

# Ambient Sediment Quality Conditions in Minnesota

Advanced data interpretation tools were used to assess sediment quality in a random and reference set of Minnesota lakes. These sediment chemistry data were also compared to other sediment quality data sets collected in Minnesota.



## Authors

Judy L. Crane, Ph.D.

Steven Hennes

## Acknowledgments

The impetus for this report came from our former supervisor, Mark Tomasek. His vision was to assess the state of sediment quality throughout Minnesota, which was something that had not been done before. While a patchwork of sediment assessment studies has been conducted in some of Minnesota's lakes, rivers, and wetlands by various government, tribal, academic, and private groups, these data had not been tied together in a cohesive manner. We were tasked with doing so. This very large task was further refined into more manageable tasks for the production of this report.

We appreciate the assistance of several external agencies for providing data files and addressing data questions. In particular, Richard Kiesling, Mark Brigham, Kathy Lee, and Laurel Woodruff of the U.S. Geological Survey (USGS) were helpful. Kent Johnson, Metropolitan Council, generously provided unpublished sediment chemistry data from the Minnesota, Mississippi, and St. Croix Rivers. Daniel Engstrom (Science Museum of Minnesota) provided sediment quality data from a 1995 - 1996 study of Minnesota lake sediments. Steve Enger [Minnesota Department of Natural Resources (MDNR)] shared historical permit records of herbicide use in Minnesota lakes.

In-house assistance was provided by several Minnesota Pollution Control Agency (MPCA) staff. Mark Gernes and Robert Murzyn provided unpublished sediment chemistry data from numerous wetlands. Deepa deAlwis addressed several data quality questions, in consultation with Scott Wade (LimnoTech), regarding newer St. Louis River Area of Concern sediment data sets. GIS support was provided by Shawn Nelson and Kris Parson. Kirk Wythers provided assistance with producing Tableau graphics of wetland data. Word processing support was provided by Jennifer Holstad. Lastly, we would like to thank our current supervisor, Bill Cole, former section manager, Katrina Kessler, and current section manager, Catherine Neuschler, for their support leading to the completion of this report.

The principal data set used in this report came from an unpublished study in which sediment quality data were collected in 2007 as an internal, agency-funded "add-on" to the federal National Lake Assessment (NLA) project. We would like to thank Frank Kohlasch, Marvin Hora (now retired), and Mark Sandusky (now retired) for MPCA supervisor and management support in securing this funding. Steve Heiskary (now retired) was the lead agency contact for the NLA project, and we would like to thank him and the field crews for collecting sediment cores for us. In particular, Steve Heiskary, Kelly O'Hara, Jesse Anderson, Matt Lindon, and Harold Wiegner, along with student interns David Tollefson and Monica Brooks, collected intact sediment core sections for us to process in 2007. Sediment samples from Cass Lake were collected by Steve Hennes (MPCA) and the Leech Lake Band. Mari Nord and Sarah Lehmann, of the U.S. Environmental Protection Agency (U.S. EPA) Region 5, and their team collected sediment samples from five lakes. The field crews were also assisted by MDNR staff and the U.S. Fish and Wildlife Service (USFWS). Metals and metalloids were analyzed by the Minnesota Department of Health. A joint powers agreement was secured with the USFWS to have other chemical and particle size analyses run by their contract laboratory, TDI-Brooks International in College Station, TX (laboratory contact: Juan Ramirez). Annette Trowbridge was our collaborator at the USFWS. Paul Hoff (MPCA) graciously allowed us to use internal funding, provided in a contract with AXYS Analytical Services Ltd. (Sidney, BC Canada), for the analysis of PBDEs in fish tissue. Fish were collected from some of the study lakes by MDNR staff, which was coordinated by Mark Briggs. Bill Scruton assisted us with a review of the quality control data

---

from the fish PBDE analyses. Sara Mueller (MPCA) assisted us greatly by adding these sediment and fish tissue data to an internal sediment quality database, and writing detailed queries using the Kaplan-Meier method for the calculation of polychlorinated dibenzo-*p*-dioxin/dibenzofuran toxic equivalents.

The draft report was reviewed by Bill Cole (MPCA), Mari Nord (U.S. EPA Region 5), and Zachary Jorgenson (St. Cloud State University).

This report is dedicated to the memory of Ed Long, the “father” of sediment quality assessment, who passed away on October 6, 2016. Ed was a mentor to Judy Crane early in her career at the MPCA. Ed was an internationally known sediment scientist while he worked for the National Oceanic and Atmospheric Administration (NOAA) in Seattle, WA. After he retired from NOAA, he continued to stay involved in sediment assessment issues, including working for the Washington State Department of Ecology until 2013. His expertise, collaborative spirit, and sense of humor will be sorely missed by those who had the privilege of working with him over the course of his career.

### **Citation**

Crane, J.L. and S. Hennes. 2016. Ambient sediment quality conditions in Minnesota. Environmental Analysis and Outcomes Division, Minnesota Pollution Control Agency, St. Paul, MN. MPCA Document Number tdr-g1-19. (<https://www.pca.state.mn.us/water/sediment-studies-twin-cities-and-statewide-sediment-investigations>)

### **Cover photo**

North Ash Lake, MN by Steve Heiskary (MPCA)

The MPCA is reducing printing and mailing costs by using the Internet to distribute reports and information to wider audience. Visit our website for more information.

MPCA reports are printed on 100% post-consumer recycled content paper manufactured without chlorine or chlorine derivatives.

## **Minnesota Pollution Control Agency**

520 Lafayette Road North | Saint Paul, MN 55155-4194 |

651-296-6300 | 800-657-3864 | Or use your preferred relay service. | [Info.pca@state.mn.us](mailto:Info.pca@state.mn.us)

This report is available in alternative formats upon request, and online at [www.pca.state.mn.us](http://www.pca.state.mn.us).

**Document number:** tdr-g1-19

# Contents

List of tables .....	vi
List of figures .....	ix
List of acronyms and abbreviations .....	xii
Executive summary .....	xx
Key findings .....	xxii
Implications .....	xxiv
Recommendations .....	xxv
Further information .....	xxv
<b>Section 1: Introduction.....</b>	<b>1</b>
What is sediment?.....	1
When can sediment become a problem? .....	2
What are sediment quality indicators? .....	4
What do we know about ambient sediment quality in Minnesota? .....	8
Purpose of this report .....	8
Audience for this report .....	8
Limitations of this report.....	9
For further information.....	9
<b>Section 2: Methods .....</b>	<b>10</b>
Search for sediment quality data sets.....	10
<i>Solicitation process</i> .....	10
<i>Evaluation process</i> .....	10
<i>Selection process</i> .....	11
MPCA’s statewide sediment survey of 54 NLAP lakes in 2007 .....	12
<i>Lake selection</i> .....	12
<i>Field sampling methods</i> .....	17
<i>Sediment processing and transport to analytical laboratories</i> .....	18
<i>Analytical methods</i> .....	20
<i>Quality assurance/quality control (QA/QC)</i> .....	24
<i>Sediment database</i> .....	27
<i>Environmental forensics</i> .....	28
<i>Statistical analyses</i> .....	30
<i>Comparisons to Level I and Level II SQTs</i> .....	36
Other sediment data sets.....	37
<i>Wetland data set</i> .....	37
<i>St. Louis River AOC data set</i> .....	38
<b>Section 3: NLAP lakes results and discussion .....</b>	<b>40</b>
TOC and particle size .....	40
<i>Background</i> .....	40
<i>Summary statistics</i> .....	40
<i>PCA analysis</i> .....	42
<i>UTL values</i> .....	43
<i>Correlation plots</i> .....	44
Metals and metalloids.....	46
<i>Background</i> .....	46
<i>Summary statistics</i> .....	49
<i>Comparisons to SQT values</i> .....	56
<i>Normalize metals and metalloids to aluminum</i> .....	59
<i>PCA analysis</i> .....	59



<i>UTL values</i> .....	63
<i>Correlation plots</i> .....	68
PAHs .....	71
<i>Background</i> .....	71
<i>Summary statistics</i> .....	74
<i>Comparisons to SQT values</i> .....	87
<i>PCA analysis</i> .....	87
<i>UTL values</i> .....	90
<i>Correlation plots</i> .....	93
<i>Environmental forensics of PAHs</i> .....	94
<i>Current and future efforts that could reduce PAH releases in Minnesota</i> .....	105
Biphenyl.....	109
<i>Background</i> .....	109
<i>Summary statistics</i> .....	109
<i>UTL values</i> .....	111
PCBs.....	112
<i>Background</i> .....	112
<i>Summary statistics</i> .....	113
<i>Comparisons to SQT values</i> .....	117
<i>UTL values</i> .....	118
Metal PEC-Qs and mean PEC-Qs .....	122
<i>Background</i> .....	122
<i>Summary statistics</i> .....	122
<i>Comparisons to SQT values</i> .....	123
<i>UTL values</i> .....	125
Legacy organochlorine pesticides .....	126
<i>Background</i> .....	126
<i>Summary statistics</i> .....	130
<i>Comparisons to SQT values</i> .....	135
<i>UTL values</i> .....	136
PCDD/Fs.....	139
<i>Background</i> .....	139
<i>Summary statistics</i> .....	140
<i>Comparisons to SQT values</i> .....	145
<i>Environmental forensics</i> .....	147
<i>UTL values</i> .....	151
PBDEs .....	154
<i>Background</i> .....	154
<i>Summary statistics: sediments</i> .....	155
<i>Comparisons to Environment Canada guidelines</i> .....	158
<i>Summary statistics: fish tissue</i> .....	158
<i>UTL values</i> .....	160
Compilation of NLAP data .....	164
<b>Section 4: Comparisons of wetland and St. Louis River AOC sediment quality to NLAP sediment quality</b> .....	<b>172</b>
Summary of wetland data .....	172
Summary of St. Louis River AOC data.....	176
Comparisons to sediment benchmarks and NLAP data .....	177
<i>SQT and NLAP UTL comparisons</i> .....	177
<i>Compilation Q-Q plots</i> .....	180
<b>Section 5: Recommendations</b> .....	<b>203</b>
Status and trends monitoring .....	203

Other sediment investigations.....	204
Data analysis and interpretation methods.....	206
Guidance and agency recommendations.....	207
Data management.....	207
Potential new developments .....	207
<b>References.....</b>	<b>209</b>
<b>Appendix A.</b>	Additional Field Sampling Information for Statewide Minnesota Lake Sediment Study (NLAP)
<b>Appendix B.</b>	MPCA QA/QC Review of Fish Tissue Results for BDEs
<b>Appendix C.</b>	Wetland Field Sampling Information
<b>Appendix D.</b>	Particle Size and TOC
<b>Appendix E.</b>	Metals and Metalloids
<b>Appendix F.</b>	PAHs
<b>Appendix G.</b>	Biphenyl
<b>Appendix H.</b>	PCBs
<b>Appendix I.</b>	Metal PEC-Qs and Mean PEC-Qs
<b>Appendix J.</b>	Legacy Pesticides
<b>Appendix K.</b>	PCDD/Fs
<b>Appendix L.</b>	BDEs and Total PBDEs with at Least One Detected Value
<b>Appendix M.</b>	Compilation of Data
<b>Appendix N.</b>	Wetland Data from Mark Gernes (MPCA)
<b>Appendix O.</b>	Sediment Quality Data from the St. Louis River Area of Concern (SLRAOC)

# List of tables

<u>Table</u>	<u>Page #</u>
1-1 Recommended Level I and Level II Sediment Quality Targets (SQTs) for the Protection of Sediment-dwelling Organisms .....	6
1-2 Additional Recommended Level I and Level II SQTs for Chemicals of Interest.....	7
2-1 Sediment Sample Site Information from the 2007 Minnesota NLAP Lakes.....	15
2-2 Acceptance Criteria for Analytical Duplicates Run by USFWS Contract Laboratories for Organic Analyses.....	26
2-3 Analytical Duplicate Anomalies in Sediment Samples Analyzed by TDI-Brooks International, Inc.....	26
2-4 Analytical Spike Anomalies in Sediment Samples Analyzed by TDI-Brooks International, Inc. ....	27
2-5 PAH Compounds Included in Different Groups of PAHs .....	29
3-1 Summary Statistics for Particle Size and TOC.....	41
3-2 Upper Tolerance Limits (UTLs) of Particle Size and TOC Data with Outliers Removed at the 5% Significance Level.....	43
3-3 Summary Statistics for Metals and Metalloids, Sorted from Low to High Nondetects .....	50
3-4 Summary Statistics for Forms of Mercury Analyzed in the 0 - 1 cm Segment of Sediment Samples Collected from the 2007 NLA Lakes in Minnesota .....	51
3-5 Comparison of Metal and Metalloid Results from the NLAP Lakes with Two Other MPCA Studies that Included Reference Lakes.....	53
3-6 Statistical Comparisons Between the NLAP and Other Sediment Studies for Metals and Selenium ...	54
3-7 Statistical Comparisons of Metals and Metalloids by Land Use Categories .....	55
3-8 Multiple Pairwise Comparisons by Land Use Categories for Selected Metals and Arsenic .....	56
3-9 Statistical Comparisons of Metals and Metalloids by Lake Surface Area Categories .....	57
3-10 Multiple Pairwise Comparisons by Lake Surface Area Categories for Manganese Based on Statistically Significant (p<0.05) Results in Table 3-9.....	57
3-11 Percentage of Metal and Metalloid Results Within Designated SQT Ranges .....	58
3-12 UTLs of Detected Metal and Metalloid Data with Outliers Removed at the 5% Significance Level .....	64
3-13 UTLs of Detected and Censored Metal and Metalloid Data with Outliers Removed at the 5% Significance Level .....	65
3-14 UTLs of Detected and Censored Forms of Mercury Analyzed in the 0 - 1 cm Segment of Sediment Samples Collected from the 2007 NLA Lakes in Minnesota .....	66
3-15 Comparison of King (2000) and Heiskary (1996) Data to NLAP UTL Values.....	67
3-16 Summary Statistics for Detected and Censored PAHs, Sorted from Low to High Nondetects .....	75
3-17 Summary Statistics for $\Sigma$ PAH Groups.....	78
3-18 Summary Statistics for PAH ESB Toxic Units .....	79
3-19 Statistical Comparisons of PAHs (with $\leq 3$ nondetects) by Major Land Use Categories .....	81
3-20 Multiple Pairwise Comparisons by Major Land Use Categories for PAHs with Significant Results in Table 3-19.....	82
3-21 Statistical Comparisons of PAHs (with $\leq 3$ nondetects) by Percent Developed Land Use Categories ...	84
3-22 Multiple Pairwise Comparisons by Developed Land Use Categories for PAHs with Statistically Significant (p<0.05) Results in Table 3-21 .....	85
3-23 Statistical Comparisons of PAHs (with $\leq 3$ nondetects) by Lake Surface Area Categories.....	86
3-24 Multiple Pairwise Comparisons by Lake Surface Area Categories for PAH Compounds with Statistically Significant (p<0.05) One-way ANOVA Results in Table 3-23.....	87
3-25 Comparison of PAH Data to the MPCA's Level I and Level II SQT Values.....	88
3-26 UTLs of Detected PAH Data with Outliers Removed at the 5% Significance Level .....	91
3-27 UTLs of Detected and Censored PAH Data with Outliers Removed at the 5% Significance Level .....	92
3-28 UTLs of $\Sigma$ PAH Groups .....	93
3-29 UTLs of PAH ESB Toxic Units.....	93

**Table**

**Page #**

3-30 Comparison of CMB8.2 Model Performance of NLAP Lakes with Two Other Sediment Studies ..... 98

3-31 Statistical Comparisons of CMB8.2 Model Performance Parameters Between the NLAP Data, Twin Cities Stormwater Pond Data (Crane 2014), and U.S. Urban Lake Data (Van Metre and Mahler 2010)..... 99

3-32 Multiple Pairwise Comparisons of CMB8.2 Model Performance Parameters by Sediment Study [NLAP, Stormwater Ponds (SWP; Crane 2014), and U.S. Urban Lakes (USUL; Van Metre and Mahler 2010)]..... 99

3-33 Statistical Comparisons of General Source Groups for CMB8.2 Model Results by Major Land Use Categories ..... 104

3-34 Multiple Pairwise Comparisons by Land Use Categories for General Source Groups with Significant Results in Table 3-33..... 104

3-35 Summary Statistics for Biphenyl ..... 110

3-36 Statistical Comparison of Biphenyl by Land Use Categories ..... 110

3-37 Multiple Pairwise Comparisons of Biphenyl by Land Use Categories ..... 110

3-38 Statistical Comparison of Biphenyl by Lake Surface Area Categories ..... 110

3-39 Multiple Pairwise Comparisons of Biphenyl by Lake Surface Area Categories ..... 111

3-40 Biphenyl UTL..... 111

3-41 Percentage of Nondetects in PCB Congeners and Total PCB Groups, Sorted from Low to High Nondetects ..... 114

3-42 Estimation of Total PCBs (Kaplan-Meier) for Lakes with <80% Nondetect Values for PCB Congeners ..... 116

3-43 Comparison of Statewide Total PCB Data to the Level I and Level II SQTs ..... 117

3-44 UTLs of Detected and Censored PCB Data with Outliers Removed at the 5% Significance Level..... 119

3-45 Summary Statistics for Metal PEC-Qs and Mean PEC-Qs..... 123

3-46 Statistical Comparisons of PEC-Qs by Land Use Categories ..... 123

3-47 Multiple Pairwise Comparisons of PEC-Qs by Land Use Categories ..... 124

3-48 Statistical Comparisons of PEC-Qs by Lake Surface Area Categories..... 124

3-49 Comparison of Mean PEC-Q Data to the MPCA's Level I and Level II SQTs ..... 124

3-50 UTLs of Metal PEC-Qs and Mean PEC-Qs ..... 125

3-51 Information on Commonly Used Organochlorine Pesticides in the U.S. .... 127

3-52 Percentage of Detected and Nondetected Pesticides and Metabolites, Sorted from High to Low Detected Compounds..... 131

3-53 Percentage of Pesticides and Metabolites (n = 30) Detected in NLAP Lake Sediments (n = 24), Sorted from High to Low Percentage of Detected Compounds ..... 132

3-54 Mean and Standard Deviation of Pesticide and Metabolite Data with <80% Nondetects, Sorted from High to Low Mean Concentrations ..... 133

3-55 Statistical Comparisons of p,p'-DDE and Total DDT by Land Use Categories..... 134

3-56 Multiple Pairwise Comparisons of p,p'-DDE and Total DDT by Land Use Categories ..... 134

3-57 Summary of Detectable DDT, DDE, and DDD Isomer Ratios ..... 135

3-58 Spearman Rank Order Correlation for Particle Size, TOC, p,p'-DDE, and Total DDT..... 135

3-59 Comparison of Statewide Pesticide and Metabolite Data to the MPCA's Level I and Level II SQT Values..... 136

3-60 UTLs of Detected and Censored Pesticide and Metabolite Data with Outliers Removed at the 5% Significance Level..... 138

3-61 Percentage of Nondetects for PCDD/F Congeners and Homolog Groups, Sorted from Low to High Nondetects ..... 141

3-62 Mean and Standard Deviation of PCDD/F Congener and Homolog Data with <80% Censored Values, as well as  $\sum$ PCDD/F Congeners ..... 142

3-63 Concentrations of  $\sum$ PCDD/F Congeners in Lake Sediment Samples ..... 143

3-64 Pairwise Statistical Comparisons Between Developed Lakes (n = 2) and the Other Lakes (n = 21) ... 144

**Table**

**Page #**

3-65 Summary Statistics for Human Health and Aquatic Life TEQs ..... 145

3-66 Spearman Rank Order Correlation of Particle Size and TOC with Individual PCDD/F Congeners  
and Homolog Groups with <5% Nondetects, as well as with  $\Sigma$ PCDD/F Congeners ..... 146

3-67 Comparison of NLAP Aquatic Life PCDD/F TEQs to the MPCA's Level I and Level II SQT Values ..... 147

3-68 UTLs of Detected PCDD/F Data with Outliers Removed at the 5% Significance Level..... 151

3-69 UTLs of Detected and Censored PCDD/F Congeners and Homologs with Outliers Removed  
at the 5% Significance Level ..... 152

3-70 UTLs of Human Health and Aquatic Life TEQs with Outliers Removed at the 5% Significance  
Level ..... 153

3-71 Percentage of Nondetects for BDE Congeners and Total PBDEs, Sorted from Low to High  
Nondetects ..... 156

3-72 Mean and SD Determined by the Kaplan-Meier Method for BDE Congeners and Total PBDEs  
with <80% NDs in Sediment Samples ..... 157

3-73 Summary Statistics for Five BDE Congeners Detected in Composite Fish Tissues ..... 159

3-74 Summary Statistics of Lipid-Normalized BDE Concentrations for Three Trophic Classes of Fish ..... 161

3-75 Statistical Comparisons of Lipid-Normalized BDE Congeners by Trophic Classes of Fish ..... 161

3-76 Multiple Pairwise Comparisons by Fish Trophic Classes for Lipid-Normalized BDEs with  
Significant One-Way ANOVA Results (Table 3-75) ..... 162

3-77 UTLs of Detected and Censored BDE Congener and Total PBDE Data in Sediment Samples  
with Outliers Removed at the 5% Significance Level ..... 163

3-78 Compilation of the Highest Pearson Product Moment Correlations (R) Based on Using  
ProUCL 5.0 Normality Designations ..... 165

3-79 Compilation of the Highest Spearman Rho Values for Selected Chemical Parameters ..... 168

4-1 Annual Chloride Fluxes in Illinois ..... 175

4-2 Comparison of Wetland and St. Louis River AOC Data to the Level I and Level II SQTs ..... 177

4-3 Comparisons of Wetland and St. Louis River AOC Data to NLAP UTL Values ..... 179

# List of figures

<u>Figure</u>	<u>Page #</u>
I	Minnesota lakes encompass a variety of land uses, including northern forests (top), agricultural areas (bottom left), and urban developments (bottom right) ..... xx
II	Location of 2007 NLA lakes in Minnesota .....xxi
III	Percentage of NLAP lakes (n = 54) within mean PEC-Q ranges corresponding to ranges of Level I and Level II SQT values.....xxii
1-1	Aerial photo of the BWCAW..... 1
1-2	Conceptual diagram of simple sediment and contaminant transport processes in lakes ..... 1
1-3	a) Example of an oxbow lake and b) a filled in stormwater pond in Woodbury, MN..... 2
1-4	Boundaries of the St. Louis River Area of Concern (AOC) ..... 3
1-5	a) Aerial view of the St. Louis River AOC and b) sediment remediation at the Hog Island/Newton Creek site along the Superior Harbor in Wisconsin..... 4
1-6	a) Collection of sediment sample for sediment chemistry measurements, b) sediment toxicity tests, and c) collection of benthic invertebrate community samples ..... 4
1-7	Freshwater benthic invertebrates typically found in clean sediment environments ..... 5
2-1	Map of random and reference lakes sampled in 2007 for Minnesota’s component of the NLA project.....13
2-2	Major land uses in the watersheds of the 2007 NLAP sediment sample sites ..... 14
3-1	Range of TOC percentages in NLAP lakes.....41
3-2	Range of percent silt in NLAP lakes..... 41
3-3	Soil parent materials in Minnesota ..... 42
3-4	PCA plot of TOC and particle size classes for the 54 NLAP lakes..... 43
3-5	Highly statistically significant correlations ( $p < 0.001$ ) were observed between particle size classes and/or TOC..... 44
3-6	Map of mineral resources in Minnesota ..... 48
3-7	Proposed location of the PolyMet Mining Corporation NorthMet mine..... 49
3-8	Correlation plot for total mercury, representing two different depth intervals for separate sediment samples from each lake..... 52
3-9	Normalization of metals and the metalloid arsenic to aluminum ..... 60
3-10	Normalization of metals and the metalloid selenium to aluminum ..... 61
3-11	PCA plot of 12 metals (including the metalloids arsenic and selenium) for the 54 NLAP lakes. .... 62
3-12	PCA plot of six metals (including the metalloid arsenic) for the 54 NLAP lakes ..... 63
3-13	Correlation plots for detected metals and vanadium (one nondetect), which had outliers removed at the 5% significance level..... 69
3-14	Correlation plots for detected metals and the metalloid arsenic, which had outliers removed at the 5% significance level ..... 70
3-15	Percentage of 34 PAHs in lake #27 – Nokomis..... 74
3-16	Range of perylene, as a percentage of $\sum\text{PAH}_{34}$ , in the NLAP lakes. .... 77
3-17	Box plots of $\sum\text{PAH}$ groups based on measured and Kaplan-Meier estimated values ..... 79
3-18	Distribution of PAH ESB Toxic Units in the study lakes. .... 80
3-19	Comparison of $\sum\text{PAH}_{13}$ concentrations to corresponding Level I and Level II SQT values ..... 88
3-20	PCA plot of 34 PAHs with $\leq 3$ nondetects ..... 89
3-21	PCA plot of 13 PAHs for the 54 NLAP lakes ..... 90
3-22	Correlation plots for detected PAHs and dibenzothiophene (one nondetect), which had outliers removed at the 5% significance level..... 94
3-23	Concentration histogram plot for lake #38 (Snail) ..... 95
3-24	Double-ratio plot of P/A vs. F/P. .... 96
3-25	Double-ratio plot for PAH compounds indicative of major emission sources from vehicles. .... 96

<u>Figure</u>	<u>Page #</u>
3-26	Comparison of measured concentrations of $\Sigma\text{PAH}_{\text{CMB}}$ with those estimated by the CMB8.2 model. .98
3-27	CMB8.2 model results for $R^2$ . ..... 98
3-28	CMB8.2 model results for Chi Square. ....98
3-29	CMB8.2 model results for percent mass. ....98
3-30	Comparison of PAH proportional values between sources used in the EPA's CMB8.2 model (open circles) and the mean profile for NLAP lakes (closed circles; uncertainty bars indicate one SD) for which that source was used in the model results ..... 101
3-31	Number of lakes for which generalized PAH sources comprised the source apportionment of PAHs. .... 102
3-32	General source apportionment of PAHs in each NLAP lake. .... 102
3-33	Source apportionment of PAHs in lakes with low concentrations of $\Sigma\text{PAH}_{\text{CMB}}$ . .... 103
3-34	Source apportionment of PAHs in BWCAW lakes. .... 103
3-35	Location of coal-fired power plants in Minnesota (designated by circles with triangles) and the Prairie Island nuclear facility ..... 106
3-36	Xcel Energy's Sherco coal-fired power plant in Becker, MN ..... 106
3-37	The installation of pollution control devices has decreased diesel emissions from Minnesota school buses ..... 107
3-38	Asphalt-based sealants are a suitable alternative to CT-sealants ..... 108
3-39	Linear regression of estimated Total PCBs (Kaplan-Meier) and Total PCBs (pesticide scan) ..... 117
3-40	Comparison of Total PCBs (pesticide scan) in NLAP lakes to the Level I and Level II SQT values ..... 118
3-41	Comparison of mean PEC-Q ranges to Level I and Level II SQTs ..... 125
3-42	Metal PEC-Q ranges in NLAP lakes ..... 125
3-43	Comparison of measured Total DDT concentrations to the MPCA's Level I and Level II SQT values. .... 137
3-44	Comparison of chlordane concentrations to the MPCA's Level I and Level II SQT values. .... 137
3-45	Aquatic life TEQs based on the Kaplan-Meier method ..... 147
3-46	Human Health TEQs based on the Kaplan-Meier method ..... 147
3-47	Mean (SD) weight percentages of PCDD/F congeners ..... 148
3-48	a) Detected PCD2378 data compared to PCD_T4, and b) the ratio of detected PCD2378 concentrations to PCD_T4 plotted for each lake ..... 149
3-49	Mean weight percentages of PCDD/F homologs in lake #36 (Red Rock) and the other 22 NLAP lakes ..... 150
3-50	Mean weight percentages of PCDD/F homologs in developed lakes versus 20 other lakes (which excluded Lake #36—Red Rock) ..... 150
3-51	Scatter plot of lead vs. indeno[1,2,3-cd]pyrene ..... 166
3-52	a) Scatter plot of C1-dibenzothiophene vs. TOC and b) zinc vs. TOC ..... 167
3-53	PCA plot of three principal components for the metals, mean PEC-Q, and $\Sigma\text{PAH}_{13}$ parameters that also have SQT values ..... 170
3-54	PCA plot of three principal components for the parameters in Figure 3-53 plus particle size fractions, TOC, and biphenyl ..... 171
4-1	Concentration ranges of chloride in wetland sediments ..... 174
4-2	Corn and soybean acreage percentage changes from 2006 to 2014 using Cropland Data Layer (CDL) results ..... 176
4-3	Concentration ranges of copper (a) and lead (b) in NLAP lakes and MPCA wetland sediments ..... 181
4-4	Concentration ranges of nickel (a) and zinc (b) in NLAP lakes and MPCA wetland sediments ..... 181
4-5	Concentration ranges of metal PEC-Qs in NLAP lake and MPCA wetland sediments ..... 182
4-6	Concentration ranges of cadmium in surficial sediments from designated sites in the St. Louis River AOC. .... 183
4-7	Concentration ranges of copper in surficial sediments from designated sites in the St. Louis River AOC ..... 184

<b>Figure</b>	<b>Page #</b>
4-8 Concentration ranges of lead in surficial sediments from designated sites in the St. Louis River AOC .....	185
4-9 Concentration ranges of mercury in surficial sediments from designated sites in the St. Louis River AOC .....	186
4-10 Concentration ranges of nickel in surficial sediments from designated sites in the St. Louis River AOC .....	187
4-11 Concentration ranges of zinc in surficial sediments from designated sites in the St. Louis River AOC .....	188
4-12 Concentration ranges of metal mean PEC-Qs in surficial sediments from designated sites in the St. Louis River AOC .....	189
4-13 Concentration ranges of mean PEC-Qs in surficial sediments from designated sites in the St. Louis River AOC .....	190
4-14 Concentration ranges of $\Sigma$ PAH <sub>13</sub> in surficial sediments from designated sites in the St. Louis River AOC .....	191
4-15 Concentration ranges of aquatic life PCDD/F TEQs (W_TEQ_KMDF) in surficial sediments from designated sites in the St. Louis River AOC .....	192
4-16 Compilation Q-Q plot for clay (%). .....	193
4-17 Compilation Q-Q plot for silt. ....	193
4-18 Compilation Q-Q plot for sand. ....	193
4-19 Compilation Q-Q plot for TOC. ....	194
4-20 Compilation Q-Q plot for aluminum. ....	194
4-21 Compilation Q-Q plot for antimony. ....	194
4-22 Compilation Q-Q plot for arsenic. ....	195
4-23 Compilation Q-Q plot for barium. ....	195
4-24 Compilation Q-Q plot for beryllium. ....	195
4-25 Compilation Q-Q plot for cadmium. ....	196
4-26 Compilation Q-Q plot for chromium. ....	196
4-27 Compilation Q-Q plot for cobalt. ....	196
4-28 Compilation Q-Q plot for copper. ....	197
4-29 Compilation Q-Q plot for iron. ....	197
4-30 Compilation Q-Q plot for lead. ....	197
4-31 Compilation Q-Q plot for manganese. ....	198
4-32 Compilation Q-Q plot for mercury. ....	198
4-33 Compilation Q-Q plot for molybdenum. ....	198
4-34 Compilation Q-Q plot for nickel. ....	199
4-35 Compilation Q-Q plot for selenium. ....	199
4-36 Compilation Q-Q plot for silver. ....	199
4-37 Compilation Q-Q plot for thallium. ....	200
4-38 Compilation Q-Q plot for vanadium. ....	200
4-39 Compilation Q-Q plot for zinc. ....	200
4-40 Compilation Q-Q plot for metal PEC-Qs. ....	201
4-41 Compilation Q-Q plot for mean PEC-Qs. ....	201
4-42 Compilation Q-Q plot for $\Sigma$ PAH <sub>13</sub> . ....	201
4-43 Compilation Q-Q plot for Total PCBs. ....	202
4-44 Compilation Q-Q plot for aquatic life PCDD/F TEQs (W_TEQ_KMDF). ....	202



# List of acronyms and abbreviations

---

AcNaph	acenaphthene
AcNaphYl	acenaphthylene
AhR	aryl hydrocarbon receptor
Al	aluminum
ANOVA	analysis of variance
ANT	anthracene
AOC	Area of Concern
As	arsenic
ATSDR	Agency for Toxic Substances and Disease Registry
AUs	animal units
AVS	acid volatile sulfide
$b_0$	intercept
$b_1$	slope
B2	probable human carcinogen
Ba	barium
BAA	benzo[a]anthracene
B[a]P	benzo[a]pyrene as used in B[a]P equivalents
BaP	benzo[a]pyrene as used in forensic source ratios
BAP	benzo[a]pyrene
BbF	benzo[b]fluoranthene as used in forensic source ratios
BBF	benzo[b]fluoranthene
BC	British Columbia
BDE	brominated diphenyl ether
BeP	benzo[e]pyrene as used in forensic source ratios
BEP	benzo[e]pyrene
BGHIP	benzo[g,h,i]perylene
BHC	benzene hexachloride (as in gamma BHC for lindane)
BkF	benzo[k]fluoranthene as used in forensic source ratios
BKF	benzo[k]fluoranthene
BMP	best management practice
BUI	beneficial use impairment
BWCAW	Boundary Waters Canoe Area Wilderness
BZ	Ballschmitter and Zell
C	possible human carcinogen
C1-DBZTP	C1-dibenzothiophenes
C1-FLUT/PYR	C1-fluoranthenes/pyrenes
C1-Naph	C1-naphthalenes
C1-PHE/ANT	C1-phenanthrenes/anthracenes
C2-DBZTP	C2-dibenzothiophenes
C2-Naph	C2-naphthalenes

# List of acronyms and abbreviations (continued)

---

C2-PHE/ANT	C2-phenanthrenes/anthracenes
C3-DBZTP	C3-dibenzothiophenes
C3-Naph	C3-naphthalenes
C3-PHE/ANT	C3-phenanthrenes/anthracenes
C4-Naph	C4-naphthalenes
C4-PHE/ANT	C4-phenanthrenes/anthracenes
CA	California
CAFOs	concentrated animal feeding operations
CCME	Canadian Council of Ministers of the Environment
CDDs	chlorinated dibenzo- <i>p</i> -dioxins
CDL	cropland data layer
cm	centimeter
CMB	chemical mass balance
Co	cobalt
CO <sub>2</sub>	carbon dioxide
Cr	chromium
CT	coal tar-based
CTD	chlorinated derivatives of triclosan
Cu	copper
cul	cultivated (agriculture) land uses
CV	coefficient of variation
CVAA	cold vapor atomic absorption
D	not classifiable as to human carcinogenicity
2D	two-dimensional
3D	three-dimensional
D1	>60% developed land uses
D2	10 - 14% developed land uses
D3	4 - 9% developed land uses
D4	0 - 3% developed land uses
DBahANT	dibenzo[a,h]anthracene
DBZTP	dibenzothiophene
DC	District of Columbia
DCDD	dichlorodibenzo- <i>p</i> -dioxin
DDA	<i>p,p'</i> -2,2-bis(chlorophenyl)acetic acid
DDCN	<i>p,p'</i> -2,2-bis(4-chlorophenyl)acetonitrile
DDD	dichlorodiphenyldichloroethane
DDE	dichlorodiphenyldichloroethylene
DDMS	<i>p,p'</i> -2,2-bis(chlorophenyl)-1-chloroethane
DDMU	2,2-bis(chlorophenyl)-1-chloroethylene
DDT	dichlorodiphenyltrichloroethane

# List of acronyms and abbreviations (continued)

---

dev	developed land uses
df	degrees of freedom
DI	deionized water
2,6-DMeNaph	2,6-dimethylnaphthalene
DNA	deoxyribonucleic acid
DNT	do not test
DP	Dechlorane Plus
DW	dry weight
E	east
E	evidence of noncarcinogenicity in humans
ECD	electron capture detection
EPA	Environmental Protection Agency
ESB	equilibrium partitioning sediment benchmark
f	female
F/P	fluoranthene to pyrene ratio
FEQGs	Federal Environment Quality Guidelines
FL	Florida
FLUT	fluoranthene
for	forested land uses
g	gram
GA	Georgia
GC	gas chromatography
GC/ECD	gas chromatography/electron capture detection
GC/MS	gas chromatography/mass spectrometry
GC/MS-NCI	gas chromatography/mass spectrometry-negative chemical ionization
GC/MS-SIM	gas chromatography/mass spectrometry-selected ion monitoring
GIS	geographic information system
GPS	global positioning system
ha	hectare
HBCDD	hexabromocyclododecane
HCA	hierarchical cluster analysis
HCB	hexachlorobenzene
HCH	hexachlorocyclohexane
HCl	hydrochloric acid
HH	human health
HH_TEQ	human health toxic equivalent
HH_TEQ_KMDF	human health calculation of TEQs using PCDD/Fs
HH_TEQ_KMDFP	human health calculation of TEQs using PCDD/Fs and coplanar PCBs
HI	Hawaii
HP	Hewlett Packard

# List of acronyms and abbreviations (continued)

---

HRGC	high resolution gas chromatography
HRGC/HRMS	high resolution gas chromatography/high resolution mass spectrometry
HRMS	high resolution mass spectrometry
HW	Hawkins Wixley
HxCDD	hexachlorodibenzo- <i>p</i> -dioxin
IA	Iowa
IBI	index of biological integrity
ICDP	indeno[1,2,3- <i>cd</i> ]pyrene
ICP	inductively coupled plasma
ICP-MS	inductively coupled plasma-mass spectrometry
ID	inner diameter in reference to GC columns
ID	identification in reference to field samples of sediments
IL	Illinois
IRIS	Integrated Risk Information System
IUPAC	International Union of Pure and Applied Chemistry
KCl	potassium chloride
kg	kilogram
KM	Kaplan-Meier calculation
KMDF	Kaplan-Meier calculation of TEQs using PCDD/Fs
KMDFP	Kaplan-Meier calculation of TEQs using PCDD/Fs and coplanar PCBs
L	liter
LOD	limit of detection
m	male
MAD	median absolute deviation (used as MAD/0.675)
MDA	Minnesota Department of Agriculture
MDEQ	Michigan Department of Environmental Quality
MDH	Minnesota Department of Health
MDL	method detection limit
MDNR	Minnesota Department of Natural Resources
1-MeNaph	1-methylnaphthalene
1-MePHE	1-methylphenanthrene
2-MeNaph	2-methylnaphthalene
mg	milligram
MI	Michigan
mm	millimeter
mm	maximum-minimum transformation
Mn	manganese
MN	Minnesota
MO	Missouri
MPCA	Minnesota Pollution Control Agency

# List of acronyms and abbreviations (continued)

---

MS	mass spectrometry
MW302-PAHs	molecular weight 302 PAHs
MWRDGC	Metropolitan Water Reclamation District of Greater Chicago
N	number of samples
N/A	not applicable
Naph	naphthalene
NC	North Carolina
NCHF	north central hardwood forest
ND	nondetect as used in relation to analytical results
ND	North Dakota
NDIR	nondispersive infrared
NDSU	North Dakota State University
NE	northeast
ng	nanogram
NGP	northern glaciated Plains
Ni	nickel
NJ	New Jersey
NLA	National Lake Assessment
NLAP	National Lake Assessment Project
NLF	northern lakes and forest
NPDES	National Pollutant Discharge Elimination System
NW	northwest
NY	New York
NYSDEC	New York State Department of Environmental Conservation
OC	organic carbon
OCDD	1,2,3,4,6,7,8,9-octachlorodibenzo- <i>p</i> -dioxin
OCDF	1,2,3,4,6,7,8,9-octachlorodibenzofuran
OH	Ohio
ON	Ontario
OR	Oregon
P/A	phenanthrene to anthracene ratio
PAC	polycyclic aromatic compounds
PAHs	polycyclic aromatic hydrocarbons
PAST	PAleontological STatistics
Pb	lead
PBDEs	polybrominated diphenyl ethers
PC1	principal component 1
PC2	principal component 2
PC3	principal component 3
PCA	principal components analysis

# List of acronyms and abbreviations (continued)

---

PCBs	polychlorinated biphenyls
PCD12378	1,2,3,7,8-pentachlorodibenzo- <i>p</i> -dioxin
PCD123478	1,2,3,4,7,8-hexachlorodibenzo- <i>p</i> -dioxin
PCD123678	1,2,3,6,7,8-hexachlorodibenzo- <i>p</i> -dioxin
PCD123789	1,2,3,7,8,9-hexachlorodibenzo- <i>p</i> -dioxin
PCD1234678	1,2,3,4,6,7,8-heptachlorodibenzo- <i>p</i> -dioxin
PCD2378	2,3,7,8-tetrachlorodibenzo- <i>p</i> -dioxin
PCD_T4	dioxins, 4TCDD, total
PCD_T5	dioxins, 5PeCDD, total
PCD_T6	dioxins, 6HxCDD, total
PCD_T7	dioxins, 7HpCDD, total
PCDD	polychlorinated dibenzo- <i>p</i> -dioxin
PCDD/Fs	polychlorinated dibenzo- <i>p</i> -dioxins/dibenzofurans
PCDF	polychlorinated dibenzofuran
PCF12378	1,2,3,7,8-pentachlorodibenzofuran
PCF123478	1,2,3,4,7,8-hexachlorodibenzofuran
PCF123678	1,2,3,6,7,8-hexachlorodibenzofuran
PCF123789	1,2,3,7,8,9-hexachlorodibenzofuran
PCF1234678	1,2,3,4,6,7,8-heptachlorodibenzofuran
PCF1234789	1,2,3,4,7,8,9-heptachlorodibenzofuran
PCF2378	2,3,7,8-tetrachlorodibenzofuran
PCF23478	2,3,4,7,8-pentachlorodibenzofuran
PCF234678	2,3,4,6,7,8-hexachlorodibenzofuran
PCF_T4	furans, 4TCDF, total
PCF_T5	furans, 5PeCDF, total
PCF_T6	furans, 6HxCDF, total
PCF_T7	furans, 7HpCDF, total
PEC	probable effect concentration
PEC-Q	probable effect concentration quotient
pg	picogram
PHE	phenanthrene
PHE/ANT	phenanthrene/anthracene
POPs	persistent organic pollutants
PYR	pyrene
Q	quantile
Q1	25 <sup>th</sup> percentile
Q2	50 <sup>th</sup> percentile (i.e., median)
Q3	75 <sup>th</sup> percentile
QA	quality assurance
QA/QC	quality assurance/quality control

# List of acronyms and abbreviations (continued)

---

QAPP	quality assurance project plan
QC	quality control
Q-Q	quantile-quantile plots
R or r	correlation coefficient
$r^2$	coefficient of determination
R-EMAP	Regional Environmental Monitoring and Assessment
rho ( $\rho$ )	correlation coefficient for the nonparametric Spearman rank order correlation test
RPD	relative percent difference
RRF	relative response factor
RRV	Red River Valley
RSD	relative standard deviation
S	south
SD	standard deviation when used with statistical results
SD	South Dakota
Se	selenium
SEM	standard error of the mean when used in regards to statistical tests
SEM	simultaneously extractable metals
SIM	selected ion monitoring
SLRAOC	St. Louis River Area of Concern
SOPs	standard operating procedures
SQT	sediment quality target
SRV	soil reference value
STORET	Storage and Retrieval database
SW	southwest
SWP	stormwater pond
TCDD	tetrachlorodibenzo- <i>p</i> -dioxin
TCEP	tris(2-chloroethyl)phosphate
TDCPP	tris(1,3-dichloro-2-propyl)phosphate
TEC	threshold effect concentration
TEF	toxic equivalency factor
TEQ	toxic equivalent
TMDL	total maximum daily load
1,6,7-TMeNaph	1,6,7-trimethylnaphthalene
TOC	total organic carbon
TPAH13	total sum of 13 PAHs that also have SQT values
TPL	Temperate Plains
TricDD	trichlorodibenzo- <i>p</i> -dioxin
TSCA	Toxic Substances Control Act
TU	Toxic Unit
TX	Texas

## List of acronyms and abbreviations (continued)

---

µg	microgram
UK	United Kingdom
UMW	Upper Midwest
UNEP	United Nations Environment Programme
UPGMA	unweighted pair group method with arithmetic mean
U.S.	United States
USDA	U.S. Department of Agriculture
USEPA	U.S. Environmental Protection Agency
USFWS	United States Fish and Wildlife Service
USGS	United States Geological Survey
USUL	U.S. urban lakes
UTL	upper tolerance limit
UTL 95-95	the 95% UTL with 95% coverage
UV	ultraviolet
V	vanadium
VA	Virginia
vs.	versus
W	west
W	aquatic life in context of PCDD/F TEQs
W_TEQ	aquatic life toxic equivalents for PCDD/Fs
W_TEQ_KMDF	aquatic life TEQs for PCDD/Fs estimated by Kaplan-Meier
W_TEQ_KMDFP	aquatic life TEQs for PCDD/Fs and coplanar PCBs estimated by Kaplan-Meier
WA	Washington
WCBP	western corn belt Plains
wet	lakes and wetlands land uses
WH	Wilson Hilferty
WHO	World Health Organization
WI	Wisconsin
WSA_Eco9	Wadeable Streams Assessment nine aggregated Omernik level 3 ecoregions
wt	weight
WWTP	wastewater treatment plant
Zn	zinc



# Executive summary

---

This report provides the first ever, overarching assessment of ambient sediment quality conditions in Minnesota. A common feature of all of Minnesota's many lakes (Figure I), rivers, streams, harbors, and wetlands is the layer of mud, or sediment, at the bottom of them. Sediment provides important habitat for bottom-dwelling (benthic) organisms, nearshore aquatic vegetation, and wildlife. It also provides a repository for a variety of contaminants that attach to particles in the water column and settle out to the sediments. Over time, layers of sediment build-up in depositional areas of waterbodies, providing a history of changes. Scientists who collect long sediment cores from these areas can obtain a wealth of information about fluctuations in contaminant concentrations over time, as well as biological impacts from changing land uses and climate. The upper, surficial sediments from randomly selected waterbodies can be used to provide an indication of "ambient" chemical and physical concentrations due to natural sources and/or diffuse anthropogenic (i.e., human activity) sources.



Figure I. Minnesota lakes encompass a variety of land uses, including northern forests (top), agricultural areas (bottom left), and urban developments (bottom right).

The purpose of this report is to assemble and evaluate ambient sediment chemistry and particle size data from Minnesota waterways. To that end, the main focus of this report is on a previously unreported sediment investigation conducted in 2007. This study was an internally-funded side project to a larger national effort funded by the U.S. Environmental Protection Agency (EPA) called the National Lake Assessment (NLA) project. The Minnesota Pollution Control Agency (MPCA) commonly referred to Minnesota's component of this nationwide 2007 study as the National Lake Assessment Project (NLAP). This NLAP terminology was also used to refer to the independent sediment samples collected from the same suite of lakes by the NLA field crews. Minnesota's component of the NLA lakes included 50 randomly selected lakes and four *a priori* reference lakes, representing different ecoregions and major land uses (Figure II). Sediment chemistry and particle size data were evaluated from one composite

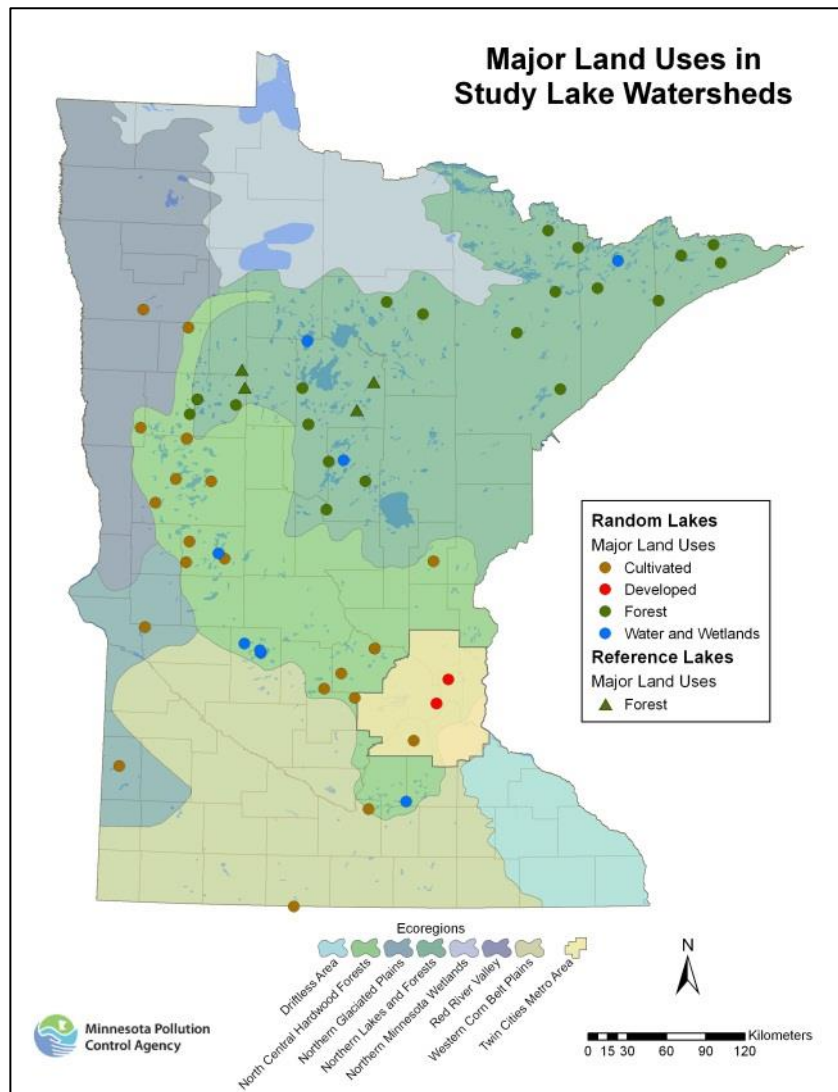


Figure II. Location of 2007 NLA lakes in Minnesota.

surficial (0 – 15 cm) sediment sample per lake (n = 54). These samples were used to provide an indication of the statistical range of more recently deposited analytes and to determine if these concentrations were influenced by major watershed land uses. The analyte list included: 19 metals and metalloids, 43 individual and alkylated homolog groups of polycyclic aromatic hydrocarbons (PAHs), biphenyl, 114 polychlorinated biphenyl (PCB) congeners, 30 legacy organochlorine pesticides and metabolites, 24 polychlorinated dibenzo-*p*-dioxins/dibenzofuran (PCDD/F) congeners and homolog groups, 55 polybrominated diphenyl ether (PBDE) congeners, total organic carbon (TOC), and particle size fractions (i.e., percent clay, silt, and sand). Due to resource limitations, PCBs, legacy pesticides, and PCDD/Fs were only measured in 23 - 24 sediment samples. In addition, a small fish survey was conducted to assess PBDEs in both whole fish and fish tissues from three different trophic species of fish collected from five NLAP lakes.

The sediment quality data were evaluated using chemical indices, making comparisons to benchmark values, conducting statistical analyses, and incorporating environmental forensic techniques to identify sources. Mean probable effect concentration quotients (PEC-Qs) were calculated to distill data from a mixture of contaminants into one unitless index. The mean PEC-Qs, along with a suite of contaminant

concentrations, were compared to their corresponding Level I and Level II sediment quality targets (SQTs) for the protection of benthic organisms. Ambient background threshold values of contaminants were calculated for the 95% upper tolerance limit (UTL) with 95% coverage. Sample values above the UTLs are likely due to increased anthropogenic contamination, point sources, or naturally high mineral deposits of certain metals and metalloids. This approach resulted in no more than a 5% false positive error rate (i.e., the chance of falsely classifying a true background concentration as a contaminated concentration). In addition, multivariate statistical methods were used to tease out relationships in complex data sets. Environmental forensic methods were also used to identify major sources of PAHs and PCDD/Fs. Finally, other agency-related sediment quality data sets, excluding known contaminated areas, were compared to the NLAP sediment data.

## Key findings

The sediment chemistry results for the *a priori* reference samples were often similar to the results from the random lake samples, excluding the urban sites. The *a priori* reference and random data were merged into one data set for the purposes of this report to yield data on ambient sediment quality conditions for this particular suite of lakes. These data were not extrapolated to Minnesota lakes, in general, although this could be done based on the probability design of the broader, nationwide NLA study. The key findings of this report include:

- **Sediment quality in this set of Minnesota lakes ranged from good to moderate based on mean PEC-Q values, an integrative measure of multiple contaminants (Figure III).** Mean PEC-Q values less than or equal to the Level I SQT value (i.e., 0.10) are protective of sediment-dwelling organisms (i.e., benthic invertebrates). Under this scenario, harmful effects are unlikely to be observed in 43% of NLAP lakes with mean PEC-Q values  $\leq 0.10$  (Figure III). Values between the Level I and Level II SQT values (i.e.,  $>0.10 - 0.60$ ) may be associated with an increased incidence of sediment toxicity in 57% of the study lakes (Figure III). No lakes exceeded the Level II SQT value of 0.60 for mean PEC-Qs, for which harmful effects on benthic invertebrates would be more likely to occur.

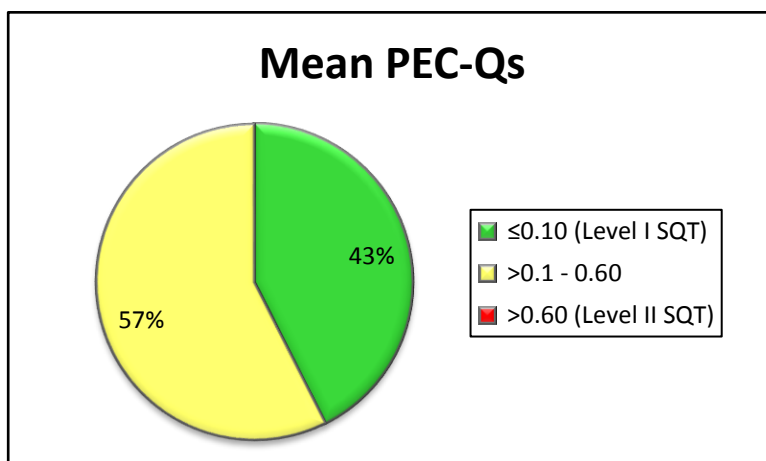


Figure III. Percentage of NLAP lakes (n = 54) within mean PEC-Q ranges corresponding to ranges of Level I and Level II SQT values.

- **On an individual basis, some contaminants exceeded their Level II SQT values in a small number of lakes.** Thus, there would be an increased likelihood of detrimental impacts to benthic invertebrates in the sediments of these lakes. Examples included:
  - Historical uses of sodium arsenite to control aquatic weeds in one urban lake (Snail Lake) resulted in the exceedance of the Level II SQT value for arsenic.
  - In a few cases, the exceedances were due to elevated anthropogenic or point source inputs [i.e., acenaphthylene, lead, sum dichlorodiphenyldichloroethane (DDD) compounds, and sum dichlorodiphenyldichloroethylene (DDE) compounds].
  - Some exceedances of metals (e.g., copper, chromium, and nickel) in a few northeastern Minnesota lakes were due to geological deposits of minerals containing these metals. Thus, the sediments were naturally enriched in these metals.
- **The sediments in two urban study lakes tended to be more contaminated than sediments in lakes from other major watershed land uses.** These differences were often statistically significant ( $p < 0.05$ ), particularly for lakes with developed (i.e., urban) versus cultivated land uses for arsenic, lead, zinc, and numerous PAH compounds. The two urban lakes included in this study were from the Minneapolis-St. Paul, MN metropolitan area (i.e., Nokomis and Snail), and they were frequent outliers that stood out as unique in the multivariate statistical analyses that were performed.
- **Mercury was below the Level I SQT value (i.e., 0.18 mg/kg dry wt.) in 81.5% of lake sediments, and no lake sediments exceeded the Level II SQT value (i.e., 1.1 mg/kg dry wt.).** Ten lakes (e.g., 18.5%) had mercury concentrations between the Level I and Level II SQT values. The highest mercury concentration of 0.57 mg/kg dry wt. occurred in Vesper, a Boundary Waters Canoe Area Wilderness lake located in northeast Minnesota. Atmospheric deposition was the most likely source of mercury to this lake.
- **Total PAH (i.e.,  $\sum\text{PAH}_{13}$ ) concentrations were below the Level I SQT value in lake sediments located outside of urban areas.** Perylene, a mostly naturally produced PAH compound not included in  $\sum\text{PAH}_{13}$ , exceeded 1 mg/kg dry wt. in four lakes. Environmental forensic techniques indicated the sediment samples from most of the lakes were dominated by pyrogenic (i.e., combustion) sources of PAHs. Source apportionment modeling of PAHs revealed that vehicle emissions and coal-related combustion were the most common sources. Coal tar-based sealant dust was also an important source in many lakes. Wood combustion was important in a smaller number of lakes.
- **Total PCBs were less than or equal to the Level I SQT value in 22 of 24 lakes, with higher values in the two urban lakes.** Certain higher chlorinated PCB congeners (i.e., 118 and 132+153) were frequently detected in most lake sediments due to their chemical persistence.
- **Dichlorodiphenyltrichloroethane (DDT) metabolites were commonly detected in a subset of 24 lakes and had the most exceedances of the Level I SQT values.** The concentrations of most other legacy organochlorine pesticides were below their corresponding Level I SQT values.
- **PCDD/F congeners and homolog groups were frequently detected.** Most aquatic life PCDD/F toxic equivalents were between the Level I and Level II SQT values. A general environmental forensic analysis of the data showed that ubiquitous combustion sources, like wood burning and automobile emissions, appear to be important. In addition, burning of household garbage is likely another important source.

- **The brominated diphenyl ether (BDE) congener results in sediment and fish tissue provided additional relevance for Minnesota’s legislative actions to prohibit products with pentaBDE and octaBDE, as well as an upcoming ban on decaBDE.**
  - BDE-209, a decaBDE, was detected in 84% of lake sediment samples (n = 52 NLAP lakes).
  - Fish at the top of the food chain (i.e., predator trophic group) had significantly higher (p<0.05) mean lipid-normalized concentrations of BDEs-47, 100 (a pentaBDE), and 153 than lower trophic fish.
- **UTL values were calculated for all ambient sediment quality data that had <80% nondetects.** The NLAP UTLs will provide another valuable tool for sediment assessment work.
- **The NLAP sediment quality data provided a valuable, random data set to compare to other MPCA study data collected from Minnesota waterways.** Sediment chemistry data from a multi-year wetland survey and newer data from the St. Louis River Area of Concern (AOC; excluding known contaminated sites) were compared to the NLAP data.
  - For the wetland data, the highest percentage of exceedances of the NLAP UTL values occurred for beryllium, silver, selenium, and vanadium.
  - For the St. Louis River AOC data, the highest percentage of exceedances of the NLAP UTL values occurred for  $\Sigma$ PAH<sub>13</sub>, aquatic life PCDD/F toxic equivalents, copper, and nickel.

## Implications

- **These results will be used to help prioritize agency activities related to ambient sediment quality, and for future status and trends work.** For the first time, sediment chemistry will be added to the 2017 NLA suite of lakes nationwide. This will give us an opportunity to reassess some of the NLAP UTLs with more data that will be collected in Minnesota. If continued, this work can help track the effectiveness of programs and regulations, such as banning coal tar-based sealants due to PAH contamination and certain flame retardants (i.e., PBDEs).
- **As urban development expands in Minnesota, we are likely to see further degradation of sediment quality in those areas.** Incorporation of best management stormwater practices can alleviate some of these issues. Further reductions of PAHs in sediment may result from Minnesota’s 2014 ban on coal tar-based sealants, expansion of Project Green Fleet from the Minneapolis-based Environmental Initiative to retrofit vehicles and equipment with diesel engines to reduce emissions, and clean energy initiatives, such as development of our state’s Clean Power Plan.
- **Bans on persistent organic chemicals may take decades to result in contaminant reductions in surficial sediments.** Several banned organochlorine pesticides and their metabolites were still detected in over half of the NLAP lake sediments, even after being banned over 30 - 40 years ago for some compounds. Although PCBs were banned in 1979, these legacy contaminants are still an important issue in urban sediments. These recalcitrant compounds continue to cycle through the environment.
- **Incorporation of buffer strips along public agricultural waterbodies may help reduce sediment and contaminant loads to agricultural waterways.** Minnesota’s 2015 landmark Buffer Law, which was amended by the Legislature and signed into law by Governor Dayton on April 25, 2016, designates an estimated 110,000 acres of land for water quality buffer strips statewide. This new law is very timely, because row crop farming has expanded substantially in central Minnesota during the past decade due to higher crop prices.

- **This report should be considered, in conjunction with other agency and stakeholder water quality reports, as part of a broader weight-of-evidence for making management decisions about water quality in Minnesota.** Governor Dayton has made water quality one of the hallmarks of his second term. This report adds to our body of knowledge about the status of sediment quality issues in Minnesota, which can impact the overlying water and aquatic life.

## Recommendations

A number of recommendations are made at the end of this report pertaining to:

- Status and trends monitoring
- Other sediment investigations that could be conducted
- Data analysis and interpretation methods
- Guidance and agency recommendations
- Data management
- Potential new developments

## Further information

For further information about this report, contact: Judy L. Crane, Ph.D. at [judy.crane@state.mn.us](mailto:judy.crane@state.mn.us) or 651-757-2293 (voice).



# Section 1: Introduction

Minnesota is known for its bountiful water resources, ranging from the pristine Boundary Waters Canoe Area Wilderness (BWCAW; Figure 1-1) in northeastern Minnesota to urban waterways affected by human development. When most people think of Minnesota's many lakes, streams, and rivers they envision clean water for recreational activities like boating, fishing, and swimming. Beneath the water surface, though, is an important component of these waterways, the bottom sediments. This report will examine ambient sediment quality in Minnesota. By this, we mean to evaluate chemical and particle size concentrations derived from natural and diffuse anthropogenic sources (i.e., "ambient") in a set of random and *a priori* reference lakes across Minnesota. In turn, these data will be compared to other surficial sediment quality data collected from Minnesota, especially for wetlands and a portion of the St. Louis River Area of Concern (AOC) in northeastern Minnesota. This report represents the first broad assessment of sediment quality conditions to be conducted across the State of Minnesota.



Figure 1-1. Aerial photo of the BWCAW; photo copyright by Jim Brandenburg.

## What is sediment?

Sediment is the mud that forms at the bottom of waterways (Figure 1-2). It is composed of loose particles of sand, silt, and clay that are intermixed with decomposed organic matter from plants, invertebrates, and animals. This material often enters waterways from surface water runoff from the surrounding watershed (e.g., erosion of land), from atmospheric deposition (e.g., dust), and from in-

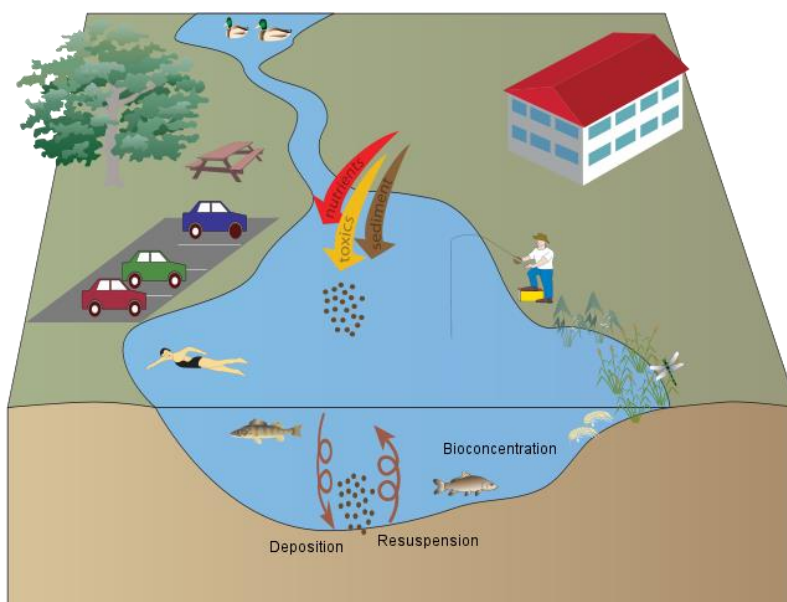


Figure 1-2. Conceptual diagram of simple sediment and contaminant transport processes in lakes (prepared by Judy Crane using the Integration and Application Network, University of Maryland Center for Environmental Science; [ian.umces.edu/imagelibrary/](http://ian.umces.edu/imagelibrary/)).

water processes (e.g., algae blooms that die and decompose). Material suspended in the water column may settle out to the sediments. As part of the natural feature of waterways, sediment provides important habitat for bottom-dwelling (i.e., benthic) organisms and nearshore aquatic vegetation. The surficial sediments can be mixed by burrowing aquatic invertebrates and some bottom feeding (i.e., benthic) fish. This material can also be resuspended due to currents (e.g., during flooding), commercial and recreational boat traffic (e.g., boat propellers), and/or wind-induced waves in shallow areas. A permanently buried layer of sediment that cannot be disturbed lies below the surficial sediments. In depositional areas, the sediment builds up over time. This provides a history of changes that can be assessed with radioisotope dating, along with chemical measurements and/or evaluations of diatoms and pollen, in sections of a sediment core.

## When can sediment become a problem?

As sediment accumulates, it can eventually fill-in sections of a waterway until it becomes upland soil. For example, oxbow lakes that form from separated sections of rivers can eventually fill in with sediment (Figure 1-3a). Another example is an urban stormwater pond that fills in with sediment after many years of service as a best management practice (BMP) for stormwater runoff (Figure 1-3b). In the case of the oxbow lake, nature is taking its course. For the stormwater pond example, cities must manage this accumulated sediment in order to preserve the benefits of the BMP to reduce suspended sediment and contaminants from reaching downstream waters and to reduce flooding of urban areas.

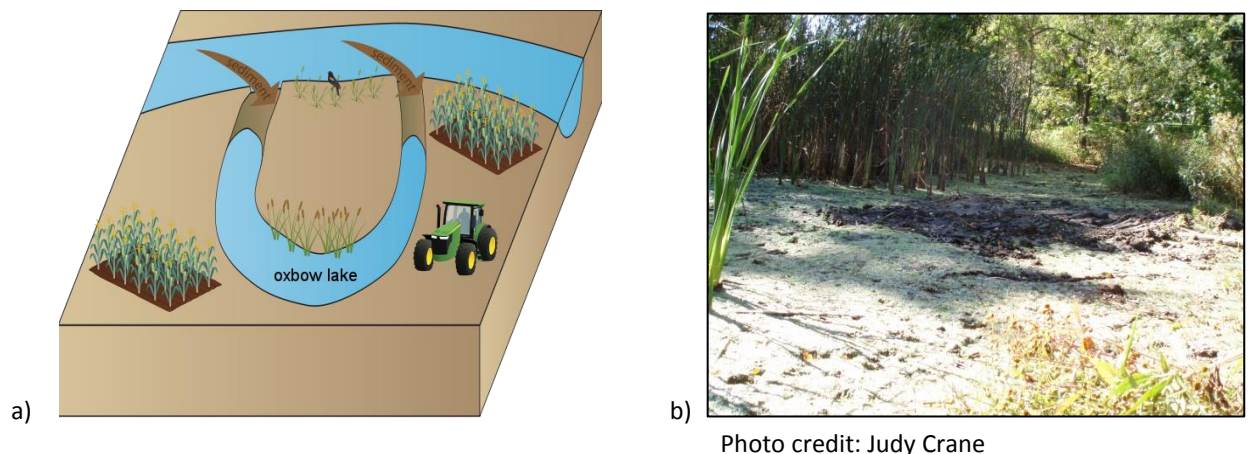


Figure 1-3. a) Example of an oxbow lake and b) a filled in stormwater pond in Woodbury, MN (diagram prepared by Judy Crane using the Integration and Application Network, University of Maryland Center for Environmental Science; [ian.umces.edu/imagelibrary/](http://ian.umces.edu/imagelibrary/)).

Accumulated sediment becomes a problem when it impairs designated uses of the waterway (e.g., navigation), impacts habitat for aquatic organisms, and/or results in the build-up of contaminants of potential concern. Contaminated sediments can become an important nonpoint source of nutrients and contaminants to the overlying water of ponds, wetlands, lakes, harbors, streams, and rivers. Several chemical and physical factors control the fate and transport of these nutrients and contaminants (Crane and Hennes 2007). Contaminated sediments can contribute to the following problems:

- Tumors and other deformities in bottom-dwelling fish
- Degraded benthic communities, which result in less food for fish and some wildlife



- Degraded fish and wildlife habitats
- Bioaccumulation of contaminants up the food chain, which may result in fish and wildlife consumption advisories for humans
- Potential human health risks from exposure to sediment-derived contaminants
- Aesthetic impairments
- Restrictions on navigational dredging and beneficial use of dredged material

Several of the above issues have contributed to beneficial use impairments (BUIs) in the St. Louis River AOC (Figure 1-4), including the Duluth-Superior Harbor (Figure 1-5a, b). A variety of government, tribal, business, academic, and nonprofit stakeholders, as well as potentially responsible parties, have contributed resources for the assessment, management, remediation, and restoration of contaminated sediment areas in this AOC (LimnoTech 2013a). Both Minnesota and Wisconsin share portions of this AOC, which is located along the southwestern edge of Lake Superior (Figure 1-4). The U.S. Environmental Protection Agency (EPA) removed the degradation of aesthetics BUI for this AOC during August 2014. Partner agencies have developed a roadmap for delisting other BUIs by 2025 (LimnoTech 2013a). Estimates for removing the remaining BUIs range from 300 - 400 million dollars (LimnoTech 2013a). The St. Louis River AOC represents the largest area in Minnesota impacted by contaminated sediments.

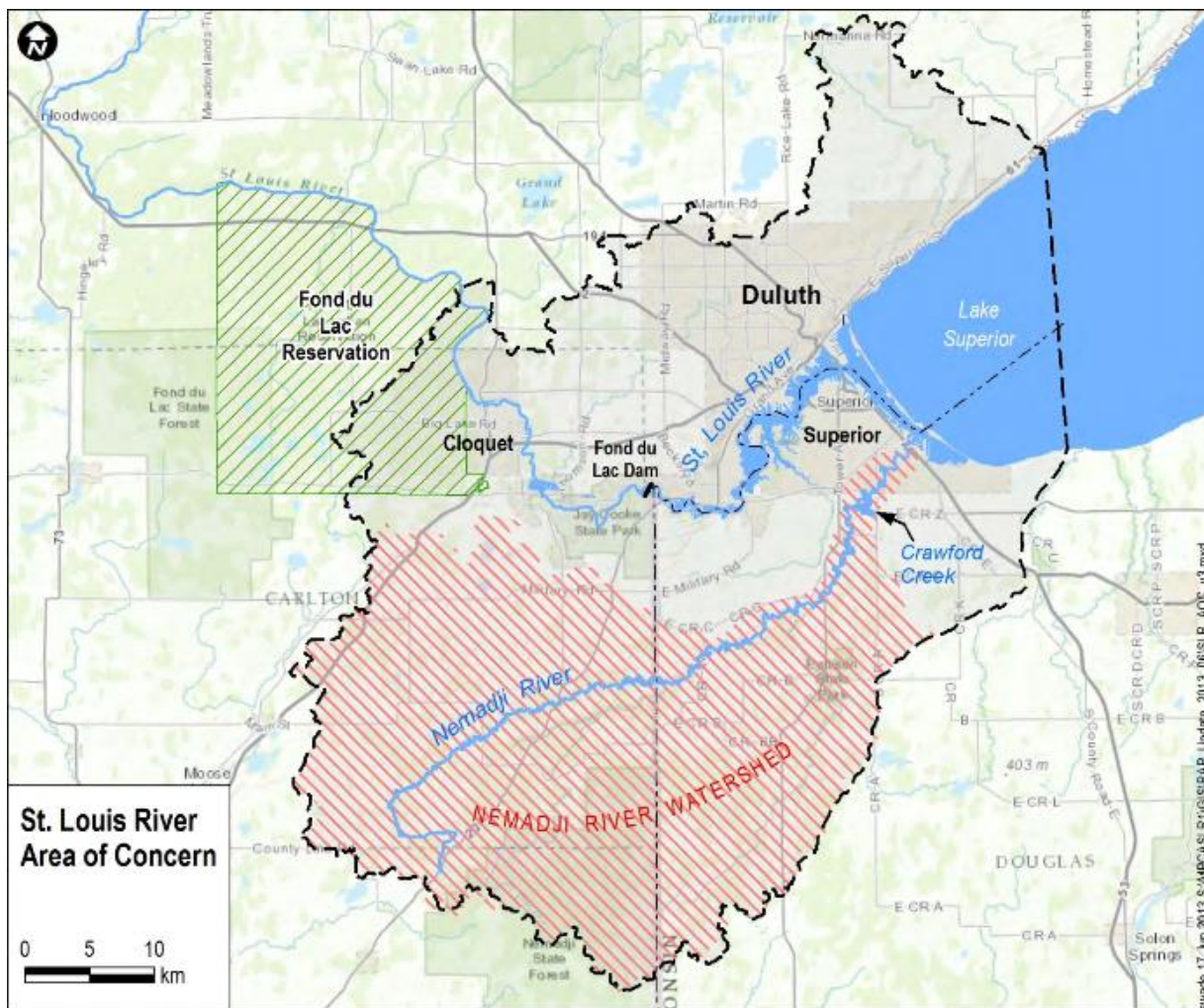


Figure 1-4. Boundaries of the St. Louis River Area of Concern (AOC).

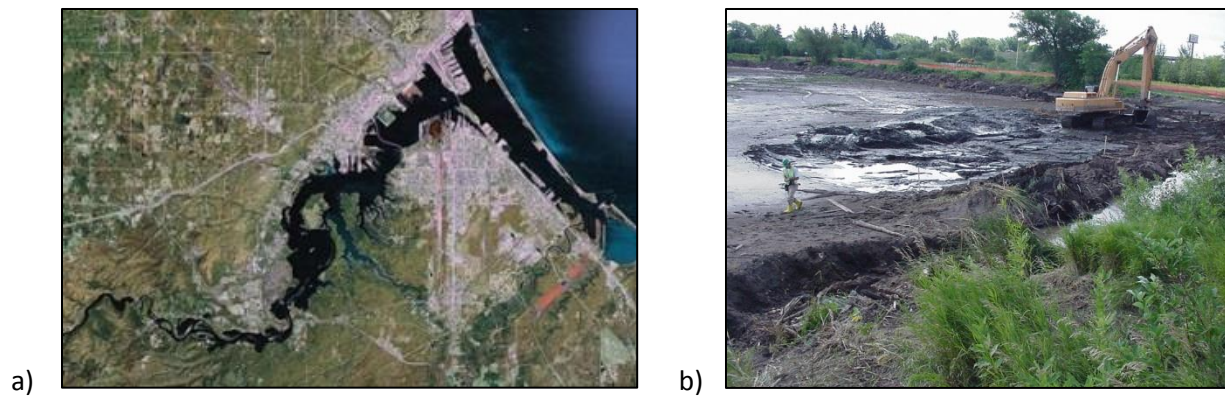


Figure 1-5. a) Aerial view of the St. Louis River AOC and b) sediment remediation at the Hog Island/Newton Creek site along the Superior Harbor in Wisconsin.

## What are sediment quality indicators?

Indicators provide a sign of ecosystem health that are meaningful and relevant to stakeholder groups, as well as to scientists. In order to assess sediment quality, scientists rely on specific indicators such as:

- Sediment chemistry (Figure 1-6a)
- Sediment toxicity tests (Figure 1-6b)
- Benthic invertebrate community structure (Figure 1-6c)
- Sediment Quality Triad, which is a tool based on associations between sediment chemistry, sediment toxicity tests, and *in situ* biological effects
- Physical characteristics (e.g., particle size, sedimentation rate)
- Tissue chemistry
- Water chemistry
- Pore water toxicity (i.e., exposure of aquatic plants, invertebrates, and/or fish larvae to interstitial water extracted from the sediments)
- Fish health (e.g., incidence of tumors, fin rot)
- Water column and elutriate toxicity, where the term elutriate refers to dilutions of sediment material



Figure 1-6. a) Collection of sediment sample for sediment chemistry measurements, b) sediment toxicity tests, and c) collection of benthic invertebrate community samples.

Sediment-related indicators provide many “tools in the toolbox” that can be used to directly assess trends in sediment quality conditions over time. These indicators are further strengthened by making comparisons with watershed variables like land use. Each indicator is composed of distinct measurements called metrics (Crane et al. 2000). An example of a metric important to sediment



chemistry is the dry weight concentration of a contaminant (e.g., mercury). Comparison of the metrics to numerical targets lets scientists assess how “clean” the sediments are in a particular area. The use of several metrics (e.g., sediment chemistry, sediment toxicity, benthic invertebrate community) provides a weight-of-evidence approach that results in more comprehensive sediment assessments.

The Minnesota Pollution Control Agency (MPCA) uses numerical sediment quality targets (SQTs) as benchmark values for making comparisons to surficial sediment chemistry measurements (Crane et al. 2000, 2002; Crane and MacDonald 2003; Crane and Hennes 2007). The SQTs are based on two types of narrative SQTs (Crane et al. 2000).

- The Level I SQTs are intended to identify contaminant concentrations below which harmful effects on benthic invertebrates (Figure 1-7) are unlikely to be observed.
- The Level II SQTs are intended to identify contaminant concentrations above which harmful effects on benthic invertebrates are likely to be observed.

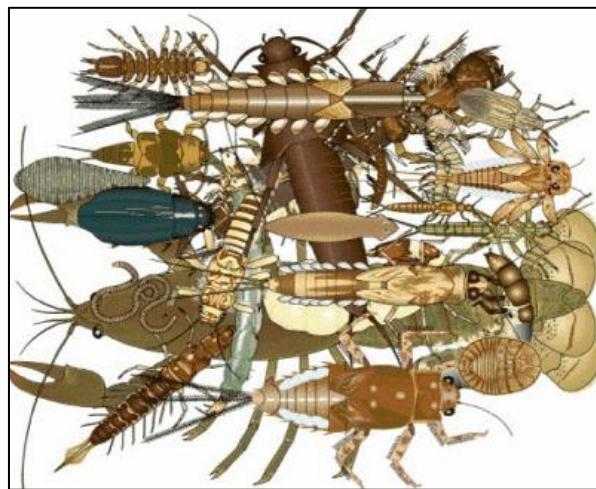


Figure 1-7. Freshwater benthic invertebrates typically found in clean sediment environments (from: <http://www.dep.wv.gov/WWE/getinvolved/sos/Pages/Benthics.aspx>).

These narrative objectives do not address the potential for bioaccumulation of certain contaminants or the associated effects on those species that consume aquatic organisms (i.e., wildlife and humans; Crane et al. 2000). The MPCA did not have enough matching sediment chemistry and toxicity data to develop SQTs specific to Minnesota. Therefore, other sediment quality guidelines were evaluated that met these narrative objectives.

The MPCA adopted Level I and Level II SQTs for a common suite of contaminants (Tables 1-1 and 1-2). These include eight metals and metalloids, 13 individual polycyclic aromatic hydrocarbons (PAHs), total PAHs ( $\Sigma\text{PAH}_{13}$ ), total polychlorinated biphenyls (PCBs), 10 organochlorine pesticides, and polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/Fs; Crane and Hennes 2007). Most of the SQTs were adopted from consensus-based sediment quality guidelines (MacDonald et al. 2000), for which most of the Level I SQTs correspond to threshold effect concentrations (TECs) and most of the Level II SQTs correspond to probable effect concentrations (PECs). Since sediments often contain a mixture of contaminants, the MPCA also uses SQT values for mean probable effect concentration quotients (PEC-Qs). The mean PEC-Qs provide a sediment assessment tool that distills data from a mixture of contaminants (i.e., certain metals,  $\Sigma\text{PAH}_{13}$ , and/or Total PCBs) into one unitless index (Crane and Hennes 2007). In addition, the mean PEC-Qs provide a way to compare sediment quality over time and space

Table 1-1. Recommended Level I and Level II Sediment Quality Targets (SQTs) for the Protection of Sediment-dwelling Organisms (Crane *et al.* 2000, 2002)

Chemical	Aquatic Life		Source <sup>†</sup>
	Level I SQT	Level II SQT	
<b>Metals (in mg/kg dry wt.)</b>			
Arsenic <sup>§</sup>	9.8	33	MacDonald et al. (2000)
Cadmium* <sup>§</sup>	0.99	5.0	MacDonald et al. (2000)
Chromium <sup>§</sup>	43	110	MacDonald et al. (2000)
Copper* <sup>§</sup>	32	150	MacDonald et al. (2000)
Lead* <sup>§</sup>	36	130	MacDonald et al. (2000)
Mercury	0.18	1.1	MacDonald et al. (2000)
Nickel <sup>§</sup>	23	49	MacDonald et al. (2000)
Zinc* <sup>§</sup>	120	460	MacDonald et al. (2000)
<b>PAHs (in µg/kg dry wt.)</b>			
2-Methylnaphthalene	20	200	CCME (1999)
Acenaphthene	6.7	89	CCME (1999)
Acenaphthylene	5.9	130	CCME (1999)
Anthracene*	57	850	MacDonald et al. (2000)
Fluorene	77	540	MacDonald et al. (2000)
Naphthalene* <sup>§</sup>	180	560	MacDonald et al. (2000)
Phenanthrene* <sup>§</sup>	200	1200	MacDonald et al. (2000)
Benz(a)anthracene* <sup>§</sup>	110	1100	MacDonald et al. (2000)
Benzo(a)pyrene* <sup>§</sup>	150	1500	MacDonald et al. (2000)
Chrysene* <sup>§</sup>	170	1300	MacDonald et al. (2000)
Dibenz(a,h)anthracene	33	140	MacDonald et al. (2000); CCME (1999)
Fluoranthene*	420	2200	MacDonald et al. (2000)
Pyrene* <sup>§</sup>	200	1500	MacDonald et al. (2000)
Total PAHs* <sup>§</sup>	1600	23000	MacDonald et al. (2000)
<b>PCBs (in µg/kg dry wt.)</b>			
Total PCBs* <sup>§</sup>	60	680	MacDonald et al. (2000)
<b>Pesticides (in µg/kg dry wt.)</b>			
Chlordane*	3.2	18	MacDonald et al. (2000)
Dieldrin*	1.9	62	MacDonald et al. (2000)
Sum DDD*	4.9	28	MacDonald et al. (2000)
Sum DDE* <sup>§</sup>	3.2	31	MacDonald et al. (2000)
Sum DDT*	4.2	63	MacDonald et al. (2000)
Total DDT*	5.3	570	MacDonald et al. (2000)
Endrin	2.2	210	MacDonald et al. (2000)
Heptachlor epoxide*	2.5	16	MacDonald et al. (2000)
Lindane (gamma-BHC)	2.4	5	MacDonald et al. (2000)
Toxaphene	0.1	32	NYSDEC (1999) <sup>‡</sup>

Table 1-1. Continued

Chemical	Aquatic Life		Source <sup>†</sup>
	Level I SQT	Level II SQT	
Mean PEC-Q	0.1	0.6	USEPA 2000a

SQT = sediment quality target; PEC-Q = probable effect concentration quotient.

<sup>†</sup> Some SQT values were rounded to two significant figures from the original source.

\* Reliable consensus-based threshold effect concentration (TEC) values that were adopted as Level I SQTs [i.e., predictive ability  $\geq 75\%$  and  $\geq 20$  samples below the TEC values (MacDonald et al. 2000)].

<sup>§</sup> Reliable consensus-based probable effect concentration (PEC) values that were adopted as Level II SQTs [i.e., predictive ability  $\geq 75\%$  and  $\geq 20$  samples predicted to be toxic (MacDonald et al. 2000)].

<sup>‡</sup> Originally based on  $\mu\text{g/g}$  organic carbon; assumed total organic carbon (TOC) = 1%.

Table 1-2. Additional Recommended Level I and Level II SQTs for Chemicals of Interest (Crane and Hennes 2007)

Chemical	Aquatic Life		Source
	Level I SQT	Level II SQT	
<i>Polychlorinated dibenzo-p-dioxins/ dibenzofurans (in ng TEQ/kg dry wt.)</i> PCDD/Fs*	0.85	21.5	CCME 1999

SQT = sediment quality target; TEQ = toxic equivalent; PCDD/Fs = polychlorinated dibenzo-*p*-dioxins/dibenzofurans.

\* Values are expressed as TEQ units, based on Van den Berg et al.'s (1998) toxic equivalency factor (TEF) values for fish. There is currently insufficient information to determine TEFs for invertebrates.

(Long et al. 2006). Based on matching sediment chemistry and sediment toxicity data sets, the mean PEC-Qs have been found to provide a reliable basis for classifying sediments as toxic or not toxic in the St. Louis River AOC, in the larger geographic areas of the Great Lakes, and elsewhere in North America (Crane et al. 2000, 2002). Thus, similar relationships would be expected at other aquatic sites in Minnesota.

## What do we know about ambient sediment quality in Minnesota?

The MPCA has limited information about sediment quality conditions throughout the state of Minnesota. Most data have been collected from contaminated areas impacted by past industrial and municipal point sources, as well as old landfills. For the St. Louis River AOC, sediment quality data from a number of stakeholders have been incorporated into different phases of a GIS-based sediment quality database (Crane 2006) that has been expanded into a data management system. This new system also includes restoration project objectives and other environmental data. The MPCA's webpage on "Contaminated Sediment Studies: St. Louis River Area of Concern" contains information on completed and in-progress sediment studies led by the MPCA and its collaborators and consultants. This webpage is available at: <https://www.pca.state.mn.us/water/sediment-studies-st-louis-river-area-concern>.

Determining ambient sediment quality is important for further assessing the ecological health of waterways and for determining ambient background concentrations of contaminants that can be compared to contaminated areas. State and Federal laws have resulted in substantial reductions in point sources of contaminants and nutrients in waterways, but nonpoint sources of pollution are a growing concern. These nonpoint sources are harder to control and include atmospheric deposition of contaminants, farm and feedlot runoff, storm sewers, failing septic systems, and runoff from urban areas (e.g., paved surfaces and lawns).

Contaminants that build up in the sediment and food chain are of particular concern, especially mercury, PCBs, PCDD/Fs, and organochlorine pesticides. PAHs are a class of ubiquitous urban contaminants that preferentially adsorb to sediment but are rapidly metabolized by fish, leading to little bioaccumulation (van der Oost et al. 2003). The ability to metabolize PAHs is highly variable in benthic invertebrates (Meador 2003). Endocrine disrupting compounds and other emerging contaminants, like certain flame retardants, are being detected in some Minnesota sediments. However, the MPCA has no SQT values for emerging contaminants.

## Purpose of this report

The purpose of this report is to assemble and evaluate ambient sediment chemistry and particle size data from multiple Minnesota waterways. This effort will give us a snapshot of the statistical range of potential contaminants of concern, and it will also allow us to determine if major land uses in the watersheds of a random set of lakes influence analyte concentrations in surficial sediments. In addition, we will compare a suite of contaminants to their corresponding Level I and Level II SQT values, use multivariate statistical techniques to tease out relationships in complex data sets, evaluate sources of PAHs and PCDD/Fs, and determine ambient background threshold values of contaminants. Other agency-related sediment quality data sets, excluding known contaminated areas, will be compared to the core lake sediment data evaluated in this report. These results will be used to help prioritize agency activities related to ambient sediment quality issues.

## Audience for this report

This report was designed to reach multiple audiences. The Executive Summary and Introduction were prepared for an educated layperson to read, such as concerned citizens, stakeholder groups, legislators, MPCA managers, and others wanting a short synopsis of this report. The technical data evaluation sections of this report include a short highlights box at the beginning of each section to provide the main points of that section. Additional technical details are provided in these sections and the appendices to describe the data evaluations in more detail, including the use of multivariate statistical and

environmental forensic techniques. These technical sections will be of greatest interest to other researchers, consultants, and agency staff. This report includes the analysis of 19,573 sample results for 281 unique chemicals, chemical groups, and physical parameters. As such, readers can pick and choose the sections of greatest interest to them.

## Limitations of this report

This report is subject to the following limitations:

- Sediment quality data from Superfund sites and sediment assessment areas designated for remedial action in the St. Louis River AOC were excluded.
- Sediment chemistry data were limited to surficial sediments (i.e., upper 15 cm or 6 inches); by excluding deeper sediment core sections, temporal differences were not assessed.
- Level I and Level II SQT values were not available for some of the contaminants included in this report.
- Other sediment quality indicators (e.g., sediment toxicity, benthic invertebrate community) were not considered due to resource issues and the paucity of data outside the St. Louis River AOC.
- Data sets from the MPCA were given higher priority than other stakeholder data sets.
- Quality assurance/quality control (QA/QC) procedures were not evaluated for non-MPCA data sets.
- Data may not be geographically representative of all ecoregions or major land uses in Minnesota.
- Stormwater ponds were not considered, even if they had a lake identification number from the Minnesota Department of Natural Resources (MDNR), because of their primary use as a stormwater BMP. However, some of the wetland data used in this report were found, after data analyses had been completed, to be from stormwater-impacted areas.
- Upland soil samples adjacent to waterbodies were not included.
- Water quality and habitat data were not assessed to provide comprehensive evaluations of waterbodies included in this report.
- The results may change as more ambient sediment chemistry data are collected in Minnesota.

## For further information

For further information about the content of this report, contact Judy L. Crane, Ph.D. at [judy.crane@state.mn.us](mailto:judy.crane@state.mn.us) or 651-757-2293 (voice).

## Section 2: Methods

---

This chapter describes how sediment quality data sets were selected, evaluated, analyzed, and incorporated into this report. In addition, the field and analytical methods for MPCA data sets not reported elsewhere are provided.

### Search for sediment quality data sets

#### Solicitation process

Multiple methods were used to select surficial sediment quality data sets collected in Minnesota since 1990. The year 1990 was used as a lower-end cut-off because better QA/QC procedures for sediment chemistry assessments in Minnesota were normally used after that time. In addition, the search was limited to sediment chemistry and particle size parameters due to the paucity of other indicators (e.g., sediment toxicity tests) beyond the St. Louis River AOC. Surficial sediments were selected because they were most relevant for biological exposures and future status and trends work. Methods for selecting sediment quality data included:

- Personal knowledge of sediment chemistry and particle size data sets
- Inventory of sediment quality studies listed on the MPCA's Contaminated Sediment webpages (<https://www.pca.state.mn.us/water/contaminated-sediments>)
- Availability of data in government databases
- Phone and/or email solicitations of staff from the MPCA, U.S. Geological Survey (USGS), U.S. Environmental Protection Agency (EPA) Region 5, U.S. Army Corps of Engineers, Metropolitan Council, University of Minnesota, and Science Museum of Minnesota's St. Croix Watershed Research Station
- Internet searches, particularly for "grey literature" and peer-reviewed journal articles

Electronic copies of sediment chemistry/particle size data sets and any associated reports were obtained, where possible.

#### Evaluation process

Information on available sediment quality data sets was compiled in a Microsoft™ Excel 2000 spreadsheet. As a first step, several non-Superfund data sets from the St. Louis River AOC, including reference and randomly collected samples, were included. Secondly, sediment quality data sets from other areas in Minnesota were compiled. Some of these studies included emerging contaminants and/or conventional contaminants lacking SQT values. In all, 54 data sets were considered. This compilation provided an overall summary of available surficial sediment chemistry/particle size data in Minnesota.

The Excel spreadsheet was populated with a number of data fields. These fields included:

- Database Study ID: for data obtained from an existing sediment database
- Study Name
- Geographic Area
- Year Sampled
- Chemical Parameters: by chemical class (e.g., metals, PAHs)
- Availability of GIS Information
- File Names
- Study Contact
- Reference(s)
- Notes



Not all data fields were filled in, because it became evident that the scope of this project would need to be refined further based on limited resources.

Next, data sets were evaluated for their relevance in determining ambient concentrations of contaminants in surficial sediments. Data sets which included randomly collected surficial sediment samples from throughout the State of Minnesota were of highest relevance. Data sets from known contaminated areas were of low relevance.

Data sets were also assessed for their availability. Electronic data sets, preferably in a database format, were preferred over paper copies. Some older, unpublished data sets were no longer available in any form from the study contacts. Requests for follow-up information from some study contacts were not fulfilled, which lessened inclusion in this report.

Data sets were evaluated based on the number of samples included in the study and the analytical methods used. Data sets with small numbers of samples were of low relevance, because comparisons to other data sets would have low statistical strength. Studies that screened the samples into certain size fractions prior to analysis were also of low relevance, because bulk sediment measurements were preferred. This situation applied primarily to USGS studies of metals and metalloids, in which about 90% of the samples were screened using a <62 micron size fraction. In addition, studies that analyzed sediments for conventional metals rather than simultaneously extractable metals (SEM) and acid volatile sulfides (AVS) were preferred. This was because the conventional metal results would be directly comparable to the MPCA's Level I and Level II SQT values.

## Selection process

Data sets were winnowed down to make the scope of this project more manageable. Top priority went to studies that included a statistically randomized study design and included surficial sediment samples from throughout the state. Only one study met these criteria: a 2007 MPCA sediment survey of 50 randomly selected and four *a priori* reference lakes led by Judy Crane and Steve Hennes. This internally-funded study used the field resources of the U.S. EPA's National Lake Assessment (NLA) project to collect surficial sediment from the deepest area of each lake. The MPCA and MDNR were strong collaborators for the Minnesota component of the nationwide NLA study (Monson and Heiskary 2008, Heiskary and Lindon 2010). The field and analytical methods of the 2007 sediment survey are described further in the Methods section. The evaluation and interpretation of this large data set was the primary focus of this ambient sediment report. Although these sediment data were not a formal part of the U.S. EPA's nationwide NLA study, they will be referred to as the National Lake Assessment Project (NLAP) sediment data throughout this report. Other MPCA staff involved in the water quality and habitat-related measures of the 2007 NLA draw of Minnesota lakes usually referred to these data as NLAP data, too (Monson and Heiskary 2008, Heiskary and Lindon 2010). In more recent surveys, MPCA staff switched to the NLA terminology.

Other large sediment quality data sets were selected to compare to the 2007 NLAP sediment study. It was of particular interest to compare sediment chemistry parameters from different water body types (e.g., river, estuary, harbor, or wetland) to the NLAP sediment samples. Data collected by the MPCA or a MPCA contractor were also of high interest due to greater agency involvement and the availability of QA/QC information. One of the studies selected included a multiyear, mostly unpublished wetland data set from Mark Gernes (MPCA). This surficial sediment data set included metals, metalloids, and chloride from wetlands located primarily in the southern half of the state.

Due to the importance of the St. Louis River AOC in northeastern Minnesota, data from multiple sediment assessment studies were considered. Sediment chemistry data from a 1995 Regional Environmental Monitoring and Assessment Program (R-EMAP) study in the lower St. Louis River AOC

represented both randomly collected surficial sites and 20 *a priori* training sites of low and high contamination (Breneman et al. 2000; Crane et al. 2005). However, SEM and AVS were measured instead of conventional metal methods, and PAHs were only analyzed by a fluorometric screening method at some sites (Peterson et al. 2002). In addition, more recent sediment quality data had been collected in this AOC as part of Great Lakes Restoration Initiative funding. Thus, the R-EMAP data were not considered further. Instead, four recent sediment quality data sets from the St. Louis River AOC were selected for this effort (Somat Engineering 2012a, b; Weston Solutions, Inc. 2012a, b). Data from known contaminated sites (LimnoTech 2013b) were excluded because these data would adversely skew the ambient data results. Even so, sediment quality conditions in this AOC may not be representative of the rest of Minnesota because of widespread legacy contamination. The field sampling and analytical methods, as well as evaluation of these data sets, will be described in a subsequent section.

## MPCA's statewide sediment survey of 54 NLAP lakes in 2007

### Lake selection

The selection of study lakes for sediment samples was the same as those selected for the Minnesota component of the 2007 nationwide NLA study, which has been described by Monson and Heiskary (2008). Briefly, the U.S. EPA developed a probability-based network of potential study lakes nationwide so that statistically valid estimates of the condition of all lakes could be obtained with a known degree of confidence. Specifically, a Generalized Random Tessellation Stratified survey design for a finite resource was used for the site selection (USEPA 2009a). The design was developed to include a representative subset of the lakes that were sampled in the EPA's 1972 National Lake Eutrophication study (USEPA 2007a, 2009a). The NLA set of lakes in the conterminous United States included natural and built freshwater lakes, ponds, and reservoirs >10 acres (i.e., 4.05 ha) in size and at least one meter in depth. The goal of the NLA survey was to address two key questions about the quality of the nation's lakes, ponds, and reservoirs (USEPA 2007a):

1. What percent of the nation's lakes are in good, fair, and poor condition for key indicators of trophic state, ecological health, and recreation?
2. What is the relative importance of key stressors such as nutrients and pathogens?

Minnesota received 41 lakes as part of the original draw of lakes for the national survey. The NLA design included an "oversample" of additional randomly selected lakes so that any state wishing to conduct a state scale survey could be accommodated. The MPCA added nine lakes to the survey in the order given from the "oversample" group to yield the 50 lakes needed for statistically-based statewide estimates of condition (Monson and Heiskary 2008; Figure 2-1). Due to drought conditions during the summer of 2007 and/or the inaccessibility of some lakes that did not have public access, some of the original draw lakes were replaced by the oversample list of randomly selected lakes. The U.S. EPA added four *a priori* reference lakes that they thought would make good candidate reference lakes, based in part on state recommendations and evaluation of aerial photographs as described by Herlihy et al. (2013; Figure 2-1). Five size classes of lakes were represented in Minnesota's component of the 2007 study (n = 54):

- A. 4 – 10 ha: 4 lakes
- B. 10 – 20 ha: 3 lakes
- C. 20 – 50 ha: 11 lakes (including 2 reference lakes)
- D. 50 – 100 ha: 13 lakes
- E. >100 ha: 23 lakes (including 2 reference lakes)

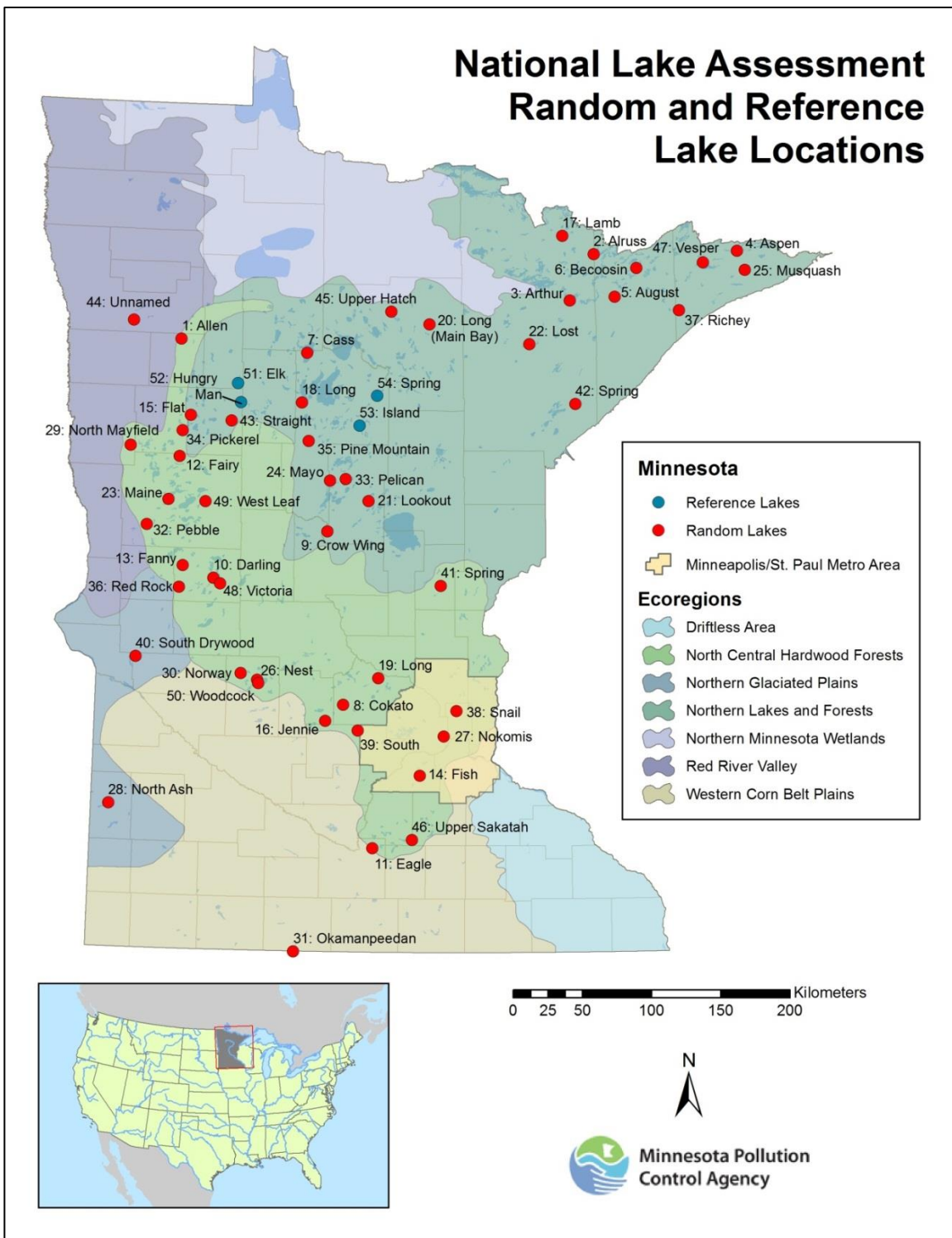


Figure 2-1. Map of random and reference lakes sampled in 2007 for Minnesota’s component of the NLA project. Sediment sampling was included for each lake as an independent, value-added project funded by the MPCA.

Other lake, watershed, ecoregion, and land use information was obtained for the NLAP lakes. In addition to surface area, the estimated volume and watershed area was compiled for each lake (Appendix A). Ecoregions in Minnesota were updated by the MDNR in September 2008, which resulted in four lakes changing ecoregions. The September 2008 ecoregion classifications are shown in Figure 2-1. This

group of ecoregions differed from the nine, aggregated Omenik Level 3 ecoregions delineated by the U.S. EPA for the continental United States (USEPA 2009b; Appendix A). Two of the Level 3 ecoregions covered Minnesota, including:

- Upper Midwest (UMW): 49 lakes (including the 4 reference lakes)
- Temperate Plains (TPL): 5 lakes

Land use type information for each lake watershed was obtained from other MPCA staff involved in the NLA project. Land use types included: developed, cultivated (i.e., agriculture), pasture and open land, forest, and lakes and wetlands (which included the surface area of the lake). The number of feedlots in each watershed was noted, too. The major land use categories for the Minnesota component of the NLA study are provided in Figure 2-2, Table 2-1, and summarized as follows:

- Developed: 2 lakes
- Cultivated: 20 lakes
- Forested: 24 lakes (including the 4 reference lakes)
- Lakes and wetlands: 8 lakes

Most of the study lakes were located in watersheds dominated by either forests or cultivated land, with a smaller number of lakes in watersheds dominated by lakes and wetlands. Only two lakes from developed watersheds in the Minneapolis-St. Paul, MN metropolitan area were included in this study.

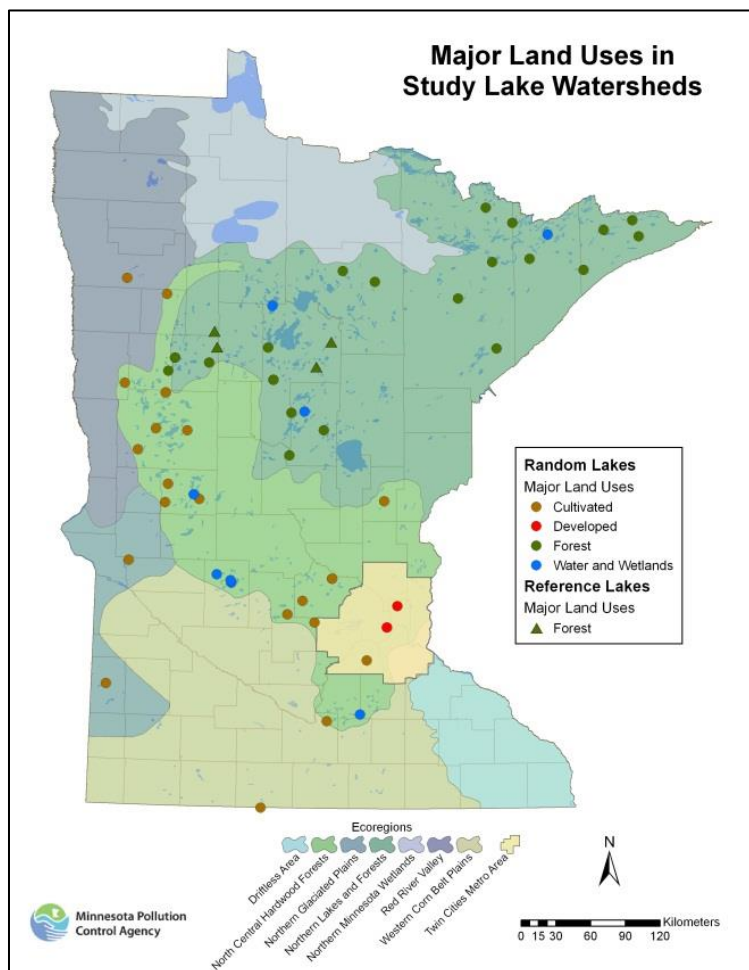


Figure 2-2. Major land uses in the watersheds of the 2007 NLAP sediment sample sites.

Table 2-1. Sediment Sample Site Information from the 2007 Minnesota NLAP Lakes

Short ID	Lake	County	Major Land Use	Station ID	CenUTM X-coordinate	CenUTM Y-coordinate
1	Allen	Mahnomen	Cultivated	440157CS07	291265	5260612
2	Alruss	St. Louis	Forested	690005CS07	589249	5321758
3	Arthur	St. Louis	Forested	690154CS07	571895	5288148
4	Aspen	Cook	Forested	160204CS07	692871	5324265
5	August	Lake	Forested	380691CS07	604245	5290895
6	Becoosin	Lake	Lakes & Wetlands	380472CS07	619923	5311767
7	Cass	Beltrami	Lakes & Wetlands	040030CS07	382139	5250364
8	Cokato	Wright	Cultivated	860263CS07	408112	4995651
9	Crow Wing	Crow Wing	Forested	180155CS07	396695	5121231
10	Darling	Douglas	Lakes & Wetlands	210080CS07	314152	5087606
11	Eagle (North)	Blue Earth	Cultivated	070060CS07	429053	4891913
12	Fairy	Otter Tail	Cultivated	560356CS07	289947	5175657
13	Fanny	Douglas	Cultivated	210336CS07	291868	5096790
14	Fish	Scott	Cultivated	700069CS07	463482	4944300
15	Flat	Becker	Forested	030242CS07	298038	5205584
16	Jennie	Meeker	Cultivated	470015CS07	394985	4984003
17	Lamb	St. Louis	Forested	690341CS07	566376	5335053
18	Long	Cass	Forested	110480CS07	378332	5214363
19	Long	Wright	Cultivated	860069CS07	433566	5014824
20	Long (Main Bay)	Itasca	Forested	310266CS07	470549	5271000
21	Lookout (Crocker)	Crow Wing	Forested	180123CS07	426418	5143039
22	Lost (Horseshoe)	St. Louis	Forested	690611CS07	542598	5256619
23	Maine (Round)	Otter Tail	Cultivated	560476CS07	281705	5144559
24	Mayo	Crow Wing	Forested	180408CS07	398509	5157935
25	Musquash	Cook	Forested	160104CS07	698556	5310304
26	Nest	Kandiyohi	Lakes & Wetlands	340154CS07	345873	5013656
27	Nokomis	Hennepin	Developed	270019CS07	480861	4972688
28	North Ash	Lincoln	Cultivated	410055CS07	238117	4924986

Table 2-1. Continued

Short ID	Lake	County	Major Land Use	Station ID	CenUTM X-coord	CenUTM Y-coord
29	North Mayfield	Clay	Cultivated	140029CS07	254495	5183897
30	Norway	Kandiyohi	Lakes & Wetlands	340251CS07	333940	5018593
31	Okamanpeedan	Martin	Cultivated	460051CS07	371798	4817170
32	Pebble	Otter Tail	Cultivated	560829CS07	265963	5126557
33	Pelican	Crow Wing	Lakes & Wetlands	180308CS07	409943	5159047
34	Pickereel	Becker	Forested	030287CS07	292061	5194318
35	Pine Mountain	Cass	Forested	110411CS07	383023	5186561
36	Red Rock	Douglas	Cultivated	210297CS07	289291	5080968
37	Richey	Cook	Forested	160643CS07	650907	5281291
38	Snail	Ramsey	Developed	620073CS07	490030	4991152
39	South	McLeod	Cultivated	430014CS07	418583	4977034
40	South Drywood	Swift	Cultivated	760149CS07	257837	5031152
41	Spring	Kanabec	Cultivated	330027CS07	478612	5081673
42	Spring	St. Louis	Forested	690129CS07	575838	5213371
43	Straight	Becker	Forested	030010CS07	327449	5201303
44	Unnamed	Polk	Cultivated	600307CS07	256715	5274580
45	Upper Hatch	Itasca	Forested	310770CS07	442983	5280200
46	Upper Sakatah	Le Sueur	Lakes & Wetlands	400002CS07	457752	4897695
47	Vesper	Cook	Forested	160414CS07	668195	5315930
48	Victoria	Douglas	Cultivated	210054CS07	319017	5083567
49	West Leaf	Otter Tail	Cultivated	560114CS07	308479	5142945
50	Woodcock (W. Woodcock)	Kandiyohi	Lakes & Wetlands	340141CS07	346720	5011319
51	Elk*	Clearwater	Forested	150010CS07	332103	5228383
52	Hungry Man*	Becker	Forested	030029CS07	334147	5214810
53	Island*	Cass	Forested	110102CS07	419943	5197592
54	Spring*	Cass	Forested	2D3008CS07	432731	5219161

\* Designated *a priori* reference lake.

## Field sampling methods

### Collection of sediment samples

Sediment samples were collected by the NLA field crews from the MPCA, U.S. EPA, and Leech Lake Band during June 26, 2007 through August 22, 2007. The Leech Lake Band was only involved in sampling Cass Lake (lake #7, Table 2-1), while the U.S. EPA field crew led the sampling of Allen (#1, Table 2-1) and the four *a priori* reference lakes (lakes #51 – 54, Table 2-1). The MPCA field crews sampled the other lakes. The NLA field crews followed the procedures in the draft Field Operations Manual (USEPA 2007a) for all their daily activities including: verifying lakes at the launch site, recording GPS coordinates, collecting and processing samples, following safety procedures, and record keeping. The crews were also given specific instructions for the collection of sediment samples for contaminant and particle size analysis, in addition to decontamination procedures to follow between sample sites. The field crews utilized motorized boats, except in the BWCAW where motorized boats were mostly prohibited. In those cases, they transported canoes and gear by foot to the study lakes; canoes were lashed together to provide a stabilized sampling platform. As part of the NLA activities, the field crews collected sediment samples with a modified K-B corer for diatom analysis and sediment mercury (USEPA 2007a). This same K-B corer was used for the collection of sediment samples for this MPCA-funded project.

A modified K-B corer with Lexan core tubes was used to collect sediment samples from the deepest location of each lake. The procedures were similar to the general coring procedures described in the NLA Field Operations Manual (USEPA 2007a). However, only the upper 15 cm of the sediment profile was collected and extruded into a large, pre-cleaned 1 L wide-mouthed glass jar with a Teflon-lined lid. For most lakes, two cores were collected in close proximity to each other, and each core was extruded into a separate labelled jar. Lakes from the BWCAW were more difficult to sample (i.e., by canoe), and only one sediment core sample was collected from each BWCAW lake. For five lakes, an extra sediment sample (i.e., field replicate consisting of two cores) was collected in close proximity to the original sample to assess field precision. Lakes with field replicates included: Fairy (#12), Flat (#15), Long (#19), Nokomis (#27), and Pine Mountain (#35). For the deeper lakes, the NLA crews had to drop the corer several times before they could obtain a cohesive sample. Sample tracking forms, specific to this independent project, were filled out in the field. Samples were stored on ice in coolers until they could be transported to refrigerators at the MPCA's Field Operations Center in St. Paul, MN.

The field crews followed a multi-step decontamination process between each lake. First at the sampling vehicle, they used a brush to wash the core tube and spatulas with Liquinox (non-phosphate detergent solution) and tap water. Next, they rinsed the core tube and Teflon® or stainless steel spatulas with tap water. This was followed by rinsing the inner core tube and spatulas with methanol. The waste solvent was captured in a solvent disposal container. The core tube and spatulas were then rinsed with deionized water. The equipment was air dried and then wrapped in foil for later use. While in the field, the K-B corer and spatulas were rinsed with lake water after collecting the NLA-specific sediment samples (i.e., diatoms and mercury), as well as between the first and second sediment chemistry core samples and between field replicates. A brush was also used to remove any visible sediment between field-collected samples.

### Collection of fish

The MPCA had an opportunity to leverage other internal funding for emerging contaminant analysis with ongoing fish collection efforts led around the state by the MDNR. Five NLAP lakes [August (#5), Cass (#7), Jennie (#16), Mayo (#24), and Nokomis (#27)] happened to be included in the MDNR's suite of lakes to be sampled for fish during June to September 2007. Funding was approved by MPCA management for the analysis of polybrominated diphenyl ethers (PBDEs) in fish tissue from these five

lakes. This data set would complement the sediment PBDE analyses for these lakes. Mark Briggs (MDNR) coordinated the collection of fish samples by MDNR Fisheries staff. For each lake, five fish were to be collected from each of the following trophic guilds: predator (northern pike or walleye), omnivore (pan fish; bluegill or yellow perch), and benthic fish (brown bullhead, yellow bullhead, or white sucker). However, the field crews forgot to collect the benthic fish from Mayo (#24) and Nokomis (#27) while they were collecting other predator and pan fish on the same sampling trip for two other MPCA studies. The field crews were not able to collect enough pan fish from one of the lakes for a field replicate so five additional predator fish (northern pike) from August (#5) were collected for the field replicate. The fish were collected with gill nets and trap nets. Weight and length measurements were taken in the field, the fish were wrapped in aluminum foil, and the fish were stored on ice in coolers until they could be transported back to the MPCA where the samples were stored in a walk-in freezer. Judy Crane and Steve Hennes selected five comparable fish for a particular species from each guild for analysis.

Frozen fish were shipped overnight on dry ice to AXYS Analytical Services Ltd. located in Sidney, British Columbia, Canada for processing and analysis. The samples were transferred to secure storage and kept at -20 °C prior to extraction. The length, sex, and age of the individual fish species were determined (Appendix A).

### **Sediment processing and transport to analytical laboratories**

The sediment samples were processed further at a laboratory at the MPCA's St. Paul office before subsamples were stored and transported to analytical laboratories. The samples were processed within one to 23 days of sample collection. For the two sediment core samples collected from most of the study lakes, Judy Crane and Steve Hennes composited the samples in a 1 L pre-cleaned Pyrex mixing cup. Large twigs and stones were removed while the samples were being homogenized with an extra-large pre-cleaned metal spoon. The BWCAW lakes and some of the other northeastern Minnesota lakes only had one sediment core sample, which was also homogenized in a 1 L pre-cleaned Pyrex mixing cup. Each homogenized sample was split-up into the following pre-cleaned containers: plastic jars for metals analysis by the Minnesota Department of Health (MDH), multiple pesticide-grade 250 mL amber glass jars with Teflon®-lined lids for organic chemical parameters, and Ziploc freezer bags for particle size samples. The sample jars were filled one-half to two-thirds full. At the time of sample processing, the full analytical component of hydrophobic organic chemicals had not been determined, pending additional internal funding for this project. One organics jar for each lake was labeled "PAHs and TOC," because these analyses were certain. Two to three jars for each lake were labeled as "extra sediment," with the intent these samples would be used for organic analyses to be determined. In addition, there was usually one other sample jar labeled as an "archive" sample for retention at the MPCA.

The sediment subsamples were stored differently, depending on the analyses. Sediment samples for 19 metals and metalloids were refrigerated and transported to the MDH Analytical Laboratory in batches for analysis soon after collection; MDH sediment lab sheets were filled out to accompany the samples. The particle size samples were stored in a MPCA cold room at 4°C, and the other sediment samples were stored in an adjoining walk-in freezer; these samples were stored until additional internal funding became available to complete a Joint Powers Agreement and subsequent contract amendment with the U.S. Fish and Wildlife Service (USFWS). The USFWS had negotiated better analytical prices than the MPCA could obtain for a small number of analytical laboratories. Thus, the MPCA was able to parlay this cost savings into a broader suite of organic contaminants to be analyzed on the sediment samples.

Even with the cost savings of using the USFWS analytical laboratories, there were insufficient funds to analyze the complete suite of organic contaminants on all of the samples. The following process was



developed on 10/10/2008 to create a short-list of samples for PCB congeners, organochlorine pesticides, and PCDD/Fs:

1. Based on the metal and metalloid results, the random samples were listed from high to low mean PEC- $Q_{\text{metals}}$  values. The number of extra amber glass jars for each lake was recorded with this list.
2. As a first cut, the random lakes with the highest mean PEC- $Q_{\text{metals}}$  values, and which also had three extra sediment samples, were selected. In order to broaden the geographic coverage of samples, lakes with only two extra sample jars were considered if their mean PEC- $Q_{\text{metals}}$  values were elevated. This resulted in the selection of two lakes from northeastern Minnesota [i.e., #4 (Aspen) and #5 (August)].
3. As a second cut, two field replicates were selected that also had three extra samples. This resulted in the selection of replicate samples for lakes #15 (Flat) and #27 (Nokomis).
4. As a third cut, the other random and reference samples were selected based on geographic coverage, watershed characteristics, and the number of extra sample jars. Two reference lakes were selected, including #52 (Hungry Man) and #53 (Island).

Judy Crane and Steve Hennes assisted Annette Trowbridge (USFWS) with preparing the electronic catalog, which was a work request with details about the field samples and parameters to be measured. The catalog was used to submit sediment samples to the USFWS contract laboratory for the following chemical and physical parameters:

- Aromatic scan for PAHs (reported in dry weight concentrations): 54 samples + 5 field replicates
- Total organic carbon (TOC; reported as a percentage): 54 samples + 5 field replicates
- Particle size (reported as percent clay, sand, and silt on a dry weight basis): 54 samples + 5 field replicates
- PBDEs (reported in dry weight concentrations): 52 samples + 5 field replicates
- Congener-specific PCB scan with organochlorine pesticide scan (reported in dry weight concentrations): 24 samples + 2 field replicates
- PCDD/F full scan (reported in dry weight concentrations): 23 samples + 2 field replicates.

Authorization to ship the sediment samples to the USFWS contract laboratory (TDI-Brooks International, College Station, TX) was provided on 5/12/2009. For jars that had been labeled as “extra,” another label was affixed to the lid to designate the chemical parameter for that sample. Three sample jars cracked while stored in the MPCA freezer for lakes #24, 43, and the field replicate for #15; those samples were replaced with “archived” samples. Due to the high moisture content of some samples, all available “extra” and “archived” sediment samples were shipped to TDI-Brooks International. All sediment samples were sent by overnight courier in large coolers packed with bubble wrap, packing peanuts, and blue ice; sample tracking forms were included in a Ziploc bag taped to the inside cover of each cooler lid. Three sediment sample jars arrived broken (i.e., the bottom was cracked off), but the samples were not compromised and were transferred to new sampling jars by laboratory staff. The temperature of the sediment samples was checked upon receipt, and the sample jars were stored in an access-controlled freezer (-20°C) until processing. Sediment samples for particle size were stored refrigerated at 4°C until processing. TDI-Brooks International shipped the sample jars for PCDD/Fs to a subcontract laboratory (Columbia Analytical Services) in Houston, TX for analysis.

## Analytical methods

### Sediment analyses by MDH

**18 metals and metalloids:** In order to determine environmentally available metals and metalloids, the sediment samples underwent a microwave extraction acid digestion step with nitric acid according to USEPA Method 3051A (USEPA 2007b). The samples were then filtered and analyzed by USEPA Method 6020 (USEPA 1994a) for 18 metals and metalloids by inductively coupled plasma – mass spectrometry (ICP-MS). This method measured ions produced by a radio-frequency inductively coupled plasma. The analyte species were nebulized, and the resulting aerosol was transported by argon gas into the plasma torch. The ions produced were entrained in the plasma gas and introduced, by means of an interface, into the MS. The ions produced in the plasma were sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences were assessed and either corrected or flagged (USEPA 1994a). Most of the analytical method detection limits were between 0.05 – 0.5 mg/kg dry wt., except for the following metals: aluminum (50 mg/kg dry wt.), barium (2.5 mg/kg dry wt.), manganese (5 mg/kg dry wt.), vanadium (1 mg/kg dry wt.), and zinc (5 mg/kg dry wt.). These reporting limits were elevated due to the high moisture content of some samples.

The QC samples followed the procedures provided in USEPA Method 6020 (USEPA 1994a). This included the use of mixed calibration standard solutions, analytical blanks, post-digestion spike additions, and one analytical duplicate per batch of 20 samples. The samples were extracted and analyzed within their extraction holding time (180 days) and analysis holding time (180 days).

**Mercury:** Subsamples of sediment were digested one of two ways as described in USEPA Method 7471A (USEPA 1994b). Next, each sample was analyzed by cold-vapor atomic absorption (CVAA; USEPA 1994b). This procedure was based on the absorption of radiation at the 253.7 nm wavelength by mercury vapor. The mercury was reduced to the elemental state and aerated from solution in a closed system. The mercury vapor then passed through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) was measured as a function of mercury concentration. Total mercury (inorganic and organic) was measured. The method detection limit and reporting limit for mercury were both 0.05 mg/kg dry wt. This was higher than MDH's normal reporting limit of 0.005 mg/kg dry wt. due to the high moisture content of some samples.

The QC samples followed the procedures provided in USEPA Method 7471A (USEPA 1994b). A calibration curve was constructed by plotting the absorbances of standards versus micrograms of mercury. Analytical blanks, spiked samples, and analytical duplicates were analyzed, too. The analysis holding time was 28 days.

### Sediment analyses by USFWS contract laboratories

Other chemical and physical analyses of sediment samples were performed by TDI-Brooks International and their subcontract laboratory (Columbia Analytical Services) for PCDD/Fs. The analytical methods were comparable to those designated by the USFWS on their web site for analytical services. TDI-Brooks International's Standard Operating Procedures (SOPs) were followed for all processes in the receipt, processing, extraction, analysis, and reporting of environmental data. As specified in the MPCA's Joint Powers Agreement with USFWS, all samples were analyzed and/or extracted within 30 days of processing the samples (e.g., thawing the frozen samples). A full description of the analytical methods was provided in the final catalog results. The moisture content of each sediment sample was run to determine how much water was in the sediment samples so that the results could be reported in dry weight measurements.

For organic contaminants (e.g., PAHs, chlorinated pesticides, and PCBs), sediment from the sample jars were composited together and these analytes were extracted, isolated, and concentrated from the

sediment matrix. The sediment samples were freeze dried, powdered, and homogenized prior to extraction. Sediments for PAHs, PCBs, and organochlorine pesticides were extracted in dichloromethane using a Dionex ASE200 Accelerated Solvent Extractor. The extracts were concentrated and then purified using alumina/silica gel chromatography columns. The resultant eluent was concentrated to a final volume of 1.0 mL before analysis. A synopsis of the important analysis steps for each group of chemical and particle size parameters is provided below. This synopsis is based on analytical methods provided by TDI-Brooks International.

**PAH analysis:** The analysis of 43 parent and alkylated PAHs, as well as biphenyl, was performed using gas chromatography/mass spectrometry (GC/MS) in selected ion monitoring (SIM) mode. The method detection limits (MDLs) for this method were low, with most compounds below 0.5 µg/kg dry wt.

Sample extracts were analyzed in a Hewlett Packard (HP) model 5890 GC and model 5972 MS operated in SIM using a capillary column. The GC was operated in splitless mode, and the capillary column was an Agilent Technologies HP-5MS (60 m x 0.25 mm ID and 0.25 µm film thickness). The carrier flow was by electronic pressure control, and the carrier gas was helium at a flow rate of 1 mL/minute. The temperature of the injection port was 300°C, and the transfer line was 290°C. The initial oven temperature was 60°C, the ramp rate was 7°C/minute to a final oven temperature of 310°C, which was held for 20 minutes. The data acquisition system allowed for the continuous acquisition and storage of all data during analysis and was capable of displaying ion abundance versus time or scan number.

Each batch of samples run on the GC/MS-SIM included a portion of the samples and the following QC samples: method blank, analytical duplicate, matrix spike, and a matrix spike duplicate.

A calibration curve was established by analyzing each of five calibration standards (analyte concentrations ranging from 0.02 to 1 mg/mL) and determining a relative response factor (RRF) for each analyte. For analyte identification, the extracted ion current profiles of the primary m/z and the confirmatory ion for each analyte must be at a maximum in the same scan or within one scan of each other. In addition, the retention time must fall within 5 seconds of the retention time of the authentic standard or alkyl homolog groups. Calibration check standards were interspersed throughout an analytical batch in order to insure the instrument's integrity. A diluted oil standard was used as a retention index solution for compounds not found in the calibration solution (e.g., alkylated PAH homolog groups). Analyte concentrations were determined using the internal standard method and analyte concentrations were corrected for surrogate recovery. The relative peak heights of the primary mass ion compared to the confirmation or secondary mass ion needed to fall within 30% of the relative intensities of these masses in a reference mass spectrum.

**Organochlorine pesticide and PCB analysis:** The analysis of 28 organochlorine pesticides and metabolites, as well as Total PCBs and 114 individual and coeluting groups of PCB congeners was performed using a high resolution GC with electron capture detection (ECD). The MDLs were generally <0.2 µg/kg dry wt.

The sample extracts were analyzed on an HP model 5890 GC equipped with an ECD. Approximately 1 mL of sample was injected using an HP model 7673A autosampler. The GC/ECD was set-up with dual columns. The primary capillary column was a J&W DB-5 (30 m x 0.24 mm ID and 0.25 µm film thickness) or equivalent. The second confirmation column was a J&W DB-17HT (30 m x 0.25 mm ID and 0.15 µm film thickness). The inlet system was splitless, and the carrier gas was helium at a flow rate of 1 mL/minute using electronic pressure control. For the analysis of standard halogenated hydrocarbons, the temperature of the injection port was 275°C and the detector was 325°C. The initial oven temperature was 100°C with a hold time of 1 minute. The ramp rate was 5°C/minute to 140°C with a hold time of 1 minute, followed by a ramp rate of 1.5°C/minute to 250°C with a hold time of 1 minute

and finally a ramp rate of 10°C/minute to 300°C with a final hold time of 5 minutes. For planar PCBs, the GC/ECD was operated in the splitless mode with helium as the carrier gas with a flow rate of 1 mL/minute. The temperature of the injection port was 275°C and the detector was 325°C. The initial oven temperature was 100°C, which was held for 1 minute. The ramp rate was 10°C/minute to 150°C, followed by a ramp rate of 6.0°C/minute to 270°C with a hold time of 3 minutes. The retention time of sample analytes needed to fall within 15 seconds of the retention time of analytes in a calibration standard or a retention index solution. The levels of toxaphene were determined using the retention index solution of a complex mixture. The data acquisition system used HP Chemstation software.

Each sample batch run through the GC/ECD included a subset of samples and the following QC samples: method blank, analytical duplicate, matrix spike, and a matrix spike duplicate.

A calibration curve was established by analyzing 2 mL each of five calibration standards (analyte concentrations ranging from 0.005 to 0.200 mg/mL) and fitting the data to a quadratic equation. Calibration check standards were interspersed throughout an analytical batch in order to ensure the instrument's integrity. An Aroclor mixture was used as a retention index solution for individual PCBs not found in the calibration solution, and individual PCB congener retention times were based on pattern recognition. Analyte concentrations were determined using the internal standard method, and analyte concentrations were corrected for surrogate recovery.

If needed, the presence of pesticides and PCBs were confirmed by GC/MS in either full scan or SIM mode. Samples were initially screened by GC/ECD and GC/MS to confirm the presence of specific analytes in a sample. When analytes were detected at 10 times the SIM limit of detection, they could be confirmed by GC/MS-SIM. In this case, the samples were analyzed on a HP 5890 GC/5972 MS. The GC was temperature-programmed and operated in splitless mode. The analytical column was an Agilent Technologies HP5MS (60 m x 0.25 mm ID and with a 0.25 µm film thickness). The carrier gas was helium with a flow rate of 1 mL/minute. The temperature of the injection port was 300°C, and the transfer line was 290°C. The oven was at an initial temperature of 60°C with a ramp time of 7°C/minute. Analytes were "confirmed" when the spectrum contained at least three of the major ions. The chromatographic peaks had to be at least three times the background noise and also had to be within one scan of each other and match the retention time of the standard run under the same conditions to be "confirmed."

**PCDD/Fs:** The analysis of 17 PCDD/F congeners that had chlorine atoms located in the 2,3,7,8 positions, as well as several homolog groups, was conducted based on adaptations to EPA Method 1613B (USEPA 1994c). These congeners encompassed the ones of highest concern for health effects in fish, wildlife, and humans. The method involved solvent extraction, clean-up, and quantification by high resolution GC (HRGC) – high resolution MS (HRMS) such that low MDLs (i.e., 0.01 µg/kg dry weight) could be obtained.

A brief summary of the PCDD/F method is provided here. A specified amount of sample was spiked with a solution containing specified amounts of each of the fifteen isotopically labeled PCDD/Fs. Next, a toluene extraction was conducted on each sediment sample. The extracts were submitted to an acidic washing treatment and dried. Following a solvent exchange step, the extracts were cleaned up by column chromatography on silica gel and activated carbon. The final extract for HRGC/HRMS was accomplished by adding 20 µL of a nonane solution containing 100 pg/µL of the following internal standard compounds: <sup>13</sup>C12-1,2,3,4-tetrachlorodibenzo-*p*-dioxin (TCDD) and <sup>13</sup>C12-1,2,3,7,8,9-hexachlorodibenzo-*p*-dioxin (HxCDD). The former was used to determine the percent recoveries of tetra- and pentachlorinated PCDD/F congeners, while the latter was used to determine the percent recoveries of the hexa-, hepta-, and octachlorinated PCDD/F congeners.

Two µL of the concentrated extract were injected into an HRGC/HRMS system capable of performing selected ion monitoring at resolving powers of at least 10,000 (i.e., 10% valley definition). The

identification of sixteen 2,3,7,8-substituted congeners, for which a <sup>13</sup>C12-labeled standard was available in the sample and the labeled standard spiking solutions, was based on their elution at their exact retention time (within 0.005 retention time units measured in the routine calibration) and the simultaneous detection of the two most abundant ions in the molecular ion region. The identification of 1,2,3,4,6,7,8,9-octachlorodibenzo-furan (OCDF) was based on its retention time relative to <sup>13</sup>C12-1,2,3,4,6,7,8,9-octachlorodibenzo-*p*-dioxin (OCDD) and the simultaneous detection of the two most abundant ions in the molecular ion region. Identification was also based on a comparison of the ratios of the integrated ion abundance of the molecular ion species to their theoretical abundance ratios. Quantitation of the individual congeners, total PCDDs, and total PCDFs was achieved in conjunction with the establishment of a multipoint (five points) calibration curve for each homolog, during which each calibration solution was analyzed once.

The QC samples included: method blanks, analytical duplicates, matrix spikes, and matrix spike duplicates.

**PBDEs:** Fifty-five individual and coeluting homolog groups of PBDE compounds were quantified, including brominated diphenyl ether (BDE)-209. The methods involved solvent extraction, clean-up, and quantification by GC/MS-Negative Chemical Ionization (GC/MS-NCI) and GC/MS-SIM. The detection limits specified in the Joint Powers Agreement with USFWS were between 0.4 to 1.9 µg/kg dry weight.

PBDEs were analyzed in sample extracts by a Thermo Trace GC and DSQ-II MS operated in SIM using a capillary column. The GC was operated in splitless mode using a PTV injection port, and the capillary column was an Agilent Technologies DB-XLB (15 m x 0.25 mm ID and 0.10 µm film thickness). The carrier gas was helium at a flow rate of 1 mL/minute and methane was used as the reactant gas with a flow rate of 2.0 mL/minute. The temperature of the injection port was 40°C (ramp to 300°C), and the transfer line was 290°C. The initial oven temperature was 110°C, the ramp rate was 7°C/minute to a final oven temperature of 280°C, and this temperature was held for 20 minutes. For analyte identification, the extracted ion current profiles of the primary *m/z* and the confirmatory ion for each analyte must be at a maximum in the same scan or within one scan of each other. In addition, the retention time must fall within 5 seconds of the retention time of the authentic standard.

The QC samples included method blanks, analytical duplicates, matrix spikes, and matrix spike duplicates.

**TOC:** The analysis of TOC was conducted by the Lloyd Kahn method (Kahn 1988). First, an aliquot of dried sediment was treated with sufficient phosphoric acid (1:1) to remove inorganic carbon prior to instrument analysis. Approximately 350 mg of treated sample was loaded into a clean, carbon-free combustion boat, which were loaded into a LECO autosampler rack assembly. Next, the dried sample was combusted at 1350°C under an oxygen atmosphere in a LECO CR-412 Carbon Analyzer. Carbon present in the samples was oxidized to form CO<sub>2</sub> gas. The sample gas flowed into a nondispersive infrared (NDIR) detection cell. The NDIR measured the mass of CO<sub>2</sub> present. The mass was converted to percent carbon based on the dry sample weight.

The QC samples included analytical duplicates.

**Particle size:** A homogenized subsample was mixed with a deflocculent solution to disaggregate the sample. A combination of sieves and settling tubes, followed by collection of material on clean paper and weighing were then used to determine the sand fraction (+4 phi). The material that passed through the sieves was added to a graduated cylinder and topped off to 1000 mL with deflocculent solution. After allowing the cylinder to stand for 24 hours at 24°C, the cylinder was thoroughly mixed. After 20 seconds, a 25 mL aliquot was withdrawn from a depth of 20 cm (representing the silt fraction). The aliquot was emptied into a tared 50 mL beaker. A second 25 mL aliquot was withdrawn from the

graduated cylinder from a depth of 10 cm at an interval of 2 hours and 3 minutes (representing the clay fraction) and placed into a tared 50 mL beaker. The 50 mL beakers were dried in an oven at 70°C to 90°C until dry. The dried samples were then weighed. The results were reported as percentages of the total sample weight.

The QC samples included analytical duplicates.

### **Fish tissue analyses by AXYS**

The fish samples were processed different ways, depending on their trophic guild and species type. Predator fish were processed as skin-on fillets (removed scales). Omnivore fish were processed as skin-on whole fish (removed scales). Benthic fish were processed as skin-on whole fish for bullheads and skin-on whole fish (removed scales) for white suckers. For each lake, five fish for each trophic guild were homogenized and composited together. The percentage of lipids in each composite sample was determined.

The extraction and analysis of BDEs in fish tissues followed EPA Method 1614 (USEPA 2007c), with some modifications developed by AXYS. Composite samples were spiked with isotopically labeled BDE surrogate standards, solvent extracted, and cleaned up on a series of chromatographic columns, which could include layered acid/base silica, Florisil, and alumina columns. The final extracts were spiked with isotopically labeled recovery (internal) standards prior to instrumental analysis. Analysis of the extracts was performed on a HRMS coupled to a HRGC equipped with a DB-5HT chromatography column (30 m x 0.25 mm ID and 0.10 µm film thickness). By using the isotope dilution/internal standard quantification procedures, the data were recovery corrected for possible losses during extraction and clean up. The results were reported as wet weight measurements.

The QC samples included three procedural blanks, a lab-generated reference sample known as the ongoing precision and recovery sample, a sample duplicate, matrix spike, and matrix spike duplicate. The duplicate was prepared from the August-2007-Yellow Perch composite sample. The matrix spike and matrix spike duplicate samples were prepared from the Nokomis-2007-Walleye composite sample.

## **Quality assurance/quality control (QA/QC)**

### **Field QA/QC**

The nationwide NLA project had a quality assurance project plan (QAPP) that was followed for all field work (USEPA 2006a, 2009a). For the extra sediment samples collected in conjunction with the NLA sampling, a separate QAPP was not prepared. The random sampling design of the NLA study insured the data were representative of Minnesota lakes from similar surface area classes. Sediment samples were collected for the intended analytes, with a few exceptions. PBDE analyses were removed from lakes #8 (Cokato) and #25 (Musquash), because of insufficient sample. Lake #8 (Cokato) was the only lake that a full 15 cm core segment could not be obtained; the upper 10 cm of sediment was sampled from this lake. As detailed earlier, there were also a few sample jars that cracked while stored in the MPCA's walk-in freezer.

Judy Crane found several data discrepancies in some site names, surface areas of NLA lakes, MDNR site IDs, updated ecoregions, as well as missing county names and sampling dates. She worked with the MPCA's internal NLA team to resolve these discrepancies, which involved confirmation or input from EPA Region 5, as needed.

Field precision was assessed through the collection and measurement of field replicates at a rate of one replicate per ten analytical samples. Thus, five field replicates, collected in close proximity to the original samples, were collected for the 50 randomly selected lake sites. This process allowed intralaboratory

precision information to be obtained on sample acquisition, handling, shipping, storage, preparation, and analysis. Both samples were carried through the steps in the measurement process together to provide an estimate of short-term precision. The principal measure of precision was the average relative percent difference (RPD) between field replicates, which was calculated as follows:

$$RPD = \frac{|D_1 - D_2| \times 100\%}{(D_1 + D_2)/2}$$

RPD = relative percent difference

D<sub>1</sub> = sample value

D<sub>2</sub> = field replicate sample value

## Analytical QA/QC

Sediment samples analyzed by the USFWS contract laboratory followed several QA/QC processes as specified by the USFWS Analytical Control Facility ([https://www.fws.gov/ecological-services/habitat-conservation/acf\\_qaqc.html](https://www.fws.gov/ecological-services/habitat-conservation/acf_qaqc.html), accessed 9/15/2016), including:

- Procedural blanks to determine the level of the target analyte in reagents, acids, sample vessels, glassware, or solvents used in the analyses. Procedural blanks were performed at a frequency of one every 10 samples.
- Analytical duplicate samples were used to assess the precision of the methods used for analysis. After the sample was homogenized, two separate subsamples were taken and analyzed. Duplicate analysis was performed at a frequency of one every 10 samples.
- Spiked samples were analyzed to assess the accuracy of the methods used for analysis. After the sample was homogenized, two separate subsamples were taken. One was processed as a sample. The second subsample had a known quantity of the targeted analyte added. Analysis of the matrix spike and the sample generated recovery numbers. Spike analysis was performed at a frequency of one every 10 samples. The control limit was exceeded if the percent recovery was greater than two times the standard deviation of the expected average.
- Calibration curves were required for each instrumental analysis of a sample batch. Calibration curves were verified immediately utilizing a mid-level calibration standard to determine if the initial calibration was acceptable for the analytical run.
- Calibration checks were done after every ten samples to check the validity of the calibration curve for the continuing sample group. The normal check was to reanalyze the mid-level standard used in the initial calibration. The acceptance coefficient of variation for this analysis had to be ≤10%.

MDH's Environmental Laboratory followed a similar QC program. Judy Crane performed a check of the metals and metalloids data from MDH and informed them of some minor edits. She also performed a QA check of the metals and metalloid data when MPCA staff entered these data into the U.S. EPA's Storage and Retrieval (STORET) database.

Analytical precision is the ability to produce the same result in repeated tests of the same sample. The principal measure of precision was the average RPD between analytical duplicates. The analytical RPD was calculated in the same manner as the field RPD, except the analytical duplicate was substituted for the field replicate. The USFWS Analytical Control Facility, at the time the catalog of NLAP sediment samples were submitted to their contract laboratory, acknowledged that an acceptable RPD will change depending on the proximity of the analyte concentration to the limit of detection (LOD). The LOD is the same as the method LOD, which is defined as the Student's t for 99% confidence times the standard deviation of seven replicate measurements of the same low level sample. Table 2-2 gives their

acceptance criteria for four classes of organic chemicals. The USFWS did not specify acceptance criteria for PBDE RPDs, although the acceptance criteria from pesticides and PCBs could be used as a default. The following acceptance criteria were used for other USFWS contract laboratory analytes:

- Average moisture RPDs should be <5%
- Average TOC RPDs should be <10%
- Average particle size RPDs should be <20%

Table 2-2. Acceptance Criteria for Analytical Duplicates Run by USFWS Contract Laboratories for Organic Analyses

Concentration <sup>1</sup> (Multiples of LOD)	Maximum Acceptable Average RPD (%)		
	Pesticides and PCBs	PAHs	PCDD/Fs
0-2 * LOD	200	200	200
2-10 * LOD	17.3	17.3	43.3
>10 * LOD	8.64	8.64	20.1

USFWS = U.S. Fish and Wildlife Service; LOD = limit of detection; RPD = relative percent difference; PAHs = polycyclic aromatic hydrocarbons; PCDD/Fs = polychlorinated dibenzo-*p*-dioxins/dibenzofurans.

<sup>1</sup> If the concentration of the analyte was less than the LOD, the USFWS Contract Laboratory took one-half the LOD for use in the RPD calculation.

For the analyses by MDH, the following QC criteria were used to assess the precision of analytical duplicates for mercury and other metals and metalloids:

Mercury: <20% RPD

Other Metals and Metalloids: <10% RPD

The RPD was calculated for each metal and metalloid that had detected data.

The principal measure of accuracy was the recovery of spiked analytes. The average recovery of most organochlorine pesticides, PCBs, and PBDEs should be between 80 – 120%, whereas it should be between 60 – 140% for PCDD/Fs and individual PCB congeners.

All of the USFWS contract laboratory data were reviewed by a Quality Assurance Officer for the data report. A large report was prepared of the analytical results, QC results, and evaluation of the data (TDI - Brooks International, Inc. 2009). The results were acceptable, except for the data anomalies listed in Tables 2-3 and 2-4. The variability of the analytical duplicates in Table 2-3 was high, partly because the

Table 2-3. Analytical Duplicate Anomalies in Sediment Samples Analyzed by TDI-Brooks International, Inc.

Analyte	Short ID	Station ID	Lake	RPD*
C3-Chrysene	19	860069CS07	Long	195
C3-Phenanthrenes/Anthracenes	19R	860069CS07R	Long	185
C4-Phenanthrenes/Anthracenes	31	460051CS07	Okamanpeedan	194

RPD = relative percent difference.

\* The analytical duplicate result was below the reporting limit for each analyte. TDI-Brooks International, Inc. used one-half the reporting limit in their calculation of the RPD.



Table 2-4. Analytical Spike Anomalies in Sediment Samples Analyzed by TDI-Brooks International, Inc.

Analyte	Short ID	Station ID	Lake	% Recovery
BDE-85	5	380691CS07	August	121
BDE-154	28	410055CS07	North Ash	121
beta-Endosulfan	7	040030CS07	Cass	24.8
beta-Endosulfan	28	410055CS07	North Ash	17.3

analytical duplicates were all below the reporting limit. These results should be considered as estimated. The spike recoveries of BDE-85 and BDE-154 in two samples were high (Table 2-4), and the results may be biased high. The spike recoveries for beta-endosulfan in Table 2-4 were low for two samples, and the results may be biased low. For the spike anomalies given in Table 2-4, each of these analytes were below the reporting limit for the corresponding sediment samples.

AXYS encountered some QC issues with the analysis of fish tissues for BDE congeners, which resulted in further discussions between AXYS and the MPCA. When AXYS first analyzed the composite fish tissue samples for BDEs, they found elevated levels of some of the hexas, heptas, and octa to the deca-BDEs in the blank and some of the samples. Bill Scruton (MPCA QA Coordinator) assisted Judy Crane and Steve Hennes with communicating our data quality expectations for tissue samples to AXYS staff. In the end, AXYS discovered the source of the lab contamination, re-ran the fish tissue samples, and an agreement was reached that AXYS would retain their QC acceptance criteria for calibration, ongoing precision and recovery samples, and sample recovery. In addition, the MPCA would utilize its own acceptance criteria to validate the data. Bill Scruton's validation letter of the data is provided in Appendix B. In his letter, some BDE compounds were considered as estimated values due to their detection and quantification in the procedural blanks.

## Sediment database

The sediment quality data and study information were added to an internal Microsoft Access 2000 statewide sediment quality database. This database was adapted from the Phase IV GIS-based sediment quality database for the St. Louis River AOC (Crane and Myre 2006). QA/QC checks of the data entry process were conducted to ensure the data were entered and processed correctly. Total chemical concentrations and important sediment chemistry benchmarks were calculated in the database.

### Total chemical concentrations

The procedures for calculating total chemical concentrations in the sediment database are summarized in Crane and Hennes (2007). These procedures included  $\Sigma\text{PAH}_{13}$ , Total PCBs, Total DDTs, and Total chlordane. In the database, the following rules were used for calculating total chemical concentrations with nondetect data (Crane and Myre 2006):

- Nondetect results were treated as one-half the reporting limit if there was a mix of nondetect and detected results (e.g.,  $<5 + 5 = 7.5$ ).
- If all the results were nondetects, then the total was calculated by summing the reporting limits (e.g.,  $<5 + <5 = 10$ ).

### Calculated benchmarks

The chemical data for certain parameters were used to calculate benchmark values relevant to ecological or human health. Benchmarks were calculated for groups of chemical classes, as well as for a compilation of different chemicals. These benchmark values were calculated in the Access 2000

sediment quality database. The U.S. EPA's PAH Equilibrium Partitioning Sediment Benchmark (ESB) Toxic Units (TU) model, for evaluating ecological risk to aquatic invertebrates, was calculated for  $\sum\text{PAH}_{34\text{-TU}}$  (Table 2-5) using final chronic values (USEPA 2003; Burgess 2009) and TOC data. Nondetect PAH data were treated as follows: 1) nondetect results were treated as one-half the reporting limit if there was a mix of nondetect and detected results, 2) if all results were nondetects, then the total was calculated by summing the reporting limits, and 3) nondetect results that had reporting limits greater than the associated Level II SQT value were excluded.

For PCDD/Fs, human health and aquatic life toxic equivalents (TEQs) were calculated by multiplying chemical values by their respective World Health Organization (WHO) toxic equivalency factors (TEFs) and summing the results. The TEFs for human health came from Van den Berg et al. (2006), whereas the TEFs for aquatic health were based on fish TEFs from Van den Berg et al. (1998). Nondetects for PCDD/Fs were treated two ways: 1) using one-half the reporting limit, and 2) using the Kaplan-Meier method of Helsel (2010) using a special set of queries developed by Sara Mueller (MPCA). Following Helsel (2010), reported concentrations of relevant analytes were multiplied by the corresponding TEF value. Nondetects were excluded from the calculations if they had the largest product (reporting limit x TEF) and were included as detects if they had the smallest product.

Mean PEC-Qs provided a screening tool to compare sediment quality between sites. The mean PEC-Qs were calculated for chemicals with reliable PECs (USEPA 2000a). These PEC values were adopted as Level II SQTs for use in Minnesota (Crane and Hennes 2007). Briefly, individual PEC-Qs (chemical concentration divided by the corresponding PEC value) were calculated for chemicals with reliable PECs [i.e., six metals,  $\sum\text{PAH}_{13}$  (Table 2-5), and Total PCBs]. Next, the mean PEC-Q for metals with reliable PECs (i.e., arsenic, cadmium, chromium, copper, lead, nickel, and zinc) were calculated. Finally, the mean PEC-Q values for the three main classes of chemicals with reliable PECs were calculated. In some cases, the mean PEC-Qs were only calculated using the mean  $\text{PEC-Q}_{\text{metals}}$  and  $\text{PEC-Q}_{\sum\text{PAH}_{13}}$  data for samples lacking Total PCB data. Nondetect data were typically treated as one-half the reporting limit. Any nondetect data that had detection limits greater than the corresponding Level II SQT values were excluded from the mean PEC-Q calculation.

## Environmental forensics

Environmental forensic procedures were used to determine sources of PAHs and PCDD/Fs in the data sets. These procedures ranged from qualitative to semi-quantitative to quantitative methods.

### PAHs

PAHs always occur as a mixture of compounds, for which changes in the assemblage of PAHs can be used to identify sources of PAHs (e.g., like a fingerprint). PAH histogram plots and source ratios were used for qualitative and semi-quantitative analysis of the data, respectively. Histogram plots of parent and alkylated PAH concentrations (generated in SigmaPlot 13.0, Systat Software, Inc., San Jose, CA) were used to assess the pattern of each parent PAH compound and its alkylated homologs. Patterns displaying a bell-shaped curve were indicative of petrogenic (i.e., oil-based) sources of PAHs, whereas patterns displaying a down gradient curve were indicative of pyrogenic (i.e., combustion-based) sources (Boehm 2006). In addition, the following diagnostic source ratios were used to identify petrogenic and pyrogenic sources of PAHs: fluoranthene:pyrene (F/P) and phenanthrene:anthracene (P/A; Budzinski et al. 1997). The following source ratios were used for determining a range of major emission sources from automobiles: benzo[b]fluoranthene:benzo[k]fluoranthene (BbF/BkF) vs. benzo[a]pyrene:benzo[e]pyrene (BaP/BeP; Dickhut et al. 2000). Double-ratio plots were generated in SigmaPlot 13.0 for these combinations of PAHs.

Table 2-5. PAH Compounds Included in Different Groups of PAHs

PAH Compound	$\Sigma$ PAH <sub>13</sub>	$\Sigma$ PAH <sub>17</sub>	$\Sigma$ PAH <sub>34-TU</sub>	$\Sigma$ PAH <sub>34</sub> for PAHs $\leq$ 3 NDs	$\Sigma$ PAH <sub>CMB</sub>
<b>Detected Data</b>					
Acenaphthene	X	X	X	X	
Acenaphthylene	X	X	X	X	
Anthracene	X	X	X	X	X
Benzo[a]anthracene	X	X	X	X	X
Benzo[a]pyrene	X	X	X	X	X
Benzo[b]fluoranthene		X	X	X	X
Benzo[g,h,i]perylene		X	X	X	X
Benzo[k]fluoranthene		X	X	X	X
Benzo[e]pyrene			X	X	X
C1-Fluorenes			X	X	
C1-Fluoranthenes/pyrenes			X	X	
C1-Naphthalenes			X	X	
C1-Phenanthrenes/anthracenes			X	X	
C2-Naphthalenes			X	X	
C3-Naphthalenes			X	X	
Chrysene	X	X	X	X	X
Fluoranthene	X	X	X	X	X
Fluorene	X	X	X	X	
Indeno[1,2,3-cd]pyrene		X	X	X	X
1-Methylnaphthalene				X	
2-Methylnaphthalene	X	X		X	
2,6-Dimethylnaphthalene				X	
1-Methylphenanthrene				X	
1,6,7-Trimethylnaphthalene				X	
Naphthalene	X	X	X	X	
Perylene			X	X	
Phenanthrene	X	X	X	X	X
Pyrene	X	X	X	X	X
<b>Detected &amp; Censored Data</b>					
Dibenzothiophene				X	
C1-Chrysenes			X	X	
C1-Dibenzothiophenes				X	
C2-Fluorenes			X	X	
C2-Phenanthrenes/anthracenes			X	X	
Dibenzo[a,h]anthracene	X	X	X	X	
C4-Naphthalenes			X		
C2-Dibenzothiophenes					
C2-Chrysenes			X		
C3-Phenanthrenes/anthracenes			X		
C3-Fluorenes			X		
C3-Chrysenes			X		
C3-Dibenzothiophenes					
C4-Chrysenes			X		
C4-Phenanthrenes/anthracenes			X		

PAH = polycyclic aromatic hydrocarbon; ND = nondetect; TU = Toxic Units; CMB = Chemical Mass Balance model.

The U.S. EPA's Chemical Mass Balance (CMB) 8.2 receptor model (Coulter 2004) was used to provide a quantitative assessment of important sources of PAHs to the study lakes. This air model has been adapted by other researchers (Li et al. 2003; Van Metre and Mahler 2010) for use in the source apportionment of PAHs in sediment. The model uses an effective variance weighted least square solution to the CMB equations, provided several model assumptions are met (Li et al. 2003; Coulter 2004). The MPCA has used this model previously for the source apportionment of PAHs in stormwater pond sediments (Crane 2014). Similar methods were followed for the NLAP sediment data set. Briefly, the model included  $\leq 12$  parent PAHs ( $\Sigma\text{PAH}_{\text{CMB}}$ ) identified in Table 2-5. A group of published PAH source profiles listed in Crane (2014) were considered for inclusion in the model, including the general categories of coal tar-based sealant (CT-sealant) dust and particulate runoff, asphalt sealant pavement dust, vehicle-related sources, coal combustion, fuel oil combustion, fireplace combustion of wood products, and used motor oil.

The model included several source inputs. Each run of the CMB8.2 model attempted to fit the source data to the ambient sediment data in  $\leq 20$  iterations using source elimination. The source profile uncertainty was set at 40% (Li et al. 2003; Van Metre and Mahler 2010; Crane 2014), and the minimum source projection was set at the default value of 0.95. The uncertainty values of the ambient PAH data from the NLAP lakes were set at 20%. Output files were generated as comma-separated value files that were imported into Microsoft Excel 2010 (Microsoft Corporation, Redmond, WA) for further analysis.

### **PCDD/Fs**

The weight percentage pattern of PCDD/F congeners and its homologs creates a unique "fingerprint" that can be used for environmental forensics work to identify sources of these compounds. The weight percentages of 17 PCDD/F congeners were calculated, and the mean and standard deviation (SD) values were plotted in a histogram plot in SigmaPlot 13.0. The results were then compared to published literature values for likely sources. Another common forensic technique is to compare patterns in 2,3,7,8-TCDD (PCD2378) concentrations with the homolog of total TCDDs (PCD\_T4), as well as ratios of these compounds. A plot of detected PCD2378 concentrations vs. PCD\_T4 concentrations, as well as a plot of the ratio of detected PCD2378 to PCD\_T4 for individual lakes were prepared in SigmaPlot 13.0. These results were compared to published literature values for sources. Finally, the percent homolog patterns of PCDD/Fs were calculated, and the mean (SD) values were plotted in SigmaPlot 13.0. The data were further broken out into different lake groups, plotted in SigmaPlot 13.0, and assessed for differences due to source type.

### **Statistical analyses**

A wide variety of statistical analyses were conducted on this sediment data set. A preliminary evaluation of the PAH data showed that the contaminant concentrations were not statistically significantly different ( $p > 0.05$ ) between the reference lakes and random lakes in the same major land use class (i.e., forested). A decision was then made to pool the reference lake data with the randomly selected lake data for all analytes. Based on the small sample size of the *a priori* reference lakes ( $n = 4$ ) and random lakes ( $n = 50$ ), it was advantageous to pool these data to increase the power of the statistical tests.

### **Normalization of metals and metalloids to aluminum**

Major components of the earth's crust, like aluminum and iron, are often used as "reference" elements to normalize "trace" metal and metalloid concentrations. Doing so, through the use of correlation plots, provides a way to visually determine "outliers" outside the 95% prediction intervals. These "outliers" may represent contaminated or naturally enriched sites beyond an anthropogenic background. Linear regression correlation plots were prepared in SigmaPlot 13.0 between individual metals and metalloids (Y-axis) with aluminum (X-axis); the 95% prediction interval was plotted along with the regression line.

Metals and metalloids were limited to those elements with <5% nondetects; the reporting limit was substituted for the nondetect value. The intercept, slope, and coefficient of determination ( $r^2$ ) values were noted. Sample values outside the 95% prediction intervals were labelled with their short ID number.

### **Total chemical groups by the Kaplan-Meier method**

Because substitution methods for nondetect values can bias the results, the Kaplan-Meier method (Helsel 2012) was used to calculate total values of PAH and PCB groups containing censored (i.e., nondetect) data. These values were used instead of total values from the sediment database. Kaplan-Meier is a nonparametric statistical technique that was developed for censored survival data, and it is also broadly applicable to estimating descriptive statistics of environmental data with <80% nondetects (Helsel 2012).

For PAHs, the mean Kaplan-Meier value was multiplied by the number of PAHs in each group. Three total PAH groups were determined in this manner for PAHs with <80% nondetects (Table 2-5). First,  $\Sigma\text{PAH}_{13}$  comprised the 13 low molecular weight and high molecular weight PAHs that have corresponding SQTs (Crane and Hennes 2007). Second,  $\Sigma\text{PAH}_{17}$  corresponded to a list of 17 PAHs used by the U.S. EPA. Third,  $\Sigma\text{PAH}_{34}$  corresponded to a subgroup of PAHs that had approximately <5% nondetects. There was also a group of 34 PAHs, with some differences from  $\Sigma\text{PAH}_{34}$ , that were used to estimate ESB Toxic Units ( $\Sigma\text{PAH}_{34\text{-TU}}$ ; Table 2-5).

Congener-specific PCB data were used to calculate Total PCBs by the Kaplan-Meier method. This was done for samples with <80% nondetects. These results should not be confused with the Total PCBs that were an analytical output of the pesticide scan.

### **Broad array of statistical analyses in ProUCL 5.0**

The U.S. EPA's ProUCL 5.0 software (<http://www2.epa.gov/land-research/proucl-software>) was used for several statistical analyses of the uncensored and censored (i.e., nondetect) data sets. The data were first set-up in Excel 2010 files for use in ProUCL 5.0. Analytes with nondetect data necessitated the creation of extra indicator columns for each analyte, where nondetects were represented by "0" and detects were represented by "1." General statistics for uncensored data sets included: number of observations, number of missing samples, minimum and maximum values, mean, SD, standard error of the mean (SEM), median absolute deviation (MAD)/0.675, skewness, kurtosis, and coefficient of variation (CV). General statistics for censored data included: number of observations, number of missing samples, number of detects, number of nondetects, % nondetects, minimum and maximum nondetect values, as well as the Kaplan-Meier mean, variance, SD, and CV. Percentiles were also provided in the general statistics output for both detected and detected plus censored data for the following groups: 10%ile, 20%ile, 25%ile (quantile 1), 50%ile (quantile 2 or the median), 75%ile (quantile 3), 80%ile, 90%ile, 95%ile, and 99%ile.

Separate outlier tests were run on raw detected and censored data sets in ProUCL 5.0. The outlier tests for censored data gave options for two substitution methods (i.e., zero or one-half the reporting limit for the nondetect value), and both procedures were used. The ProUCL Technical Guidance (Singh and Singh 2013) indicates that it should not matter how the nondetect observations are treated for the identification of high outliers. Dixon's outlier test was used when there were  $\leq 25$  detected samples; this method had the restriction that only one outlier could be specified at the 5% significance level. Rosner's outlier test was used to identify up to 10 outliers in data sets with  $\geq 25$  detected samples. Both outlier tests assumed that the data followed a normal distribution without the suspected outliers. However, since the Dixon and Rosner tests may not identify all potential outliers in a data set, the resulting reduced data set may still not follow a normal distribution (Singh and Singh 2013). If there are multiple

outliers, both outlier tests may suffer from masking effects. Graphical displays of the data, including box plots and quantile-quantile (Q-Q) plots, were used to further identify outliers or multiple populations of data. Multiple and single box plots of both detected and censored data groups were generated in ProUCL 5.0. Standard normal Q-Q plots of the raw data were generated for individual analytes and calculated values. The Q-Q plots provided a graphical method to test the approximate normality of a data set. A linear pattern displayed by the majority of the data suggests approximate normality. However, data points well separated from the linear pattern represent outlying observations not belonging to the main dominant population of data, and jumps (or breaks) in the Q-Q plot may suggest the presence of multiple populations of data (Singh and Singh 2013). Professional judgment was used to identify additional outliers or separate populations of data based on a review of the outlier tests and graphical displays of data.

After removing outliers and/or separate populations of data from the dominant population of raw data, ProUCL 5.0 was used to estimate several types of background threshold values. As part of this process, goodness of fit tests for normal, gamma, and log distributions were run. Background threshold values were calculated for each distribution, as well as for nonparametric distribution-free background statistics. The 95% one-sided upper tolerance limits (UTLs) with 95% coverage were of greatest interest for the NLAP data set. The UTL represents a confidence limit on a percentile of the population, rather than a confidence limit on the mean (Singh and Singh 2013). The 95% UTL with 95% coverage (hereafter generally referred to as the UTL or UTL95-95) represents the value below which 95% of the population values are expected to fall with 95% confidence. Another way of thinking of this is that it represents a 95% upper confidence limit for the 95% percentile. Therefore, a UTL95-95 provides coverage for 95% of all current and future potential observations from the background population (or comparable to background) with a confidence coefficient of 0.95. By chance, a UTL95-95 can classify 5% of background observations as not coming from the background population with a confidence coefficient of 0.95; this represents the false positive error rate. Sample values above the UTL95-95 may also be due to increased anthropogenic contamination or naturally high mineral deposits of certain metals and metalloids. UTLs for normally distributed data were preferred over those derived from gamma distributed data. Both distributions were better than log distributed data. When the data were not normally distributed and the gamma distribution was used, the gamma UTL upper limits were estimated two different ways: 1) the Wilson Hilferty (WH) method, and 2) the Hawkins Wixley (HW) method. Professional judgment can be used to select the upper limit value of interest. For data with <80% nondetects, the Kaplan-Meier versions of the UTL95-95 calculations were performed. The ProUCL 5.0 guidance recommends not computing UTLs on data sets containing less than eight to ten observations (Singh and Singh 2013).

ProUCL 5.0 has some limitations in terms of the presentation options for certain work products. Spreadsheets produced in ProUCL were saved as Excel 2010 files, whereas graphs were saved as Bitmap (.bmp) images. The formatting options of graphs were limited while working in ProUCL 5.0. Graph .bmp images were pasted into Word 2010, re-sized, and outliers were noted on the Q-Q plots by pasting Word text boxes on top of the Q-Q plots.

### **Correlations between analytes**

Correlations procedures were used to measure the strength of association between analytes. With correlations, it does not matter which variable is dependent or independent. Correlations were run in SigmaPlot 13.0, and the type of correlation depended on whether the data passed the Shapiro-Wilk normality test. For normally distributed data, the parametric Pearson product moment correlation was run; this method assumes constant variance of the residuals. For data that were not normally distributed, the nonparametric Spearman rank order correlation was run; this method finds the correlation of data measured by rank or orders.

The correlation coefficients for the parametric and nonparametric methods have similar intent, but different names. The correlation coefficient for the parametric (Pearson) test is  $r$ , while it is  $\rho$  for the nonparametric (Spearman) test. These values vary between -1 and +1. A correlation coefficient near +1 indicates there is a strong positive relationship between the two variables, with both increasing together. A correlation coefficient near -1 indicates there is a strong negative relationship between the two variables, with one decreasing as the other increases. A correlation coefficient of zero indicates no relationship between the two variables.

The p-value produced by both methods is the probability of being wrong in concluding there is a true association between the variables (SigmaPlot 13.0 User's Manual). The smaller the p-value, the greater the probability that the variables are correlated. When  $p < 0.05$ , the independent variable can usually be used to predict the dependent variable.

Several correlations were run on part or all of the NLAP data that were measured in all of the sediment samples. Correlations were limited to those parameters with <5% nondetects, in which the reporting limit was substituted for the nondetect value. For the correlations run on a compilation of all of the NLAP data with <5% nondetects, outliers (as determined using ProUCL 5.0) were removed from the data set.

### **Statistical comparisons of groups**

**Multiple comparisons:** A portion of the sediment quality data were analyzed to determine if major land use practices in the lake watersheds had any influence on ambient chemical concentrations and particle size ranges. Data were primarily limited to those analytes and particle size classes measured or calculated from data collected from all 54 lakes, including: TOC, particle size, metals and metalloids, PAHs, biphenyl, metal PEC-Qs, and mean PEC-Qs. Four major land use classes were considered, including: cultivated, developed, forested, and lakes and wetlands. The data were further restricted to analytes that were either always detected or had approximately <5% nondetects. In this case, nondetects were substituted at the full reporting limit. Including higher percentages of substituted data would artificially skew the statistical analyses (Helsel 2012).

A one-way Analysis of Variance (ANOVA) was run in SigmaPlot 13.0 for each group of analytes measured in all the lake sediment samples. The raw data were organized by land use categories. If the data passed the Shapiro-Wilk normality test and the Brown-Forsythe equal variance test, then the one-way ANOVA continued. If the data did not pass either of these tests, then a natural log transformation was performed. If that transformation did not work, a square root transformation was conducted. The null hypothesis for this test was that there would be no difference in the distribution of values between the different land use groups. If the one-way ANOVA determined the differences in the mean values among the land use groups were greater than would be expected by chance, then a statistically significant ( $p < 0.05$ ) result was obtained. In order to determine the pairs of land use groups that were statistically different, the Holm-Sidak method was used for all pairwise multiple comparisons. This method is more powerful than the Tukey and Bonferroni pairwise tests, because it is able to detect statistical differences that these other two tests do not when dealing with unequal sample size (SigmaPlot 13.0 User's Guide). For the four major land use groups, there were six possible pairwise comparisons.

If the raw or transformed data failed either the normality test or the equal variance test, then a Kruskal-Wallis one-way ANOVA on Ranks was initiated in SigmaPlot 13.0. This test does not assume all the sample data were drawn from normally distributed populations with equal variances. This nonparametric procedure tests the null hypothesis of no significant differences between the medians of land use groups, but does not determine which groups are different or the size of these differences (SigmaPlot 13.0 User's Manual). If the differences in the median values among the land use groups were greater than would be expected by chance, then a statistically significant difference ( $p < 0.05$ ) was

determined. To isolate the group or groups that differed from the others, Dunn's method was used to assess multiple comparisons. This was the only test option because of the unequal sample sizes of data among the land use groups. If a group was not found to be significantly different than another group ( $p > 0.05$ ), then all groups with ranks in between the rank sums of these two groups were also assumed not to be statistically different. As a result, a "Do Not Test" message appeared for these other comparisons (SigmaPlot 13.0 User's Manual).

A similar statistical process was followed for assessing whether chemical concentrations or sediment benchmarks with <5% nondetects varied by surface area classes of study lakes. In this case, the statistical analyses were limited to the following parameters that were measured or calculated from data collected from each lake: metals and metalloids, PAHs, biphenyl, metal PEC-Qs, and mean PEC-Qs.

Finally, statistical comparisons were made to assess whether the percentage of developed land uses in the surrounding lake watersheds had any influence on PAH concentrations with <5% nondetect values. A similar statistical process was followed as for the watershed land use and surface area comparisons. Lakes were divided into the following four groups:

- D1 = >60% developed land uses (n = 2)
- D2 = 10 – 14% developed land uses (n = 11)
- D3 = 4 – 9% developed land uses (n = 20)
- D4 = 0 – 3% developed land uses (n = 21)

**Pairwise comparisons:** Pairwise statistical comparisons of the raw or grouped data were conducted using either the Student's t-test, if the data were normally distributed, or the nonparametric Mann-Whitney rank sum test if the Shapiro-Wilk normality test failed. These analyses were run in SigmaPlot 13.0. The p-values to reject normality or equal variance were both set at 0.050.

### Principal components analysis

Principal component analysis (PCA) is a multivariate statistical technique used to reduce the complexity of data sets to its most important components. PCA is very useful for explaining sources of variability in the data and representing the data with fewer variables while preserving most of the total variance. Each principal component represents a linear combination of the original variables. The first principal component accounts for the greatest amount of variation, while each subsequent principal component accounts for as much of the remaining variation, as possible, and is orthogonal to all of the previous principal components (Johnson et al. 2004). PCA analysis was run in SigmaPlot 13.0 on analytes which were measured in all 54 lake samples and which had approximately <5% nondetects. The reporting limit was substituted for the few nondetect values allowed. Although Helsel (2012) has discussed multivariate methods for censored data, a decision was made not to try them since this was a relatively small data set for running PCA analysis. Fifty samples are a general lower limit for running PCA analyses (Barrett and Kline 1981). PCA creates optimized linear combinations of variables that tend to over fit the data, and inflated error rates may occur when sample size is too small (Osborne and Costello 2004). Thus, it did not seem appropriate to use Helsel's (2012) approach for chemicals that had a higher number of nondetects (i.e., number of detected compounds would be <50).

PCA analysis is sensitive to variance in the data so raw data were not used. A few different approaches were used to normalize the data, including dividing groups of individual PAH compounds or metals and metalloids by their respective total values and also normalizing metal and metalloid data to aluminum. These procedures reduced variance in the data, but still resulted in some chemicals (e.g., perylene) having much higher variance than the other analytes. In PCA, the analytes with the highest mean and variance usually have the greatest influence on the analysis (Johnson et al. 2004). Thus, a better approach was sought for transforming the data. Ultimately, the range transformation (also known as the



maximum-minimum transformation) was used on all the raw data prior to running each PCA. The range transformation was performed as follows for each group of analytes:

$$x'_{ij} = (x_{ij} - x_{\min j}) / (x_{\max j} - x_{\min j})$$

where the transformed value ( $x'_{ij}$ ) represents the difference between the raw value ( $x_{ij}$ ) minus the minimum value in the group ( $x_{\min j}$ ) divided by the difference in the largest ( $x_{\max j}$ ) and smallest ( $x_{\min j}$ ) values. For each column of data for a particular analyte, this transformation resulted in values between 0 and 1.0. The range transformation produces variances that are similar (e.g., homogeneous). The range transformation has two advantages: 1) it does not force the data to conform to a theoretical distribution and 2) all values are non-negative (Johnson et al. 2004). The range transformation was also run on some normalized data sets, which were then processed by PCA. However, the PCA was sufficient on the raw data that were range transformed.

The PCA analyses were run on groups of similar compounds (e.g., metals and metalloids, PAHs), as well as mixtures of contaminants, contaminant indices (e.g., mean PEC-Qs), and particle size. The matrix for the analyses could be set-up in SigmaPlot 13.0 using either the correlation or covariance matrix. The correlation matrix is used on analytes with different units, while the covariance matrix is used on parameters which have the same units. Both matrices were tried in some early PCA analyses, but ultimately the covariance matrix was used for the final PCA analyses since all of the range transformed data were unitless. The significance level for hypothesis testing was set at 0.050 with a confidence level of 95%. The selection method for components was either selected for the average eigenvalue, minimum eigenvalue (e.g., 1.0), or number of components (e.g., three). The Henze-Zinker normality test was used with a p value to reject of 0.050. In all, 51 combinations of variables were run through PCA analysis, of which seven combinations are presented in this report.

SigmaPlot 13.0 produced a report of each PCA analysis, in addition to three types of result graphs. The graphs included scree plots, component loading plots, and component score plots. The PCA component scores listed in the PCA report also identified potential outliers for site IDs with p-values <0.05. These results aided in the interpretation of the PCA analysis. Since SigmaPlot 13.0 could not produce three-dimensional (3D) graphs of the component scores within the PCA module, the component scores for three components were copied from the report into a new SigmaPlot 13.0 section and worksheet. Next, the 3D graphing tool was used in SigmaPlot 13.0 to generate a 3D graph. Although it was not possible to plot site IDs on the 3D graphs, they could be obtained by clicking on a point and seeing the corresponding component scores highlighted in the worksheet. These component scores were linked to the site IDs. The site IDs were written on a hard copy of the 3D graph.

Hierarchical cluster analysis (HCA) was conducted to identify similar groups of samples on each 3D graph of PCA component scores. The three columns of components scores from the PCA report were copied into the free PAleontological STATistics (PAST) version 3.0 software (<http://folk.uio.no/ohammer/past/>). The HCA was conducted three different ways. Two ways set the algorithm to “Paired Group (UPGMA)” with a similarity index of either “Euclidean” or “Gower.” The third way set the algorithm to “Ward’s Method” with a similarity index of “Euclidean.” The HCA plots provided tree-like dendrograms of similar sample IDs. Four to seven major groups of samples, depending on potential outliers, were selected from the HCA plots to identify groups on the 3D plots. In all cases, the “Paired Group (UPGMA)” algorithm with the “Gower” similarity index worked the best at identifying discrete groups on the 3D plots.

The 3D plots were revised in SigmaPlot 13.0 to identify sample sites by the major land uses in each lake watershed. The major land use categories and number of samples in each category included: cultivated (n = 20), developed (n = 2), forested (n = 24), and lakes and wetlands (n = 8). Data from the four reference sites (all from forested land uses) were pooled with the random sites. Based on the HCA

groupings, either circles, ellipses, or other shapes were drawn around similar site IDs on each 3D PCA plot. As such, two-dimensional shapes were drawn on a 3D graph to identify similar groups of samples. It was not technically feasible to encompass similar samples with a 3D shape in SigmaPlot 13.0.

### **CMB8.2 model**

Several statistical procedures were used to prepare the measured  $\sum\text{PAH}_{\text{CMB}}$  data and for evaluating source profile data for inclusion in the CMB8.2 model. PAH proportional values (i.e., individual PAH concentrations divided by  $\sum\text{PAH}_{\text{CMB}}$ ) were calculated and assessed for normality using the Shapiro-Wilk test in SigmaPlot 13.0. A Spearman rank order correlation was run when the data were not normally distributed. The linear dependence between PAH proportional values of normally distributed sources and sediment data were assessed using Pearson product moment correlations ( $r$ ) and the statistical significance ( $p$ ) of the correlations. The sediment data were evaluated several different ways to select the best sources to include in the model. Due to the widespread geographic coverage of the samples in Minnesota, the best approach ended up being to run each sample independently through the model with an assortment of source options that were significantly correlated to the sediment data. Graphs comparing the PAH proportional values for the sources and groups of lakes using those sources were prepared in SigmaPlot 13.0.

Several statistical measures were used to assess the performance of each model run. These measures included Chi square, coefficient of determination ( $R^2$ ) values, the percent mass estimated by the model, and the T-statistic (Coulter 2004). Chi square is the weighted sum of squares of the differences between the calculated and measured fitting species concentrations; values less than one were preferred (indicating a very good fit to the data), whereas values between one and two were also acceptable.  $R^2$  values near 1.0 indicated that the source contribution estimates explained the measured concentrations very well, but other  $R^2$  values  $>0.8$  were acceptable, too. Percent mass represented the percent ratio of the sum of the model-calculated source contribution estimates to the measured mass concentration, and ratios approaching 100% were most ideal; ratios between 80 and 120% were also acceptable. The T-statistic that appeared with the source contribution estimates provided additional information to assess model performance because it could be indicative of collinearity among the source profiles when it was  $<2.0$  (Coulter 2004).

Additional summary statistics were run of the model results. The mean RPD between measured and modeled  $\sum\text{PAH}_{\text{CMB}}$  concentrations was calculated. The model performance of  $R^2$ , Chi square, and percent mass was compared to two other sediment studies that used the model for the source apportionment of PAHs: 1) a Minneapolis-St. Paul, MN (Twin Cities) metropolitan area stormwater pond sediment study (Crane 2014), and 2) a U.S. urban lake sediment study (Van Metre and Mahler 2010). SigmaPlot 13.0 was used to run either a one-way ANOVA or Kruskal-Wallis one-way ANOVA on ranks, depending on whether the data passed normality and equal variance tests. The data were transformed with a natural log or square root transformation, as needed. Any significant ANOVA results triggered multiple pairwise tests to determine the pairs of values that were statistically significant ( $p<0.05$ ).

### **Comparisons to Level I and Level II SQTs**

Sediment chemistry data were compared to analogous Level I and Level II SQT values (Tables 1-1 and 1-2; Crane and Hennes 2007). This included a suite of eight metals and metalloids, 13 low molecular weight and high molecular weight PAHs,  $\sum\text{PAH}_{13}$ , Total PCBs, 10 legacy organochlorine pesticides, mean PEC-Qs, and PCDD/F TEQs for aquatic life. The percentage of analytes within designated SQT ranges were calculated in Excel 2010, including:

- $\leq$ Level I SQT
- $>$ Level I SQT to  $\leq$ Level II SQT

- >Level II SQT

Summary tables of the results were assembled in Excel 2010. In addition, GIS maps were prepared in ArcMap 9.2, 9.3, and 10.1 for a short-list of analytes compared to their respective SQT values.

## Other sediment data sets

The NLAP sediment quality data provided a valuable, random data set to compare to other study data collected from Minnesota waterways. In particular, sediment chemistry data from a wetland survey and newer data from the St. Louis River AOC were selected for this comparison.

## Wetland data set

The MPCA's wetland staff collected surficial sediments from a number of large depressional wetlands during July to September of 1995, 1999, 2001, 2002, and 2003. Part of this data set was used as ancillary measurements for projects that developed benthic invertebrate and vegetation indices of biological integrity (IBI; Gernes and Helgen 1999, 2002). Another portion of this data set was never evaluated. After 2003, sediment sampling for nutrients and chemical parameters was discontinued in the MPCA's wetland work.

The wetland data included sites from reference areas, as well as disturbed areas in agricultural and urban watersheds (Appendix C). This broad range of sites from least disturbed to disturbed was important for the MPCA's IBI work (Gernes and Helgen 1999, 2002). The field sampling procedures for collecting these wetland samples is provided in Appendix C, which was based on methods described in Gernes and Helgen (1999, 2002). Composite sediment samples of the upper 5 cm were usually analyzed by the University of Minnesota Soils Analytical Laboratory. Metals and metalloids were analyzed using ICP techniques after 10% nitric acid digestion (Gernes and Helgen 1999, 2002). Chloride was extracted using charcoal and analyzed in a Technicon autoanalyzer with the mercury (II) thiocyanate method (Gernes and Helgen 1999). The 2003 samples were sent to MDH, and they subcontracted the metal and metalloid analyses to the University of Minnesota Soils Analytical Laboratory. MDH conducted the analyses of several conventional parameters in the 2003 samples, including chloride.

Wetland staff provided three Excel spreadsheets of sediment data that had been queried from an internal Access wetland database. The types of data fields differed in each spreadsheet. A new composite spreadsheet was generated for parameters of interest. Duplicate and lab duplicate samples were excluded, and only the most recent data from a site were used. For analytes containing both detected and nondetected data, an additional column was added to designate detected data as a "1" and nondetected data as a "0." This was done in order to make the spreadsheet compatible with ProUCL 5.0. Mean metal PEC-Qs were calculated per the procedures of Crane and Hennes (2007), which included substituting one-half the reporting limit for nondetected data. This compilation worksheet was copied to a new Excel spreadsheet for use in ProUCL 5.0. The data for calcium, magnesium, phosphorus, potassium, sodium, and sulfur were deleted, in part because the data were in different units.

Most of the same statistical analyses were run in ProUCL 5.0 as done on the NLAP and St. Louis River AOC data sets. These analyses included: general statistics, outlier tests, box plots, and individual Q-Q plots. Compilation Q-Q plots were also generated for analytes measured in the NLAP, wetland, and/or St. Louis River AOC data sets.

Sediment quality parameters were also compared to sediment benchmark values. Data were compared to corresponding Level I and Level II SQT values, and the results were compiled in a table. For a short list of chemical parameters, GIS maps were generated in ArcMap 10.3.1 to compare the data to

corresponding Level I and Level II SQTs. In addition, the data for chloride and a short-list of metals were reformatted and run in Tableau 9.0 to provide interactive views of the data in relation to SQT values and concentration ranges. The wetland sediment chemistry results were also compared to corresponding NLAP UTL values, and the results were compiled in a table.

## **St. Louis River AOC data set**

Newer sediment quality data from the Minnesota side of the St. Louis River AOC were used for this evaluation. These data (Somat Engineering 2012a, b; Weston Solutions, Inc. 2012a, b) were previously added to the data management system (i.e., database) for the St. Louis River AOC (LimnoTech 2013b). Bay West LLC, under contract with the MPCA's Duluth office, used database version SLR\_AOC\_DB\_07.02.01.mdb to query contaminant data from these studies. This query corresponded to database study ID's #67, 69, 72, and 74. Their query was designed to exclude Superfund sites and sediment assessment areas needing remedial action. In addition, the query excluded sample midpoint data >15 cm. Data from the Wisconsin side of the AOC were mostly excluded. In all, this data set included areas of the upper, middle, and lower St. Louis River, as well as the lower estuary section of the river and the Duluth/Superior Harbor. Data parameters included particle size, TOC, metals and metalloids, PAHs, PCBs, aquatic life TEQs for PCDD/Fs, metal PEC-Qs, and mean PEC-Qs. The field sampling and analytical procedures were described in the study reports (Somat Engineering 2012a, b; Weston Solutions, Inc. 2012a, b). For study ID #69 (Weston Solutions 2012a), the data for PAHs, pesticides, certain metal samples, metal PEC-Qs, and mean PEC-Qs were previously redacted from the database per U.S. EPA's determination of QA/QC issues with some or all of these data (MPCA memorandum from Nelson T. French and Luke Charpentier to St. Louis River AOC data users, January 30, 2015); the report for study ID #69 (Weston Solutions 2012a) contains these data of unknown quality. In the case of the metal PEC-Q data, all of the data were redacted even though much of the data were acceptable. These metal PEC-Q data were not recalculated for this report.

The Excel spreadsheet containing Bay West's query was modified to meet the needs of this data analysis. Duplicate samples were removed, and data from the 0 - 15 cm depth interval were selected. Extra columns were added for data that contained both detected and censored data, per ProUCL 5.0 guidance (Singh and Singh 2013), to designate a "1" for detected data and a "0" for nondetect data. Data for each analyte were compiled into separate ProUCL-ready worksheets. These worksheets contained 42 data fields for each analyte. A new Excel spreadsheet, containing a compressed version of the data, was developed. The new spreadsheet contained the contaminant concentration data, as well as the associated column of ones and zeroes if an analyte had both detected and nondetected data, respectively.

During the process of evaluating the data, several data discrepancies were discovered. These discrepancies were discussed with the MPCA's QA/QC Coordinator for the St. Louis River AOC data management system, who consulted with LimnoTech as needed. Erroneous detection limit values for some silver and selenium values were corrected in the database. Negative particle size values were noted for clay and/or silt for three samples in Study ID #69, and a decision was made to exclude these data from ProUCL 5.0. In addition, a negative TOC value from this same study was also excluded. After conducting some statistical analyses in ProUCL 5.0, additional data discrepancies were found and the analyses were re-run. This included excluding some samples with depth intervals >15.2 cm (the samples had initially been included due to the midpoint depth being <15.2 cm). There were also three analytes with zero values for data, instead of the reporting limit; this included cadmium (one value), selenium (68 values), and Total PCBs (277 values). These data issues were not resolved, and were left as zeroes in the data analyses. After completing the statistical analyses and GIS mapping of the data, it was discovered that aquatic life PCDD/F TEQ data calculated by Kaplan-Meier (TEQ\_KMDF\_W) were added to a later

version of the database (SLR\_AOC\_DB\_07.03.00.mdb) for study #69. These new data were added to the rest of the PCDD/F TEQ data, and the ProUCL 5.0 analyses and GIS map were revised. In addition, new analytical data (Study ID 87), which were collected to replace the uncertain data in study ID #69, became available in a subsequent update of the database (SLR\_AOC\_DB\_07.04.00). However, there was not enough time to incorporate these new data (particularly PAHs, metal PEC-Qs, and mean PEC-Qs) in this report.

Most of the same statistical analyses were run in ProUCL 5.0 as done on the NLAP and wetland data sets. These analyses included: general statistics, outlier tests, box plots, and individual Q-Q plots. Compilation Q-Q plots were also generated for analytes measured in the NLAP, St. Louis River AOC, and/or wetland data sets.

Sediment quality parameters were also compared to sediment benchmark values. Data were compared to corresponding Level I and Level II SQT values, and the results were compiled in a table. For a short list of chemical parameters, GIS maps were generated in ArcMap 10.3.1 to compare the data to corresponding Level I and Level II SQTs. The St. Louis River AOC sediment chemistry and particle size results were also compared to corresponding NLAP UTL values, and the results were compiled in a table.

## Section 3: NLAP lakes results and discussion

---

This section will provide an assessment and evaluation of the sediment chemistry and particle size data sets from the 2007 NLAP lakes. Groups of similar parameters are presented first, followed by a compilation of the analytes included at all of the sampling sites.

### TOC and particle size

#### *Highlights:*

- Spatial differences in TOC and particle size fractions were observed across the state.
- TOC was significantly higher ( $p < 0.05$ ) in lakes dominated by forests than by lakes in cultivated or lake and wetland watersheds.
- PCA analysis, in conjunction with HCA analysis, allowed the visual observation of outliers and groups of similar samples by land uses for TOC and particle size classes.
- UTL values were calculated for these parameters.

### Background

TOC and particle size are important ancillary measurements of sediment quality studies. These variables can aid in interpreting data on contaminant concentrations. For example, concentrations of hydrophobic organic contaminants may be normalized to TOC to further define the bioavailability of sediment-bound contaminants (Di Toro et al. 1991). Sediment particles with a smaller particle size (i.e., silt and clay) have a greater surface area for becoming enriched in contaminants than the sand fraction. In addition, both TOC and particle size are important features for determining suitable habitat for benthic organisms and aquatic vegetation.

### Summary statistics

#### TOC

TOC spanned a wide range of percentiles. The average was 14.2% with a SD of 7.1% (Table 3-1). TOC is naturally high in the Northern Lakes and Forests ecoregion due to abundant organic detritus produced within and entering lakes, wetlands, and peat bogs in these watersheds (Figure 3-1). TOC varied between low and medium ranges in the North Central Hardwood Forests ecoregion. TOC concentrations were in the lowest range in the Northern Glaciated Plains and Western Corn Belt Plains ecoregions. For example, farmed land in watersheds in the Western Corn Belt Plains reduces the diversity and quality of organic carbon sources to these lakes. Based on land use classifications, a one-way ANOVA indicated significant ( $p = 0.002$ ) differences in the mean values of TOC between land use groups. Pairwise multiple comparisons with the Holm-Sidak method showed that mean TOC values from lakes dominated by forests were significantly higher ( $p = 0.003$ ) than lakes in cultivated land uses and were also significantly greater ( $p = 0.035$ ) than lakes where lakes and wetlands dominated land uses. No other land use pairs were significantly different ( $p > 0.05$ ). Other summary statistics, percentile distributions, and a box plot of the TOC data are available in Appendix D.

Table 3-1. Summary Statistics for Particle Size and TOC

Parameter	N	Number Detects	Number NDs	% NDs	Mean (%)	SD (%)
Clay	54	54	0	0	23.5	17.4
Sand	54	54	0	0	34.9	21.0
Silt	54	54	0	0	41.7	18.6
TOC	54	54	0	0	14.2	7.1

N = number of samples; ND = nondetect, SD = standard deviation; TOC = total organic carbon.

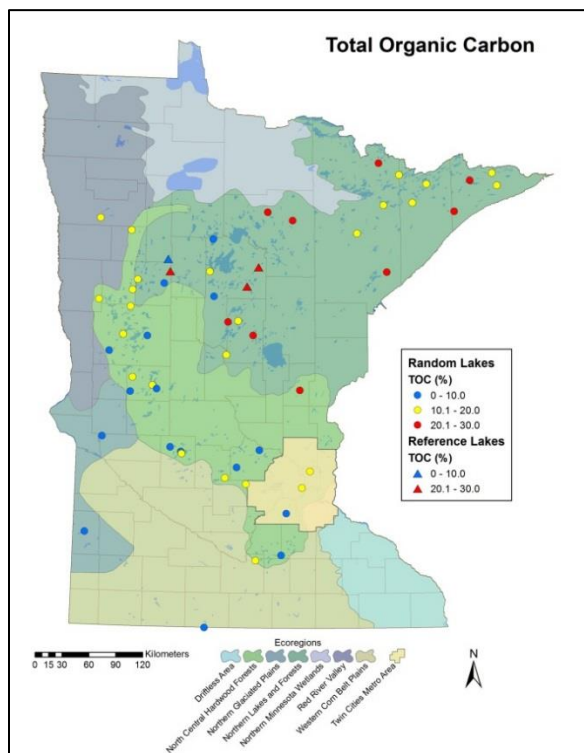


Figure 3-1. Range of TOC percentages in NLAP lakes.

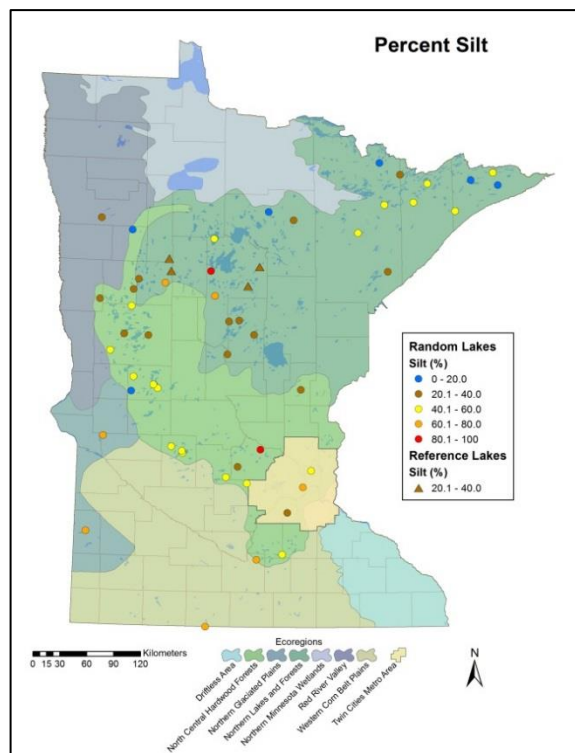


Figure 3-2. Range of percent silt in NLAP lakes.

### Particle size

Particle size was representative of depositional areas in the center of each NLAP lake. Particle size was dominated by the silt and sand fractions, followed by clay (Table 3-1). Percent silt varied throughout the state, but tended to be higher in the lower half of the state, particularly in agricultural and highly urbanized areas (Figure 3-2). This area is dominated by glacial till deposited by glaciers between ten and twenty thousand years ago (Figure 3-3; Anderson et al. 2001). The hard rock, Canadian Shield portions of northeastern Minnesota were not as conducive to the formation of silt particles in area lakes (Figures 3-2 and 3-3). However, there were no significant differences in the median values of percent silt ( $p = 0.06$ ) and percent clay ( $p = 0.553$ ) between major land use classes as determined by a Kruskal-Wallis one-way ANOVA on ranks test. In addition, there was no significant difference ( $p = 0.657$ ) in the mean values of percent sand between major land use classes as determined by a one-way ANOVA. The data

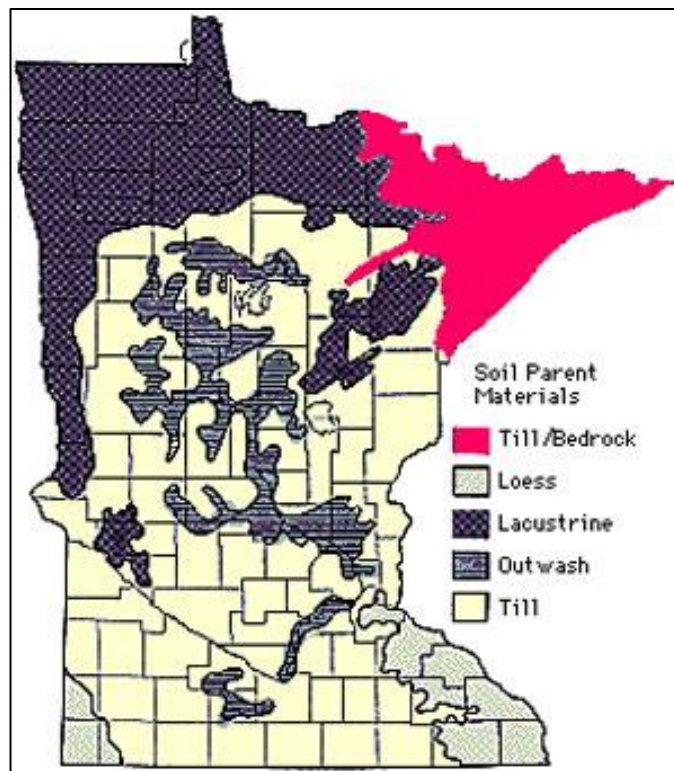


Figure 3-3. Soil parent materials in Minnesota (Anderson et al. 2001).

were not evaluated further by ecoregions. Other summary statistics, percentile distributions, and box plots of particle size data are available in Appendix D.

### PCA analysis

Four variables were included in the 3D PCA analysis of the particle size and TOC data (Figure 3-4). This 3D plot gave a better assessment of statistical outliers than a two-dimensional (2D) PCA plot. The supporting information for the PCA analysis is provided in Appendix D, including the scree plot, component loadings plots, and component score plots. The inclusion of three components accounted for 100% of the variance in the data. Based on the Eigenvectors of the covariance matrix, the major contributors to principal components 1 (PC1), 2 (PC2), and 3 (PC3) were sand, clay, and TOC, respectively (Appendix D). The percentage of variance explained by the three components for each variable is provided in Appendix D. Three samples (#19, 36, and 47) were outliers due to their statistically significant ( $p < 0.05$ ) component scores (Appendix D). Site 19 (Long Lake in Wright county) had the highest percentage of silt (i.e., 97.4%) in any of the samples. Site 36 (Red Rock Lake) had the highest percentage of sand (79.2%) and lowest percentage of TOC (0.57%) in the study lakes. Red Rock stood out as having the most compact and “hard” sediments when the samples were processed from the field collections. Site 47 (Vesper, a BWCAW lake) had the highest percentage of clay (78%), as well as elevated TOC (20.4%). These sites were further distinguished from most of the rest of the data set when the component scores were run through HCA using the paired group (UPGMA) algorithm and the Gower similarity index (Appendix D). Five clusters of samples were selected to display on the PCA graph (Figure 3-4). Four of the five clusters were comprised of either forested or cultivated land uses or a combination of these major land uses. The other cluster had the largest group of samples comprising a mixture of the four land use classes. The top cluster of six forested and two cultivated land use samples tended to have higher sand and TOC fractions than the other samples.



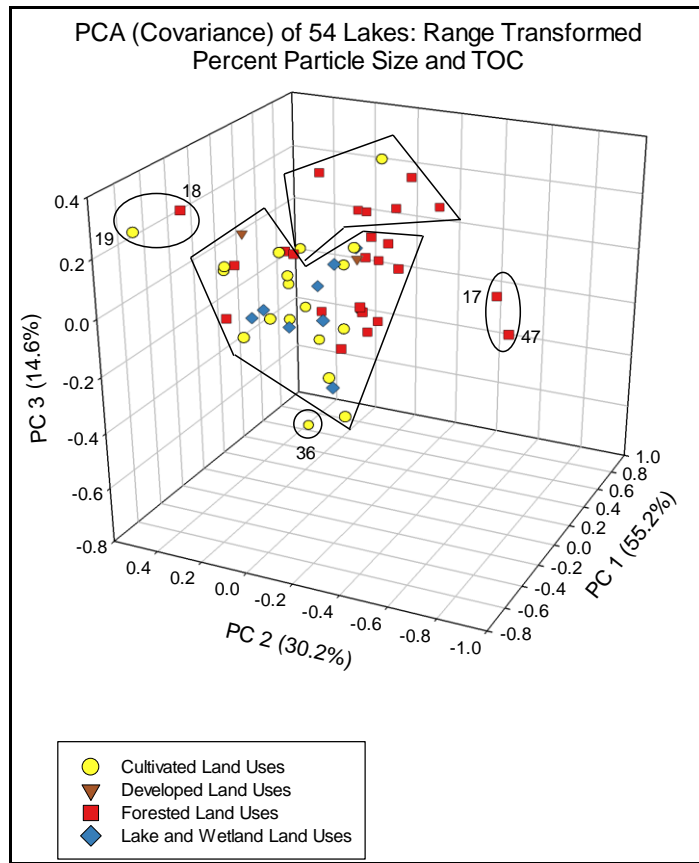


Figure 3-4. PCA plot of TOC and particle size classes for the 54 NLAP lakes. The PCA was run using a covariance matrix, and the data were range transformed.

### UTL values

UTL values were calculated in ProUCL 5.0 for TOC and particle size fractions (Table 3-2). Although the PCA results showed three outliers in the component scores based on a compilation of four variables, Rosner’s outlier test at the 5% significance level for the individual raw data indicated only one sample (i.e., 47) was significantly different from the other samples for the clay fraction. Silt, sand, and TOC did not have significant outliers. Q-Q plots (Appendix D) were also reviewed for statistical outliers and other distinct populations of data. Environmental lake sediment data above these UTL values would be more unusual due to natural geologic or anthropogenic influences on the surrounding watershed or in-lake processes.

Table 3-2. Upper Tolerance Limits (UTLs) of Particle Size and TOC Data with Outliers Removed at the 5% Significance Level (units in percent)

Parameter	N	Potential Outliers at 5% Significance Level (lake ID numbers)	Normal Distribution
			95% UTL with 95% Coverage
Clay (%)	53	47	54.7
Silt (%)	54		79.7
Sand (%)	54		77.7
TOC (%)	54		28.6

UTL = Upper Tolerance Limit.

## Correlation plots

Particle size and TOC regression correlation plots were developed after removing a potential outlier at the 5% significance level (i.e., from Table 3.2). The scatter plots of clay (%) vs. silt (%), as well as TOC (%) vs. clay (%) did not exhibit significant correlation coefficients ( $p > 0.05$ ). However, highly significant ( $p < 0.001$ ) Pearson correlation coefficients were observed between pairs of other particle size and/or TOC variables (Figure 3-5). The plot of TOC (%) vs. sand (%) was the only graph to display a positive correlation. That is, as the percentage of sand increased, so did the percentage of TOC. This result was contrary to some other studies. In Slip C, a boat slip in Duluth Harbor, MN, TOC (%) displayed a strong

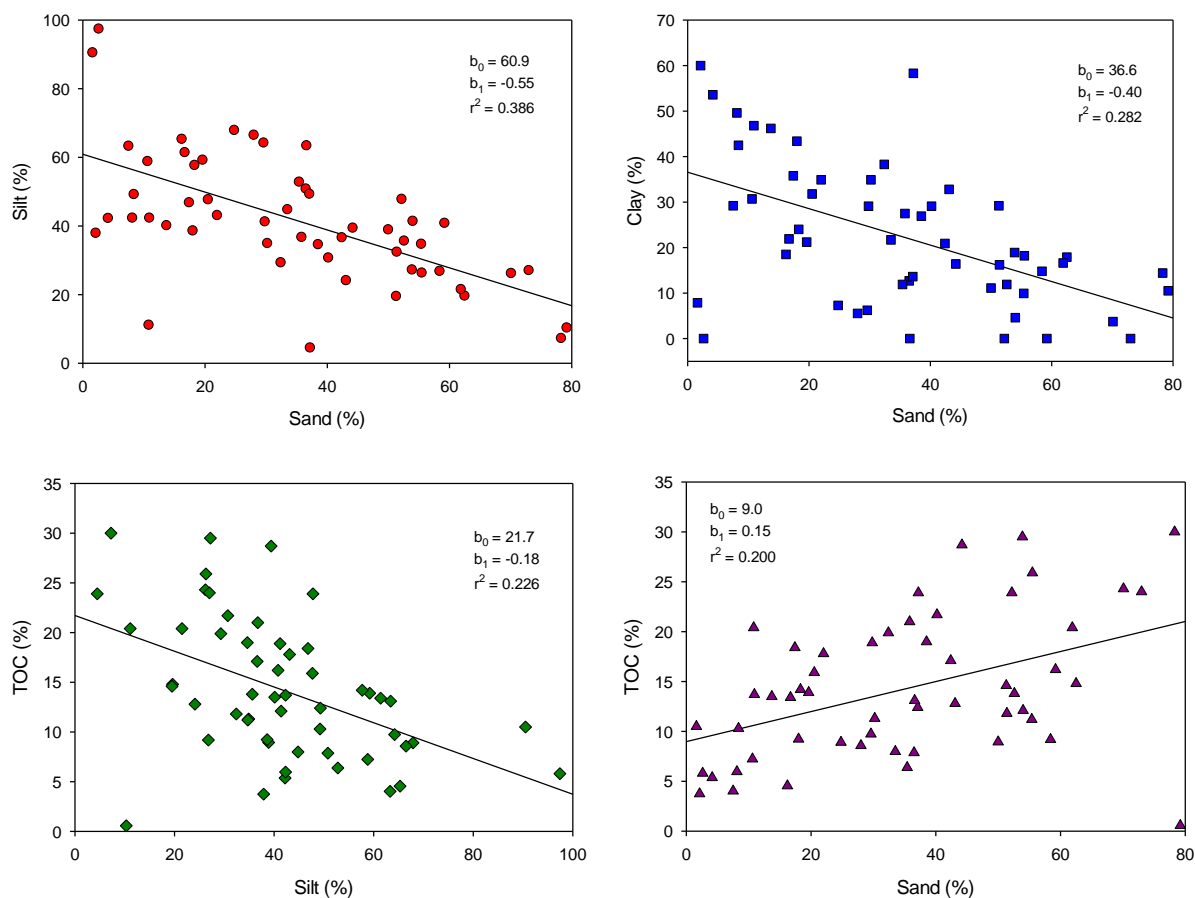


Figure 3-5. Highly statistically significant correlations ( $p < 0.001$ ) were observed between particle size classes and/or TOC (only one outlier was removed for clay at the 5% significance level). Linear regression terms:  $b_0$  = intercept,  $b_1$  = slope, and  $r^2$  = coefficient of determination.

negative correlation to the percentage of sand and gravel ( $> 53 \mu\text{m}$ ;  $r = -0.782$ ) and positive correlations to the percentages of silt ( $r = 0.794$ ) and clay ( $r = 0.707$ ; Crane 1999). Similarly, significant ( $p < 0.05$ ) Spearman rho ( $\rho$ ) correlations were found between % TOC and % sand ( $\rho = -0.736$ ), % silt ( $\rho = 0.853$ ), and % clay ( $\rho = 0.778$ ) in Lake Roosevelt and Upper Columbia River sediments in Washington state (Era and Serdar 2001). The particle size and TOC analyses of the NLAP samples were based on freeze-dried sediments. However, this method of drying should not affect the results. Keiser et al. (2014) evaluated the effects of drying methods on grain-size analyses, and freeze drying produced the most consistent results. Since the NLAP sediment samples were composed of only one composite sample from the deepest part of each lake, these data represent a broad geographic area encompassing wide-scale

watershed inputs that may not be representative of relationships observed in focused studies of limited geographic range (e.g., boat slip).

## Metals and metalloids

### *Highlights:*

- Mean values of arsenic, barium, lead, and zinc varied significantly ( $p < 0.05$ ) for the following pairwise comparisons of major watershed land use classes:
  - Arsenic, lead, and zinc were each significantly higher ( $p < 0.05$ ) in lakes with developed land uses than the other two or three major land uses;
  - Barium was significantly higher ( $p < 0.05$ ) in lakes with cultivated land uses than forests;
  - Lead and zinc were each significantly higher ( $p < 0.05$ ) in lakes with forests than cultivated land uses; and
  - Lead was significantly higher ( $p < 0.05$ ) in lakes with lake and wetland land uses than cultivated land uses.
- Statistical comparisons of the metals and metalloids by the five NLA surface area classes were hampered by the small number of lakes in some classes. Manganese was the only parameter with a statistically significant ( $p < 0.05$ ) result. However, multiple pairwise comparisons were inconclusive.
- The metal and metalloid concentrations, including mercury, were low (i.e., less than Level I SQT values) in the majority of lakes.
- Some metals (e.g., chromium, copper, and nickel) were naturally enriched in portions of northeastern Minnesota, due to geological deposits of minerals containing these metals. In a few cases, these metals exceeded the Level II SQT values.
- Historical uses of sodium arsenite in Snail Lake (#38), an urban lake, contributed to arsenic concentrations that exceeded the Level II SQT value.
- Statistical outlier tests were better at determining outliers than normalizing metal concentrations to aluminum.
- Multivariate statistical methods (i.e., PCA in conjunction with HCA) were useful for grouping similar lakes together.
- UTL values were calculated for metals and metalloids with  $< 80\%$  nondetect values.
- Correlation plots of metals and metalloids (excluding statistical outliers) showed that several of them co-occurred.

### **Background**

Metals and metalloids occur in sediments from both natural and anthropogenic sources. Metals (e.g., copper, nickel, and zinc) are typically hard, shiny, and have good electrical and thermal properties. Metalloids include elements like arsenic and antimony, which have physical/chemical properties in between or comprising a mixture of metals and nonmetals (Lombi and Holm 2010). Selenium is commonly described as a metalloid in environmental chemistry literature (Chapman et al. 2010). Aluminum is sometimes classified as a metalloid, although it is commonly classified as a metal. For this report, antimony, arsenic, and selenium will be considered as metalloids. The term “heavy metals” refers to metals and metalloids that have a relatively high density, can cause adverse effects at low

concentrations, and tend to accumulate in the food chain; examples of heavy metals include mercury, arsenic, cadmium, chromium, and lead (Tchounwou et al. 2012). However, the list of metals and metalloids included under the “heavy metals” category has not been used consistently by regulators, environmental scientists, and chemists, prompting some to suggest this terminology be abandoned (Duffus 2002). In this report, metals and metalloids will be referred to by their element name and general classification as metals or metalloids.

Metals and metalloids are found in various mineral complexes in the earth’s crust. Physical and chemical weathering of rocks releases dust and rock fragments directly into waterways, as well as to the ground to be incorporated into soil. Erosion of the soil during rain and snowmelt runoff events, in addition to airborne transport of dust during wind events, provides other transport pathways for metals and metalloids to enter streams, rivers, lakes, and wetlands. Divalent metals (e.g., barium, cadmium, lead, and zinc) that are freely dissolved in water have a positive charge, and these metals are attracted to the negative charge on clay particles suspended in the water column. These complexes can then be transported in the water column or settle out to the bottom sediments. Other metals can be scavenged by particles and removed to the sediments, as well.

When metals and metalloids are naturally enriched in rock, it may be economically feasible for mining companies to extract them. Gold was discovered in northern Minnesota during the short-lived Vermilion Lake gold rush of 1865-66 and during a more productive extraction on Little American Island in Rainy Lake in 1893 (<http://www.dnr.state.mn.us/education/geology/digging/history.html>; accessed 12/15/2015). Minnesota is currently the largest producer of iron ore and taconite (i.e., lower grade iron ore) in the U.S. (<http://www.dnr.state.mn.us/education/geology/digging/mining.html>; accessed 12/15/2015). Iron ore used to be mined on the Cuyuna, Mesabi, and Vermilion iron ranges, but only the Mesabi Range is mined today (Figure 3-6). Manganese, copper, nickel, and titanium have also been discovered in mineable quantities in Minnesota, but have not previously been of high enough quality to mine (Figure 3-6). However, PolyMet Mining Inc. has been seeking approval during the past 10 years to build an open pit copper-nickel mine (i.e., NorthMet project) in northeastern Minnesota near Hoyt Lakes. If approved, the metals would be extracted from sulfide ore in the Duluth Complex during the 20-year period of the permit (Figure 3-7). The company would also extract cobalt and small amounts of precious metals (e.g., platinum, palladium, gold, and silver; <http://www.polymetmining.com/northmet-project/overview/>; accessed 12/15/2015). The MDNR determined on March 3, 2016 that the environmental impact statement for the proposed NorthMet project met the state’s standards for adequacy (<http://news.dnr.state.mn.us/2016/03/03/dnr-deems-polymet-mine-environmental-impact-statement-adequate/>; accessed 4/18/2016). More than 20 types of local, state, and federal approvals and permits are needed for this proposed project to advance. In addition, the U.S. Forest Service and U.S. Army Corps of Engineers must complete their records of decision. One of the challenges with this type of nonferrous mine is the need for long term treatment of wastewater and waste rock due to the formation of acid mine drainage, which is harmful to aquatic life and makes some metals more soluble and toxic.

Besides mining, other human-based activities contribute metals and metalloids to the environment. These activities can include: smelting, electroplating, and other industrial processes that have metal residues in their waste streams (Shine et al. 1995). Releases of wastewater treatment plant (WWTP) effluent to waterways can introduce low concentrations of metals and metalloids into receiving waters. Vehicle traffic can be a source of metals to road dust that can subsequently wash-off to waterways. For example, copper is released from abraded brake linings in cars and trucks (TDC Environmental 2004). Zinc is also released in abraded tire particles from vehicles (Councell et al. 2004). In the past, some lakes have been treated with algicides and herbicides, like copper sulfate and sodium arsenite, to reduce algae and noxious weed growth in lakes (Förstner 1976). Coal and oil-fired power plants are major

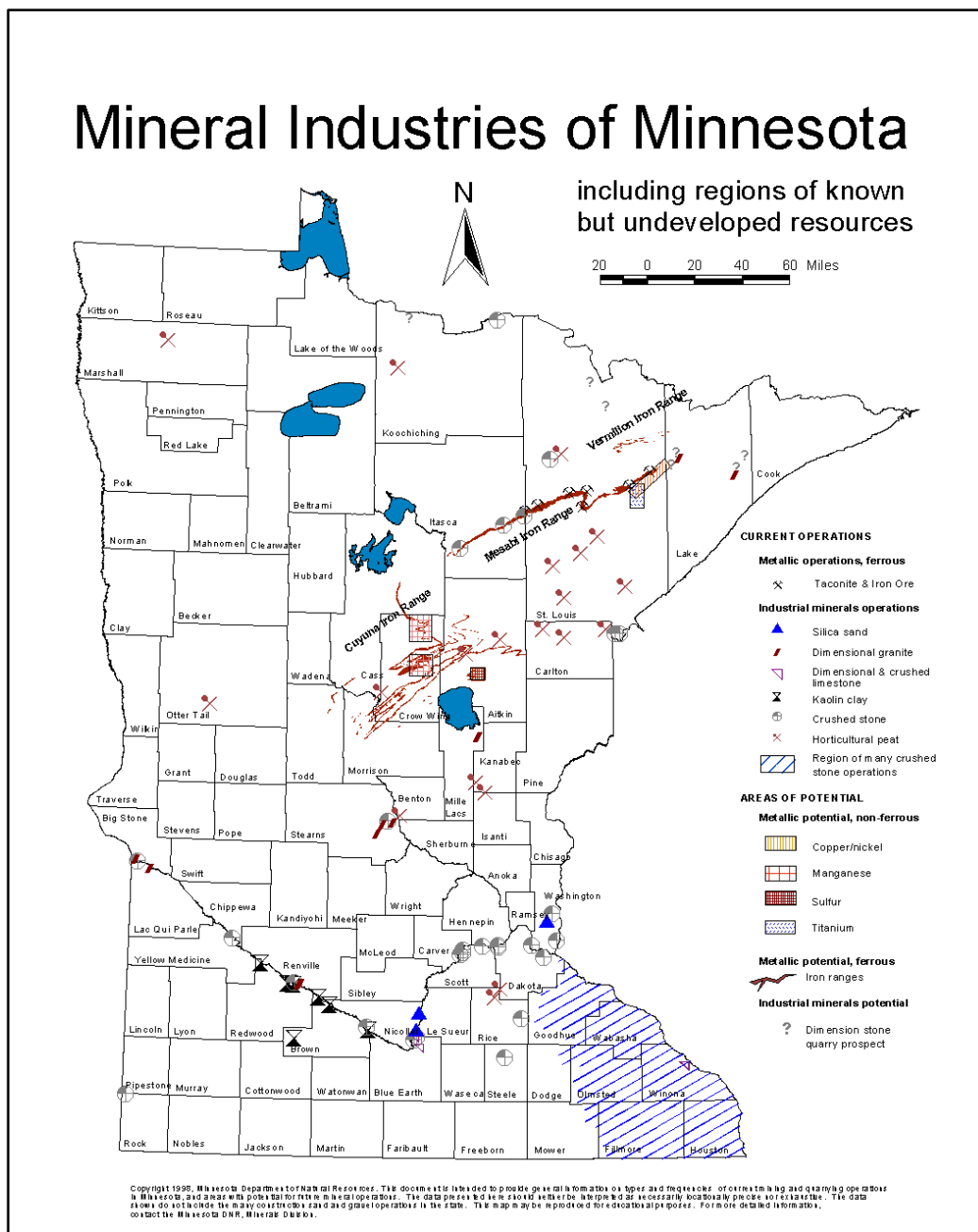


Figure 3-6. Map of mineral resources in Minnesota (MDNR website: [http://images.dnr.state.mn.us/education\\_safety/education/geology/digging/minmap.gif](http://images.dnr.state.mn.us/education_safety/education/geology/digging/minmap.gif)).

contributors of mercury, arsenic, chromium, and nickel to U.S. air pollution (<https://www3.epa.gov/mats/powerplants.html>; accessed 4/18/2016), some of which can be transported and deposited to lakes. Most of the mercury found in Minnesota's lakes and rivers is due to atmospheric deposition, of which 90% comes from other states and countries (MPCA 2013). Certain bacteria can convert mercury to methylmercury in aquatic sediments, where it can build-up in the food chain and accumulate in fish tissue (Hsu-Kim et al. 2013). Twenty-four of the 54 NLAP study lakes have fish advisories for mercury (<http://www.health.state.mn.us/divs/eh/fish/eating/specpoplakes.pdf>; accessed 4/18/2016).

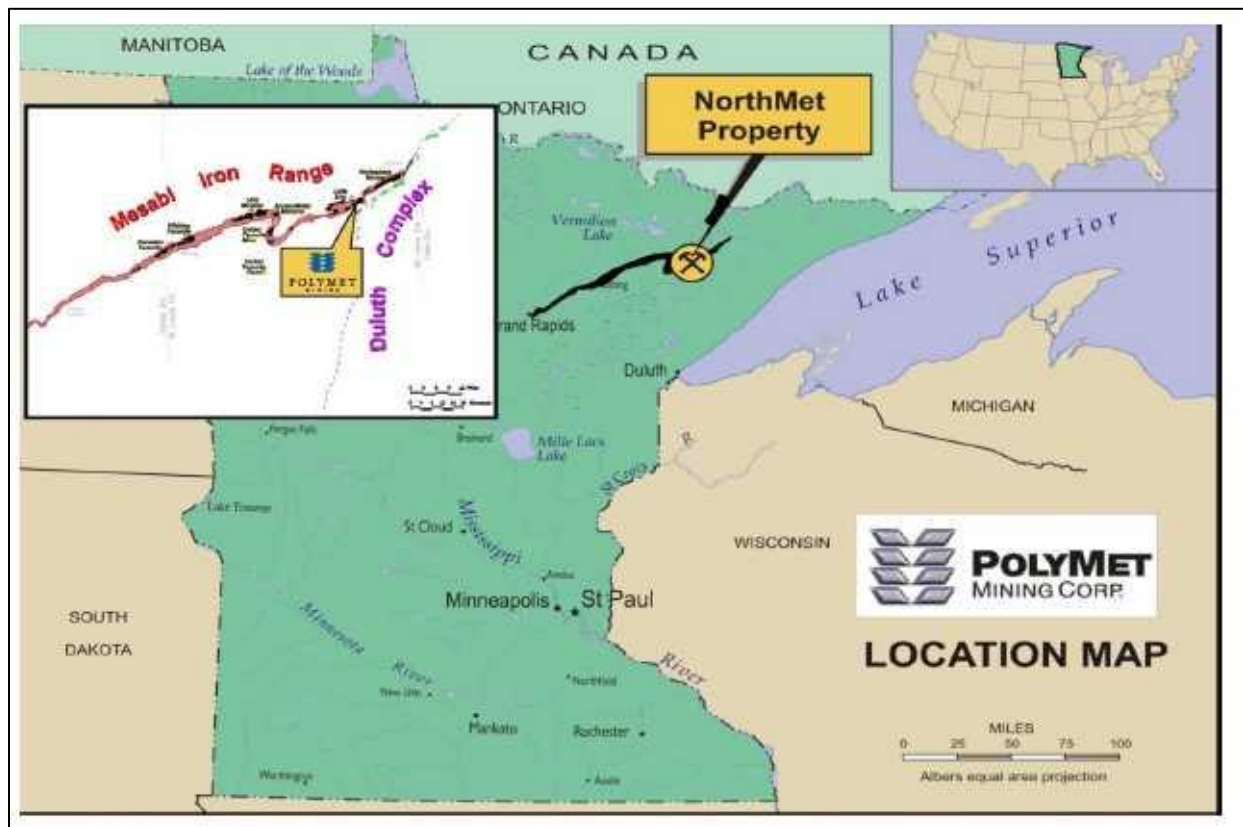


Figure 3-7. Proposed location of the PolyMet Mining Corporation NorthMet mine (source accessed 12/15/2015: <http://www.sec.gov/Archives/edgar/data/866028/000106299313002016/form20fx21x1.jpg>).

The natural and anthropogenic release of metals and metalloids to waterbodies can have potential detrimental effects on biota and human health, depending on the physical/chemical factors that affect their bioavailability. The biogeochemistry of metals and metalloids in aquatic systems has been reviewed by Mason (2013). Factors influencing metal and metalloid availability and toxicity in sediments are discussed by Chapman et al. (1999). Particular features of the mercury cycle in the environment are described by Wentz et al. (2014). Fish are useful bio-indicators of metal contamination, especially of mercury, cadmium, copper, lead, and zinc; these metals can accumulate in fish tissues, interfere with reproduction, weaken the immune system, and induce pathological changes (Authman et al. 2015). A weight-of-evidence approach is useful for assessing effects of metals and metalloids on benthic organisms in sediment. De Castro-Català et al. (2016) proposed using invertebrate communities, toxicity bioassays, and the toxic unit approach as complementary assessment tools for determining the ecotoxicity of sediments in rivers. A review of the environmental occurrence of certain metals and metalloids, production and use, potential for human exposure, and molecular mechanisms of toxicity, genotoxicity, and carcinogenicity is provided by Tchounwou et al. (2012).

## Summary statistics

### NLAP data

Summary statistics for the metals and metalloids are provided in Table 3-3. Ten metals and metalloids were detected in all of the NLAP sediment samples, whereas seven metals and metalloids were detected in  $\leq 80\%$  of samples. Antimony and thallium were not detected in any sediment samples. It was

Table 3-3. Summary Statistics for Metals and Metalloids, Sorted from Low to High Nondetects

Metal or Metalloid	N	Number Detects	Number NDs	% NDs	Mean (mg/kg dry wt.)*	SD (mg/kg dry wt.)*
<b>Detected Data</b>						
Aluminum	54	54	0	0	14330.0	7255.0
Arsenic	54	54	0	0	10.5	12.6
Barium	54	54	0	0	212.7	84.2
Chromium	54	54	0	0	35.0	19.8
Cobalt	54	54	0	0	5.7	4.0
Copper	54	54	0	0	25.4	35.6
Lead	54	54	0	0	34.1	30.9
Manganese	54	54	0	0	1148.0	1478.0
Nickel	54	54	0	0	16.0	10.9
Zinc	54	54	0	0	61.4	29.2
<b>Detected &amp; Censored Data</b>						
Selenium	54	53	1	1.9	1.9	0.63
Vanadium	54	53	1	1.9	34.3	18.5
Cadmium	54	48	6	11.1	0.52	0.33
Molybdenum	54	43	11	20.4	1.9	1.2
Beryllium	54	24	30	55.6	0.42	0.20
Mercury	54	22	32	59.3	0.10	0.10
Silver	54	19	35	64.8	0.16	0.073
Antimony	54	0	54	100	-	-
Thallium	54	0	54	100	-	-

N = number of samples; ND = nondetect; SD = standard deviation.

\* The Kaplan-Meier method was used to calculate mean and SD values for censored data sets that had <80% nondetects.

surprising that mercury was not detected in 59% of samples since this element is so ubiquitous and frequently detected in sediment samples. In the future, more sediment may need to be collected for metal and metalloid analyses. The mass of available sediment was low for the mercury analyses, which contributed to higher reporting limits than expected. Additional summary statistics, percentiles, box plots, and Q-Q plots (with outliers noted at the 5% significance level) are provided in Appendix E.

The concentrations of metals and metalloids in the surficial sediments varied widely. Aluminum had the highest mean concentration of 14,330 mg/kg dry wt. (Table 3-3), which is consistent with its high abundance in the earth's crust (i.e., most abundant metal and third most abundant element; Rudnick and Gao 2003). Aluminum also spanned a wide concentration range from 1430 mg/kg dry wt. in lake #43 (Straight) to 31,500 mg/kg dry wt. in lake #46 (Upper Sakatah). Natural metal concentrations may vary by orders of magnitude depending on the sediments' mineralogy, grain size, and organic content (Carvalho et al. 2002). Manganese is another important component of the earth's crust, and it had the second highest mean concentration in the NLAP lake sediments (Table 3-3). Barium and zinc were also prevalent metals. Mercury was highest in lakes located in northeastern Minnesota.



### Additional NLA mercury data

As part of the nationwide NLA project in 2007, the U.S. EPA and USGS collaborated on the analysis of total mercury and methyl mercury on the 0 - 1 cm sediment core section collected from each lake (USEPA 2009a). The raw data were provided by the U.S. EPA in cooperation with the USGS. The Minnesota component of this data set was used to provide additional information about the distribution of mercury in the study lake sediments. A summary of these data are provided in Table 3-4. Additional summary statistics, percentiles, box plots, and Q-Q plots (with outliers noted at the 5% significance level) are provided in Appendix E.

Table 3-4. Summary Statistics for Forms of Mercury Analyzed in the 0 - 1 cm Segment of Sediment Samples Collected from the 2007 NLA Lakes in Minnesota

Forms of Mercury	N	Number Missing	Number Detects	Number NDs	% NDs	Mean*	SD*
Total Mercury (mg/kg dry wt.)	38	16	36	2	5.3	0.13	0.11
Methyl Mercury (µg/kg dry wt.)	39	15	35	4	10.3	0.63	0.48

NLA = National Lake Assessment; N = number of samples; ND = nondetect; SD = standard deviation.

\* The Kaplan-Meier method was used to calculate mean and SD values for censored data sets that had <80% nondetects.

The mercury data from the 0 – 15 cm depth interval were compared to the total mercury data from the 0 - 1 cm depth interval. Both measurements represent different forms of mercury (i.e., total mercury) that are converted to inorganic mercury before being measured by CVAA spectrometry. The “total mercury” terminology, as used by the U.S. EPA and USGS, was kept with the 0 – 1 cm depth interval samples to help distinguish it further from the 0 – 15 cm samples. Both types of samples were analyzed by different laboratories with their own unique sample processing and analytical digestion methods. Even so, the mean and SD values were comparable (Tables 3-3 and 3-4) for this limited data set. There were a number of missing data from the 0 – 1 cm core segments due to insufficient sediment mass for the chemical analyses (Table 3-4). For lakes that had detected total mercury data for both core segments, the results were plotted in Figure 3-8. The data were comparable ( $r^2 = 0.947$ ), despite spanning different spatial time periods for these sediment samples. This result may represent a consistent atmospheric source of mercury over recent time periods. At four mercury deposition network sites across Minnesota, no significant trends were observed in total mercury concentrations in precipitation during 1996 – 2005 (Wentz et al. 2014). Thus, atmospheric inputs of mercury through rainfall held steady during this time period. Sediment reconstruction of mercury from dated sediment cores collected from 55 Minnesota lakes during the mid-1990s indicated that mercury emissions in Minnesota peaked in the 1970s (Engstrom et al. 2007).

Although the mercury concentrations were low in the NLAP lakes, compared to other metals and metalloids (Table 3-3), this element is of high concern because of its potential to transform to methylmercury. Methylmercury bioaccumulates in aquatic food webs and has led to fish advisories throughout Minnesota. The MPCA is working on a plan with stakeholders to reach a 2025 goal to reduce in-state emissions of mercury by 76% from 2005 levels (MPCA 2009). Achievement of this goal should help reduce the bioaccumulation of methyl mercury in fish caught from Minnesota lakes and streams.

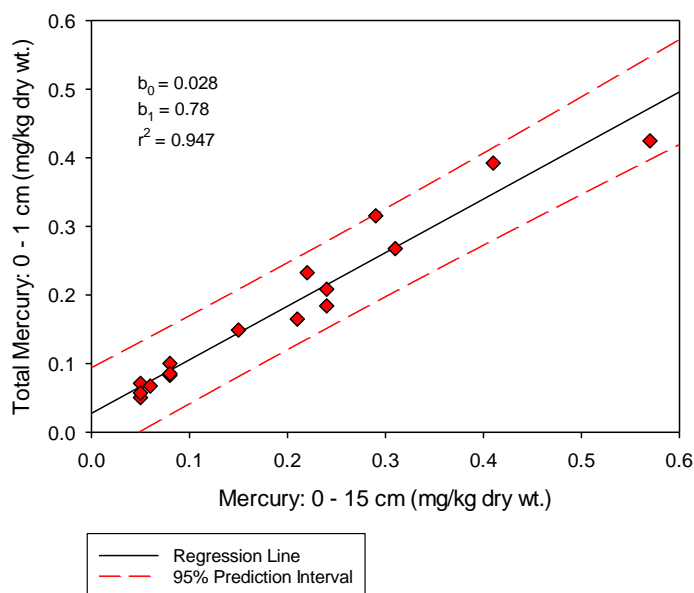


Figure 3-8. Correlation plot for total mercury, representing two different depth intervals for separate sediment samples from each lake. Only those samples that were collected and detected in both core sections were plotted. Linear regression terms:  $b_0$  = intercept,  $b_1$  = slope, and  $r^2$  = coefficient of determination.

The methyl mercury concentrations in the 0 – 1 cm sediment sections were low, averaging 0.63  $\mu\text{g}/\text{kg}$  dry wt. (Table 3-4). For the 26 NLA lakes in which methyl mercury and total mercury were detected in each 0 – 1 cm core segment, the ratio of methyl mercury to total mercury was calculated. The ratio averaged 0.50% with a SD of 0.36% and a median of 0.40%. These ratios were comparable to the methyl mercury to total mercury ratios calculated from an older study of Minnesota lakes ( $n = 49$ ). Dated sediment cores from this older study represented the time period from 1994 to 1997 and showed the following similar results: mean = 0.54%, SD = 0.59%, and median = 0.35% (Engstrom et al. 2007 and unpublished methyl mercury data supplied by Daniel Engstrom, St. Croix Watershed Research Station, Science Museum of Minnesota to Judy Crane on 12/10/2013).

Total mercury and methyl mercury were also analyzed in a surface water sample from each NLA lake in 2007. For the Minnesota component of this nationwide study, the median total mercury concentration was 0.526  $\text{ng}/\text{L}$  ( $n = 53$ ), while the median methyl mercury concentration was 0.053  $\text{ng}/\text{L}$  ( $n = 51$ ; Monson and Heiskary 2008). The median methyl mercury fraction of total mercury was 9.2% in these lake water samples, and this result indicates the efficiency of conversion of total mercury to methylmercury in a particular aquatic system (Monson and Heiskary 2008).

### Comparison of NLAP data to two other MPCA studies

The metal and metalloid data from the NLAP sediment study were compared to two older lake sediment studies from the MPCA, which also included reference lakes (Heiskary 1996; King 2000). These other data sets had a more limited analyte list, for which the original data were re-analyzed in ProUCL 5.0 to calculate summary statistics for detected and censored data. The mean and SD values for corresponding metals and the metalloid selenium are provided in Table 3-5. In addition, statistical tests were run in SigmaPlot 13.0 to assess for statistical differences in the means or medians of these groups of data. For data that had only one or two nondetect values, the full reporting limit was substituted. For cadmium and mercury, statistical comparisons were not made due to the higher number of nondetect values in

Table 3-5. Comparison of Metal and Metalloid Results from the NLAP Lakes with Two Other MPCA Studies that Included Reference Lakes

Study	2007 NLAP Lakes	King (2000)	Heiskary (1996) <sup>§</sup>
Sample Year	2007	1996	1992 & 1993
N	54	9	35
Depth Interval	0 - 15 cm	0 - 8 cm	0 - 3 cm or 0 - 5 cm
Ecoregion Coverage	NCHF, NGP, NLF, RRV, WCBP	NLF	NCHF, NLF, WCBP
Metal or Metalloid	Mean (SD) mg/kg dry wt.	Mean (SD) mg/kg dry wt.	Mean (SD) mg/kg dry wt.
Cadmium	0.52* (0.33*)	not calculable <sup>†</sup>	1.8* (1.0*)
Chromium	35.0 (19.8)	23.6 (13.2)	29.4 (17.3)
Copper	25.4 (35.6)	27.0* (25.1*)	29.8* (22.0*)
Lead	34.1 (30.9)	33.3* (15.4*)	50.3* (21.5*)
Mercury	0.10* (0.10*)	0.1 (0.1)	0.11* (0.11*)
Nickel	16.0 (10.9)	20.0 (11.0)	not analyzed
Selenium	1.9* (0.63*)	0.98 (0.57)	not analyzed

NLAP = National Lake Assessment Project; N = number of samples; NCHF = North Central Hardwood Forests; NGP = Northern Glaciated Plains; NLF = Northern Lakes and Forests; RRV = Red River Valley; WCBP = Western Corn Belt Plains; SD = standard deviation.

<sup>§</sup> Included 28 reference lakes and seven lakes, which currently or historically received municipal wastewater treatment plant effluent.

\* The Kaplan-Meier method was used to calculate mean and SD values for censored data sets that had <80% nondetects.

<sup>†</sup> The reporting limits were too high, and all values were reported as <5 mg/kg dry wt.

these data sets (Tables 3-3 and 3-5). With mercury, similar mean and SD concentrations were observed across studies (Table 3-5), indicating a uniform atmospheric source of mercury to these lakes. For chromium, copper, lead, nickel, and selenium, natural log and square root transformations of the data were applied when the statistical comparisons of the raw data failed the Shapiro-Wilk normality test. For most of these data, except nickel, nonparametric statistical methods were run to assess for differences in median values between each study.

The statistical comparisons between the NLAP sediment and historical studies for chromium, copper, lead, nickel, and selenium are provided in Table 3-6. The results were not statistically significant ( $p > 0.05$ ) for chromium and nickel (Table 3-6). Statistically significant differences ( $p = 0.007$ ) in median values of copper were observed between the Heiskary (1996) and NLAP sediment studies (Table 3-6). However, this significance appeared to be due to seven impacted lakes included in the Heiskary (1996) study; these lakes received current or historical inputs of municipal WWTP effluent. When these seven lakes were removed from the Heiskary (1996) data set, no significant differences ( $p = 0.066$ ) were observed between the median values of all three sediment studies (Table 3-6). Lead, on the other hand, showed statistically significant differences ( $p < 0.05$ ) in median values between the NLAP and Heiskary (1996) data sets, regardless of whether the seven impacted lakes were included or not (Table 3-6). The cause for higher median values of lead in Heiskary's (1996) study is unknown, although these lakes could have been potentially impacted by the historical atmospheric deposition of lead emissions from vehicles. Lead was gradually phased out in gasoline, and it was totally banned by the Clean Air Act on January 1, 1996 (Siver and Wozniak 2001;

Table 3-6. Statistical Comparisons Between the NLAP and Other Sediment Studies for Metals and Selenium

Metal or Metalloid	Study Comparisons	Transformation of Data	Statistical Method	Statistical Result
Chromium	NLAP, King (2000), & Heiskary (1996)	none <sup>1</sup>	Krusakal-Wallis One-Way ANOVA on Ranks	Not Significant (p = 0.096)
Copper	NLAP, King (2000) <sup>2</sup> , & Heiskary (1996) <sup>2</sup>	none <sup>1</sup>	Krusakal-Wallis One-Way ANOVA on Ranks	<b>Significant (p = 0.01)</b>
	Heiskary (1996) <sup>2</sup> vs. NLAP	none <sup>1</sup>	Dunn's Method	<b>Significant (p = 0.007)</b>
	Heiskary (1996) <sup>2</sup> vs. King (2000) <sup>2</sup>	none <sup>1</sup>	Dunn's Method	Not Significant (p = 0.742)
	King (2000) <sup>2</sup> vs. NLAP	none <sup>1</sup>	Dunn's Method	Not Significant (p = 1.000)
Copper <sup>3</sup>	NLAP, King (2000) <sup>2</sup> , & Heiskary (1996) <sup>2</sup>	none <sup>1</sup>	Krusakal-Wallis One-Way ANOVA on Ranks	Not Significant (p = 0.066)
Lead	NLAP vs. Heiskary (1996) <sup>2</sup>	none <sup>1</sup>	Mann-Whitney Rank Sum Test	<b>Significant (p&lt;0.001)</b>
Lead <sup>3</sup>	NLAP vs. Heiskary (1996) <sup>2</sup>	none <sup>1</sup>	Mann-Whitney Rank Sum Test	<b>Significant (p = 0.002)</b>
Nickel	NLAP vs. King (2000)	natural log	t-test	Not Significant (one-tailed p = 0.123) <sup>†</sup>
Selenium	NLAP <sup>2</sup> vs. King (2000)	none <sup>1</sup>	Mann-Whitney Rank Sum Test	<b>Significant (p&lt;0.001)</b>

NLAP = National Lake Assessment Project; ANOVA = Analysis of Variance.

<sup>1</sup> Both the natural log and square root transformations did not pass either the Shapiro-Wilk normality test or the equal variance test (Brown-Forsythe) so that a one-way ANOVA could be run.

<sup>2</sup> When only one or two nondetects were present, the full reporting limit was substituted before conducting the statistical test method.

<sup>3</sup> Excluded impacted lakes from Heiskary (1996).

<sup>†</sup> The power of the performed test was below the desired power of 0.800, meaning less likelihood of detecting a difference when one actually exists.

<https://www.epa.gov/aboutepa/epa-takes-final-step-phaseout-leaded-gasoline>, accessed 4/26/2016). Leaded gasoline was a major source of lead emissions to the atmosphere, and dated sediment cores in reservoirs showed peaks in lead concentrations corresponding to the historical use of leaded gasoline (Callender and Van Metre 1997; Juracek and Ziegler 2006). Although the deeper (i.e., 0 - 15 cm) surficial sediments of the NLAP samples probably encompass part of the time period of Heiskary's more shallow samples (i.e., 0 - 5 cm), more recent deposition of sediments in the NLAP lakes should be lower in lead. Thus, there would be a dilution effect of the historical lead concentrations. For selenium, statistically significant differences (p<0.001) were observed in the median values of the NLAP and King (2000) sediment samples. The lower selenium values in King's (2000) study were all from reference lakes located in the Northern Lakes and Forests ecoregion.

### Statistical comparisons by major watershed land uses

Statistical comparisons were run on the NLAP metals and metalloids data to determine if land use had any influence on mean or median concentrations (with ≤1 nondetects). Due to the small sample size of some land use categories (e.g., n = 2 for developed land uses), this affected the power of the statistical

results for cobalt and vanadium (Table 3-7). Initially, either parametric or nonparametric ANOVAs were run on the raw data (Appendix E). However, natural log or square root transformations were useful in allowing more parametric ANOVAs to be run. Thus, one-way ANOVAs were run on either raw or transformed data, except for manganese (Table 3-7). Neither transformation helped to allow a one-way ANOVA to be run for manganese. There were no statistically significant differences ( $p>0.05$ ) in the means of aluminum, cobalt, nickel, selenium, and vanadium by major land use category (i.e., developed, cultivated, forested, and lakes and wetlands; Table 3-7). Median values of manganese were also not influenced ( $p>0.05$ ) by major land use categories (Table 3-7). The following parameters had statistically significant differences ( $p<0.05$ ) in the mean concentrations of major land use categories: arsenic, barium, chromium, copper, lead, and zinc (Table 3-7).

Table 3-7. Statistical Comparisons of Metals and Metalloids by Land Use Categories

Metal or Metalloid	Transformation of Data	p-value	
		One-Way ANOVA	Kruskal-Wallis One-Way ANOVA on Ranks
Aluminum	not needed	0.879	
Arsenic	natural log	0.003*	
Barium	natural log	0.045*	
Chromium	natural log	0.028*	
Cobalt	natural log	0.374†	
Copper	natural log	0.019*	
Lead	square root	<0.001*	
Manganese	none <sup>1</sup>		0.504
Nickel	natural log	0.786	
Selenium	natural log	0.911	
Vanadium	not needed	0.390†	
Zinc	not needed	0.002*	

ANOVA = analysis of variance.

\* Statistically significant difference ( $p<0.05$ ).

† The power of the performed test was below the desired power of 0.800, meaning less likelihood of detecting a difference when one actually exists.

<sup>1</sup> Both the natural log and square root transformations did not pass either the Shapiro-Wilk normality test or the equal variance test (Brown-Forsythe) so that a one-way ANOVA could be run.

The Holm-Sidak method used the results of the significant one-way ANOVAs (Table 3-7) to run multiple pairwise comparisons. None of the pairwise comparisons were statistically significant ( $p>0.05$ ) for chromium and copper (Table 3-8). For barium, the forested and cultivated land uses were the only pair displaying statistically significant differences ( $p<0.05$ ; Table 3-8). Mean values of barium were higher in watersheds dominated by cultivated land uses than those dominated by forests. Mean values of arsenic and lead were both significantly higher ( $p<0.05$ ) in watersheds dominated by developed land uses than the other three major land uses (Table 3-8). In addition, mean values of lead were also significantly higher ( $p<0.05$ ) in watersheds dominated by either forests or lakes and wetlands compared to cultivated land uses (Table 3-8). Mean values of zinc were significantly higher ( $p<0.05$ ) in lakes dominated by developed land uses than either those dominated by cultivated land uses or lakes and wetlands (Table 3-

Table 3-8. Multiple Pairwise Comparisons by Land Use Categories for Selected Metals and Arsenic. Pairs Shaded "Yes" are Significantly Different ( $p < 0.05$ ) from Each Other as Determined Using the Holm-Sidak Method.

Metal or Metalloid	$p < 0.05$					
	dev vs. cul	dev vs. wet	dev vs. for	for vs. cul	for vs. wet	wet vs. cul
Arsenic <sup>1</sup>	Yes	Yes	Yes	No	No	No
Barium <sup>1</sup>	No	No	No	Yes	No	No
Chromium <sup>1</sup>	No	No	No	No	No	No
Copper <sup>1</sup>	No	No	No	No	No	No
Lead <sup>2</sup>	Yes	Yes	Yes	Yes	No	Yes
Zinc	Yes	Yes	No	Yes	No	No

dev = developed; cul = cultivated; for = forested; wet = lakes and wetlands.

<sup>1</sup> Based on natural log transformation of data.

<sup>2</sup> Based on square root transformation of data.

8). In addition, the mean value of zinc in lakes dominated by forests was significantly higher ( $p < 0.05$ ) than lakes in agricultural areas with cultivated land uses (Table 3-8). Lead and zinc are common urban contaminants, and were both elevated enough in the two lakes included in the developed land uses to be able to discern significant differences between some other land use categories. In the future, it would be advantageous to conduct a study in which there were an equal number of lakes in each land use category at a higher frequency (e.g.,  $n > 20$  lakes) to provide greater statistical power for pairwise comparisons.

### Statistical comparisons by surface area categories

The NLAP metal and metalloid data were also compared by the five surface area categories included in the nationwide NLA study design. Due to the small number of samples in some surface area categories, six metals had one-way ANOVA results where the power of the performed test was below the desired power of 0.800 (Table 3-9). Manganese was the only parameter with a statistically significant ( $p < 0.05$ ) result (Table 3-9). The result of the Kruskal-Wallis one-way ANOVA on ranks for manganese was used by Dunn's method for multiple pairwise comparisons. Dunn's method is not as sensitive as the parametric Holm-Sidak method, but it is the only option for a nonparametric test with unequal sample size. Surface area categories E and A were not statistically different ( $p > 0.05$ ) from each other for manganese (Table 3-10). The other nine pairwise comparisons for manganese were given a "Do Not Test" classification (Table 3-10). This result occurs for a comparison when no significant difference ( $p > 0.05$ ) is found between the two rank sums that enclose that comparison. Not testing the enclosed rank sums is a procedural rule. A result of "Do Not Test" should be treated as if there is no significant difference between the rank sums, even though one may appear to exist. For future NLA projects, comparisons by surface area categories may need to be done on a regional basis to increase the number of sediment samples, and power, of these statistical tests.

### Comparisons to SQT values

The NLAP sediment results for seven metals and the metalloid arsenic were compared to their corresponding Level I and Level II SQT values. Concentrations were below the Level I SQT values for most of the sediment samples, meaning conditions were protective of sediment-dwelling organisms for these elements (Table 3-11). Chromium and lead had the highest percentage of samples (31.5 and 27.8%, respectively), which were between the Level I and Level II SQT values. Cadmium, mercury, and zinc did

Table 3-9. Statistical Comparisons of Metals and Metalloids by Lake Surface Area Categories

Metal or Metalloid	Transformation of Data	p-value	
		One-Way ANOVA	Kruskal-Wallis One-Way ANOVA on Ranks
Aluminum	not needed	0.308 <sup>†</sup>	
Arsenic	none <sup>1</sup>		0.874
Barium	not needed	0.744	
Chromium	natural log	0.378 <sup>†</sup>	
Cobalt	natural log	0.056 <sup>†</sup>	
Copper	none <sup>1</sup>		0.104
Lead	natural log	0.613	
Manganese	none <sup>1</sup>		0.016*
Nickel	natural log	0.137 <sup>†</sup>	
Selenium	natural log	0.560	
Vanadium	not needed	0.417 <sup>†</sup>	
Zinc	not needed	0.068 <sup>†</sup>	

ANOVA = analysis of variance.

<sup>†</sup> The power of the performed test was below the desired power of 0.800, meaning less likelihood of detecting a difference when one actually exists.

<sup>1</sup> Both the natural log and square root transformations did not pass either the Shapiro-Wilk normality test or the equal variance test (Brown-Forsythe) so that a one-way ANOVA could be run.

\* Statistically significant difference (p<0.05).

Table 3-10. Multiple Pairwise Comparisons by Lake Surface Area Categories for Manganese Based on Statistically Significant (p<0.05) Results in Table 3-9

Metal	Dunn's Method: p<0.05	
	E vs. A	Nine Other Pairwise Comparisons
Manganese	No	DNT

DNT = do not test.

Surface Area Categories: A = 4 - 10 ha; E = >100 ha.

not have any exceedances of the corresponding Level II SQT values, while the other chemicals were exceeded in one or two lakes. Exceedances of the Level II SQT values indicated harmful effects on sediment-dwelling organisms were likely to be observed (Crane et al. 2000, Crane and Hennes 2007). The two developed lakes (#27 and 38) exceeded the Level II SQT for lead, which was likely due to urban contamination from stormwater runoff and other sources. The Level II SQT exceedances for chromium (lake #3), copper (lake #6), and nickel (lakes #5 and 6) occurred in lakes from northeastern Minnesota where these metals are naturally high in geological minerals. Lake #6 (Becoosin) is located in the protected BWCAW, and would thus only receive air-derived anthropogenic inputs of contaminants besides naturally-derived runoff from the local watershed. Arsenic exceeded the Level II SQT value in lakes #38 (Snail) and 51 (Elk).

Table 3-11. Percentage of Metal and Metalloid Results Within Designated SQT Ranges (n = 54)

Metal or Metalloid	Percent of Samples (n = 54)		
	≤ Level I SQT	> Level I SQT to ≤ Level II SQT	> Level II SQT
Arsenic	75.9	20.4	3.7
Cadmium	88.9	11.1	0
Chromium	70.4	27.8	1.8
Copper	87.0	11.1	1.8
Lead	64.8	31.5	3.7
Mercury	81.5	18.5	0
Nickel	88.9	7.4	3.7
Zinc	94.4	5.6	0

SQT = sediment quality target.

The high arsenic concentration of 73.2 mg/kg dry wt. in Snail Lake (#38) appeared to be due to past treatments of arsenic compounds to control aquatic macrophytes and algae. Snail Lake has had frequent problems with submerged vegetation, chara, filamentous algae, and snails that cause swimmer’s itch. Under Minnesota law, aquatic plants growing in public waters are the property of the state (<http://www.dnr.state.mn.us/shorelandmgmt/apg/regulations.html>; accessed 7/6/2015). Sodium arsenite increased in use in Minnesota in 1954 and was used to eradicate aquatic vegetation (Minnesota Conservation Department 1959), and it was used through 1969 as determined from historical lake permits to destroy or control aquatic vegetation or organisms. For nearly 60 years, Snail Lake has been one of the more highly treated lakes in Minnesota. The MDNR records for Snail Lake listed the chemicals it was treated with from 1957 – 1981. After that time period, however, generic guidance was given for MDNR-approved aquatic herbicides or algaecides that were used. Several permits from 1957, 1958, 1959, 1961, and 1962 indicated Snail Lake was treated with sodium arsenite to control aquatic plants. Copper sulfate continues to be used in this lake to control snails causing swimmer’s itch and for filamentous algae. The U.S. Army sampled surficial sediments in Snail Lake during September 1999, and the average arsenic concentration of 10 samples was 52.4 mg/kg dry wt. (U.S. Army 2004); this average also exceeded the Level II SQT value for arsenic. High arsenic concentrations have also been measured in surficial sediments from several Wisconsin lakes treated with sodium arsenite (three references as cited in Tanner and Clayton 1990). Arsenic is likely to remain high in Snail Lake for some time. For a lake in Michigan that was treated with sodium arsenite in 1957, Siami et al. (1987) developed a model that predicted it would take more than 100 years for arsenic levels to reach pretreatment concentrations in the surficial sediments.

The source of the high arsenic concentration of 67.5 mg/kg dry wt. in Elk Lake (#51) is less certain. Elk Lake is a “super-sentinel” deep-water lake, which is included in a group of 24 lakes being studied by the MDNR to understand the effects of environmental stressors such as climate change (<http://www.dnr.state.mn.us/fisheries/slice/sentinel.html>; accessed 4/21/2016). It is located in Itasca State Park with road access and a group campsite along its shore, with no other development (O’Hara et al. 2011). Thus, it is located in a pristine area. A quick review of MDNR’s old paper permit records did not reveal any records for Elk Lake. However, records could have been missed or arsenic compounds could have been illegally disposed of in this lake. Further sampling is warranted to evaluate if other areas of Elk Lake have elevated arsenic concentrations in the sediment.



## Normalize metals and metalloids to aluminum

Naturally occurring metals and metalloids in soil and sediment usually exist in predictable proportions to other elements (Myers and Thorbjornsen 2004). Major components of the earth's crust, like aluminum and iron, are often used as "reference" elements to normalize "trace" metal and metalloid concentrations. As discussed by Carvalho et al. (2002; and references therein), lithium, manganese, and TOC have also been used to normalize metal and metalloid concentrations. Doing so, through the use of correlation plots, provides a way to visually determine "outliers" outside the 95% prediction interval. These "outliers" may represent contaminated or naturally enriched sites beyond an anthropogenic background.

For the NLAP sediment data, aluminum was selected to assess "outliers" in correlation plots with other metals and metalloids. Using aluminum as a reference element has several advantages, including: 1) it is naturally abundant, 2) anthropogenic contributions are uncommon, particularly outside of developed watersheds, and 3) it often associates with clay minerals, which due to their negative charge, also concentrate many trace metals and metalloids (Windom et al. 1989; Hanson et al. 1993; Daskalakis and O'Connor 1995). Some researchers automatically perform a log transformation of their data prior to preparing correlation plots with aluminum and trace metals (Carvalho et al. 2002). For the NLAP sediment data, aluminum was normally distributed at the 5% significance level as determined by ProUCL 5.0 software. A decision was made not to transform the NLAP data in the correlation plots provided in Figures 3-9 and 3-10 for metals and metalloids that had  $\leq 1$  nondetect value. The coefficient of determination ( $r^2$ ) values were very low ( $<0.07$ ) for arsenic, barium, copper, lead, and selenium (Figures 3-9 and 3-10), indicating aluminum did not co-occur with these metals and metalloids. Weaker  $r^2$  values ( $>0.07$  and  $<0.30$ ) were noted for chromium, cobalt, manganese, and zinc (Figures 3-9 and 3-10). Nickel ( $r^2 = 0.451$ ) and vanadium ( $r^2 = 0.786$ ) showed the strongest co-occurrences with aluminum (Figure 3-10). One to three lakes were noted on each correlation plot as potential outliers (Figures 3-9 and 3-10). Statistical outlier tests were also run in ProUCL 5.0, and those results will be discussed in a subsequent section.

## PCA analysis

PCA analysis of the metal and metalloid data was performed with two different groups of parameters. First, the analysis was run on the 10 metals and two metalloids that had  $\leq 1$  nondetect value. This list included: aluminum, arsenic, barium, chromium, cobalt, copper, lead, manganese, nickel, selenium, vanadium, and zinc. The scree plot, component loading plots, and component score plots are provided in Appendix E. Three principal components accounted for 69.3% of the variance in the data (Figure 3-11). Each principal component is a linear combination of the original variables, after each original variable has been centered about its mean. The Eigenvectors in PC1 were highest for aluminum, vanadium, and zinc, while barium contributed the most to PC2. Arsenic and barium contributed the greatest Eigenvectors to PC3 (Appendix E). Thus, the data set was compressed down to four metals and the metalloid arsenic for accounting for most of the variance. The unexplained variance ranged from 8.0% for aluminum to 86.8% for selenium (Appendix E). Two significant outliers ( $p < 0.05$ ) were noted from the component scores, including: lakes #38 (Snail) and 51 (Elk; Figure 3-11; Appendix E). The groups on this plot were based on the HCA set-up with the paired group (UPGMA) algorithm and the Gower similarity index (Appendix E). Lakes #38 and 51 had the highest arsenic concentrations measured in this study, respectively, and each lake is noted as a unique group on Figure 3-11. Three other groups were distinguished, but they could have just as easily been included in one large group. There is some professional judgment involved with selecting the HCA distance cut-off for distinguishing between clusters as shown in Appendix E. Of the three larger clusters, the two lower ones concentrated lakes from cultivated land uses in addition to a smaller number of lakes from forested and

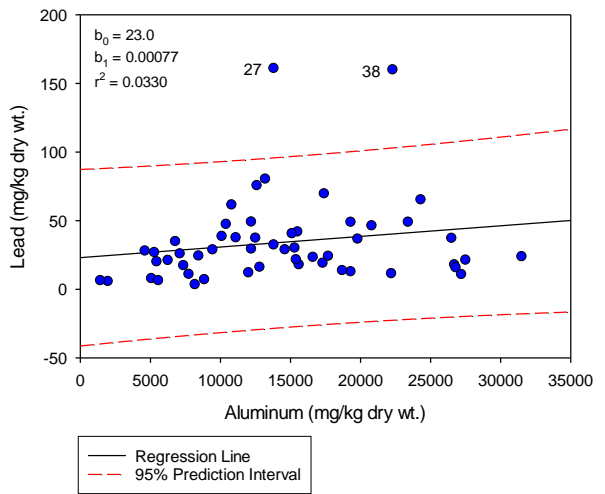
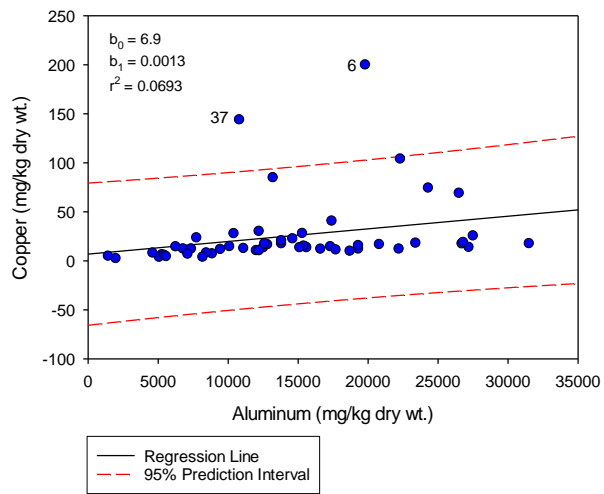
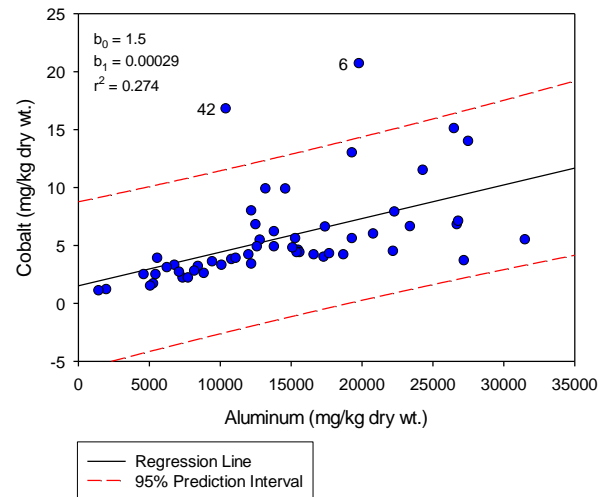
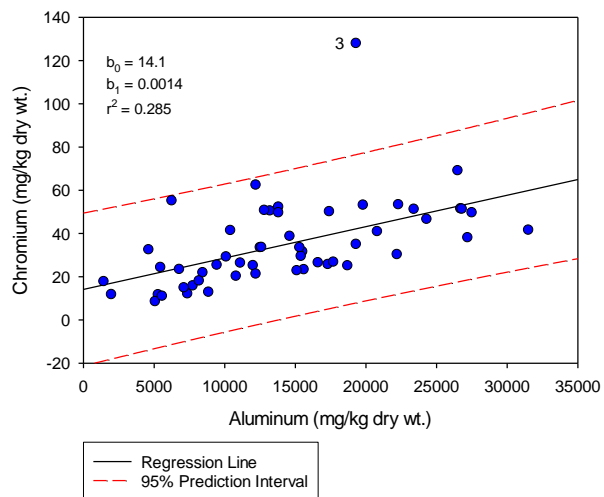
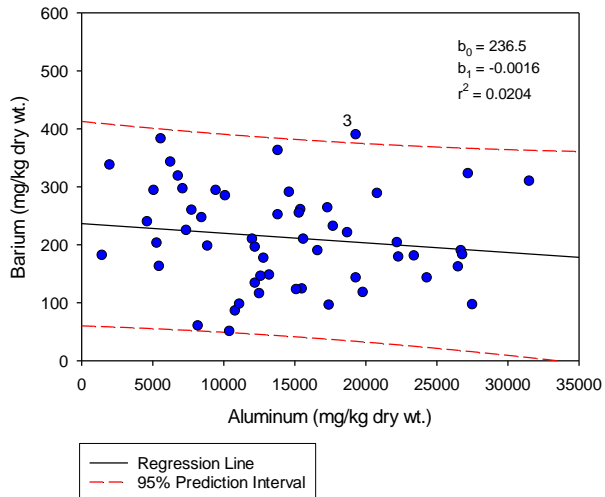
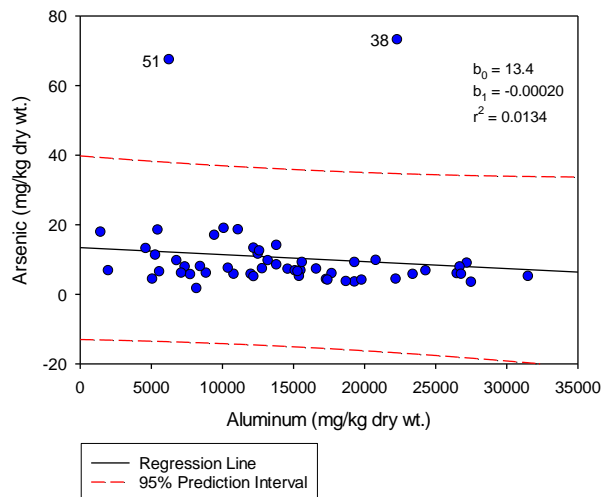


Figure 3-9. Normalization of metals and the metalloid arsenic to aluminum. “Outliers” appear outside the 95% prediction intervals. Linear regression terms:  $b_0$  = intercept,  $b_1$  = slope, and  $r^2$  = coefficient of determination.

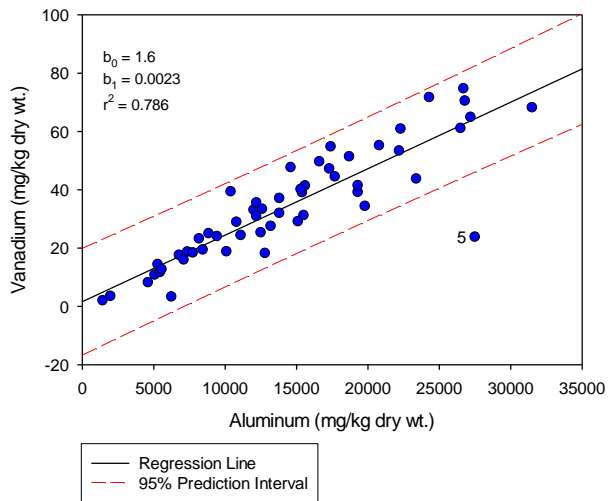
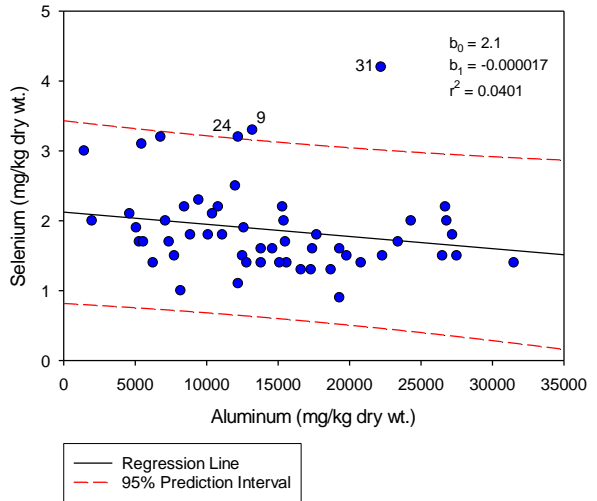
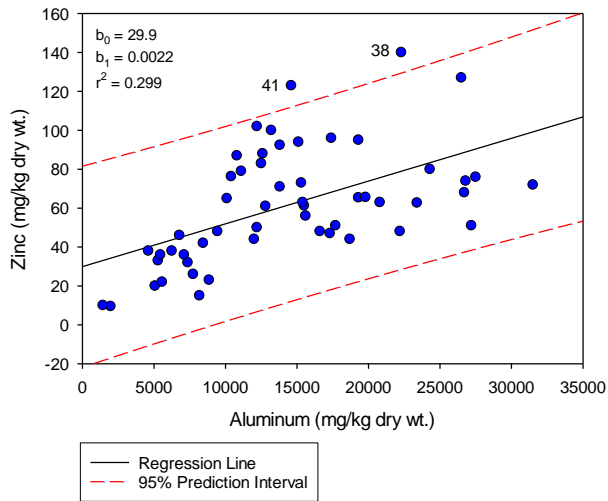
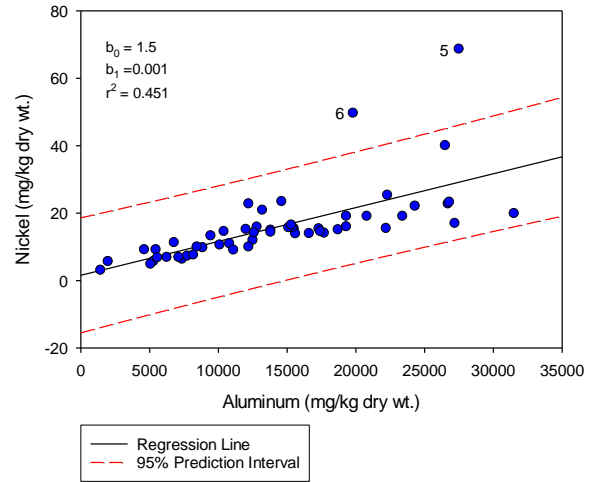
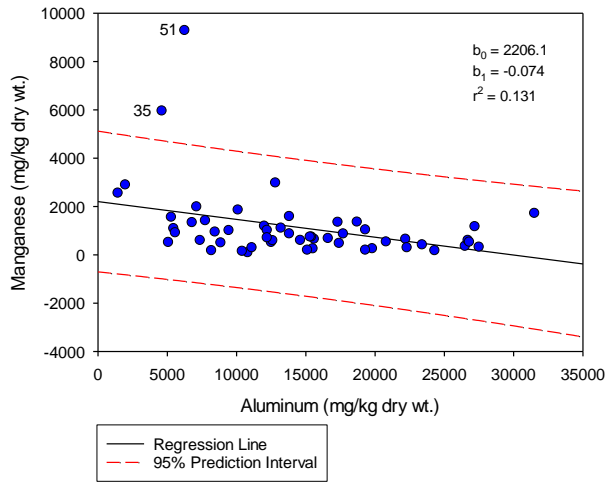


Figure 3-10. Normalization of metals and the metalloid selenium to aluminum. “Outliers” appear outside the 95% prediction intervals. Linear regression terms:  $b_0$  = intercept,  $b_1$  = slope, and  $r^2$  = coefficient of determination.

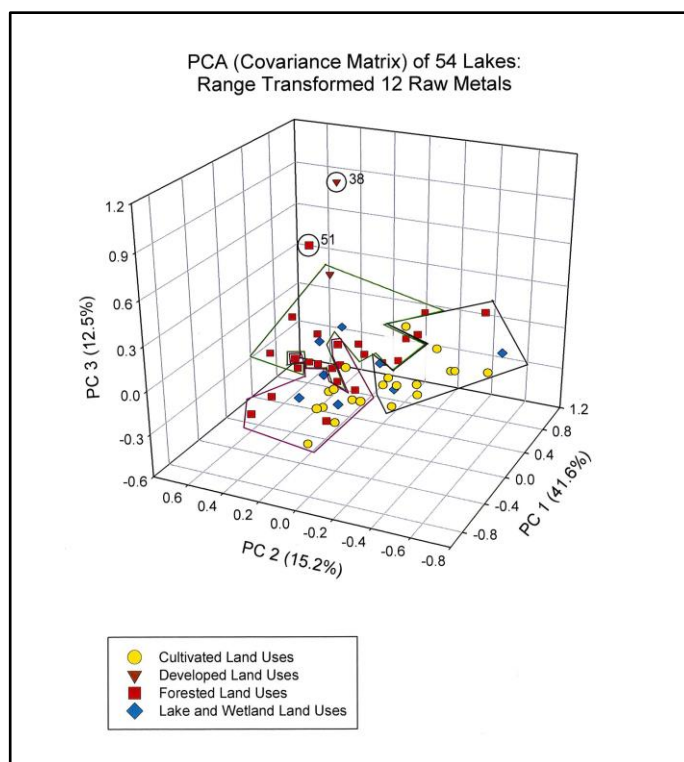


Figure 3-11. PCA plot of 12 metals (including the metalloids arsenic and selenium) for the 54 NLAP lakes.

lake/wetland land uses. The top of the three large clusters was dominated by lakes from forested land uses.

The second PCA analysis was limited to a subset of metals and metalloids that also had SQT values, including: five metals (chromium, copper, lead, nickel, and zinc) and the metalloid arsenic (hereafter lumped with the other metals for this discussion). This plot was more relevant for metals of interest to the MPCA. The scree plot, component loading plots, and component score plots are provided in Appendix E. Three principal components accounted for 81.3% of the variance in the data (Figure 3-12). The Eigenvectors in PC1 were highest for zinc and lead, while arsenic and nickel contributed the most to PC2. Copper and chromium contributed the greatest Eigenvectors to PC3 (Appendix E). The unexplained variance ranged from 8.4% for copper to 31.3% for arsenic (Appendix E). Five significant outliers ( $p < 0.05$ ) were noted from the component scores, including: lakes #3 (Arthur), 5 (August), 6 (Becoosin), 37 (Richey) and 38 (Snail; Figure 3-12; Appendix E). Lakes #3, 5, 6, and 37 are located in northeast Minnesota where naturally-derived concentrations of copper, nickel, chromium, and some zinc are higher in the mineralogical composition of the surrounding soils. The other outlier, #38, is an urban lake with elevated arsenic, lead, and zinc concentrations. The seven groups on this plot were based on the HCA set-up with the paired group (UPGMA) algorithm and the Gower similarity index (Appendix E). Lake #6 had the highest copper concentration. Lakes #3 and 4 had elevated nickel and zinc. Lake #3 was high in chromium. The cluster of lakes #37, 47, and 9 were generally elevated in zinc and some lead. Lakes #27 and 51 had similar chromium and copper concentrations, but differed in the magnitude of some other metals (e.g., lead and zinc). All other lakes, encompassing cultivated, forested, and lakes and wetlands land uses, were clustered together in one group. If the clusters were compressed further, lakes #3, 4, and 5 would form one cluster, and lakes #9, 37, and 47 would form a cluster with the largest number of lakes in the center of the PCA diagram (Appendix E). Lakes #6 and 38 were the most distinct clusters.

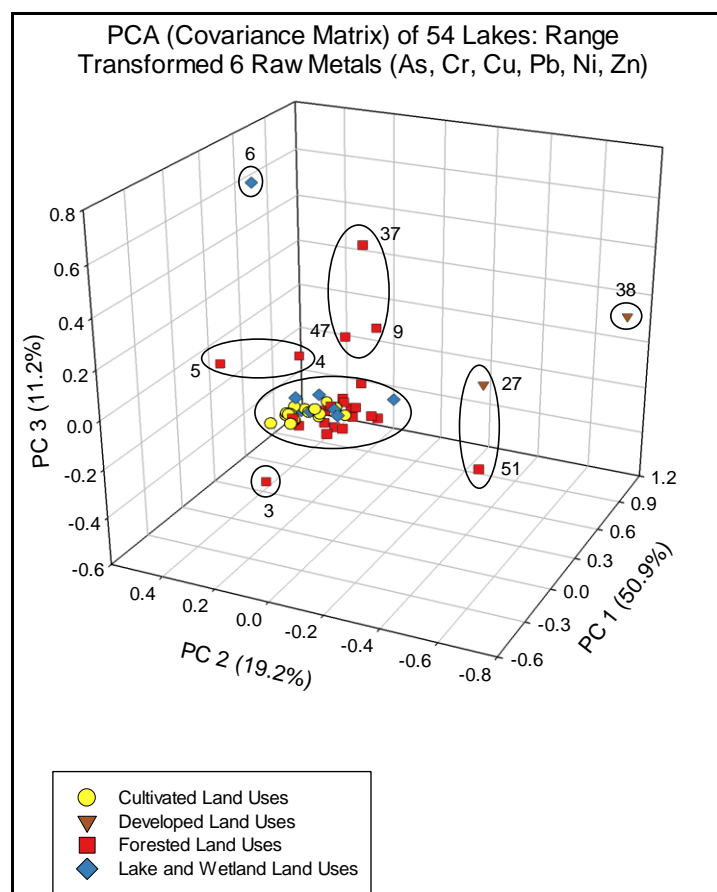


Figure 3-12. PCA plot of six metals (including the metalloid arsenic) for the 54 NLAP lakes.

## UTL values

UTL values were calculated in ProUCL 5.0 for metals and metalloids that had <80% nondetect values (Tables 3-12 and 3-13). In addition, UTLs were calculated for the total mercury and methyl mercury analyses of 0 – 1 cm sediment core fractions (Table 3-14). Prior to estimating UTL values, outliers were removed at the 5% significance level as determined using the outlier tests in ProUCL 5.0. The results from these statistical outlier tests provided a more rigorous and uniform procedure for determining outliers, than estimating outliers by normalizing metals and metalloids to aluminum (Figures 3-9 and 3-10). For molybdenum, there were not any statistical outliers, but 10 upper values appeared to form a separate population of data from visual interpretation of the Q-Q plot (Appendix E); these upper data points were excluded from the UTL calculations. Outliers are noted on the Q-Q plots provided in Appendix E. Aluminum, barium, and zinc did not have any statistical outliers (Table 3-12), while cadmium and vanadium were the only metals with censored data that did not have any outliers (Table 3-13). The UTLs either followed a normal or gamma distribution after any outliers or separate populations of data were removed.

In comparison to the seven metals and the metalloid arsenic that have Level I and Level II SQT values (Table 1-1), the UTL values exceeded the corresponding Level I SQT values for all elements, except copper. For cadmium, mercury, nickel, and zinc, the exceedances were slight. For arsenic, chromium, and lead, the exceedances were more substantial, but were still below the Level II SQT values. These exceedances are based on a small data set. After new NLA sediment sampling takes place in 2017, the

Table 3-12. UTLs of Detected Metal and Metalloid Data with Outliers Removed at the 5% Significance Level (units in mg/kg dry wt.)

Metal or Metalloid	N	Potential Outliers Removed at 5% Significance Level (lake ID numbers)	Normal Distribution*	Gamma Distribution*	
				95% Approx. Gamma UTL with 95% Coverage	
			95% UTL with 95% Coverage	WH	HW
Aluminum	54		29132		
Arsenic	52	38, 51	-	18.2	18.6
Barium	54		384.5		
Chromium	53	3	-	73.1	75.2
Cobalt	49	3, 4, 5, 6, 42	-	10.4	10.6
Copper	47	4, 6, 9, 25, 37, 38, 47	27.5		
Lead	52	27, 38	67.2		
Manganese	49	19, 22, 35, 43, 51	1784		
Nickel	51	4, 5, 6	25.1		
Zinc	54		121		

UTL = Upper Tolerance Limit; WH = Wilson Hilferty; HW = Hawkins Wixley.

\* UTLs for normally distributed data were preferred over those derived from gamma distributed data. When the data were not normally distributed, the gamma distribution was used to estimate UTL values. Gamma UTLs are calculated using two different methods for which professional judgment can be used to select the value of interest.

2007 and 2017 sediment data can be combined to assess their usefulness for calculating UTL values. In addition, there may be a need to calculate regional UTL values for certain metals (e.g., copper, nickel) that are naturally high in portions of northeast Minnesota. The SQT and UTL values have different purposes, and it is not necessary for the UTL values to be less than the Level I SQT values. However, this may point out the conservative nature of some Level I SQT values compared to the corresponding UTL values. This issue should be taken into consideration for remediation decisions at small, uncomplicated sediment sites where individual SQTs or mean PEC-Qs may be used as remediation goals (Crane and Hennes 2007).

The NLAP UTL values were compared to the corresponding sediment data sets from King (2000) and Heiskary (1996). For King's (2000) study of nine reference lakes in the Northern Lakes and Forests ecoregion, the UTL values were not exceeded for cadmium, chromium, lead, and selenium (Table 3-15). The higher exceedances of copper and nickel in these lakes (King 2000) were consistent with naturally higher levels of these metals in portions of far northeastern Minnesota. Mercury was similarly elevated above the NLAP UTL value in both studies (Table 3-15). The NLAP UTL for copper was exceeded in 37.1% of Heiskary's (1996) study lakes (n = 35; Table 3-15), particularly in those lakes receiving current or historical WWTP effluent. Only two of the eight Heiskary (1996) study lakes exceeding the NLAP lead UTL were impacted by WWTP effluents. The rest were split between lakes in the Western Corn Belt Plains and North Central Hardwood Forest ecoregions; some of these lakes had substantial urban land uses in their watersheds (Heiskary 1996).

Over 68% of Heiskary's (1996) study lakes exceeded the UTL of 1.5 – 1.6 mg/kg dry wt. for cadmium (Table 3-15), for which most of the exceedances (up to 3.8 mg/kg dry wt.) were from lakes located in

Table 3-13. UTLs of Detected and Censored Metal and Metalloid Data with Outliers Removed at the 5% Significance Level (units in mg/kg dry wt.; <80% Nondetects)

Metal or Metalloid	N (# detects)	% Nondetects	Potential Outliers Removed at 5% Significance Levels (lake ID numbers)*	Normal Distribution and KM Estimates†	Gamma Distribution and KM Estimates†	
					95% Approx. Gamma UTL w/ 95% Coverage	
					WH	HW
Beryllium	53 (23)	56.6	25	0.77		
Cadmium	54 (48)	11.1		-	1.5	1.6
Mercury	53 (21)	60.4	47	0.26		
Molybdenum	44 (33)	25	1, 10, 13, 18, 29, 30, 32, 38, 48, 51	2.6		
Selenium	48 (47)	2.1	9, 10, 18, 24, 31, 43	2.4		
Silver	53 (18)	66	4	0.25		
Vanadium	54 (53)	1.8		72.1		

KM = Kaplan-Meier; UTL = Upper Tolerance Limit; WH = Wilson Hilferty; HW = Hawkins Wixley.

\* Molybdenum did not have any significant outliers at the 5% significance level. However, its Q-Q plot appeared to have two separate distributions. The upper distribution of data was deleted as noted here. The upper distribution did not include any lakes from northeast Minnesota or south of the Minneapolis-St. Paul metropolitan area. When all 54 data points were considered, the data displayed a lognormal distribution and the 95% Kaplan-Meier UTL with 95% coverage was 5.9 mg/kg dry wt.

† UTLs for normally distributed data were preferred over those derived from gamma distributed data. When the data were not normally distributed, the gamma distribution was used to estimate UTL values. Gamma UTLs are calculated using two different ways for which professional judgment can be used to select the value of interest.

Table 3-14. UTLs of Detected and Censored Forms of Mercury Analyzed in the 0 - 1 cm Segment of Sediment Samples Collected from the 2007 NLA Lakes in Minnesota. Outliers were Removed at the 5% Significance Level.

Forms of Mercury	N (# detects)	% Nondetects	Potential Outliers Removed at 5% Significance Levels (lake ID numbers)*	Normal Distribution and KM Estimates†	Gamma Distribution and KM Estimates†	
					95% Approx. Gamma UTL w/ 95% Coverage	
				95% UTL with 95% Coverage	WH	HW
Total Mercury (mg/kg dry wt.)	38 (36)	5.3			0.47	0.51
Methyl Mercury (µg/kg dry wt.)	38 (34)	10.5	12	1.4		

UTL = Upper Tolerance Limit; NLA = National Lake Assessment; KM = Kaplan Meier; WH = Wilson Hilferty; HW = Hawkins Wixley.


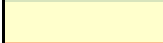



† UTLs for normally distributed data were preferred over those derived from gamma distributed data. When the data were not normally distributed, the gamma distribution was used to estimate UTL values. Gamma UTLs are calculated using two different methods for which professional judgment can be used to select which value to use.



Table 3-15. Comparison of King (2000) and Heiskary (1996) Data to NLAP UTL Values

Metal or Metalloid	King (2000)		Heiskary (1996)	
	Percent <UTL	Percent ≥UTL	Percent <UTL	Percent ≥UTL
Cadmium	100	0	31.4	68.6
Chromium	100	0	97.1	2.9
Copper	66.7	33.3	62.9	37.1
Lead	100	0	77.1	22.9
Mercury	88.9	11.1	91.4	8.6
Nickel	77.8	22.2	N/A	N/A
Selenium	100	0	N/A	N/A

NLAP = National Lake Assessment Project; UTL = upper tolerance limit; N/A = not applicable.

Values ≥UTL	Shading
>0 to ≤10%	
>10 to ≤20%	
>20 to ≤30%	
>30 to ≤40%	
>40%	

either the Western Corn Belt Plains ecoregion or which also received historical or current WWTP effluent. This result was surprising for the agricultural sites. Although phosphate fertilizers contain varying amounts of cadmium as contaminants from phosphate rock (Page et al. 1987; De Boo 1990), it seems unlikely that this source would contribute to the high cadmium concentrations observed in Heiskary's (1996) study. The MDH conducted a screening evaluation of arsenic, cadmium, and lead levels in fertilizer products sold in Minnesota (MDH 1999), and the only product that exceeded risk-based California standards for cadmium was used around houses in urban areas. Measurable quantities of cadmium were found in only 8.6% of primary (nitrogen, phosphate, and potassium) and micronutrient fertilizer products in the fall of 1997 and spring of 1998 (MDH 1999). For another study that included agricultural and urban watershed uses, the levels of cadmium measured in surficial (0 - 3 cm) sediments from pools in the Upper Mississippi River downstream from the Twin Cities, MN to Davenport, IA varied from 1.2 – 3.2 mg/kg dry wt.; some of the higher values were observed downstream of WWTP outfalls (Beauvais et al. 1995). One of Heiskary's (1996) study lakes (Nest) was also sampled for the NLAP study, and the results for cadmium varied by over an order of magnitude. Cadmium was 1.5 mg/kg dry wt. in the surficial sediment sample collected from Nest in 1992 (Heiskary 1996), and it was <0.1 mg/kg dry wt. in the surficial sediment sample collected from a comparable area in 2007. While sediments can be very heterogeneous, and these sediments represent different time periods of collection, some of these differences may also be due to changes in WWTP operations. Nest received indirect input from the Belgrade WWTP stabilization pond, which flowed to the Crow River and then Nest (Heiskary 1996). The cadmium values from Heiskary's (1996) study may be biased high, but cannot be proved without doing a follow-up study. For example, radioisotope dating and metals analysis of discrete segments of sediment cores from some of Heiskary's study lakes could be done to obtain the historical record of metal concentrations in these samples.

## Correlation plots

For the metals and the metalloid arsenic that were detected in all the sediment samples, regression correlation plots were developed after removing potential outliers at the 5% significance level (Figures 3-13 and 3-14). The same statistical outliers identified for the NLAP UTLs (Table 3-12), as well as the separate population of manganese samples (Table 3-12), were excluded from the correlation plots. Vanadium was also included since it only had one nondetect value, which was substituted with the reporting limit. Although selenium had one nondetect value, it did not display a significant correlation with any of the other metals or arsenic. The correlations in Figures 3-13 and 3-14 were all highly statistically significant ( $p < 0.001$ ), except for lead versus arsenic. Arsenic was not normally distributed, and it had a significant Spearman rho correlation with lead ( $p < 0.05$  and  $> 0.001$ ). The graph of lead versus arsenic is based on a linear correlation for a Pearson correlation, which is why the  $r^2$  value is very low (Figure 3-14). Cobalt and chromium were also not normally distributed; graphs with these metals were highly statistically significant ( $p < 0.001$ ) based on a Spearman rho correlation. Most of the graphs showed a high level of co-occurrence among pairs of metals, especially with nickel and metals like cobalt, aluminum, vanadium, and zinc (Figure 3-13). This finding is also consistent with the component loadings of metals and metalloids for the PCA plot of 10 metals and two metalloids (Appendix E). Barium and manganese were correlated with each other, but not with many other metals and metalloids. These metals also tracked with each other on the previously mentioned component loading graphs (Appendix E). In comparison, a survey of sediments from 14 minimally impacted lakes in northeastern Washington State also showed the best Pearson correlation coefficient for barium was with manganese (Johnson et al. 2011).

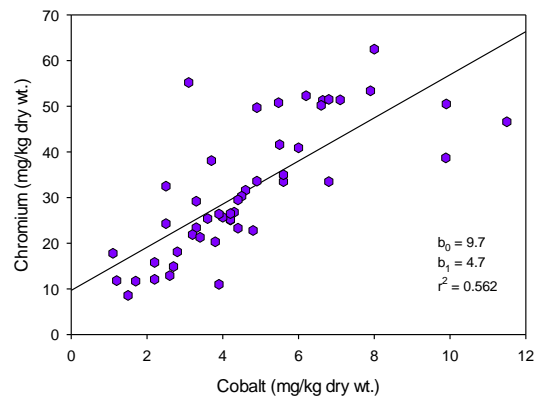
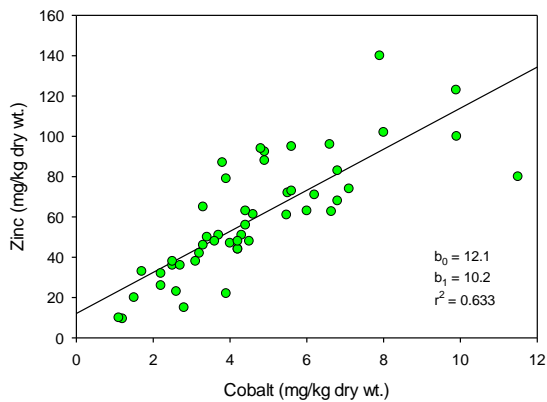
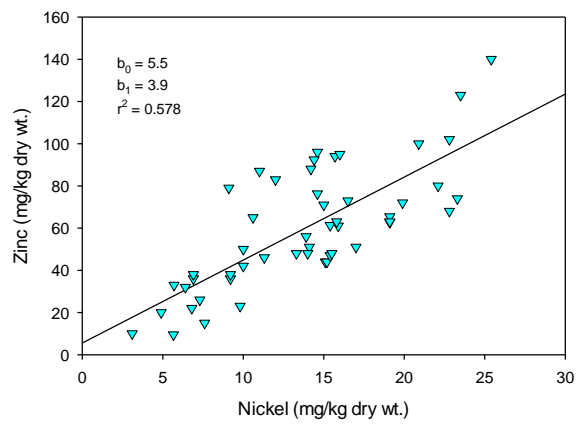
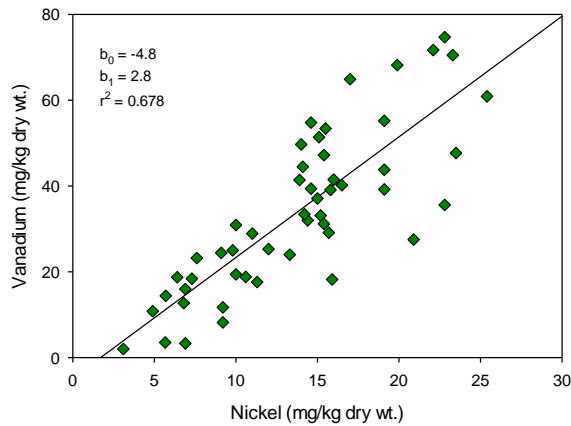
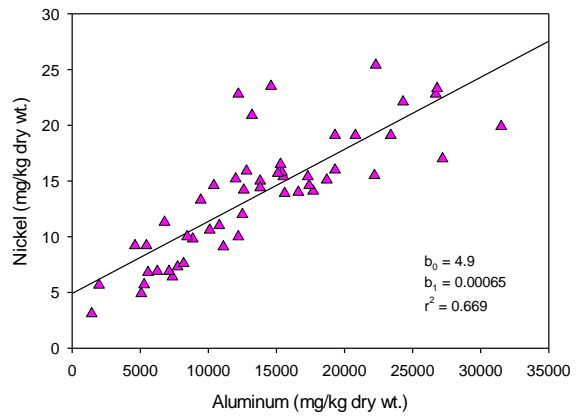
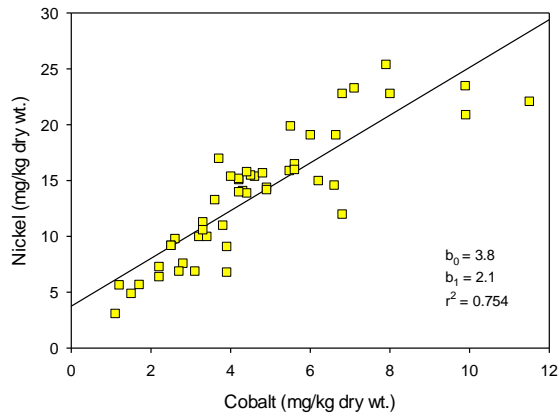


Figure 3-13. Correlation plots for detected metals and vanadium (one nondetect), which had outliers removed at the 5% significance level. For each graph,  $b_0$  = intercept,  $b_1$  = slope, and  $r^2$  = coefficient of determination.

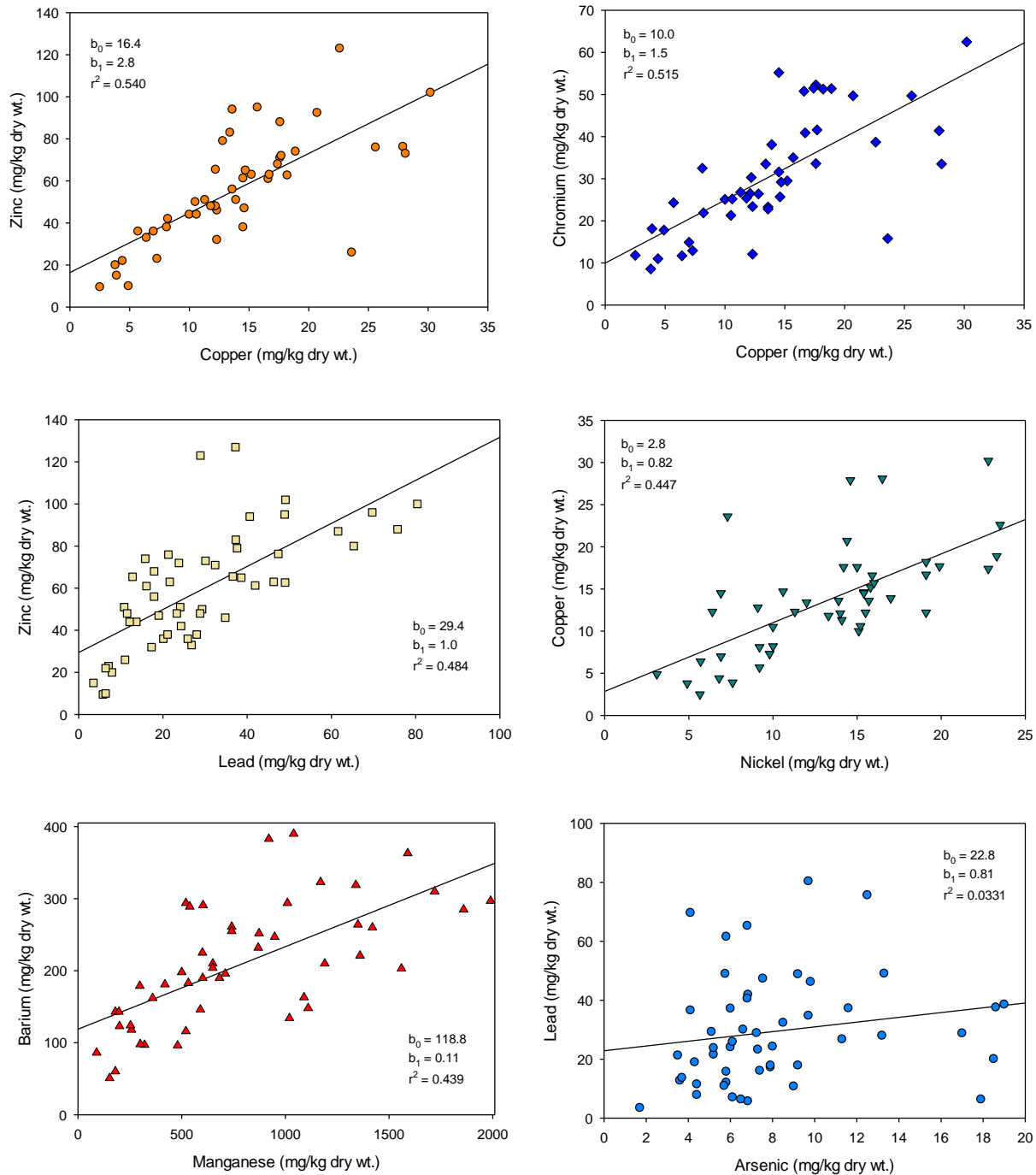


Figure 3-14. Correlation plots for detected metals and the metalloid arsenic, which had outliers removed at the 5% significance level (except for manganese, which had a separate population of samples removed). For each graph,  $b_0$  = intercept,  $b_1$  = slope, and  $r^2$  = coefficient of determination.

## PAHs

### *Highlights:*

- PAHs are ubiquitous in lake sediments throughout Minnesota and occur as a mixture of compounds.
- Perylene had a unique distribution compared to the other PAHs, and it is produced naturally in lake sediments.
- PAH ESB Toxic Units were below 1.0 for all samples, indicating that benthic organisms in sampled lakes are not likely to encounter adverse effects through narcosis.
- Lakes dominated by watersheds with developed land uses had the largest number of significant results ( $p < 0.05$ ) compared to three other major land uses for a broad suite of PAHs and  $\Sigma$ PAH groups; in all cases, concentrations were higher in the lakes with developed watersheds. For seven PAHs, significant differences ( $p < 0.05$ ) were observed between cultivated and forested land uses; higher concentrations were observed in the sediments of lakes surrounded by forests.
- Multiple pairwise comparisons were also made based on the percentage of developed land uses in each lake watershed.
- For naphthalene and four alkylated naphthalenes, there were significant differences ( $p < 0.05$ ) between lakes in NLA surface area category D (50 – 100 ha) versus surface area class E (>100 ha). The two urban lakes in category D contributed to higher mean concentrations of these PAH compounds.
- Most sample concentrations were less than their corresponding Level I SQT values, which would be protective of benthic organisms.
- The highest concentrations of  $\Sigma$ PAH<sub>13</sub> occurred in two developed lakes (#27 and 38), with values between the Level I and Level II SQT values.
- Multivariate statistical methods were used on two groups of PAH compounds to identify similar groups of lakes, as well as outliers.
- UTLs were calculated for PAH compounds with <80% nondetects, as well as for  $\Sigma$ PAH groups and PAH ESB Toxic Units.
- Regression correlation plots showed that PAHs of the same ring structure tended to have the strongest correlations with each other.
- Environmental forensic techniques indicated the samples were dominated by pyrogenic (i.e., combustion) sources of PAHs. In addition, the source apportionment of PAHs was dominated by vehicle emissions and coal-related combustion sources. CT-sealant dust was also an important source.
- Additional efforts in the energy and transportation sectors in Minnesota will likely result in future reductions of some PAH sources to the environment.

## Background

PAHs are persistent organic pollutants, which include hundreds of individual compounds (Douben 2003). Their structures include two or more benzene rings and may contain other fused ring structures. These compounds always occur as mixtures in the environment. The PAHs most commonly analyzed in

environmental samples include parent (i.e., unsubstituted benzene rings fused together) and alkylated PAHs, which include methyl (also known as alkyl) substitutions on the associated parent PAH compound. There can be one to four alkyl substitutions on an alkylated PAH, and these substitutions are designated as C1-, C2-, C3-, or C4-parent PAH name (e.g., C4-chrysene). More recently, other PAH compounds and derivatives have emerged in environmental samples, including: molecular weight 302 PAHs (MW302-PAHs), heterocyclic PAHs (where one of the carbons within the ring is replaced by nitrogen, oxygen, or sulfur), nitrated PAHs, and oxygenated PAHs (Titaley et al 2016). For the purposes of this report, ambient concentrations of parent and alkylated PAHs will be discussed, along with a limited number of heterocyclic PAHs (e.g., dibenzofuran). Much of this background section is based on a previous literature review by Crane et al. (2010).

A brief review of the environmental chemistry and ecotoxicity of PAHs from sediment-related exposures was provided in Crane et al. (2010). In addition, an overview of the partitioning and bioavailability of PAHs in sediments and soils was provided by Burgess et al. (2003). The physical and chemical characteristics of PAHs vary with molecular weight, which affects their distribution and fate in the environment. The general physical/chemical properties of PAHs include: high melting and boiling points, low vapor pressure, and very low water solubility (especially with increasing molecular mass; ATSDR 1995; Douben 2003; Achten and Andersson 2015). Low molecular weight PAHs, like naphthalene and other 2 to 3 ring group PAHs, are more water soluble than the higher molecular weight PAHs, like pyrene and other 4 to 7 ring PAHs (Neff 1979). Even so, PAHs are hydrophobic (i.e., avoid water) so they preferentially partition to organic carbon and particles in air, land, and water. The presence of black carbon (e.g., soot) increases the sorption of PAHs, too (Cornelissen et al. 2005). Thus, PAHs readily accumulate in sediment after entering lakes and streams.

PAHs are found naturally in coal and petroleum products and can be formed through the incomplete combustion of organic matter. The main sources of PAHs in sediments are due to petrogenic (i.e., oil-based) and pyrogenic (i.e., combustion-based) sources, and to a lesser extent to natural diagenic processes (e.g., oxidation of microbial- or plant-derived compounds; Battelle Memorial Institute et al. 2003). PAHs from pyrogenic sources are ubiquitous in the environment, whereas PAHs from petrogenic sources are more likely to be due to point sources like oil spills or refineries (Burgess et al. 2003). The PAHs from pyrogenic sources are enriched in 4 – 6 ring PAHs, and petrogenic PAHs are enriched in 2 – 3 ring PAHs. In the past decade, coal tar-based sealants have emerged as an important source of PAHs in urban areas where these sealants are used to protect and beautify asphalt driveways and parking lots (Mahler et al. 2012). In the Minneapolis-St. Paul, MN metropolitan area, coal tar-based sealant particulate wash-off and dust sources were estimated to contribute 67.1% of PAH concentrations in stormwater pond sediments, followed by vehicle-related sources (29.5%), and pine wood combustion particles (3.4%; Crane 2014).

Since PAHs preferentially adsorb to sediment, aquatic organisms and piscivorous wildlife that spend time in or near sediment are more likely to be exposed to these chemicals (Crane et al. 2010). The bioavailable fraction of PAHs in sediment and pore water is of concern when assessing risk to these ecological receptors. The age of the PAH-contaminated sediments can also affect bioavailability, with freshly contaminated sediments being more bioavailable than aged sediments (Alexander 2000; Volkering and Breure 2003). In addition, plant detritus may be an important sorbent for PAHs that can subsequently release PAHs into the water column or pore water (Rockne et al. 2002). Since PAHs occur in mixtures, display different mechanisms of toxicity, and are susceptible to transformation reactions, the joint action of PAHs in mixtures and with other contaminants have been the subject of much research (Altenburger et al. 2003).

PAHs are rapidly metabolized by fish, leading to little bioaccumulation (Lemaire et al. 1990). Thus, biomagnification of PAHs is not expected for food webs involving fish (Meador 2003). However, naphthalene, naphthol, and/or unidentified metabolite(s) can accumulate in fish brain tissues, which may impair normal brain function (Valdez Domingos et al. 2011). Fish exposed to PAH contamination have exhibited chronic effects, including: fin erosion, liver abnormalities, cataracts, skin tumors, and immune system impairments leading to increased susceptibility to disease (ATSDR 1995). In addition, PAHs may cause biochemical effects in fish through induction of mixed-function oxygenase enzymes (or cytochrome-P450), genetic effects through the formation of DNA adducts, potential reproductive toxicity, developmental effects to larval and juvenile fish, and potential behavioral effects (Akcha et al. 2003; Payne et al. 2003).

Benthic invertebrates exposed to sediment-related PAHs are susceptible to a number of detrimental effects. Some of these effects include: inhibited reproduction, delayed emergence, sediment avoidance, and mortality (ATSDR 1995). The ability to metabolize PAHs is highly variable in invertebrates (Meador 2003). For example, natural populations of benthic invertebrates in the St. Louis River AOC accumulated lower concentrations of high molecular weight PAHs than laboratory exposed invertebrates (Thijssen 1997). Factors that affect PAH accumulation include: organism behavior, laboratory artifacts, organism size, and seasonal changes in physiology, behavior, and environmental inputs (Meador 2003). Food web transfer of PAHs may occur in some invertebrates that are not able to effectively metabolize these compounds (Meador 2003).

A nonspecific narcosis-like mode of action is the most important mechanism by which acute effects occur in benthic invertebrates (Van Brummelen et al. 1998). Narcosis results in the degradation of cell membranes. The U.S. EPA's narcosis model requires the measurement of 18 parent and 16 groups of alkylated PAHs (i.e., group of 34 PAHs) in sediments to calculate the number of PAH ESB Toxic Units available to benthic organisms (USEPA 2003). Sediment concentrations of the 34 PAHs are used along with their expected sediment/water/lipid partitioning behavior to calculate a hazard quotient, referred to as a TU, which is used as a benchmark for predicting the toxicity of PAHs to benthic invertebrates (Hawthorne et al. 2006).

Certain PAHs can act as photosensitizing agents in the presence of solar ultraviolet (UV) radiation (Crane et al. 2010). Ankley et al. (2003) provided a literature review on assessing risks from photoactivated toxicity of PAHs to aquatic organisms, and they noted a number of studies showing that UV radiation can greatly increase the toxicity of PAHs in a broad phylogenetic spectrum of aquatic organisms. Field collected amphipods (scuds) from the lower St. Louis River and Duluth Harbor, MN were exposed to UV light, and the results indicated that organisms residing in PAH-contaminated environments accumulated PAH concentrations sufficient to be at risk for photoactivated toxicity (Diamond et al. 2003). In a different laboratory experiment, the spectral characteristics of UV light were shown to be an important factor in predicting photoinduced sediment toxicity from exposure to PAHs (Diamond et al. 2000).

Some PAH compounds can be hazardous to human health. Human health risks depend on: 1) the toxicological properties of the PAHs and other co-occurring contaminants, 2) the manner in which the person contacts the chemical (i.e., exposure pathway), 3) the concentrations of the contaminants, 4) how often the exposure occurs, 5) how long the exposure occurs, and 6) how much of the chemical is absorbed into the body during each exposure event (Villanacci and Beauchamp 2003). The U.S. EPA has classified the following seven PAH compounds as probable human carcinogens (Group B2), indicating sufficient evidence of carcinogenesis in animals, but inadequate evidence in humans: benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz[a,h]anthracene, and indeno[1,2,3-cd]pyrene (USEPA 1999). The MDH considers 19 priority carcinogenic PAHs (MDH 2016), including the EPA list, for which the MPCA is evaluating use of this MDH

guidance. Because benzo[a]pyrene is frequently detected in environmental samples at relatively high concentrations and has a high level of toxicity compared to other PAH compounds, it is often selected as a surrogate for other PAH compounds (Muller 2002). Benzo[a]pyrene (B[a]P) equivalents are widely used to assess human health risks of carcinogenic PAHs. Other PAH compounds have mutagenic and teratogenic properties, too (Luch 2005).

## Summary statistics

### Parent and alkylated PAHs

PAHs are ubiquitous in Minnesota lake sediments. Twenty-eight individual or PAH groups were detected in sediment samples from all 54 NLAP lakes (Table 3-16). This assemblage was dominated by parent PAHs and low molecular weight alkylated PAHs and groups. Atmospheric deposition of PAHs, with subsequent removal to the bottom sediments, is the most likely transport pathway for PAHs to enter the majority of study lakes that did not have watersheds with developed land uses. The other 15 individual PAHs or alkylated groups had one to 42 nondetects, with the C2- to C4-alkylated PAH groups having the highest number of nondetects (Table 3-16). In particular, the C4-chrysenes and C4-phenanthrenes/anthracenes were not detected in nearly 78% of lakes (Table 3-16). These alkylated PAHs are more common in oil-based material so it is not surprising that they displayed a higher frequency of nondetects in a broad distribution of Minnesota lakes. In the northern Alberta oil sands region, these types of alkylated PAHs were frequently detected in sediment cores from the Peace-Athabasca Delta (Hall et al. 2012; Jautzy et al. 2015). In contrast, Minnesota is a non-oil producing state (<http://www.eia.gov/state/?sid=MN>; accessed 5/11/2016).

The mean concentrations of PAHs varied by two orders of magnitude in the NLAP lake sediments. Mean concentrations of PAHs ranged from 1.5 µg/kg dry wt. for 1,6,7-trimethylnaphthalene to 283.7 µg/kg dry wt. for perylene (Table 3-16). Fluoranthene had the second highest mean concentration of PAHs at 109.7 µg/kg dry wt. (Table 3-16). For lakes with developed land uses, fluoranthene was the dominant PAH compound as shown in the histogram plot for lake #27 (Nokomis; Figure 3-15). This plot also shows

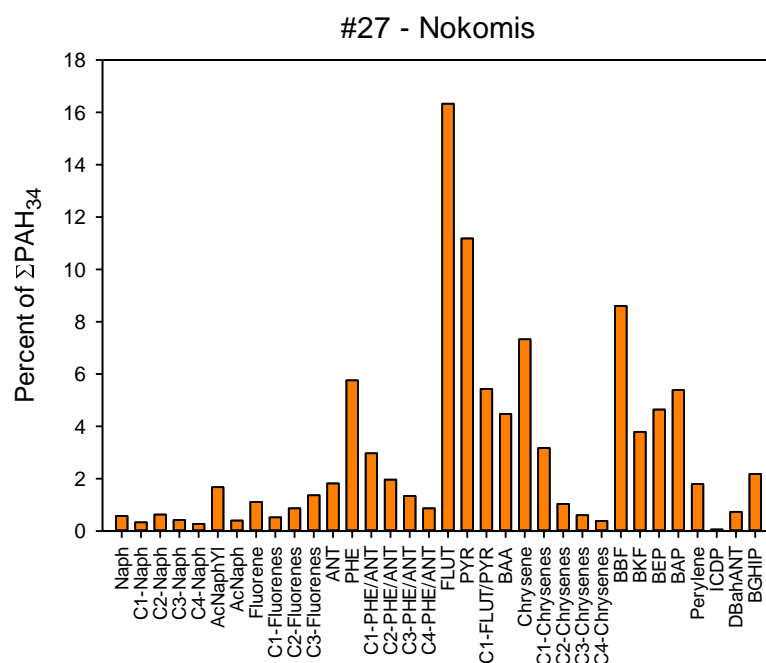


Figure 3-15. Percentage of 34 PAHs in lake #27 – Nokomis.



Table 3-16. Summary Statistics for Detected and Censored PAHs, Sorted from Low to High Nondetects

PAH Compound	Abbreviation	N	Number Detects	Number NDs	% NDs	Mean (µg/kg dry wt.)*	SD (µg/kg dry wt.)*
<b>Detected Data</b>							
Acenaphthene	AcNaph	54	54	0	0	16.3	10.6
Acenaphthylene	AcNaphYl	54	54	0	0	8.7	28.0
Anthracene	ANT	54	54	0	0	11.7	30.5
Benzo[a]anthracene	BAA	54	54	0	0	31.1	77.8
Benzo[a]pyrene	BAP	54	54	0	0	34.2	96.4
Benzo[b]fluoranthene	BBF	54	54	0	0	53.2	151.2
Benzo[g,h,i]perylene	BGHIP	54	54	0	0	21.8	39.4
Benzo[k]fluoranthene	BKF	54	54	0	0	31.8	70.9
Benzo[e]pyrene	BEP	54	54	0	0	38.5	81.9
C1-Fluorenes	C1-Fluorenes	54	54	0	0	26.1	15.8
C1-Fluoranthenes/pyrenes	C1-FLUT/PYR	54	54	0	0	43.7	93.4
C1-Naphthalenes	C1-Naph	54	54	0	0	10.2	6.7
C1-Phenanthrenes/anthracenes	C1-PHE/ANT	54	54	0	0	36.7	51.9
C2-Naphthalenes	C2-Naph	54	54	0	0	48.0	50.2
C3-Naphthalenes	C3-Naph	54	54	0	0	15.3	8.5
Chrysene	Chrysene	54	54	0	0	57.1	128.4
Fluoranthene	FLUT	54	54	0	0	109.7	282.0
Fluorene	Fluorene	54	54	0	0	41.1	30.4
Indeno[1,2,3-cd]pyrene	ICDP	54	54	0	0	18.6	21.2
1-Methylnaphthalene	1-MeNaph	54	54	0	0	5.2	3.5
2-Methylnaphthalene	2-MeNaph	54	54	0	0	9.8	6.5
2,6-Dimethylnaphthalene	2,6-DMeNaph	54	54	0	0	59.6	79.4
1-Methylphenanthrene	1-MePHE	54	54	0	0	9.6	12.9
1,6,7-Trimethylnaphthalene	1,6,7-TMeNaph	54	54	0	0	1.5	1.4
Naphthalene	Naph	54	54	0	0	16.4	11.3
Perylene	Perylene	54	54	0	0	283.7	361.7
Phenanthrene	PHE	54	54	0	0	70.4	103.1
Pyrene	PYR	54	54	0	0	78.4	193.2

Table 3-16. Continued

PAH Compound or Group	Abbreviation	N	Number Detects	Number NDs	% NDs	Mean ( $\mu\text{g}/\text{kg}$ dry wt.)*	SD ( $\mu\text{g}/\text{kg}$ dry wt.)*
<b>Detected &amp; Censored Data</b>							
Dibenzothiophene	DBZTP	54	53	1	1.9	4.6	6.5
C1-Chrysenes	C1-Chrysenes	54	52	2	3.7	57.7	61.5
C1-Dibenzothiophenes	C1-DBZTP	54	52	2	3.7	7.1	7.2
C2-Fluorenes	C2-Fluorenes	54	52	2	3.7	56.5	45.3
C2-Phenanthrenes/anthracenes	C2-PHE/ANT	54	52	2	3.7	30.2	34.6
Dibenzo[a,h]anthracene	DBahANT	54	51	3	5.6	4.5	12.6
C4-Naphthalenes	C4-Naph	54	49	5	9.3	20.3	11.5
C2-Dibenzothiophenes	C2-DBZTP	54	43	11	20.4	7.1	12.9
C2-Chrysenes	C2-Chrysenes	54	42	12	22.2	51.4	51.5
C3-Phenanthrenes/anthracenes	C3-PHE/ANT	54	36	18	33.3	18.7	31.6
C3-Fluorenes	C3-Fluorenes	54	34	20	37.0	17.1	25.1
C3-Chrysenes	C3-Chrysenes	54	29	25	46.3	52.5	87.6
C3-Dibenzothiophenes	C3-DBZTP	54	19	35	64.8	5.0	17.0
C4-Chrysenes	C4-Chrysenes	54	12	42	77.8	9.9	21.1
C4-Phenanthrenes/anthracenes	C4-PHE/ANT	54	12	42	77.8	7.0	17.9

PAH = polycyclic aromatic hydrocarbon; N = number of samples; ND = nondetect; SD = standard deviation.

\*The Kaplan-Meier method was used to calculate mean and SD values for censored data sets that had <80% nondetects.

a classic pyrogenic distribution of decreasing proportions of the parent and alkylated homologs for phenanthrene (PHE) and C1 to C4-phenanthrene/anthracene (PHE/ANT) homologs, as well as for chrysene and C1 to C4-chrysenes. This type of distribution occurs when a petrogenic source, like fuel, is combusted and emitted in vehicle emissions; PAHs associated with particles in vehicle emissions can be transported to lakes and deposited to sediments. Additional summary statistics, percentiles, and box plots are provided in Appendix F. Histogram plots of the concentration ranges of the 34 PAHs in each lake are also provided in Appendix F.

Perylene, a five-ringed PAH, had a more unique distribution than the other PAH compounds. Perylene ranged from 5.1  $\mu\text{g}/\text{kg}$  dry wt. in lake #15 (Flat) to 1640  $\mu\text{g}/\text{kg}$  dry wt. in lake #46 (Upper Sakatah). It tended to be lowest in the study lakes from northwestern Minnesota (i.e., lakes #15, 1, 44, 52, and 12, ordered in increasing concentration). Concentrations exceeded 1000  $\mu\text{g}/\text{kg}$  dry wt. in four lakes (i.e., #32, 4, 3, and 46). On a percentage basis, perylene comprised over 40% of  $\Sigma\text{PAH}_{34}$  in eight lakes and <10% of  $\Sigma\text{PAH}_{34}$  in 20 lakes (Figure 3-16). Sanders et al. (2002) also found that perylene constituted a large percentage of total PAHs in the upper Savannah River, GA and that it was distinctly separated from the other five-ringed PAHs.

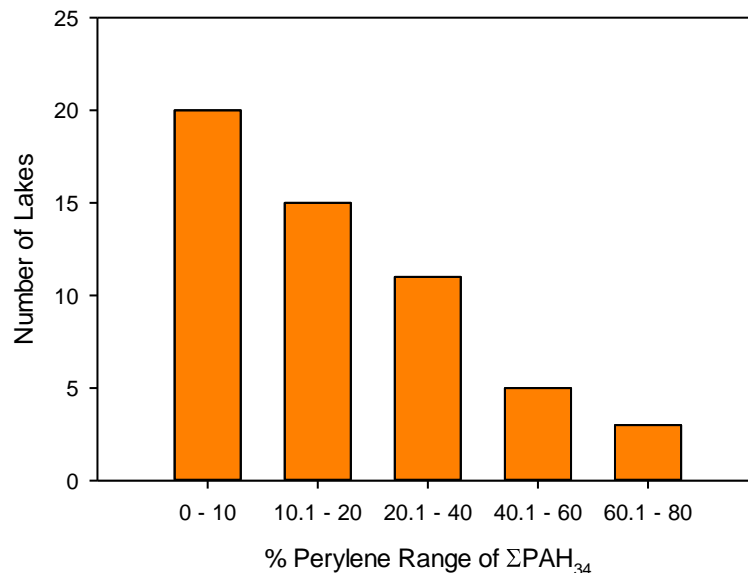


Figure 3-16. Range of perylene, as a percentage of  $\Sigma\text{PAH}_{34}$ , in the NLAP lakes.

Several researchers have noted that perylene concentrations increase with sediment depth in the Great Lakes region (Simcik et al. 1996; Silliman et al. 2001; Slater et al. 2013), in Finland and Norway (Christensen et al. 2007), in Malaysia (Bakhtiari et al. 2009), and in China (Han et al. 2015). Although deeper sediment cores were not collected from the NLAP lakes, it seems likely that a portion of these lakes would exhibit higher perylene concentrations at depth. In many sediment studies, perylene does not associate well with pyrogenic PAHs resulting from atmospheric deposition (Slater et al. 2013). Perylene is produced naturally in anoxic sediments, but its precursor has not been identified. Some researchers think that perylene originates mainly from *in situ* biogenic diagenesis under anoxic conditions and that this process is microbially mediated (Silliman et al. 2000; Han et al. 2015). Christensen et al (2007) observed that watersheds with a lot of peat and bogs can lead to high levels of perylene in lake sediments. North central and northeastern Minnesota have the greatest concentration of peatland in the U.S. (>6 million acres) after Alaska

([http://www.dnr.state.mn.us/snas/coniferous\\_peatlands.html](http://www.dnr.state.mn.us/snas/coniferous_peatlands.html); accessed 5/12/2016). Lake #3 (Arthur), which had high perylene concentrations, is also located in an area of northeastern Minnesota designated by the MDNR as having extensive peatlands. Perylene was high in other parts of the state, so there are likely other organic material sources important for the formation of perylene in sediments. In urban areas, anthropogenic sources of perylene may be a factor. Products such as coal tar pitch contain perylene (ATSDR 2002a), and it has been measured in other combustion products (Lima et al. 2005). Coal tar pitch is used to make coal tar-based sealants, which were banned in Minnesota in 2014 (Crane 2014). There appeared to be an anthropogenic source of perylene to a group of stormwater pond sediments in the Minneapolis-St. Paul, MN metropolitan area (Crane 2014). For the two NLAP lakes from developed land uses (i.e., lakes #27 and 38), there were not enough data to evaluate whether anthropogenic sources contributed to concentrations of perylene in these lakes.

### ΣPAH groups

The summary statistics for ΣPAH groups is provided in Table 3-17. The assemblage of PAHs in each total group is provided in Table 2-5. The mean concentration of ΣPAH<sub>34</sub> was nearly three times greater than the mean of ΣPAH<sub>13</sub>. However, these mean ΣPAH groups were relatively low in concentration. Additional summary statistics and percentiles are provided in Appendix F.

Table 3-17. Summary Statistics for ΣPAH Groups

Total PAH Group	N	Number of Lakes for Which the Kaplan-Meier Method was used to Calculate Total Values*	Mean (µg/kg dry wt.)	SD (µg/kg dry wt.)
ΣPAH <sub>13</sub>	54	3	489.3	980.5
ΣPAH <sub>17</sub>	54	3	614.7	1244.0
ΣPAH <sub>34</sub>	54	52	1428.0	1739.0

PAH = polycyclic aromatic hydrocarbon; N = number of samples; SD = standard deviation.

\* See Table F-1 in Appendix F for the list of lakes.

A box plot of the ΣPAH groups is given in Figure 3-17. This box plot consistently showed three lakes with the highest sediment concentrations: lakes #27 (Nokomis), 38 (Snail), and 32 (Pebble; Figure 3-17). As discussed in the subsequent section on UTLs, these three lakes were statistical outliers at the 5% significance level for each ΣPAH group. These outliers were removed from each random lake data set, and an ANOVA was run in SigmaPlot 13.0 to test the null hypothesis of no significant differences between the three outliers, the 47 other random samples, and the four reference samples. The Shapiro-Wilk normality test failed for each ΣPAH group, and natural log and square root transformations did not result in a normal distribution of the data. A Kruskal-Wallis one-way ANOVA on ranks was run on the raw data of each ΣPAH group. There was a statistically significant difference ( $p = 0.015$ ) for the three categories of samples for each ΣPAH group. Dunn's method was used to isolate the group or groups that differed from the others. ΣPAH<sub>13</sub> and ΣPAH<sub>17</sub> had similar results in that the difference of the rank sums was statistically significant ( $p < 0.05$ ) for the outliers versus the random samples, with the outliers having higher median values. However, the differences in the rank sums were not significant ( $p > 0.050$ ) for the outliers versus the reference groups (probably due to the small sample size of both groups) and for the reference versus the random sample groups. For ΣPAH<sub>34</sub>, the difference in the rank sums of the outliers versus the reference samples was not significant ( $p > 0.05$ ). This result was probably due to the small sample size of the outliers and random samples, as well as the inclusion of perylene in the total values.

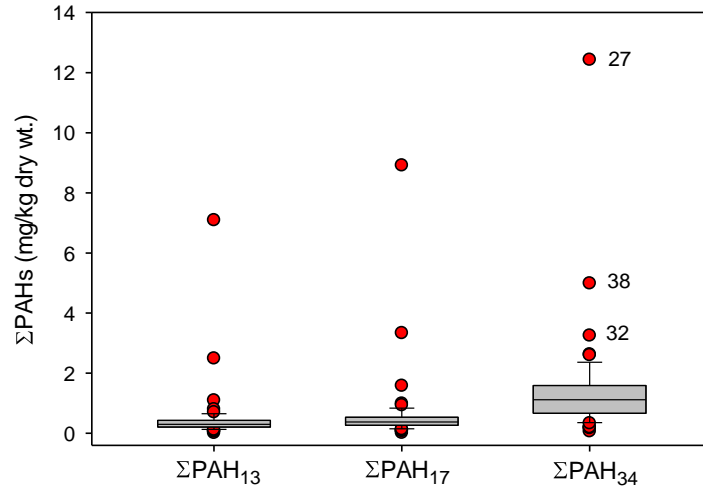


Figure 3-17. Box plots of  $\Sigma$ PAH groups based on measured and Kaplan-Meier estimated values. The three highest data points correspond to outliers for #27 (Nokomis), 38 (Snail), and 32 (Pebble), respectively.

The pairwise comparisons of the outliers versus the random samples, as well as the random versus the reference samples were given a “Do Not Test” classification for  $\Sigma$ PAH<sub>34</sub>. This result occurs for a comparison when no significant difference ( $p > 0.05$ ) is found between the two rank sums that enclose that comparison. Not testing the enclosed rank sums is a procedural rule. A result of “Do Not Test” should be treated as if there is no significant difference between the rank sums, even though one may appear to exist.

Another statistical method was run on the outlier data ( $n = 3$ ) and the pooled random and reference sample data ( $n = 51$ ) for each  $\Sigma$ PAH group. The Shapiro-Wilk normality test failed for each  $\Sigma$ PAH group, and natural log and square root transformations did not help to make the data either normal or to pass the Brown-Forsythe equal variance test. The results of a Mann-Whitney rank sum test of the raw data showed that the median values of the three outliers combined (i.e., #27, 32, and 38) were significantly greater ( $p = 0.004$ ) than the corresponding median values of the other 51 sediment samples for each  $\Sigma$ PAH group. For all other analyses, the reference data were pooled with the random data.

### PAH ESB Toxic Units

The calculated risk indicators were all low for PAHs. Summary statistics for the PAH ESB Toxic Units are provided in Table 3-18. All values were below 1.0 (Figure 3-18), indicating that benthic organisms in these lakes are not likely to encounter adverse effects through narcosis (i.e., resulting in the alteration of cell membrane function; Burgess 2009). Additional summary statistics, percentiles, and box plot of ESB Toxic Units are provided in Appendix F.

Table 3-18. Summary Statistics for PAH ESB Toxic Units

Parameter	N	Minimum	Maximum	Mean	SD	Skewness	Kurtosis
PAH ESB Toxic Units	54	0.0025	0.13	0.017	0.019	4.2	21.8

PAH = polycyclic aromatic hydrocarbon; ESB = equilibrium partitioning sediment benchmark; N = number of samples; SD = standard deviation.

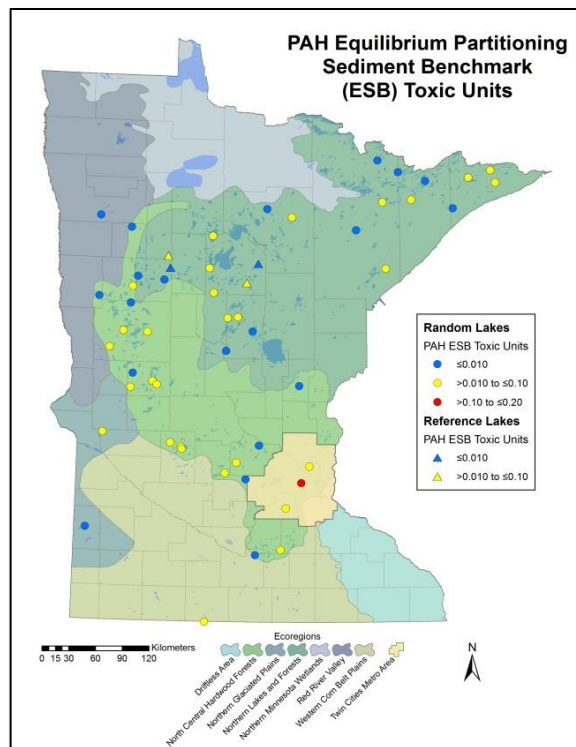


Figure 3-18. Distribution of PAH ESB Toxic Units in the study lakes.

### Statistical comparisons by major watershed land uses

Statistical comparisons were run to assess whether major watershed land uses had any influence on PAH concentrations in the study lake sediments. Individual PAH compounds (e.g., dibenzothiophene) were limited to those with ≤3 nondetect values (i.e., <5% nondetects; Table 3-16). The only PAH compounds or groups that were normally distributed, based on the raw data, were four alkylated naphthalene compounds. For the other PAH compounds and groups, natural log and square root transformations were tested to assess whether the transformed data would pass the normality and equal variance tests. When successful, a one-way ANOVA was run. Otherwise, the nonparametric Kruskal-Wallis one-way ANOVA on ranks was run on the raw data. In all, one-way ANOVAs were run on 19 PAH compounds, with the remainder run with the nonparametric method (Table 3-19). Categorization by land uses in 31 of the 37 PAHs and groups were statistically significant ( $p < 0.05$ ; Table 3-19). Perylene was among the six PAH compounds that did not show significant differences ( $p > 0.05$ ) by land use (Table 3-19).

Next, multiple pairwise comparisons were run for the four different land use categories to isolate the group or groups that differed from the others. The parametric Holm-Sidak method gave the most robust results for those PAHs run with a one-way ANOVA. Dunn's method was used for the nonparametric comparisons. For 13 parent and alkylated PAHs, significant differences ( $p < 0.05$ ) were observed between developed watersheds and the three other major land uses (Table 3-20); in all cases, the mean developed concentrations were greater than the other land use categories. For 15 other individual and  $\Sigma$ PAH groups, there were significant differences between the developed and cultivated land use groups (Table 3-20). C1-fluorenes, C2-fluorenes, and indeno[1,2,3-cd]pyrene were the only PAH compounds that did not have significant differences ( $p > 0.05$ ) between the developed and other land use categories (Table 3-20). For seven parent and alkylated PAHs, significant differences ( $p < 0.05$ ) were observed between forested and cultivated land uses (Table 3-20); the mean or median concentrations in the

Table 3-19. Statistical Comparisons of PAHs (with ≤3 nondetects) by Major Land Use Categories

PAH Compound or Group	Transformation of Data	p-value	
		One-Way ANOVA	Kruskal-Wallis One-Way ANOVA on Ranks
Acenaphthene	square root	0.005*	
Acenaphthylene	none <sup>1</sup>		0.017*
Anthracene	none <sup>1</sup>		0.075
Benzo[a]anthracene	none <sup>1</sup>		0.009*
Dibenzo[a,h]anthracene	natural log	<0.001*	
Benzo[a]pyrene	none <sup>1</sup>		0.020*
Benzo[b]fluoranthene	natural log	<0.001*	
Benzo[g,h,i]perylene	natural log	<0.001*	
Benzo[k]fluoranthene	none <sup>1</sup>		0.013*
Benzo[e]pyrene	none <sup>1</sup>		0.060
C1-Chrysenes	square root	<0.001*	
C1-Dibenzothiophenes	square root	<0.001*	
C1-Fluorenes	square root	0.025*	
C1-Fluoranthenes/Pyrenes	none <sup>1</sup>		0.014*
C1-Naphthalenes	not needed	<0.001*	
C1-Phenanthrenes/Anthracenes	none <sup>1</sup>		0.005*
C2-Fluorenes	square root	0.029*	
C2-Naphthalenes	none <sup>1</sup>		0.219
C2-Phenanthrenes/Anthracenes	none <sup>1</sup>		0.002*
C3-Naphthalenes	not needed	<0.001*	
Chrysene	none <sup>1</sup>		0.026*
Dibenzothiophene	none <sup>1</sup>		0.023*
Fluoranthene	none <sup>1</sup>		0.040*
Fluorene	none <sup>1</sup>		0.259
Indeno[1,2,3-cd]pyrene	natural log	0.005*	
1-Methylnaphthalene	not needed	<0.001*	
2-Methylnaphthalene	not needed	<0.001*	
2,6-Dimethylnaphthalene	natural log	0.475	
1-Methylphenanthrene	natural log	<0.001*	
1,6,7-Trimethylnaphthalene	natural log	0.004*	
Naphthalene	square root	<0.001*	
Perylene	natural log	0.700	
Phenanthrene	square root	<0.001*	
Pyrene	none <sup>1</sup>		0.036*
∑PAH <sub>13</sub>	none <sup>1</sup>		0.048*
∑PAH <sub>17</sub>	none <sup>1</sup>		0.029*
∑PAH <sub>34</sub>	none <sup>1</sup>		0.025*

PAH = polycyclic aromatic hydrocarbon; ANOVA = Analysis of Variance.

<sup>1</sup> Both the natural log and square root transformations did not pass either the Shapiro-Wilk normality test or the equal variance test (Brown-Forsythe) so that a one-way ANOVA could be run.

\* Statistically significant (p<0.05).

Table 3-20. Multiple Pairwise Comparisons by Major Land Use Categories for PAHs with Significant Results in Table 3-19. Pairs Shaded "Yes" are Significantly Different ( $p < 0.05$ ) from Each Other.

PAH Compound or Group	p<0.05					
	dev vs. cul	dev vs. wet	dev vs. for	for vs. cul	for vs. wet	wet vs. cul
Acenaphthene <sup>1,‡</sup>	Yes	No	No	No	No	No
Acenaphthylene <sup>§</sup>	Yes	No	DNT	No	DNT	DNT
Benzo[a]anthracene <sup>§</sup>	Yes	No	DNT	No	DNT	DNT
Dibenzo[a,h]anthracene <sup>2,‡</sup>	Yes	Yes	Yes	No	No	No
Benzo[a]pyrene <sup>§</sup>	Yes	DNT	No	DNT	DNT	No
Benzo[b]fluoranthene <sup>2,‡</sup>	Yes	Yes	Yes	Yes	No	No
Benzo[g,h,i]perylene <sup>2,‡</sup>	Yes	Yes	Yes	Yes	No	Yes
Benzo[k]fluoranthene <sup>§</sup>	Yes	DNT	No	DNT	DNT	No
C1-Chrysenes <sup>1,‡</sup>	Yes	Yes	Yes	No	No	No
C1-Dibenzothiophenes <sup>1,‡</sup>	Yes	Yes	Yes	No	No	No
C1-Fluorenes <sup>1,‡</sup>	No	No	No	No	No	No
C1-Fluoranthenes/Pyrenes <sup>§</sup>	Yes	No	DNT	No	DNT	DNT
C1-Naphthalenes <sup>‡</sup>	Yes	Yes	Yes	No	No	No
C1-Phenanthrenes/Anthracenes <sup>§</sup>	Yes	No	DNT	No	DNT	DNT
C2-Fluorenes <sup>1,‡</sup>	No	No	No	Yes	No	No
C2-Phenanthrenes/Anthracenes <sup>§</sup>	Yes	No	DNT	Yes	DNT	No
C3-Naphthalenes <sup>‡</sup>	Yes	Yes	Yes	Yes	No	No
Chrysene <sup>§</sup>	Yes	DNT	No	DNT	DNT	No
Dibenzothiophene <sup>§</sup>	Yes	No	DNT	No	DNT	DNT
Fluoranthene <sup>§</sup>	Yes	No	DNT	No	DNT	DNT
Indeno[1,2,3-cd]pyrene <sup>2,‡</sup>	No	No	No	Yes	No	No
1-Methylnaphthalene <sup>‡</sup>	Yes	Yes	Yes	No	No	No
2-Methylnaphthalene <sup>‡</sup>	Yes	Yes	Yes	No	No	No
1-Methylphenanthrene <sup>2,‡</sup>	Yes	Yes	Yes	Yes	No	No
1,6,7-Trimethylnaphthalene <sup>2,‡</sup>	Yes	Yes	Yes	No	No	No
Naphthalene <sup>1,‡</sup>	Yes	Yes	Yes	No	No	No
Phenanthrene <sup>1,‡</sup>	Yes	Yes	Yes	No	No	No
Pyrene <sup>§</sup>	Yes	No	DNT	No	DNT	DNT
∑PAH <sub>13</sub> <sup>§</sup>	Yes	No	DNT	No	DNT	DNT
∑PAH <sub>17</sub> <sup>§</sup>	Yes	No	DNT	No	DNT	DNT
∑PAH <sub>34</sub> <sup>§</sup>	Yes	No	DNT	No	DNT	DNT

PAH = polycyclic aromatic hydrocarbon; dev = developed; cul = cultivated; for = forested; wet = lakes and wetlands; DNT = do not test.

<sup>1</sup> Based on square root transformation of data.

<sup>2</sup> Based on natural log transformation of data.

<sup>‡</sup> The Holm-Sidak method was used for these pairwise multiple comparisons.

<sup>§</sup> Dunn's method was used for these pairwise multiple comparisons.



forested land use categories were always higher. Benzo[g,h,i]perylene was the only PAH compound with a significant difference ( $p < 0.05$ ) in the lakes and wetlands land uses versus cultivated land uses (Table 3-20); the mean value was higher in the lakes and wetlands classification. All other pairwise comparisons were either not significant or were given a “Do Not Test” classification (Table 3-20). In the future, it would be advantageous to conduct a study in which there were an equal number of lakes in each land use category at a higher frequency (e.g.,  $n > 20$  lakes) to provide greater statistical power.

### Statistical comparisons by percentage ranges of developed land uses

Most of the study lake watersheds encompassed a range of developed land uses (Table A-3 in Appendix A), with only two lakes (i.e., #27 and 38) dominated by urban development. In order to conduct a more nuanced evaluation than the previous one on major land uses, statistical comparisons were made to assess whether the percentage of developed land uses in the surrounding lake watersheds had any influence on PAH concentrations. Lakes were divided into the following four groups:

- D1 = >60% developed land uses ( $n = 2$ )
- D2 = 10 – 14% developed land uses ( $n = 11$ )
- D3 = 4 – 9% developed land uses ( $n = 20$ )
- D4 = 0 – 3% developed land uses ( $n = 21$ )

Individual PAHs were limited to those with  $\leq 3$  nondetect values (i.e., <5% nondetects). The only PAH compounds or groups that were normally distributed, based on the raw data, were four alkylated naphthalene compounds. For the other PAH compounds and groups, natural log and square root transformations were tested to assess whether the transformed data would pass the normality and equal variance tests. When successful, a one-way ANOVA was run. Otherwise, the nonparametric Kruskal-Wallis one-way ANOVA on ranks was run on the raw data. Due to the small sample size of the D1 and D2 groups, the power of some statistical results was affected (Table 3-21). In all, one-way ANOVAs were run on 22 PAH compounds and  $\Sigma\text{PAH}_{34}$ , with the remainder run with the nonparametric method (Table 3-21). The results of the parametric and nonparametric statistical methods showed that 22 of the 37 individual and PAH groups were statistically significant ( $p < 0.05$ ; Table 3-21). Perylene was one of the 15 PAH compounds and groups that did not show significant differences ( $p > 0.05$ ) among the percentage ranges of developed land uses (Table 3-21).

Next, multiple pairwise comparisons were run for the four ranges of developed land uses to isolate the group or groups that differed from the others. For 16 PAHs and  $\Sigma\text{PAH}_{34}$ , significant differences ( $p < 0.05$ ) were observed between D1 (>60% developed land uses) and the other three ranges of developed land uses (Table 3-22); in all cases, the mean D1 concentrations exceeded the other range groups. Three PAHs (i.e., dibenzo[a,h]anthracene, C1-phenanthrenes/anthracenes, and pyrene) only had significant differences ( $p < 0.05$ ) in D1 vs. D3 (Table 3-22); in all cases, the median concentration of D1 was higher. The only other significant differences occurred for two alkylated PAHs. There were significant differences ( $p < 0.05$ ) between groups D2 versus D4 and D4 versus D3 for 1-methylphenanthrene (Table 3-22); in both instances, D4 had a higher mean concentration. In addition, there was a significant difference ( $p < 0.05$ ) between groups D4 versus D3 for 1,6,7-trimethylnaphthalene (Table 3-22), where the lakes in group D4 had a higher mean concentration of this PAH compound. For these last three significant results, it was interesting that higher mean concentrations were noted in lakes with the smallest percentage of developed land uses. The lakes comprising group D4 were all located in the northern half of Minnesota and had the following major land uses: forested (17 lakes), lakes and wetlands (2 lakes), and cultivated (2 lakes). There may be a regional atmospheric source for 1-methylphenanthrene and 1,6,7-trimethylnaphthalene, and these compounds may be deposited or retained longer in the D4 lakes than lakes in the D2 and D3 groups.

Table 3-21. Statistical Comparisons of PAHs (with ≤3 nondetects) by Percent Developed Land Use Categories

PAH Compound or Group	Transformation of Data	p-value	
		One-Way ANOVA	Kruskal-Wallis One-Way ANOVA on Ranks
Acenaphthene	square root	0.065 <sup>1</sup>	
Acenaphthylene	none <sup>2</sup>		0.077
Anthracene	none <sup>2</sup>		0.090
Benzo[a]anthracene	none <sup>2</sup>		0.071
Dibenzo[a,h]anthracene	none <sup>2</sup>		0.042*
Benzo[a]pyrene	natural log	<0.001*	
Benzo[b]fluoranthene	natural log	<0.001*	
Benzo[g,h,i]perylene	natural log	<0.001*	
Benzo[k]fluoranthene	none <sup>2</sup>		0.048*
Benzo[e]pyrene	natural log	0.001*	
C1-Chrysenes	square root	<0.001*	
C1-Dibenzothiophenes	square root	<0.001*	
C1-Fluorenes	square root	0.204 <sup>1</sup>	
C1-Fluoranthenes/Pyrenes	natural log	<0.001*	
C1-Naphthalenes	not needed	<0.001*	
C1-Phenanthrenes/Anthracenes	none <sup>2</sup>		0.012*
C2-Fluorenes	none <sup>2</sup>		0.090
C2-Naphthalenes	natural log	0.033*	
C2-Phenanthrenes/Anthracenes	square root	<0.001*	
C3-Naphthalenes	not needed	<0.001*	
Chrysene	none <sup>2</sup>		0.103
Dibenzothiophene	none <sup>2</sup>		0.050
Fluoranthene	none <sup>2</sup>		0.054
Fluorene	none <sup>2</sup>		0.067
Indeno[1,2,3-cd]pyrene	natural log	0.127 <sup>1</sup>	
1-Methylnaphthalene	not needed	<0.001*	
2-Methylnaphthalene	not needed	<0.001*	
2,6-Dimethylnaphthalene	natural log	0.053 <sup>1</sup>	
1-Methylphenanthrene	natural log	<0.001*	
1,6,7-Trimethylnaphthalene	natural log	<0.001*	
Naphthalene	square root	<0.001*	
Perylene	natural log	0.827	
Phenanthrene	square root	<0.001*	
Pyrene	none <sup>2</sup>		0.049*
∑PAH <sub>13</sub>	none <sup>2</sup>		0.108
∑PAH <sub>17</sub>	none <sup>2</sup>		0.082
∑PAH <sub>34</sub>	square root	<0.001*	

PAH = polycyclic aromatic hydrocarbon; ANOVA = Analysis of Variance.

<sup>1</sup> The power of the performed test was below the desired power of 0.800, meaning less likelihood of detecting a difference when one actually exists.

<sup>2</sup> Both the natural log and square root transformations did not pass either the Shapiro-Wilk normality test or the equal variance test (Brown-Forsythe) so that a one-way ANOVA could be run.

\* Statistically significant (p<0.05).

Table 3-22. Multiple Pairwise Comparisons by Developed Land Use Categories for PAHs with Statistically Significant ( $p < 0.05$ ) Results in Table 3-21. Pairs Shaded “Yes” are Significantly Different ( $p < 0.05$ ) from Each Other.

PAH Compound or Group	$p < 0.05$					
	D1 vs. D3	D1 vs. D4	D1 vs. D2	D2 vs. D3	D2 vs. D4	D4 vs. D3
Dibenzo[a,h]anthracene <sup>§</sup>	Yes	No	DNT	No	DNT	DNT
Benzo[a]pyrene <sup>1,‡</sup>	Yes	Yes	Yes	No	No	No
Benzo[b]fluoranthene <sup>1,‡</sup>	Yes	Yes	Yes	No	No	No
Benzo[g,h,i]perylene <sup>1,‡</sup>	Yes	Yes	Yes	No	No	No
Benzo[k]fluoranthene <sup>§</sup>	No	DNT	DNT	DNT	DNT	DNT
Benzo[e]pyrene <sup>1,‡</sup>	Yes	Yes	Yes	No	No	No
C1-Chrysenes <sup>2,‡</sup>	Yes	Yes	Yes	No	No	No
C1-Dibenzothiophenes <sup>2,‡</sup>	Yes	Yes	Yes	No	No	No
C1-Fluoranthenes/Pyrenes <sup>1,‡</sup>	Yes	Yes	Yes	No	No	No
C1-Naphthalenes <sup>‡</sup>	Yes	Yes	Yes	No	No	No
C1-Phenanthrenes/Anthracenes <sup>§</sup>	Yes	DNT	No	DNT	DNT	No
C2-Naphthalenes <sup>1,‡</sup>	No	No	No	No	No	No
C2-Phenanthrenes/Anthracenes <sup>2,‡</sup>	Yes	Yes	Yes	No	No	No
C3-Naphthalenes <sup>‡</sup>	Yes	Yes	Yes	No	No	No
1-Methylnaphthalene <sup>‡</sup>	Yes	Yes	Yes	No	No	No
2-Methylnaphthalene <sup>‡</sup>	Yes	Yes	Yes	No	No	No
1-Methylphenanthrene <sup>1,‡</sup>	Yes	Yes	Yes	No	Yes	Yes
1,6,7-Trimethylnaphthalene <sup>1,‡</sup>	Yes	Yes	Yes	No	No	Yes
Naphthalene <sup>2,‡</sup>	Yes	Yes	Yes	No	No	No
Phenanthrene <sup>2,‡</sup>	Yes	Yes	Yes	No	No	No
Pyrene <sup>§</sup>	Yes	No	DNT	No	DNT	DNT
$\Sigma$ PAH <sub>34</sub> <sup>2,‡</sup>	Yes	Yes	Yes	No	No	No

PAH = polycyclic aromatic hydrocarbon; D1 = >60% developed land uses (n = 2); D2 = 10 - 14% developed land uses (n = 11); D3 = 4 - 9% developed land uses (n = 20); D4 = 0 - 3% developed land uses (n = 21); DNT = do not test.

<sup>1</sup> Based on natural log transformation of data.

<sup>2</sup> Based on square root transformation of data.

<sup>§</sup> Dunn's method was used for these pairwise multiple comparisons.

<sup>‡</sup> The Holm-Sidak method was used for these pairwise multiple comparisons.

### Statistical comparisons by lake surface area

The PAH data with  $\leq 3$  nondetects (i.e., <5% nondetects) were also compared by the five surface area categories included in the NLA study design. C1-fluorenes were the only PAHs to pass the normality and equal variance requirements based on the raw data. Transformations of the data (i.e., natural log and square root) were tried with the other PAH compounds and groups. One-way ANOVAs were run on 23 PAH compounds, with the remainder run with the nonparametric method (Table 3-23). Due to the small number of samples in some surface area categories, eight PAHs had one-way ANOVA results where the power of the performed test was below the desired power of 0.800 (Table 3-23). Only six, low molecular weight PAHs had statistically significant ( $p < 0.05$ ) results (Table 3-23).

Table 3-23. Statistical Comparisons of PAHs (with ≤3 nondetects) by Lake Surface Area Categories

PAH Compound or Group	Transformation of Data	p-value	
		One-Way ANOVA	Kruskal-Wallis One-Way ANOVA on Ranks
Acenaphthene	square root	0.651	
Acenaphthylene	none <sup>1</sup>		0.641
Anthracene	none <sup>1</sup>		0.252
Benzo[a]anthracene	none <sup>1</sup>		0.823
Dibenzo[a,h]anthracene	natural log	0.560	
Benzo[a]pyrene	natural log	0.417 <sup>2</sup>	
Benzo[b]fluoranthene	natural log	0.484	
Benzo[g,h,i]perylene	natural log	0.667	
Benzo[k]fluoranthene	natural log	0.375 <sup>2</sup>	
Benzo[e]pyrene	natural log	0.473	
C1-Chrysenes	none <sup>1</sup>		0.883
C1-Dibenzothiophenes	none <sup>1</sup>		0.346
C1-Fluorenes	not needed	0.673	
C1-Fluoranthenes/Pyrenes	natural log	0.208 <sup>2</sup>	
C1-Naphthalenes	square root	0.016*	
C1-Phenanthrenes/Anthracenes	none <sup>1</sup>		0.267
C2-Fluorenes	square root	0.791	
C2-Naphthalenes	natural log	0.036*	
C2-Phenanthrenes/Anthracenes	none <sup>1</sup>		0.356
C3-Naphthalenes	square root	0.292 <sup>2</sup>	
Chrysene	none <sup>1</sup>		0.794
Dibenzothiophene	natural log	0.121 <sup>2</sup>	
Fluoranthene	none <sup>1</sup>		0.440
Fluorene	none <sup>1</sup>		0.523
Indeno[1,2,3-cd]pyrene	natural log	0.884	
1-Methylnaphthalene	square root	0.022*	
2-Methylnaphthalene	square root	0.017*	
2,6-Dimethylnaphthalene	natural log	0.057 <sup>2</sup>	
1-Methylphenanthrene	natural log	0.162 <sup>2</sup>	
1,6,7-Trimethylnaphthalene	natural log	0.015*	
Naphthalene	square root	0.025*	
Perylene	natural log	0.425	
Phenanthrene	natural log	0.104 <sup>2</sup>	
Pyrene	none <sup>1</sup>		0.412
∑PAH <sub>13</sub>	none <sup>1</sup>		0.535
∑PAH <sub>17</sub>	none <sup>1</sup>		0.391
∑PAH <sub>34</sub>	none <sup>1</sup>		0.309

PAH = polycyclic aromatic hydrocarbon; ANOVA = Analysis of Variance.

<sup>1</sup> Both the natural log and square root transformations did not pass the Shapiro-Wilk normality test so that a one-way ANOVA could be run.

<sup>2</sup> The power of the performed test was below the desired power of 0.800, meaning less likelihood of detecting a difference when one actually exists.

\* Statistically significant ( $p < 0.05$ ).

The Holm-Sidak method was used to isolate the group or groups that differed from the others. The surface area categories D versus E were significantly different ( $p < 0.05$ ) for five of the six naphthalene and alkylated naphthalene compounds (Table 3-24). In all cases, the mean values were higher in lakes included in surface area category D (i.e., 50 – 100 ha). This category included the two developed lakes (i.e., #27--Nokomis and #38--Snail), which were statistical outliers for most of these six compounds. All other pairwise comparisons were not significant ( $p > 0.05$ ). Assessing lakes by surface area class was less useful than by major land use categories in the lake watersheds.

Table 3-24. Multiple Pairwise Comparisons by Lake Surface Area Categories for PAH Compounds with Statistically Significant ( $p < 0.05$ ) One-way ANOVA Results in Table 3-23. Pairs Shaded “Yes” are Significantly Different ( $p < 0.05$ ) from Each Other.

PAH Compound	Holm-Sidak Method: $p < 0.05$		
	C vs. E	D vs. E	8 Other Pairwise Comparisons
C1-Naphthalenes <sup>1</sup>	No	Yes	No
C2-Naphthalenes <sup>2</sup>	No	No	No
1-Methylnaphthalene <sup>1</sup>	No	Yes	No
2-Methylnaphthalene <sup>1</sup>	No	Yes	No
1,6,7-Trimethylnaphthalene <sup>2</sup>	No	Yes	No
Naphthalene <sup>1</sup>	No	Yes	No

PAH = polycyclic aromatic hydrocarbon; ANOVA = Analysis of Variance.

Surface Area Categories: C = 20 - 50 ha; D = 50 - 100 ha; E = >100 ha.

<sup>1</sup> Based on square root transformation of data.

<sup>2</sup> Based on natural log transformation of data.

## Comparisons to SQT values

Concentrations of PAH compounds and  $\Sigma\text{PAH}_{13}$  were compared to their corresponding Level I and Level II SQT values. Most of the concentrations of individual PAHs and  $\Sigma\text{PAH}_{13}$  were less than the corresponding Level I SQT values, except for acenaphthene and acenaphthylene (Table 3-25). For these two low molecular weight PAHs, the Level I SQT values may be too conservative. Acenaphthene had the highest percentage of samples exceeding the Level I SQT value (83.3%), and acenaphthylene was the only PAH compound to exceed the Level II SQT value for one lake (Table 3-25). For the rest of the PAH compounds and  $\Sigma\text{PAH}_{13}$ , only a few lakes exceeded the corresponding Level I SQT value and were also less than or equal to the Level II SQT value. In most cases, concentrations of PAHs in the two developed lakes were within this intermediate range of SQT values (Figure 3-19).

## PCA analysis

PCA analysis of the PAH data was performed with two different groups of parameters. First, the analysis was run on the 34 PAH compounds that were detected or had  $\leq 3$  nondetect values (Table 2-5). Supporting information from the scree plot, component loading plots, and component score plots are provided in Appendix F. Three principal components accounted for 82.9% of the variance in the data (Figure 3-20). The Eigenvectors in PC1 were similar for most of the PAH compounds since many of them co-occur. Those PAH compounds least represented in PC1 included: perylene, indeno[1,2,3-cd]pyrene, 2,6-dimethylnaphthalene, and C2-naphthalene. For PC2, 2,6-dimethylnaphthalene and C2-naphthalene contributed the greatest Eigenvectors. For PC3, C2-fluorenes, C1-fluorenes, acenaphthene, and fluorene

Table 3-25. Comparison of PAH Data to the MPCA's Level I and Level II SQT Values

PAHs	Percent of Samples (n = 54)		
	≤ Level I SQT	> Level I to ≤ Level II SQT	> Level II SQT
2-Methylnaphthalene	96.3	3.7	0
Acenaphthene	16.7	83.3	0
Acenaphthylene	74.1	24.1	1.8
Anthracene	98.1	1.9	0
Fluorene	90.7	9.3	0
Naphthalene	100.0	0	0
Phenanthrene	96.3	3.7	0
Benzo[a]anthracene	94.4	5.6	0
Benzo[a]pyrene	94.4	5.6	0
Chrysene	94.4	5.6	0
Dibenzo[a,h]anthracene	98.1	1.9	0
Fluoranthene	96.3	3.7	0
Pyrene	96.3	3.7	0
ΣPAH <sub>13</sub>	96.3	3.7	0

PAH = polycyclic aromatic hydrocarbon; SQT = sediment quality target.

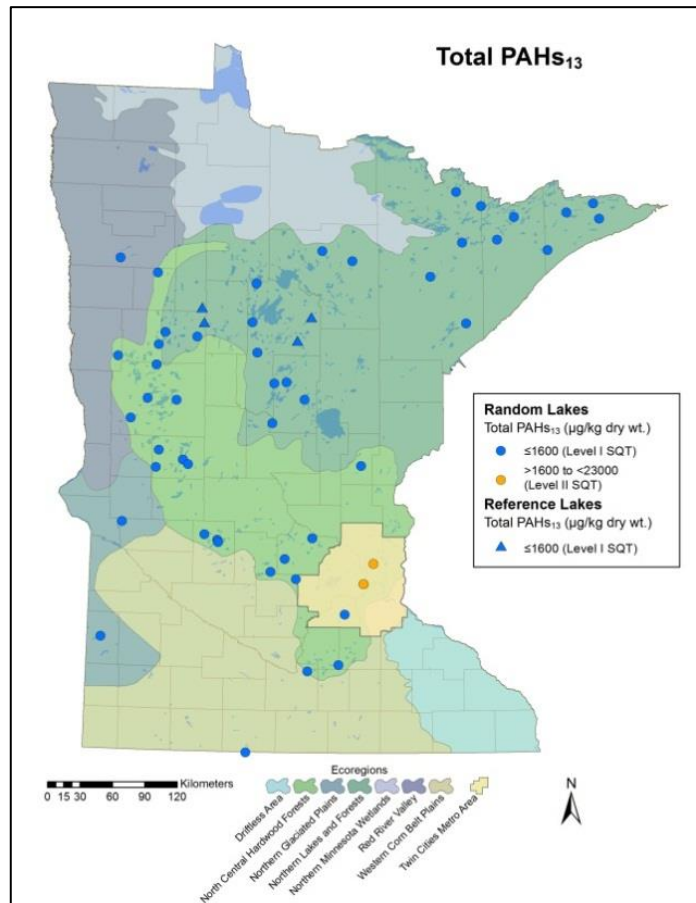


Figure 3-19. Comparison of ΣPAH<sub>13</sub> concentrations to corresponding Level I and Level II SQT values.

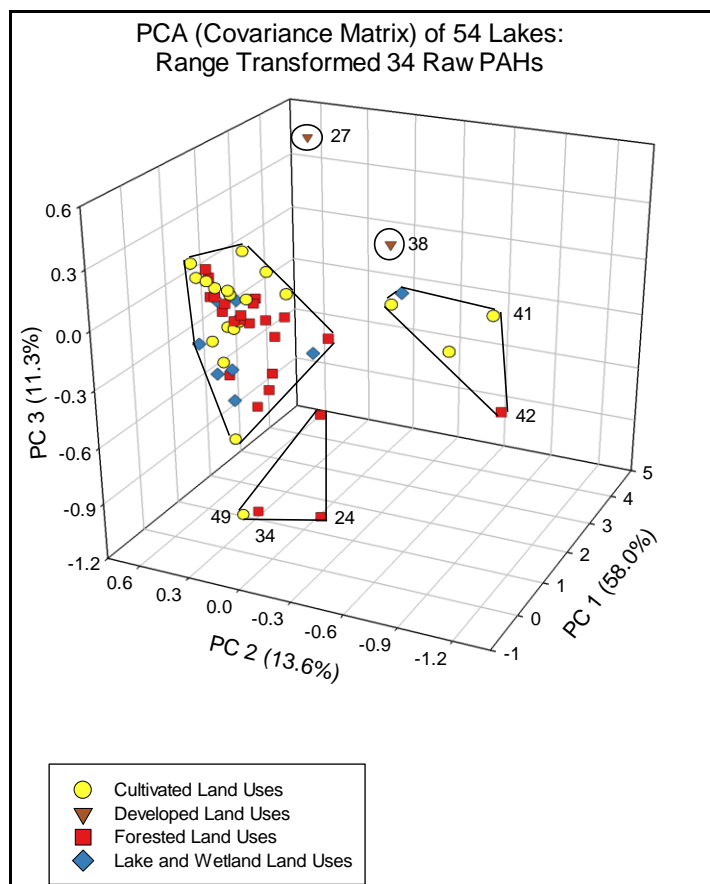


Figure 3-20. PCA plot of 34 PAHs with  $\leq 3$  nondetects. Based on the component scores, outliers included: lakes #24, 27, 34, 41, 42, and 49.

contributed the greatest Eigenvectors (Appendix F). With running this PCA analysis, only two PAH compounds were reduced from the component loadings: perylene and indeno[1,2,3-cd]pyrene. The unexplained variance ranged from 1.4% for C2-naphthalene to 92.6% for perylene (Appendix F). Six significant outliers ( $p < 0.05$ ) were noted from the component scores, including: lakes #24 (Mayo), 27 (Nokomis), 34 (Pickerel), 41 (Spring--330027), 42 (Spring—690129), and 49 (West Leaf; Figure 3-20; Appendix F). The five groups noted on this PCA plot (Figure 3-20) were based on the HCA set-up with the paired group (UPGMA) algorithm and the Gower similarity index (Appendix F). Most lakes were grouped together, which may be more representative of atmospheric sources of PAHs to these lakes. The two developed lakes, which also had the highest PAH concentrations, were distinct from each other and the rest of the lakes. Lake #27, in particular, was the most distinct in its assemblage of 32 dominant PAHs than the rest of the lakes (Appendix F).

The second PCA analysis was run on the 13 PAH compounds that also have corresponding SQT values (Table 2-5). The scree plot, component loading plots, and component score plots are provided in Appendix F. Three principal components accounted for 95.5% of the variance in the data (Figure 3-21). The Eigenvectors in PC1 were similar for all 13 PAH compounds since they co-occur (Appendix F). For PC2, acenaphthene and fluorene contributed the greatest Eigenvectors. For PC3, naphthalene and 2-methylnaphthalene contributed the greatest Eigenvectors (Appendix F). With running this PCA analysis, none of the 13 PAH compounds were reduced from the component loadings. The unexplained variance ranged from 0.22% for pyrene to 12.0% for fluorene (Appendix F). Three significant outliers ( $p < 0.05$ ) were noted from the component scores, including: lakes #24 (Mayo), 27 (Nokomis), and 49 (West Leaf;

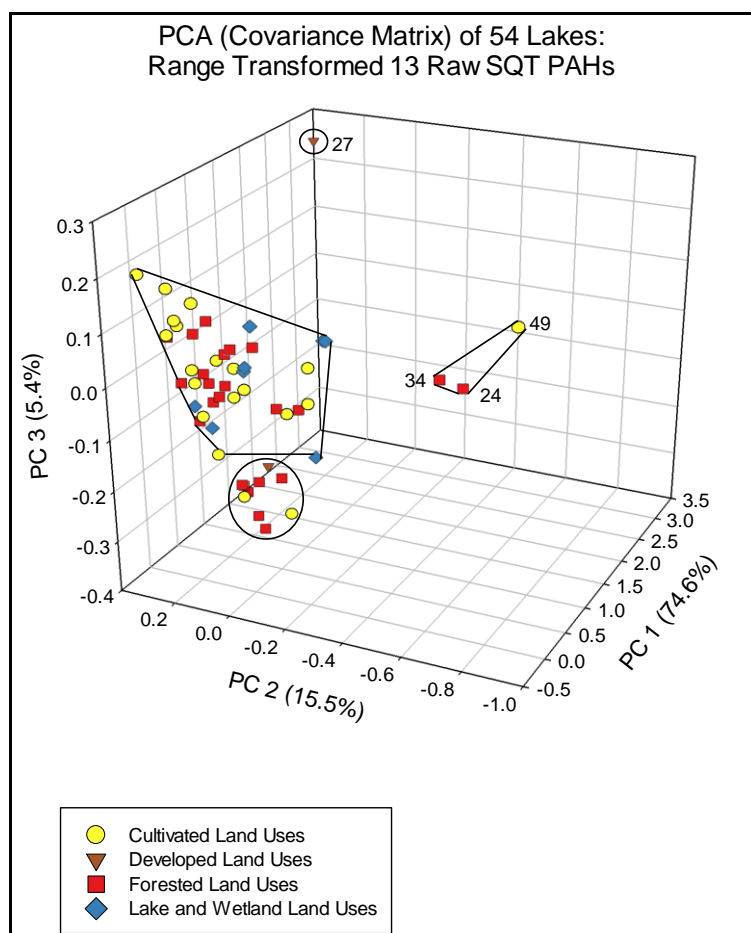


Figure 3-21. PCA plot of 13 PAHs for the 54 NLAP lakes. The outliers included lakes #24, 27, and 49.

Figure 3-21; Appendix F). The four groups noted on the PCA plot (Figure 3-21) were based on the HCA set-up with the paired group (UPGMA) algorithm and the Gower similarity index (Appendix F). Most lakes were grouped together, which may be more representative of atmospheric sources of PAHs to these lakes. Lakes #24, 34, and 49 were grouped together; all three of these lakes are located in the northcentral Minnesota, but there was no obvious reason why these lakes would cluster together. Lake #27 was the most distinct in its assemblage of 13 PAHs than the rest of the lakes (Appendix F).

## UTL values

UTL values were calculated in ProUCL 5.0 for the PAH compounds that had <80% nondetect values (Tables 3-26 and 3-27). In addition, UTLs were calculated for total PAH groups (Table 3-28) and for PAH ESB Toxic Units (Table 3-29). Prior to estimating UTL values, outliers were removed at the 5% significance level as determined using the outlier tests in ProUCL 5.0. Outliers based on these statistical tests are noted on the Q-Q plots provided in Appendix F. Of the PAH compounds detected in all 54 lakes, the C1-fluorenes were the only group that did not have any statistical outliers (Table 3-26). The C2-fluorenes and C4-naphthalenes were the only PAHs with censored data that did not have any statistical outliers (Table 3-27). The UTLs either followed a normal or gamma distribution after the removal of outliers. The two developed lakes, #27 and 38, were the most common outliers. The only PAH compounds or alkylated groups with outliers that did not include either lakes #27 or 38 were: perylene, C2-chrysenes, C3-chrysenes, and C4-chrysenes (Tables 3-26 and 3-27).



Table 3-26. UTLs of Detected PAH Data with Outliers Removed at the 5% Significance Level (units in µg/kg dry wt.)

PAH Compound	N	Potential Outliers Removed at 5% Significance Level (lake ID numbers)	Normal Distribution*	Gamma Distribution*	
				95% Approximately Gamma UTL with 95% Coverage	
			95% UTL with 95% Coverage	WH	HW
Acenaphthene	53	27	-	42.3	44.7
Acenaphthylene	51	24, 27, 38	-	10.9	11.4
Anthracene	52	27, 38	14.9		
Benzo[a]anthracene	49	24, 27, 32, 38, 47	-	41.0	43.8
Benzo[a]pyrene	51	27, 32, 38	-	43.5	46.0
Benzo[b]fluoranthene	51	27, 32, 38	-	74.3	79.1
Benzo[g,h,i]perylene	50	27, 32, 38, 47	30.5		
Benzo[k]fluoranthene	50	27, 32, 38, 47	36.5		
Benzo[e]pyrene	50	9, 27, 32, 38	-	69.1	74.2
C1-Fluorenes	54		58.3		
C1-Fluoranthenes/Pyrenes	50	27, 32, 38, 41	-	72.7	76.9
C1-Naphthalenes	52	27, 38	17.9		
C1-Phenanthrenes/Anthracenes	52	27, 38	61.6		
C2-Naphthalenes	48	23, 38, 39, 41, 42, 50	-	90.3	94.4
C3-Naphthalenes	52	27, 38	26		
Chrysene	49	24, 27, 32, 38, 47	64.3		
Fluoranthene	51	27, 32, 38	-	162.3	172.1
Fluorene	50	24, 27, 34, 49	69.9		
Indeno[1,2,3-cd]pyrene	51	32, 38, 47	33.1		
1-Methylnaphthalene	52	27, 38	9.4		
2-Methylnaphthalene	52	27, 38	17.2		
2,6-Dimethylnaphthalene	47	22, 23, 38, 39, 41, 42, 50	-	113.9	122.2
1-Methylphenanthrene	51	27, 38, 47	-	21.9	23.1
1,6,7-Trimethylnaphthalene	50	27, 38, 41, 42	-	3.4	3.5
Naphthalene	53	27	32.8		
Perylene	49	3, 4, 5, 32, 46	-	670.6	726.5
Phenanthrene	52	27, 38	-	147.7	156.3
Pyrene	49	24, 27, 32, 38, 47	-	106.7	113.7

PAH = polycyclic aromatic hydrocarbon; N = number of samples; UTL = Upper Tolerance Limit; WH = Wilson Hilferty; HW = Hawkins Wixley.

\* UTLs for normally distributed data were preferred over those derived from gamma distributed data. When the data were not normally distributed, the gamma distribution was used to estimate UTL values. Gamma UTLs were calculated two different ways, for which professional judgment can be used to select the value of interest.

Table 3-27. UTLs of Detected and Censored PAH Data with Outliers Removed at the 5% Significance Level (units in µg/kg dry wt.)

PAH Compound	N (# detects)	% Nondetects	Potential Outliers Removed at 5% Significance Level (lake ID numbers)	Normal Distribution and KM Estimates*	Gamma Distribution and KM Estimates*	
				95% UTL with 95% Coverage	95% Approx. Gamma UTL w/ 95% Coverage	
					WH	HW
Dibenzo[a,h]anthracene	51 (48)	5.9	27, 32, 38	5.2		
C1-Chrysenes	52 (50)	3.8	24, 27	-	166.7	187.7
C1-Dibenzothiophenes	52 (50)	3.8	27, 38	11.2		
C2-Chrysenes	52 (40)	23.1	24, 25	-	212.5	263.4
C2-Dibenzothiophenes	52 (41)	21.2	27, 38	11.3		
C2-Fluorenes	54 (52)	3.7		-	186.5	205.7
C2-Phenanthrenes/Anthracenes	52 (50)	3.8	27, 38	48.7		
C3-Chrysenes	52 (27)	48.1	24, 25	149.5		
C3-Dibenzothiophenes	52 (17)	67.3	27, 38	8.0		
C3-Fluorenes	52 (32)	38.5	27, 38	38.4		
C3-Phenanthrenes/Anthracenes	50 (32)	36.0	20, 27, 38, 47	32.2		
C4-Chrysenes	53 (11)	79.2	25	41.0		
C4-Naphthalenes	54 (49)	9.2		43.9		
C4-Phenanthrenes/Anthracenes	53 (11)	79.2	27	28.3		
Dibenzothiophene	52 (51)	1.9	27, 38	7.6		

UTL = Upper Tolerance Limit; PAH = polycyclic aromatic hydrocarbon; N = number of samples; KM = Kaplan-Meier; WH = Wilson Hilferty; HW = Hawkins Wixley.

\* UTLs for normally distributed data were preferred over those derived from gamma distributed data. When the data were not normally distributed, the gamma distribution was used to estimate UTL values. Gamma UTLs were calculated two different ways, for which professional judgment can be used to select the value of interest.

Table 3-28. UTLs of  $\Sigma$ PAH Groups (units in  $\mu\text{g}/\text{kg}$  dry wt.)

$\Sigma$ PAH Group*	N	Potential Outliers at 5% Significance Level (lake ID numbers)	Normal Distribution
			95% UTL with 95% Coverage
$\Sigma$ PAH <sub>13</sub>	51	27, 32, 38	636.0
$\Sigma$ PAH <sub>17</sub>	51	27, 32, 38	793.0
$\Sigma$ PAH <sub>34</sub>	51	27, 32, 38	2340.0

UTL = Upper Tolerance Limit; PAH = polycyclic aromatic hydrocarbon.

\* The Kaplan-Meier method was used to estimate  $\Sigma$ PAH groups for lakes that had censored data values.

Table 3-29. UTLs of PAH ESB Toxic Units

Parameter	N	Potential Outliers at 5% Significance Level (lake ID numbers)	Normal Distribution
			95% UTL with 95% Coverage
PAH ESB Toxic Units	49	27, 31, 32, 38, 46	0.023

UTL = Upper Tolerance Limit; PAH = polycyclic aromatic hydrocarbon; ESB = equilibrium partitioning sediment benchmark.

The UTL values were compared to corresponding Level I and Level II SQT values. The UTLs for both acenaphthene and acenaphthylene (Table 3-26) exceeded the corresponding Level I SQT values, but were below the Level II SQT values. The UTLs for the other 11 PAH compounds and  $\Sigma$ PAH<sub>13</sub> were all below the corresponding Level I SQT values. The SQT and UTL values have different purposes, and it is not necessary for the UTL values to be less than the Level I SQT values. Given the number of exceedances of the Level I SQT values in the study lakes for acenaphthene and acenaphthylene (Table 3-25), the corresponding UTL values are more useful benchmark values than the Level I SQTs. This information should be taken into consideration for remediation decisions at small sediment sites (e.g., boat slips) where the SQT values may be used to develop sediment quality remediation targets (Crane and MacDonald 2003).

## Correlation plots

Regression correlation plots were developed for PAH compounds having the same number of rings. For each plot, potential outliers were removed at the 5% significance level (Figure 3-22); these were the same outliers identified for the UTLs (Tables 3-26 and 3-27). The correlations in Figure 3-22 were all highly statistically significant ( $p < 0.001$ ) based on either a Pearson product moment or Spearman rank order correlation. The highest  $r^2$  value (0.987) occurred for the following 6-ring PAH compounds, which were normally distributed: indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene. These compounds are very hydrophobic and stable in sediments. The only other pair of normally distributed PAH compounds in Figure 3-22 were C1-naphthalene and naphthalene; these two-ring PAH compounds are more volatile and water soluble and had a lower  $r^2$  value of 0.805. The other correlation plots in Figure 3-22 included 3-, 4-, and 5-ring PAHs, for which at least one PAH compound was not normally distributed. As shown in the PCA analysis, these correlation plots demonstrate the high level of co-occurrence of most PAH compounds. PAHs of the same ring structure tended to have the strongest correlations with each other.

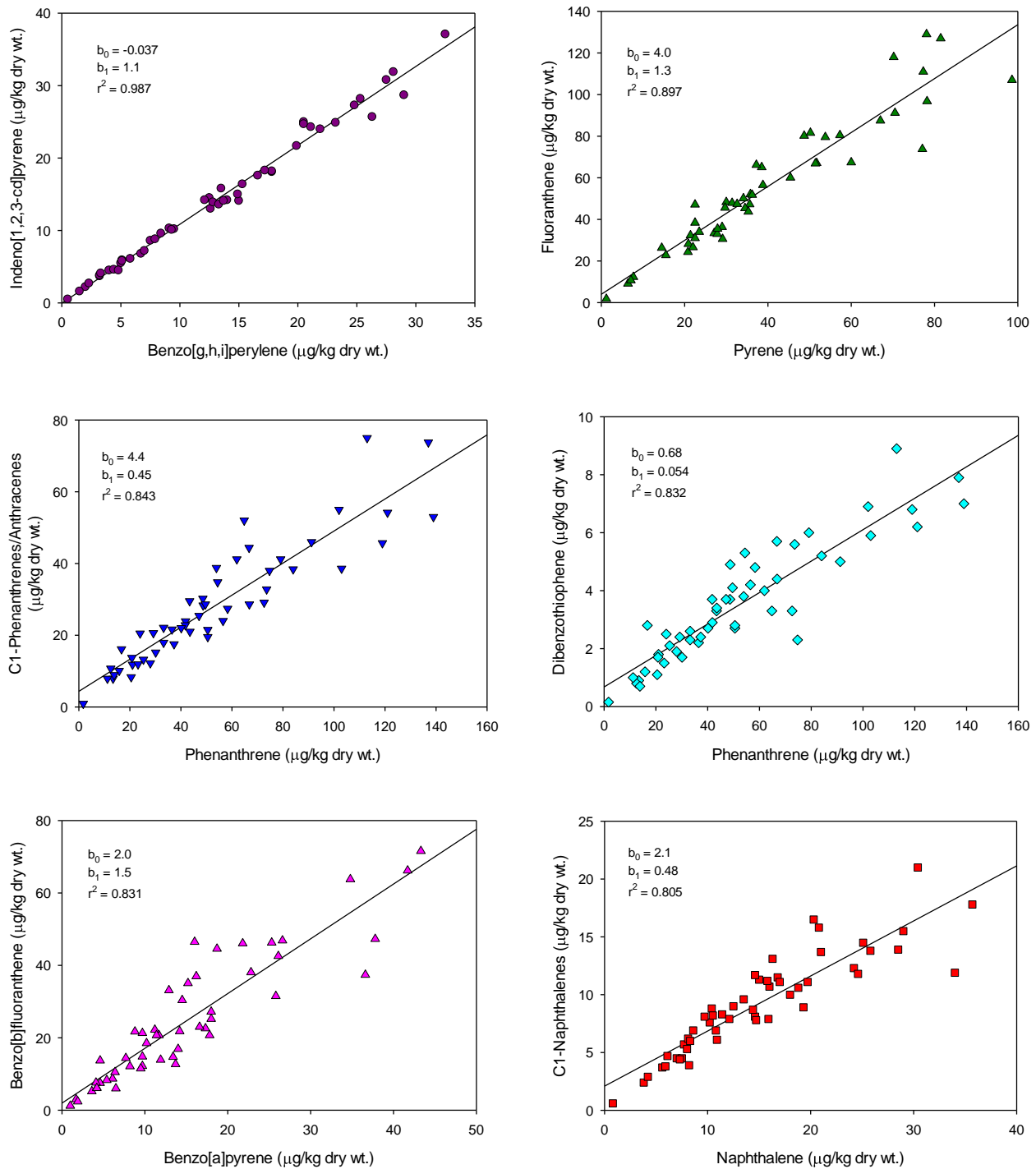


Figure 3-22. Correlation plots for detected PAHs and dibenzothiophene (one nondetect), which had outliers removed at the 5% significance level. For each graph,  $b_0$  = intercept,  $b_1$  = slope, and  $r^2$  = coefficient of determination.

## Environmental forensics of PAHs

The distribution of PAHs in sediment provides a unique pattern or “fingerprint” that gives clues to the types of sources responsible for this pattern. Environmental forensic techniques are used to compare sample “fingerprints” with known source “fingerprints” (e.g., coal combustion, vehicle emissions) to

allocate sources of PAHs. The simplest type of analysis involves creating concentration histogram plots of the parent and alkylated PAHs in each sediment sample. Next, the plots are visually examined for evidence of petrogenic (i.e., oil-based) or pyrogenic (i.e., combustion-based) sources of PAHs. Other techniques range from simple diagnostic PAH source ratios to statistical ordination techniques, such as principal components analysis, to quantitative mixing models (Boehm 2006). The U.S. EPA's CMB8.2 model has been adapted from identifying sources of PAHs in air samples to quantitatively determining the source apportionment of PAHs in sediment (Li et al. 2003; Van Metre and Mahler 2010; Crane 2014).

Histogram plots of the 43 PAHs analyzed in each lake are provided in Appendix F. Figure 3-23 shows the range of concentrations of PAHs in the histogram plot for lake #38 (Snail). This urban lake contains higher concentrations of most parent PAHs than their alkylated homologs, which are indicated by the downward sloping lines on Figure 3-23. Such a pattern is typical of pyrogenic sources of PAHs. In contrast, petrogenic PAHs have low concentrations of parent PAHs, and the concentration histogram plots of the low molecular weight parent and associated alkylated homologs display a bell-shaped curve. None of the study lakes displayed these types of bell-shaped curves for low molecular weight PAHs (Appendix F). Visual observation of the histogram plots of the study lakes (Appendix F) indicates pyrogenic sources of PAHs are important. In addition, the high concentrations of perylene in some lakes are indicative of a diagenic source for this PAH compound.

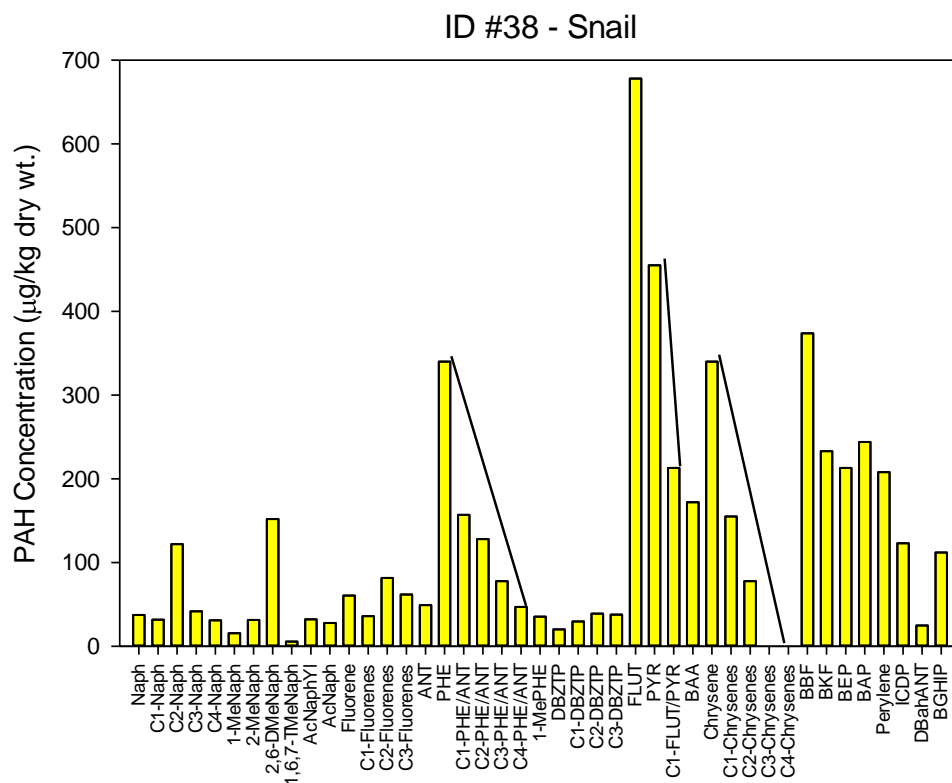


Figure 3-23. Concentration histogram plot for lake #38 (Snail). Note the decreasing trend in phenanthrene (PHE) and its homologs [C1 – C4-phenanthrene/anthracene (PHE/ANT)], pyrene (PYR) and its homolog [C1-fluoranthene/pyrene (C1-FLUT/PYR)], and chrysene and its homologs (C1 – C4-chrysenes). These trends are indicative of pyrogenic sources of PAHs.

PAH source ratios were used for semi-quantitative analysis of the data. Diagnostic source ratios of F/P and P/A have been used to distinguish between petrogenic and pyrogenic sources of PAHs (Budzinski et al. 1997). A double-ratio plot of these parameters (Figure 3-24) indicated that the samples were dominated by pyrogenic sources. This was because the F/P ratio was  $>1$  and the P/A ratio was  $<10$  for most samples (Budzinski et al. 1997). Lake #20 (Long—Main Bay) had a F/P ratio of 0.96, which would round-up to 1.0. For P/A ratios between 10 and 15 in Figure 3-24, these values are considered indeterminate relative to source (Gao et al. 2007). A double-ratio plot was also generated for BbF/BkF vs. BaP/BeP (Figure 3-25) and compared to a range of major emission sources from automobiles (Dickhut et al. 2000). The two urban lakes (#27 and 38) were not within the range of vehicle emissions being a major source of PAHs. Four lakes completely intersected the major vehicle emission ranges of both source ratios: #1 (Allen), #37 (Richey), #39 (South), and #40 (South Drywood). These lakes

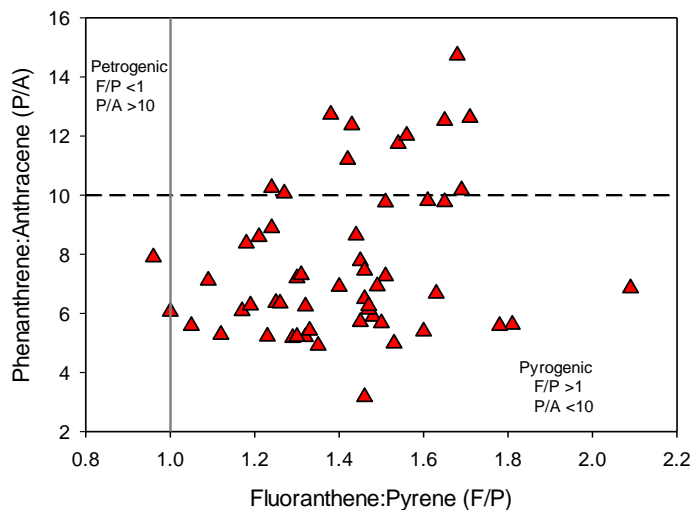


Figure 3-24. Double-ratio plot of P/A vs. F/P.

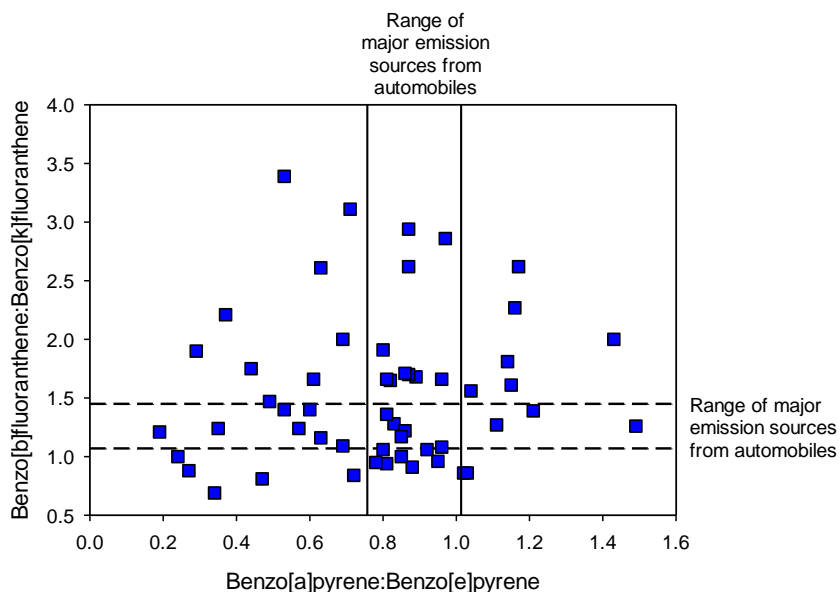


Figure 3-25. Double-ratio plot for PAH compounds indicative of major emission sources from vehicles.

represented a wide geographic range of Minnesota, which would indicate atmospheric transport of vehicle emissions provide a widespread source of PAHs to Minnesota lake sediments.

Double-ratio plots do not provide a complete understanding of all sources of PAHs. These plots do not account for varying rates of weathering or enrichment of PAH compounds and work best at sites dominated by a single source (Battelle Memorial Institute et al. 2003). The use of PAH ratios for atmospheric samples has also shown that these ratios can produce contradictory source results (Katsoyiannis et al. 2011). Quantitative modeling is the only way to provide a rigorous assessment of PAH sources in environmental samples.

Two-hundred and seventy (270) runs of the CMB8.2 model were made using different combinations of source profiles for the 12 PAH compounds in  $\Sigma\text{PAH}_{\text{CMB}}$  (Table 2-5). For 104 runs, lakes were grouped by major land use and whether they were random or reference lakes. However, not all lakes within each of these categories had satisfactory model results. Ultimately, each lake was run individually through the model to obtain the combination of sources that resulted in the best model fit. This meant that no samples were excluded from the CMB8.2 model, residual uncertainty was minimized, the T-statistic that appeared with the source contribution estimates was  $>2.0$  for the major source(s), and model performance was acceptable for  $R^2$  (i.e.,  $>0.8 - 1.0$ ), Chi Square (i.e.,  $<1.0$  preferred, between  $1.0 - 2.0$  acceptable) and percent mass (i.e.,  $80 - 120\%$ ; Coulter 2004). To assist with winnowing down the number of sources to use in the model, a Shapiro-Wilk normality test on the PAH proportional values for all sources and lake sediment samples was run. Normally distributed data were run through a Pearson product moment correlation, and a Spearman rank order correlation was used for data not normally distributed. The results of these correlation analyses were used to select a subset of source(s) with the most significant correlations to the sediment data (i.e., generally  $p < 0.001$ ). This subset of sources was tested in different combinations for each lake, and the PAH proportional values for these sources are provided in Table F-10 of Appendix F. For lake #40 (South Drywood), acceptable model results were obtained with only using a single PAH source of either diesel emissions or residential coal combustion. The results of the double-ratio plot for BbF/BkF vs. BaP/BeP (Figure 3-25) was used to select diesel as the source since lake #40 was one of four lakes intersecting the ranges of major emissions from automobile sources in this plot. Lake #40 is located in west-central Minnesota in a primarily agricultural area. Diesel emissions from farm equipment and truck traffic would be a reasonable source of PAHs to this lake.

The final CMB8.2 modeling results selected for each lake were within the acceptability requirements of the model (Table F-11 of Appendix F). There was no collinearity between any of the model sources, which was good. Calculated concentrations of  $\Sigma\text{PAH}_{\text{CMB}}$  were similar to measured concentrations (Figure 3-26; Table F-11 of Appendix F). The mean RPD between measured and calculated  $\Sigma\text{PAH}_{\text{CMB}}$  concentrations in the model was 4.7% with a SD of 4.8%; the median RPD was 2.7%. The model performance for  $R^2$ , Chi Square, and percent mass are displayed in Figures 3-27 to 3-29, respectively; individual sample results are provided in Table F-11 of Appendix F.

The CMB8.2 model performance results were also compared to analogous values from two other sediment studies (Van Metre and Mahler 2010; Crane 2014) that used the CMB8.2 model for the source apportionment of PAHs. All three sediment studies had acceptable model performance results (Table 3-30). There were statistically significant differences ( $p < 0.001$ ) among the studies for  $R^2$ , Chi Square, and percent mass (Table 3-31). Next, multiple pairwise comparisons were run to determine which studies differed from the others for these model performance parameters. For  $R^2$  and Chi Square, statistically significant ( $p < 0.05$ ) differences were observed between the Twin Cities stormwater pond study (Crane 2014) and each of the other two studies (Table 3-32). However, no statistically significant ( $p > 0.05$ ) differences were observed between the NLAP lakes and those from a national group of urban lakes (Van

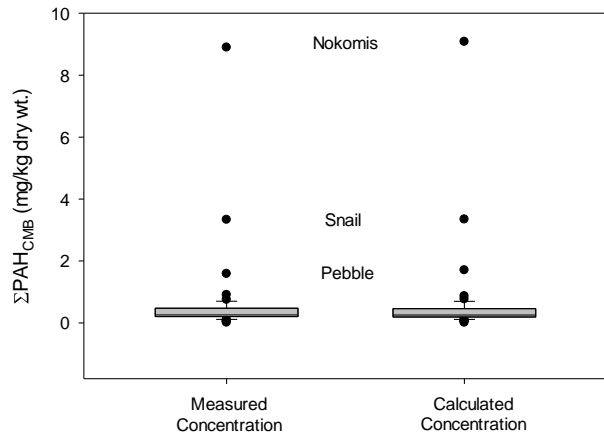


Figure 3-26. Comparison of measured concentrations of  $\Sigma\text{PAH}_{\text{CMB}}$  with those estimated by the CMB8.2 model.

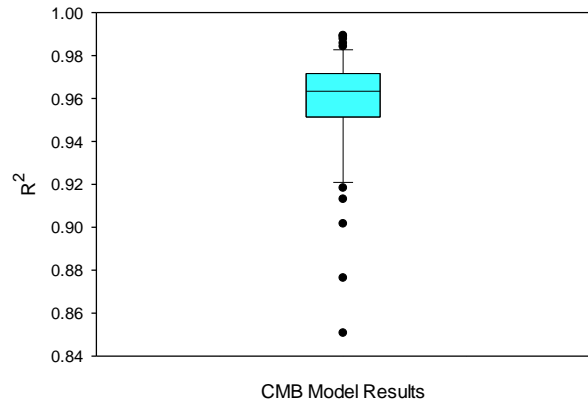


Figure 3-27. CMB8.2 model results for  $R^2$ .

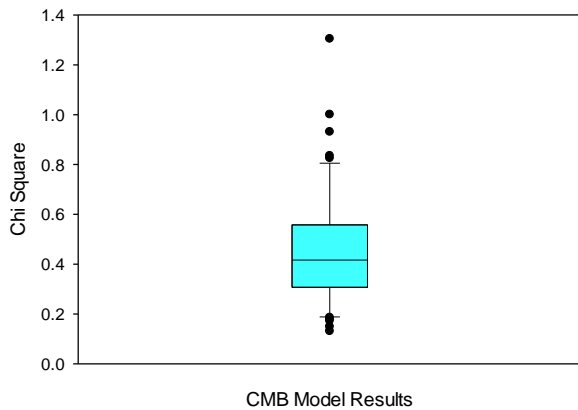


Figure 3-28. CMB8.2 model results for Chi Square.

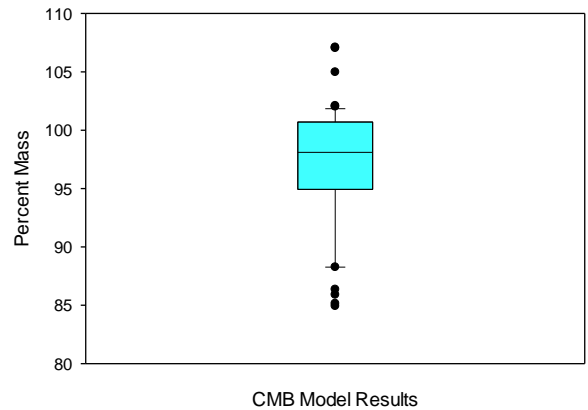


Figure 3-29. CMB8.2 model results for percent mass.

Table 3-30. Comparison of CMB8.2 Model Performance of NLAP Lakes with Two Other Sediment Studies

Sediment Study	Statistical Parameter	Model Performance		
		$R^2$	Chi Square	Mass (%)
54 NLAP Lakes (this study)	Mean	0.957	0.456	96.8
	SD	0.027	0.223	5.5
15 Twin Cities Stormwater Ponds (Crane 2014)	Mean	0.981	0.249	100.3
	SD	0.0090	0.140	1.2
40 U.S. Urban Lakes (Van Metre and Mahler 2010)	Range of Mean Values from Four Models	0.93 - 0.96	0.54 - 0.94	99 - 104

CMB8.2 = chemical mass balance model version 8.2; NLAP = National Lake Assessment Project;  $R^2$  = coefficient of determination; SD = standard deviation; U.S. = United States.



Table 3-31. Statistical Comparisons of CMB8.2 Model Performance Parameters Between the NLAP Data, Twin Cities Stormwater Pond Data (Crane 2014), and U.S. Urban Lake Data (Van Metre and Mahler 2010)

Parameter	Transformation of Data	p-value	
		One-Way ANOVA	Kruskal-Wallis One-Way ANOVA on Ranks
R <sup>2</sup>	none <sup>1</sup>		<0.001*
Chi Square	natural log	<0.001*	
Mass (%)	none <sup>1</sup>		0.010*

CMB8.2 = chemical mass balance model version 8.2; NLAP = National Lake Assessment Project; U.S. = United States; ANOVA = analysis of variance; R<sup>2</sup> = coefficient of determination.

<sup>1</sup> Both the natural log and square root transformations did not pass the Shapiro-Wilk normality test so that a one-way ANOVA could be run.

\* Statistically significant (p<0.05).

Table 3-32. Multiple Pairwise Comparisons of CMB8.2 Model Performance Parameters by Sediment Study [NLAP, Stormwater Ponds (SWP; Crane 2014), and U.S. Urban Lakes (USUL; Van Metre and Mahler 2010)]

Model Performance Parameter	p<0.05		
	NLAP vs. SWP	USUL vs. SWP	NLAP vs. USUL
R <sup>2</sup> , §	Yes	Yes	No
Chi Square <sup>1, ‡</sup>	Yes	Yes	No
Mass (%) <sup>§</sup>	DNT	DNT	No

CMB8.2 = chemical mass balance model version 8.2; NLAP = National Lake Assessment Project; SWP = stormwater ponds; U.S. = United States; USUL = U.S. urban lakes; R<sup>2</sup> = coefficient of determination; DNT = do not test.

<sup>1</sup> Based on natural log transformation of the data.

§ Dunn's method was used for these pairwise multiple comparisons.

‡ The Holm-Sidak method was used for these pairwise multiple comparisons.

Metre and Mahler 2010) for R<sup>2</sup> and Chi Square (Table 3-32). These results indicated the model performance was significantly better for sediment samples collected from a limited geographic area (e.g., Minneapolis-St. Paul, MN metropolitan area for Crane 2014) than those from a statewide and national assemblage of lakes. On a percent mass basis, the difference of ranks between the NLAP lakes and national lakes (Van Metre and Mahler 2010) was not significant (p>0.05; Table 3-32); this resulted in the other two pairwise comparisons being labeled “Do Not Test” (Table 3-32). A result of “Do Not Test” should be treated as if there is no significant difference between the rank sums, even though one may appear to exist.

The source apportionment of PAHs in each NLAP lake was effectively accomplished with the CMB8.2 model. Individual results for each lake are provided in Table F-12 of Appendix F. A total of 12 source profiles were used for the entire lake data set, for which each lake typically used two or three sources. Two lakes used one source, four lakes used four sources, and one lake used five sources (Table F-12 of Appendix F). Lakes that had a common source were grouped together so that the mean and SD of PAH

proportional values for the 12 PAHs used in the calculation of  $\sum\text{PAH}_{\text{CMB}}$  could be compared to the analogous PAH proportional values of the common source profile. A Shapiro-Wilk normality test was conducted of the PAH proportional values for the 12 source profiles and their associated groups of NLAP lakes. For those groups passing normality, a Pearson product moment correlations was run. A Spearman rank order correlation was run on all the groups. Graphs comparing the PAH proportional values for the sources and their associated sample lakes are provided in Figure 3-30 for those groups with the strongest correlations. The remaining plots are provided in Figure F-1 of Appendix F. In particular, the mean PAH proportional values for lakes were highly correlated to both the CT-sealant dust: Austin, TX #2 source and the coal emissions average source (Figure 3-30). For vehicle emission sources, the PAH proportional values for diesel vehicle particulate emissions were similar to the higher molecular weight PAH proportional values from lakes using this source, while the traffic tunnel air source more closely aligned with lower molecular weight PAHs from lakes using this source (Figure 3-30). For the pine wood soot particles #1 source, it was similar to the PAH proportional values of lakes using this source, except for fluoranthene and pyrene. The model considered the best mix of source profiles to approximate the ambient sediment data so it was not necessary for all source PAH compounds to be in sync with the ambient data.

The source apportionment results were further generalized into overarching source categories of CT-sealant pavement dust, vehicle emissions, coal-related combustion, and wood combustion (Table F-13 of Appendix F, Figure 3-31). Most NLAP lakes had two to three results in these broad source categories (Table F-13 of Appendix F). Vehicle emissions and coal-related combustion were tied as the most prevalent sources of PAHs to sediments in 41 lakes. It was surprising that CT-sealant pavement dust was a source of PAHs to sediment in 32 lakes. However, Van Metre et al. (2012a) estimated that PAH emissions from new CT-sealant applications each year (~ 1000 Mg) are larger than annual vehicle emissions of PAHs for the U.S. Thus, there could be long-range transport of CT-sealant dust particles that could be deposited via wet and dry deposition to Minnesota lakes. Wood combustion was a source of PAHs in 12 lakes. Most of the NLAP lakes, outside of the urban core of the Minneapolis-St. Paul metropolitan area, had low concentrations of  $\sum\text{PAH}_{13}$  (i.e. below the Level I SQT value). While PAH concentrations in most of these lake sediments are not of concern, it is helpful to go through this modeling exercise to create a baseline source apportionment that could be used for evaluating the results of federal and state actions in the future (e.g., clean air regulations, improvements in vehicle performance). Sediments provide a historical record of contaminant fluxes, and radioisotope dating of cores, coupled with source apportionment modeling, could provide stronger evidence of changes as a result of regulations or management actions.

The source apportionment of PAHs, by general source categories, was also displayed visually for each lake. For Figure 3-32, CT-sealant dust and coal-related combustion were the dominant sources of PAHs in surficial sediments of the three lakes (i.e., #27, 38, and 32) with the highest  $\sum\text{PAH}_{\text{CMB}}$  concentrations. In comparison, CT-sealant dust and particulate wash off were dominant sources of PAHs to stormwater pond sediments in the Minneapolis-St. Paul, MN metropolitan area, accounting for 67.1% of modeled  $\sum\text{PAH}_{\text{CMB}}$  concentrations (Crane 2014). These three lakes were removed from Figure 3-33 to more closely view the general source apportionment of PAHs in the other lakes with modeled  $\sum\text{PAH}_{\text{CMB}} < 1.0$  mg/kg dry wt. Atmospheric deposition was probably the main transport pathway for PAHs from these sources to be deposited on lakes and their surrounding watersheds. Of particular interest were the BWCAW lakes where motorized vehicles and boats are prohibited from most of the park. The modeled source apportionment of PAHs in four lakes from the remote BWCAW area is provided in Figure 3-34. These lakes are listed from west to east direction, and vehicle emissions comprised the major source to each lake. Coal-related combustion also contributed small amounts of PAHs to Alruss (#2) and Becosin (#6) lakes.

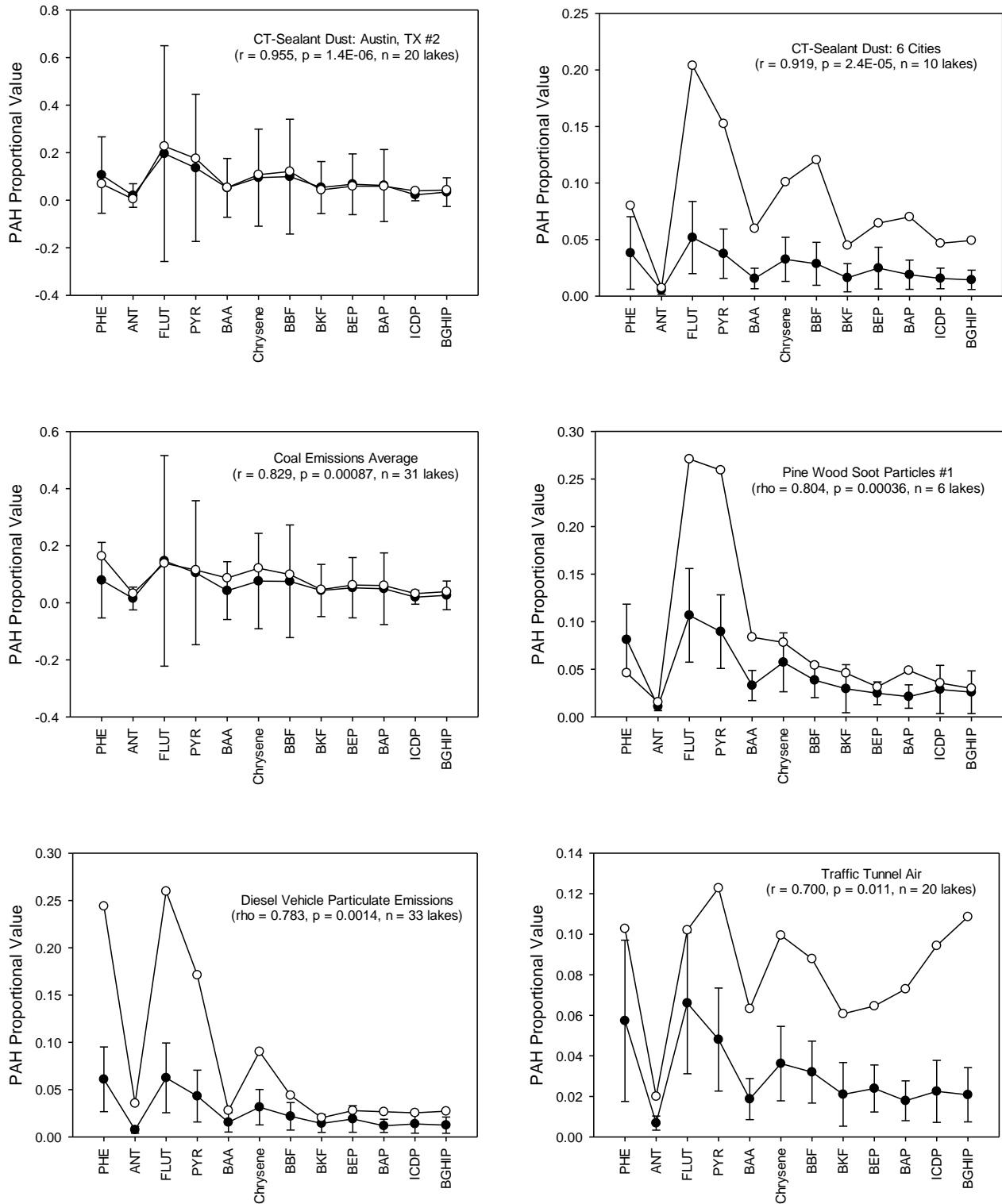


Figure 3-30. Comparison of PAH proportional values (i.e., individual PAH concentration normalized to  $\Sigma\text{PAH}_{\text{CMB}}$  concentration) between sources used in the EPA's CMB8.2 model (open circles) and the mean profile for NLAP lakes (closed circles; uncertainty bars indicate one SD) for which that source was used in the model results. PAHs range from low molecular weight to high molecular weight compounds along the x-axis. Either Pearson's r or Spearman's rho values, associated p values, and number of NLAP lakes in each group are given in parentheses; p values <0.05 are significant.

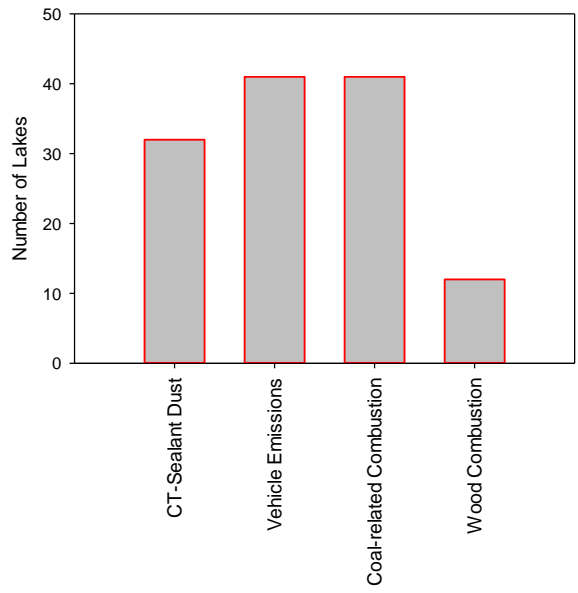


Figure 3-31. Number of lakes for which generalized PAH sources comprised the source apportionment of PAHs.

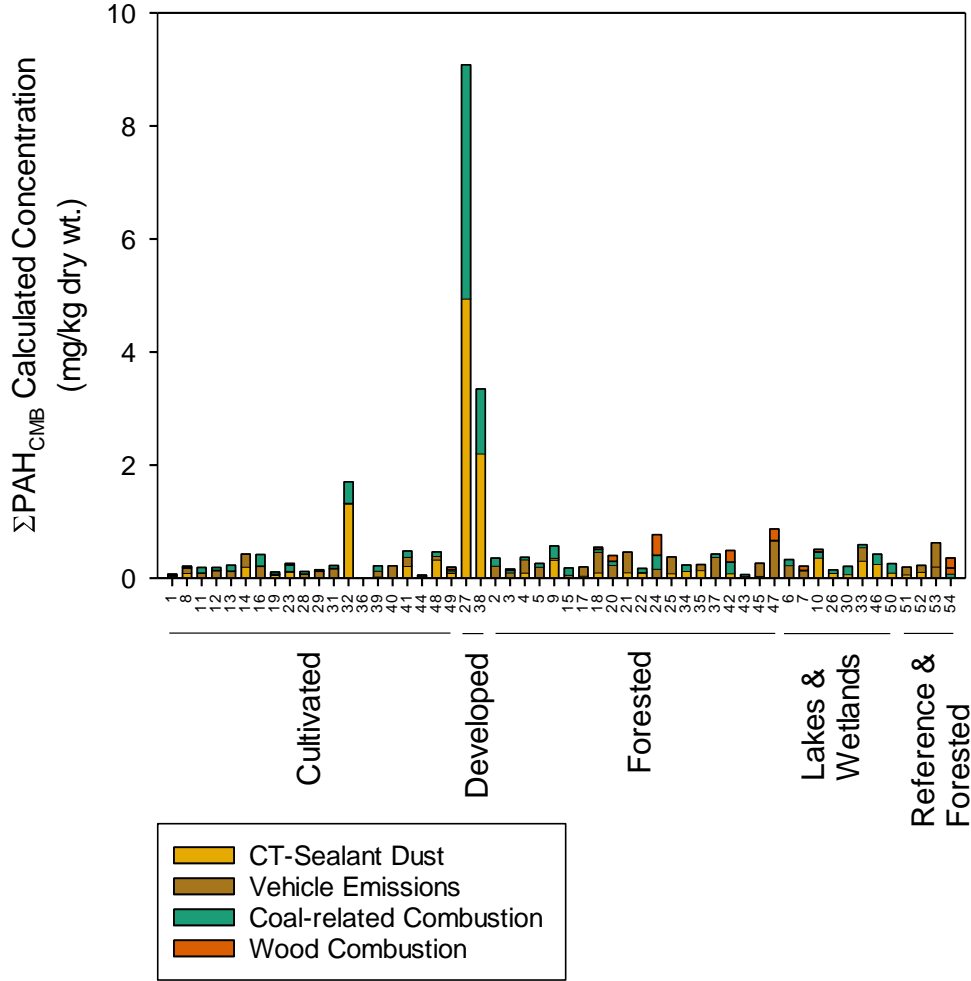


Figure 3-32. General source apportionment of PAHs in each NLAP lake.

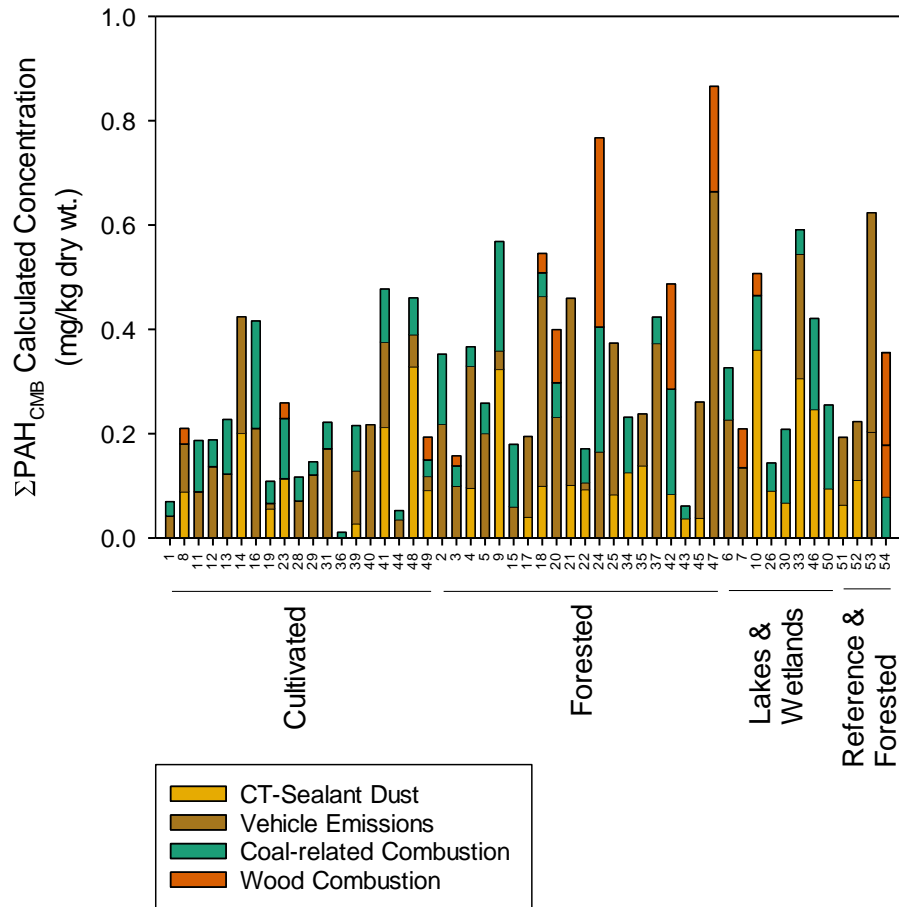


Figure 3-33. Source apportionment of PAHs in lakes with low concentrations of  $\Sigma\text{PAH}_{\text{CMB}}$ .

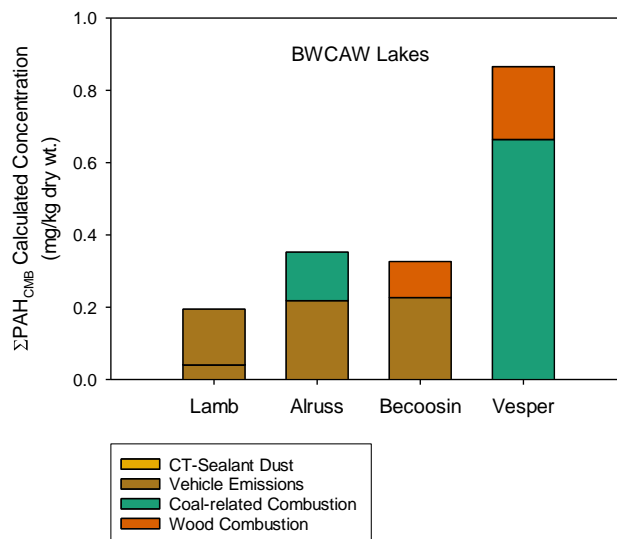


Figure 3-34. Source apportionment of PAHs in BWCAW lakes.

The CMB8.2 modeling results were evaluated further to test the null hypothesis of no significant differences in the mass concentrations of each major PAH source category between the four major land use groups (Table 3-33). Since the raw data failed the Shapiro-Wilk normality test, both natural log and square root transformations of the data were tried. Only a square root transformation of the mass concentrations attributed to vehicle emissions allowed a one-way ANOVA to be run; the result was statistically significant ( $p = 0.008$ ; Table 3-33). The transformations did not improve the normality of the other three source groups. Therefore, Kruskal-Wallis one-way ANOVAs on ranks were conducted on the mass compositions of these modeled  $\Sigma\text{PAH}_{\text{CMB}}$  concentrations. The results for both CT-sealant dust and coal-related combustion were statistically significant ( $p < 0.05$ ; Table 3-33). There was not a statistically significant difference ( $p = 0.498$ ) in the median values of  $\Sigma\text{PAH}_{\text{CMB}}$  in the land use groups for the wood combustion source category.

Table 3-33. Statistical Comparisons of General Source Groups for CMB8.2 Model Results by Major Land Use Categories

General Source Groups for CMB8.2 Model	Transformation of Data	p-value	
		One-Way ANOVA	Kruskal-Wallis One-Way ANOVA on Ranks
CT-sealant Dust	none <sup>1</sup>		0.039*
Vehicle Emissions	square root	0.008*	
Coal-related Combustion	none <sup>1</sup>		0.038*
Wood Combustion	none <sup>1</sup>		0.498

CMB8.2 = chemical mass balance model version 8.2; ANOVA = analysis of variance; CT-sealant = coal tar-based sealant.

<sup>1</sup> Both the natural log and square root transformations did not pass either the Shapiro-Wilk normality test or the equal variance test (Brown-Forsythe) so that a one-way ANOVA could be run.

\* Statistically significant ( $p < 0.05$ ).

For each of the three source categories with significant results, multiple pairwise comparisons were used to isolate the land use categories that differed from the others. For CT-sealant dust, there was no significant difference ( $p > 0.05$ ) in the rank sums between developed and cultivated land uses; all other pairwise comparisons were designated as “Do Not Test” (Table 3-34). For the vehicle emissions source,

Table 3-34. Multiple Pairwise Comparisons by Land Use Categories for General Source Groups with Significant Results in Table 3-33

General Source Groups for CMB8.2 Model	p < 0.05					
	dev vs. cul	dev vs. wet	dev vs. for	for vs. cul	for vs. wet	wet vs. cul
CT-sealant Dust <sup>§</sup>	No	DNT	DNT	DNT	DNT	DNT
Vehicle Emissions <sup>1,‡</sup>	No	No	No	No	No	No
Coal-related Combustion <sup>§</sup>	DNT	DNT	No	DNT	DNT	DNT

CMB8.2 = chemical mass balance model version 8.2; dev = developed; cul = cultivated; for = forested; wet = lakes and wetlands; CT-sealant = coal tar-based sealant; DNT = do not test.

<sup>1</sup> Based on square root transformation of data.

<sup>§</sup> Dunn's method was used for these pairwise multiple comparisons.

<sup>‡</sup> The Holm-Sidak method was used for these pairwise multiple comparisons.

there were no significant differences ( $p > 0.05$ ) between any combinations of pairwise land uses (Table 3-34). For coal-related combustion, there was no significant difference ( $p > 0.05$ ) between forested and developed land uses; all other multiple pairwise comparisons were designated as “Do Not Test” (Table 3-34). As previously mentioned, a result of “Do Not Test” should be treated as if there is no significant difference between the rank sums, even though one may appear to exist. Future NLA surveys would benefit from a larger sample size in order to assess potential land use variations more rigorously.

Although the CMB8.2 model provided a rigorous source apportionment of  $\Sigma\text{PAH}_{\text{CMB}}$  in lake sediments from throughout Minnesota, this model has several important limitations (Li et al. 2003; Van Metre and Mahler 2010; Crane 2014). These limitations include: 1) the model results are sensitive to uncertainty in the input data, which is often not well defined (Van Metre and Mahler 2010); 2) the source profiles are limited by a common number of PAHs (i.e., 12 parent PAHs), and a broader suite of PAHs would allow more detailed and unique source profiles to be developed; 3) source profiles were obtained from several literature sources, which may have varying data quality objectives and adherence to QA/QC protocols; 4) no source profiles were available for ethanol plants (21 in Minnesota; <http://www.eia.gov/state/analysis.cfm?sid=MN>, accessed 6/2/2016) or for the combustion of biofuels, which may be more important in the future as these fuels increase in use in Minnesota; and 5) source results can be misinterpreted if important sources are excluded from the model. Another limitation with interpreting the results is that the sediment core samples were not dated, and the sample lakes are likely to have different sedimentation rates. Thus, the historical record of PAH accumulation in the top 15 cm of each lake is likely to vary. A shorter depth interval (e.g., 0 – 2 cm or 0 – 5 cm) would provide a better assessment of more recent sources of PAHs.

## Current and future efforts that could reduce PAH releases in Minnesota

### Electrical generation in Minnesota

The source apportionment modeling showed that coal-related combustion was a major source of PAHs to many NLAP lakes, although the mass contribution varied by lake (Table F-13 in Appendix F). This general category includes coal-fired power plants, which are the dominant source of electricity in Minnesota. About 44% of the electricity generated in Minnesota during 2015 came from coal-fired electric power plants (<http://www.eia.gov/state/?sid=MN>; accessed 6/2/2016). Xcel Energy’s Sherburne County (Sherco) power plant in Becker, MN is the state’s largest (Figures 3-35 and 3-36), producing more than twice the electricity of each of the next two largest power plants in the state, the Clay Boswell coal-fired plant and the Prairie Island nuclear facility (Figure 3-35; <http://www.eia.gov/state/analysis.cfm?sid=MN>, accessed 6/2/2016). Several small coal-fired power plants are located throughout Minnesota (Figure 3-35).

Actions have been taken by two coal-fired power plants, which should indirectly result in reductions in PAH emissions. The Sherco Power Plant (Figures 3-35 and 3-36) has been implicated in contributing haze to Voyageur’s National Park, MN and the nearby BWCAW, as well as Isle Royale, MI (<http://www.startribune.com/feb-14-xcel-energy-denies-becker-plant-causes-haze-over-voyageurs/191055391/>; accessed 6/3/2016). Xcel Energy agreed to reduce coal plant emissions in 2015 to settle litigation on this issue (<http://www.startribune.com/xcel-agrees-to-cut-coal-plant-emissions-to-settle-suit-over-haze-in-national-parks/303954781/>; accessed 6/3/2016). In addition, Xcel plans to reduce the Sherco plant’s sulfur dioxide emissions by 50% by 2017 to reduce haze. In Fergus Falls, SD, the coal-burning Big Stone power plant, operated by Otter Tail Power Co., is installing advanced pollution controls to protect Minnesota natural areas, such as the BWCAW (<http://www.startribune.com/suit-says-feds-must-curb-air-pollution-over-natural-areas/182258021/>; accessed 6/3/2016).

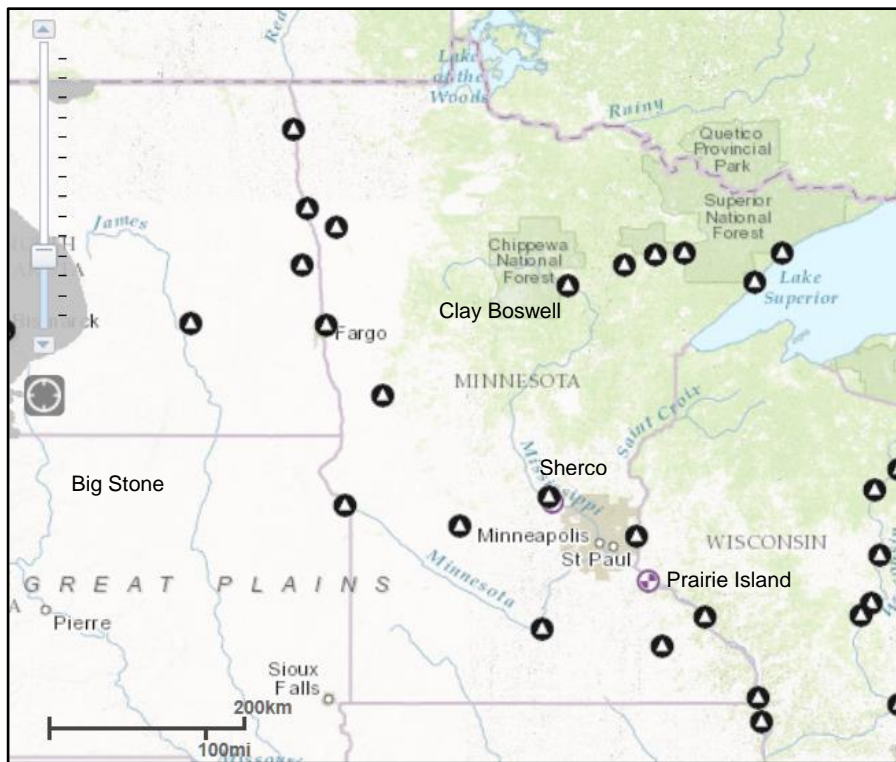


Figure 3-35. Location of coal-fired power plants in Minnesota (designated by circles with triangles) and the Prairie Island nuclear facility (<http://www.eia.gov/state/?sid=MN>; accessed 6/2/2016).



Figure 3-36. Xcel Energy's Sherco coal-fired power plant in Becker, MN.

The U.S. EPA released a draft plan on August 3, 2015, known as the Clean Power Plan, which would require a 40% reduction in Minnesota's emissions of carbon dioxide by 2030 (<http://www2.epa.gov/cleanpowerplan/clean-power-plan-existing-power-plants#CPP-final>; accessed 10/5/2015). This plan would have implications for the operation of the Sherco plant since it is the state's largest emitter of carbon dioxide (<http://www.startribune.com/epa-mandates-likely-mean-changes-at-sherco-coal-plant/328589051/>; accessed 10/5/2015). The plan will ensure that coal-fired power plants operate more cleanly and efficiently,

which would subsequently reduce PAH emissions as a by-product of reducing carbon dioxide emissions. Xcel Energy announced on October 5, 2015 its intent to cease coal-fired generation at Sherco Units 1 and 2 in 2026 and 2023, respectively, while adding new renewable sources of energy



(<http://www.jdsupra.com/legalnews/breaking-news-xcel-energy-announces-47975/>; accessed 10/6/2015). It would still retain coal-fired generation at Sherco Unit 3, which is a newer unit. In all, Xcel proposes achieving 60% carbon emission reductions by 2030. In recent developments, the U.S. Supreme Court stayed implementation of the Clean Power Plan on February 9, 2016 pending judicial review (<https://www.epa.gov/cleanpowerplan/clean-power-plan-existing-power-plants#CPP-final>; accessed 6/3/2016). States can still move forward to reduce carbon pollution from power plants and seek EPA guidance and assistance. On February 10, 2016, Minnesota Governor Mark Dayton announced Minnesota would keep moving forward on clean energy initiatives, including the development of our state's Clean Power Plan (<https://www.pca.state.mn.us/air/clean-power-plan-101>; accessed 6/3/2016). Additional information about the MPCA's work on this plan is available at: <https://www.pca.state.mn.us/clean-power-plan-minnesota>.

### **Diesel emissions in Minnesota**

Diesel vehicle particulate emissions were an important source of PAHs in 33 NLAP lake sediments (Table F-12 in Appendix F). Expansion of Project Green Fleet from the Minneapolis-based Environmental Initiative can further decrease diesel emissions in Minnesota. During the past 10 years of this voluntary program, pollution control devices have been installed on 3200 school buses (Figure 3-37; <http://www.environmental-initiative.org/our-work/clean-air/project-green-fleet>; accessed 6/3/2016). In addition, efforts to retrofit, repower, or upgrade more than 1,300 heavy-duty diesel engines including trucks, transit buses, trains, tugboats, and construction equipment have been made. These efforts have reduced particulate matter emissions equivalent to removing 750,000 cars from the road annually. Reducing these emissions may lessen atmospheric inputs of PAHs to Minnesota waterways, although sources from other states and countries may still impact Minnesota's airshed. The MPCA has estimated more than 500,000 on and off-road diesel engines continue to operate in Minnesota and could be retrofitted (David Thornton, MPCA, <http://midwestenergynews.com/2015/09/24/from-boats-to-buses-minnesota-program-helps-clean-up-diesel-emissions-vw/>; accessed 6/3/2016).



Figure 3-37. The installation of pollution control devices has decreased diesel emissions from Minnesota school buses.

### **Ban on CT-sealants in Minnesota**

Product bans on CT-sealants can decrease PAHs in the environment because suitable alternatives either have much lower concentrations of PAHs (i.e., asphalt-based sealants; Figure 3-38) or no PAHs (i.e., acrylic sealants; Crane et al. 2010). Minnesota became the second state in the U.S. to prohibit the statewide sale and use of CT-sealants as of January 1, 2014 (Crane 2014). Previously, 29 municipalities in Minnesota had passed local bans on this product (Crane 2014). Nationwide, the State of Washington, District of Columbia, and several local units of government in other states have passed bans on CT-sealants, as well (MPCA 2016a). Even with bans in place, old CT-sealant surfaces on parking lots and



Figure 3-38. Asphalt-based sealants are a suitable alternative to CT-sealants, shown here being applied to an asphalt driveway.

driveways will continue to abrade and release CT-sealant dust to the environment unless the surfaces are re-sealed with alternative products. PAHs can also continue to volatilize from old CT-sealed surfaces to the atmosphere (Van Metre et al. 2012b), although the greatest volatilization losses occur within 16 days of application (Van Metre et al. 2012a). The most effective way to reduce further PAH losses from old CT-sealed surfaces is to remove the top layers of sealant from asphalt pavement by a grinding or shot blasting technique (<https://www.pca.state.mn.us/water/sealcoat-removal-contractors>; accessed 6/3/2016).

In lieu of removal actions, it could take decades for PAH concentrations in urban sediments to decrease substantially after bans are implemented. Pavlowsky (2012) estimated that it could take  $\geq 20$  years to achieve an 80 – 90% decrease in PAH concentrations in stream and pond sediments if Springfield, MO enacted a ban on CT-sealants. Atmospheric transport of CT-sealant dust from areas that allow usage of this product could potentially be deposited in areas encompassed by local or statewide bans. Even with bans on CT-sealants, other sources of PAHs (e.g., vehicle emissions) will continue to contribute PAHs to the environment. However, any reductions or elimination of one major source will eventually result in overall reductions in PAH concentrations in surficial sediments, particularly in urban areas.

# Biphenyl

## *Highlights:*

- Low concentrations of biphenyl were detected in the sediments of each study lake.
- Biphenyl was significantly greater ( $p < 0.05$ ) in lake sediments from developed land uses than those from each of the other three major land uses (i.e., cultivated, forested, and lakes and wetlands).
- Biphenyl was significantly greater ( $p < 0.05$ ) in lake sediments in surface area class D (50 – 100 ha, which contained the developed lakes) than those in surface area class E (>100 ha).
- Atmospheric deposition may be a common source of biphenyl to most lake sediments outside of urban areas.
- UTL values ranged between 19.6 – 20.4  $\mu\text{g}/\text{kg}$  dry wt.

## Background

Although biphenyl was included in the extended list of PAHs, it does not have the fused ring structure of PAH compounds. Thus, it is considered as a separate aromatic hydrocarbon compound for this report. Biphenyl occurs naturally in coal tar, crude oil, and natural gas, and it is released to the environment by the incomplete combustion of mineral oil and coal in addition to vehicle emissions (World Health Organization 1999). Historically, it was used as the starting material for the commercial production of PCBs. Biphenyl is also used as an intermediate in the production of other organic compounds, such as emulsifiers, optical brighteners, crop protection products, and plastics (World Health Organization 1999). The most common applications of biphenyl since 2009 are in final products, including: heat transfer fluids, dyestuff carriers for textiles, preservatives for citrus fruit (no longer allowed in the U.S. and European Union), dyestuff carriers for copying paper, and solvents for pharmaceutical production (Danish EPA 2015). Biphenyl is included on the Danish EPA's List of Undesirable Substances because it: 1) causes skin irritation, 2) causes serious eye irritation, 3) may cause respiratory irritation, 4) is very toxic to aquatic life, and 5) is very toxic to aquatic life with long lasting effects (Danish EPA 2015). Environment Canada and Health Canada (2014) concluded that ambient concentrations of biphenyl in the environment do not constitute a danger to human life or health.

## Summary statistics

Biphenyl was detected in the surficial sediments of each study lake at relatively low concentrations (Table 3-35). The mean biphenyl concentration was 7.8  $\mu\text{g}/\text{kg}$  dry wt. (Table 3-35), with a median value of 6.9  $\mu\text{g}/\text{kg}$  dry wt. (Appendix G). The concentrations ranged from a low of 0.7  $\mu\text{g}/\text{kg}$  dry wt. in Red Rock (#36) to a high of 26.6  $\mu\text{g}/\text{kg}$  dry wt. in Nokomis (#27) in Minneapolis, MN. The Nokomis (#27) sample was an outlier at the 5% significance level (Appendix G). Vesper (#47), a remote BWCAW lake, had a similar concentration of over 13  $\mu\text{g}/\text{kg}$  dry wt. as Snail Lake (#38) in the Twin Cities metropolitan area. Atmospheric deposition would be the major source category of biphenyl into Vesper. Additional summary statistics, percentiles, a box plot, and a Q-Q plot with identification of the #27 outlier are provided in Appendix G.

The mean concentrations of biphenyl were compared separately in lakes from different major land use categories and surface area classes. There was a statistically significant difference ( $p = 0.014$ ) in the mean values of biphenyl from different land use groups (Table 3-36). Pairwise comparisons showed the

Table 3-35. Summary Statistics for Biphenyl

Parameter	N	Number Detects	Number NDs	% NDs	Mean (µg/kg dry wt.)	SD (µg/kg dry wt.)
Biphenyl	54	54	0	0	7.8	5.2

N = number of samples; ND = nondetect.

Table 3-36. Statistical Comparison of Biphenyl by Land Use Categories

Parameter	Transformation of Data	p-value
		One-Way ANOVA
Biphenyl	square root	0.014*

ANOVA = analysis of variance.

\* Statistically significant (p<0.05).

mean value of biphenyl in lakes with developed land uses was significantly greater (p<0.05) than the mean values in each of the other three major land uses (i.e., cultivated, forested, and lakes and wetlands; Table 3-37).

Table 3-37. Multiple Pairwise Comparisons of Biphenyl by Land Use Categories. Pairs Shaded "Yes" are Significantly Different (p<0.05) from Each Other.

Parameter	p<0.05					
	dev vs. cul	dev vs. wet	dev vs. for	for vs. cul	for vs. wet	wet vs. cul
Biphenyl <sup>1,‡</sup>	Yes	Yes	Yes	No	No	No

dev = developed; cul = cultivated; for = forested; wet = lakes and wetlands.

<sup>1</sup> Based on square root transformation of the data.

<sup>‡</sup> The Holm-Sidak method was used for these pairwise multiple comparisons.

There was a statistically significant difference (p = 0.006) in the mean values of biphenyl from five different lake surface area categories (Table 3-38). Pairwise comparisons showed that only lakes in surface area class D (50 – 100 ha, which included the developed lakes) were significantly greater (p<0.05) than those lakes in surface area class E (>100 ha; Table 3-39). For the pairs of land use categories and surface area classes that were not significantly different (p>0.05) from each other (Tables 3-37 and 3-39), atmospheric deposition of biphenyl may be a common source pathway to these lake watersheds.

Table 3-38. Statistical Comparison of Biphenyl by Lake Surface Area Categories

Parameter	Transformation of Data	p-value
		One-Way ANOVA
Biphenyl	natural log	0.006*

ANOVA = analysis of variance.

\* Statistically significant (p<0.05).

Table 3-39. Multiple Pairwise Comparisons of Biphenyl by Lake Surface Area Categories. The Pair Shaded "Yes" is Significantly Different ( $p < 0.05$ ) from Each Other.

Parameter	$p < 0.05$	
	D vs. E	Nine Other Pairs of Lake Surface Area Categories
Biphenyl <sup>1,‡</sup>	Yes	No

D = 50 - 100 ha; E = >100 ha.

<sup>1</sup> Based on natural log transformation of the data.

<sup>‡</sup> The Holm-Sidak method was used for these pairwise multiple comparisons.

## UTL values

Biphenyl does not have a SQT value or other freshwater sediment quality guideline. U.S. EPA Region III developed freshwater sediment screening benchmarks, and they used a value of 1.22 mg/kg dry wt. for biphenyl (Pluta 2006). This benchmark is nearly an order of magnitude higher than ambient concentrations measured in the NLAP lakes (Table 3-35). Since this benchmark is designed to be protective of sensitive species, the ambient biphenyl concentrations measured in the NLAP lake sediments probably present a low risk to sediment-dwelling organisms.

The Q-Q plot for biphenyl (Appendix G) was reviewed for statistical outliers and other distinct populations of data in preparation for calculating the UTLs. The UTL values for biphenyl ranged from 19.6 – 20.4  $\mu\text{g}/\text{kg}$  dry wt. after removing Nokomis (#27) as an outlier (Table 3-40). Only two other lakes exceeded this UTL range, including Flat (#15) and South Drywood (#40). Both of these lakes are located in western Minnesota under different major land uses (forested for Flat and cultivated for South Drywood).

Table 3-40. Biphenyl UTL (units in  $\mu\text{g}/\text{kg}$  dry wt.)

Parameter	N	Potential Outliers Removed at 5% Significance Level (lake ID numbers)	Gamma Distribution*	
			95% Approximately Gamma UTL with 95% Coverage	
			WH	HW
Biphenyl	53	27	19.6	20.4

N = number of samples; UTL = Upper Tolerance Limit; WH = Wilson Hilferty; HW = Hawkins Wixley.

\* UTLs for normally distributed data were preferred over those derived from gamma distributed data. When the data were not normally distributed, the gamma distribution was used to estimate UTL values. Gamma UTLs were calculated two different ways, for which professional judgment can be used to select the value of interest.

## PCBs

### *Highlights:*

- Total PCBs were low in most of the sediment samples, except for two developed lakes in the Twin Cities metropolitan area. Although PCBs were banned in 1979, these legacy contaminants are still an important issue in urban areas.
- The following congeners were detected most frequently in surficial sediment samples: 118, 132+153, 77+110, and 180. All of these congeners are more highly chlorinated and persistent in the environment. Congeners 77 and 118 also exhibit toxicity and structural features similar to 2,3,7,8-TCDD.
- Total PCBs determined from a pesticide scan were similar in concentration to Total PCBs summed by congeners using the Kaplan-Meier method.
- UTLs were calculated for individual congeners, co-eluting congener groups, and Total PCBs.

### **Background**

PCBs are a group of legacy and non-legacy contaminants, which are highly persistent in the environment. Most of these hydrophobic organic chemicals were manufactured in the U.S. as Aroclor mixtures of select PCB congeners; production ran from 1929 until these compounds were banned by the U.S. government in 1979 (Johnson et al. 2006). However, exemptions were allowed a few years later under the Toxic Substances Control Act (TSCA) for their use in controlled manufacturing processes (up to 50 ppm) and as unintentional contaminants in products such as inks and dyes (Moll 1982). PCBs were among the 12 persistent organic pollutants (POPs) initially recognized under the 2001 Stockholm Convention for causing adverse effects on humans and ecosystems (<http://chm.pops.int/TheConvention/ThePOPs/The12InitialPOPs/tabid/296/Default.aspx>, accessed 2/4/2016). Although PCBs have been banned by most developed countries, they are still produced and used in some developing countries. India ratified the Stockholm POPs Treaty in 2006 with the intent to ban the use of PCBs by 2025 and adopt measures to reduce or eliminate releases from stock piles and waste by 2028 (Press Trust of India 2015). Because of PCBs physical-chemical properties (Johnson et al. 2006), these compounds can exhibit long-range transport, particularly in air, with subsequent deposition in countries far from their source. Thus, their use in developing countries can impact countries that have previously banned PCBs. PCBs will continue cycling through the environment for some time, even if these compounds are banned globally.

Nonlegacy PCB congeners are produced during manufacturing processes in the U.S. and abroad (Prairie Research Institute 2015). These nonlegacy congeners differ from the historical PCB congeners included in commercial Aroclor mixtures (Grossman 2013). PCB 11 (3,3'-dichlorobiphenyl) was consistently detected in commercial azo and phthalocyanine pigments used in household paint, and it could be considered as a key indicator of nonlegacy PCBs (Hu and Hornbuckle 2010). PCB 11 is also inadvertently formed during the production of diarylide yellow pigments, which are used in a variety of consumer goods (e.g., newspapers, cardboard, magazines, cereal boxes, plastic bags; Rodenburg et al. 2010). It is also a significant nonlegacy PCB source to the lower Great Lakes (Khairy et al. 2015). Other nonlegacy PCB congeners include the following heavily chlorinated congeners: PCBs 206, 207, 208, and 209 (Hu et al. 2011). More than 50 PCB congeners have been detected in commercial paint pigments in patterns that differ from any Aroclor "fingerprints" (Hu and Hornbuckle 2010). Some of these nonlegacy congeners (e.g., PCB 11) are not commonly measured in environmental samples, because commercial



and government analytical labs have focused on legacy PCBs in the past. As more laboratories expand their congener list to include nonlegacy PCB congeners, the inclusion of PCB 11, in particular, may be enough to trigger exceedances of water quality standards for Total PCBs in some areas (Rodenburg et al. 2010).

PCBs continue to be of concern to ecological and human health. Because PCBs are lipophilic, these compounds accumulate in fatty tissues. In the U.S., 23% of all fish advisories in 2011 were due to PCBs; these advisories spanned 6.1 million lake acres and 132,000 river miles (USEPA 2013a). Minnesota's fish consumption advisories for PCBs are designed to protect children from developmental problems and to reduce the lifetime risk of cancer from consuming contaminated fish (MDH, <http://www.health.state.mn.us/divs/eh/fish/faq.html>, accessed 2/17/2016). MDH has issued fish advisories for six Minnesota lakes, none of which were NLAP lakes. Lake Nokomis (#27) used to have several fish advisories for PCBs (primarily for carp), but those advisories were rescinded (<http://fishadvisoryonline.epa.gov/AdvisoryDetails.aspx?ADVNUM=9250>, accessed 2/17/2016). Twelve rivers in Minnesota have fish advisories for PCBs, including multiple stretches of the Mississippi River, St. Croix River, and St. Louis River (MDH, <http://www.health.state.mn.us/divs/eh/fish/eating/sitespecific.html>, accessed 2/17/2016). These river advisories include a variety of bottom feeding and sport fishes, and most restrictions are limited to one meal per week. New work in Green Bay, WI has demonstrated invasive species (i.e., quagga mussels and their invasive predator, round gobies) may mobilize PCBs out of sediments into the food web (Macksasitorn et al. 2015). This mobilization provides another way for harmful concentrations of PCBs to build-up in fish and the piscivorous wildlife and humans who consume fish.

## Summary statistics

PCB congeners and Total PCBs (from a pesticide scan) were measured in a subset of 24 NLAP lakes. Total PCBs were also estimated using the Kaplan-Meier method for lakes with <80% nondetects of PCB congeners. Table 3-41 shows the percentage of nondetects for these analytes. None of the lakes had a complete set of congeners detected. This finding is not surprising since different groups of congeners were used in different commercial Aroclor mixtures, and the congener patterns undergo weathering in the environment over time. The following congeners were detected most frequently in surficial sediment samples: 118, 132+153, 77+110, and 180 (Table 3-41). All of these congeners are more highly chlorinated and persistent in the environment. Congeners 77 and 118 also exhibit toxicity and structural features similar to 2,3,7,8-TCDD (Van den Berg et al. 1998). Thirteen individual or coeluting groups of congeners were not detected in any samples, including five congeners with dioxin-like properties (Table 3-41). This set of nondetected congeners included two coeluting groups of dichloro-PCBs (i.e., 5+8 and 7+9). These lower chlorinated congeners are more water soluble and volatile than higher chlorinated congeners and are also more easily biodegraded or metabolized by microorganisms in the environment (Abramowicz 1990; Johnson et al. 2006). PCB 209 was also not detected in any samples; this highly chlorinated congener is a nonlegacy PCB. Another nonlegacy PCB congener, 206, was only detected in one sample [#42-Spring (690129)]. The nonlegacy PCB congeners of 11, 207, and 208 were not analyzed in these sediment samples.

Total PCBs (pesticide scan) were detected in 22 of the 24 lakes, and Total PCBs (Kaplan-Meier) were estimated in 12 lakes (Table 3-41). The estimated Total PCBs (Kaplan-Meier) ranged from 7.3 – 79.1 µg/kg dry wt. (Table 3-42). The highest concentrations were observed in the Twin Cities metropolitan area in Nokomis (#27) and Snail (#39) lakes. The mean of the Total PCB (Kaplan-Meier) concentrations in these two urban lakes were significantly higher ( $p < 0.001$ ) than the mean of the other lakes when a t-test was run. In addition, the median of the Total PCB (pesticide scan) concentrations in these two urban

Table 3-41. Percentage of Nondetects in PCB Congeners and Total PCB Groups, Sorted from Low to High Nondetects

BZ Congener Number* or Total PCB Group	Homolog Group (-biphenyl)	N	Number Detects	Number NDs	% NDs
118†	Pentachloro-	24	22	2	8.3
132+153	Hexachloro-	24	22	2	8.3
Total PCBs (pesticide scan)		24	22	2	8.3
77†+110	Tetrachloro- & Pentachloro-	24	21	3	12.5
180	Heptachloro-	24	21	3	12.5
138+160	Hexachloro-	24	16	8	33.3
87+115	Pentachloro-	24	15	9	37.5
70	Tetrachloro-	24	14	10	41.7
16+32	Trichloro-	24	13	11	45.8
88	Pentachloro-	24	13	11	45.8
52	Tetrachloro-	24	12	12	50.0
105†	Pentachloro-	24	12	12	50.0
Total PCBs (sum congeners; Kaplan-Meier)		24	12	12	50.0
18	Trichloro-	24	11	13	54.2
90+101	Pentachloro-	24	11	13	54.2
123†+149	Pentachloro- & Hexachloro-	24	11	13	54.2
146	Hexachloro-	24	11	13	54.2
37+42+59	Trichloro- & Tetrachloro-	24	10	14	58.3
56+60	Tetrachloro-	24	10	14	58.3
187	Heptachloro-	24	10	14	58.3
28	Trichloro-	24	9	15	62.5
49	Tetrachloro-	24	9	15	62.5
61+74	Tetrachloro-	24	9	15	62.5
170+190	Heptachloro-	24	9	15	62.5
178	Heptachloro-	24	9	15	62.5
199	Octachloro-	24	9	15	62.5
47+48+75	Tetrachloro-	24	8	16	66.7
97	Pentachloro-	24	8	16	66.7
22+51	Trichloro- & Tetrachloro-	24	7	17	70.8
44	Tetrachloro-	24	7	17	70.8
66	Tetrachloro-	24	7	17	70.8
99	Pentachloro-	24	7	17	70.8
128	Hexachloro-	24	7	17	70.8
129	Hexachloro-	24	7	17	70.8
20+33+53	Trichloro- & Tetrachloro-	24	6	18	75.0
41+64	Tetrachloro-	24	6	18	75.0



Table 3-41. Continued

BZ Congener Number* or Total PCB Group	Homolog Group (-biphenyl)	N	Number Detects	Number NDs	% NDs
95	Pentachloro-	24	6	18	75.0
156 <sup>†</sup> +171+202	Hexachloro- & Heptachloro- & Octachloro-	24	6	18	75.0
196+203	Octachloro-	24	6	18	75.0
29	Trichloro-	24	5	19	79.2
43	Tetrachloro-	24	5	19	79.2
46	Tetrachloro-	24	5	19	79.2
174	Heptachloro-	24	5	19	79.2
185	Heptachloro-	24	5	19	79.2
137+176	Hexachloro- & Heptachloro-	24	4	20	83.3
183	Heptachloro-	24	4	20	83.3
191	Heptachloro-	24	4	20	83.3
45	Tetrachloro-	24	3	21	87.5
82	Pentachloro-	24	3	21	87.5
84	Pentachloro-	24	3	21	87.5
141+179	Hexachloro- & Heptachloro-	24	3	21	87.5
157 <sup>†</sup> +173+200	Hexachloro- & Heptachloro- & Octachloro-	24	3	21	87.5
167 <sup>†</sup>	Hexachloro-	24	3	21	87.5
1	Chloro-	24	2	22	91.7
24+27	Trichloro-	24	2	22	91.7
25	Trichloro-	24	2	22	91.7
26	Trichloro-	24	2	22	91.7
31	Trichloro-	24	2	22	91.7
40	Tetrachloro-	24	2	22	91.7
107	Pentachloro-	24	2	22	91.7
151	Hexachloro-	24	2	22	91.7
172	Heptachloro-	24	2	22	91.7
177	Heptachloro-	24	2	22	91.7
189 <sup>†</sup>	Heptachloro-	24	2	22	91.7
194	Octachloro-	24	2	22	91.7
201	Octachloro-	24	2	22	91.7
15	Dichloro-	24	1	23	95.8
92	Pentachloro-	24	1	23	95.8
158	Hexachloro-	24	1	23	95.8
195+208	Octachloro- & Nonachloro-	24	1	23	95.8
205	Octachloro-	24	1	23	95.8
206	Nonachloro-	24	1	23	95.8
5+8	Dichloro-	24	0	24	100.0
7+9	Dichloro-	24	0	24	100.0

Table 3-41. Continued

BZ Congener Number* or Total PCB Group	Homolog Group (-biphenyl)	N	Number Detects	Number NDs	% NDs
77 <sup>†</sup>	Tetrachloro-	24	0	24	100.0
81 <sup>†</sup>	Tetrachloro-	24	0	24	100.0
83	Pentachloro-	24	0	24	100.0
85	Pentachloro-	24	0	24	100.0
86	Pentachloro-	24	0	24	100.0
114 <sup>†</sup> +122+131	Pentachloro- & Hexachloro-	24	0	24	100.0
126 <sup>†</sup>	Pentachloro-	24	0	24	100.0
136	Hexachloro-	24	0	24	100.0
166	Hexachloro-	24	0	24	100.0
169 <sup>†</sup>	Hexachloro-	24	0	24	100.0
209	Decachloro-	24	0	24	100.0

PCB = polychlorinated biphenyl; ND = nondetect.

\* BZ refers to Ballschmiter and Zell's 1980 publication in which they provided this numbering system for PCB congeners.

<sup>†</sup> PCB congeners with toxicity and structural features similar to 2,3,7,8-TCDD (i.e., dioxin-like).

Table 3-42. Estimation of Total PCBs (Kaplan-Meier) for Lakes with &lt;80% Nondetect Values for PCB Congeners

Lake ID #	Number of PCB Congeners	% NDs	KM Mean (µg/kg dry wt.)	Total PCBs (Kaplan-Meier)* (µg/kg dry wt.)
11	83	75.9	0.142	11.8
19	83	79.5	0.0885	7.3
21	83	79.5	0.199	16.5
27	83	54.2	0.879	73.0
32	83	71.1	0.301	25.0
33	83	69.9	0.288	23.9
38	83	42.2	0.953	79.1
39	83	49.4	0.368	30.5
41	83	69.9	0.429	35.6
42	83	65.1	0.339	28.1
50	83	42.2	0.331	27.5
53	83	69.9	0.183	15.2

PCBs = polychlorinated biphenyls; ND = nondetect; KM = Kaplan-Meier.

\*Total PCBs were estimated by multiplying the Kaplan-Meier mean by the total number of PCB congeners in each sample.

lakes were significantly higher ( $p < 0.05$ ) than the median of the other lakes when a Mann-Whitney rank sum test was run. The estimated Total PCB (Kaplan-Meier) values were highly correlated ( $r = 0.998$ ) to Total PCBs by the pesticide scan (Figure 3-39). The pesticide scan Total PCBs consistently

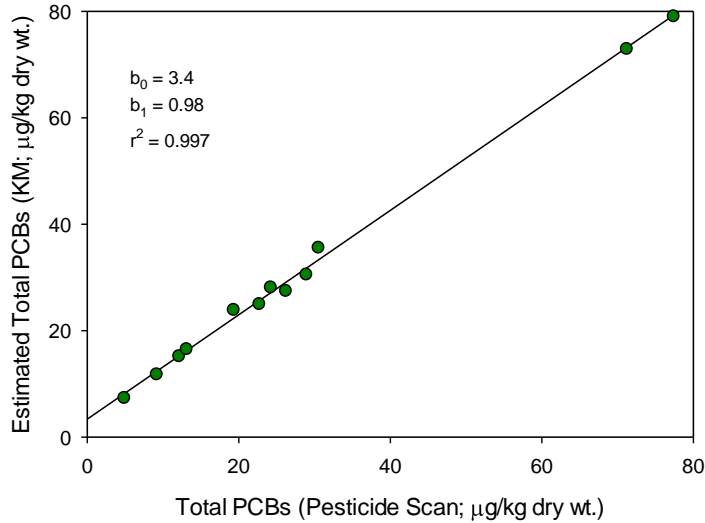


Figure 3-39. Linear regression of estimated Total PCBs (Kaplan-Meier) and Total PCBs (pesticide scan). For the linear regression,  $b_0$  = intercept,  $b_1$  = slope, and  $r^2$  = coefficient of determination.

underestimated the Kaplan-Meier Total PCBs. This regression relationship is promising as a cost effective way to use pesticide scan Total PCB data to estimate congener-specific Total PCBs:

$$\text{Estimated Total PCBs (Kaplan-Meier)} = 3.4 + 0.98(\text{Total PCBs}_{\text{pesticide scan}})$$

Appendix H contains additional summary results of these PCB data. This includes additional summary statistics, percentiles, box plots, and Q-Q plots for PCB congeners and Total PCBs (pesticide scan and estimated by Kaplan-Meier). Outliers are noted on these Q-Q plots. In addition, box plots and Q-Q plots of PCB congeners in study lakes with <80% nondetects are also provided.

### Comparisons to SQT values

Both groups of Total PCBs were compared to the MPCA’s Level I and Level II SQT values (Table 3-43). Sediments from most lakes were below the Level I SQT value of 60 μg/kg dry wt., with only the two urban lakes (#27 and 39) exceeding it. No lakes exceeded the Level II SQT value of 680 μg/kg dry wt.

Table 3-43. Comparison of Statewide Total PCB Data to the Level I and Level II SQTs

Total PCBs	Percent of Samples (n = 24)		
	≤ Level I SQT	> Level I to ≤ Level II SQT	> Level II SQT
Total PCBs (pesticide scan)	91.7	8.3	0
Total PCBs (Kaplan-Meier)	91.7	8.3	0

PCB = polychlorinated biphenyl; SQT = sediment quality target.

Figure 3-40 shows a graphical view of these results for Total PCBs (pesticide scan). For many of these lakes, atmospheric deposition of PCBs may be a major transport mechanism to the lake itself and the surrounding watershed. Application of WWTP biosolids on agricultural land and subsequent runoff to lakes could be a transport pathway for biosolids containing low concentrations of PCBs (Meijer et al.

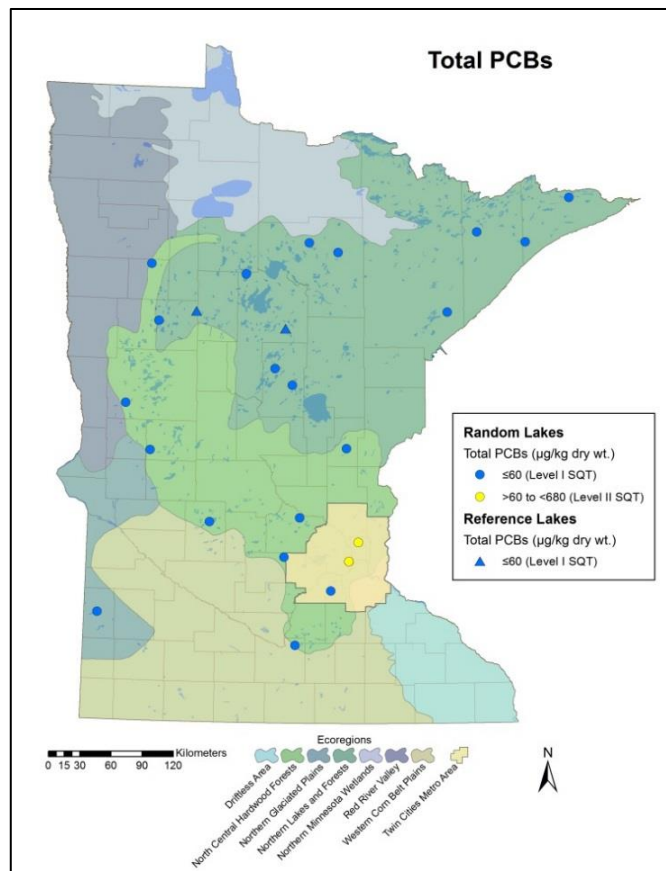


Figure 3-40. Comparison of Total PCBs (pesticide scan) in NLAP lakes to the Level I and Level II SQT values.

2003). Atmospheric deposition, as well as urban stormwater input may be important sources of PCBs to Nokomis (#27) and Snail (#38). Relatively high concentrations of PCBs have been found in concrete and masonry buildings built between 1950 and 1980, particularly due to the use of PCBs in interior and exterior caulk (Klosterhaus et al. 2014). Rain and snowmelt runoff from these buildings contributes PCBs in urban stormwater, which can eventually be deposited with particles in urban stormwater pond and lake sediments.

## UTL values

The UTL values for PCB congeners with <80% nondetects and for Total PCB groups are provided in Table 3-44. The following PCB congeners had the highest UTL values (from highest to lowest values): 52, 47+48+75, 170+190, 90+101, 97, and 22+51. Most of these congeners were in the tetra- or higher homolog groups, and none of these congeners had dioxin-like properties. The lowest UTL values were observed for the following PCB congeners (from lowest to highest values): 187, 185, 88, 156+171+202, 105, and 196+203. These congeners were in the penta- or higher homolog groups. Both 105 and 156 display dioxin-like properties. The two Total PCB groups had comparable values. Eleven individual or coeluting congeners had one or both urban lakes (#27, 38) as statistical outliers, which indicates there were additional urban sources of these congeners to the lake watersheds other than the ambient PCB concentrations observed in outstate Minnesota (i.e., outside the Twin Cities metropolitan area).

Table 3-44. UTLs of Detected and Censored PCB Data with Outliers Removed at the 5% Significance Level (units in µg/kg dry wt.)

PCB Congener(s) or Total PCBs	N (# detects)	% Nondetects	Potential Outliers Removed at 5% Significance Levels (lake ID numbers)	Normal Distribution and KM Estimates*	Gamma Distribution and KM Estimates*	
				95% UTL with 95% Coverage	95% Approx. Gamma UTL with 95% Coverage	
					WH	HW
16+32	23 (12)	47.8	28	1.8		
18	24 (11)	54.2	-	1.5		
20+33+53	24 (6)	75	-	1.7		
22+51	24 (7)	70.8	-	2.8		
28	23 (8)	65.2	20	1.5		
29	24 (5)	79.2	-	0.65		
37+42+59	24 (10)	58.3	-	1.7		
41+64	23 (5)	78.3	27	0.60		
43	24 (5)	79.2	-	1.0		
44	24 (7)	70.8	-	1.4		
46	24 (5)	79.2	-	0.82		
47+48+75	24 (8)	66.7	-	4.5		
49	23 (8)	65.2	41	1.8		
52	24 (12)	50	-		4.3	4.7
56+60	24 (10)	58.3	-	2.2		
61+74	24 (9)	62.5	-		1.6	1.7
66	24 (7)	70.8	-	1.2		
70	24 (14)	41.7	-	2.7		
77+110	22 (19)	13.6	27, 38 <sup>†</sup>	0.99		
87+115	22 (13)	40.9	27 <sup>§</sup> , 38 <sup>§</sup>	0.65		
88	22 (11)	50	27, 38 <sup>†</sup>	0.33		
95	24 (6)	75	-	1.1		
97	24 (8)	66.7	-	3.0		

Table 3-44. Continued

PCB Congener(s) or Total PCBs	N (# detects)	% Nondetects	Potential Outliers Removed at 5% Significance Levels (lake ID numbers)	Normal Distribution and KM Estimates*	Gamma Distribution and KM Estimates*	
				95% UTL with 95% Coverage	95% Approx. Gamma UTL with 95% Coverage	
					WH	HW
99	24 (7)	70.8	-	1.1		
90+101	24 (11)	54.2	-		3.2	3.4
105	23 (11)	52.2	27		0.40	0.40
118	22 (20)	9.1	27 <sup>†</sup> , 38		2.1	2.2
123+149	22 (9)	59.1	27, 38 <sup>†</sup>	0.54		
128	24 (7)	70.8	-	0.52		
129	24 (7)	70.8	-	0.82		
132+153	22 (20)	9.1	27, 38 <sup>†</sup>	1.2		
138+160	20 (12)	40	27, 38 <sup>†</sup> , 41 <sup>†</sup> , 50 <sup>†</sup>	0.65		
146	24 (11)	54.2	-	0.96		
156+171+202	23 (5)	78.3	27	0.36		
170+190	23 (8)	65.2	32	3.8		
174	24 (5)	79.2	-	1.5		
178	24 (9)	62.5	-	0.71		
180	24 (21)	12.5	-	1.2		
185	24 (5)	79.2	-	0.22		
187	22 (8)	63.6	27, 38 <sup>†</sup>	0.20		
196+203	24 (6)	75	-	0.43		
199	24 (9)	62.5	-	0.82		
Total PCBs (pesticide scan)	22 (20)	9.1	27 <sup>†</sup> , 38	33.7		
Total PCBs (Kaplan-Meier) <sup>‡</sup>	22 (10)	54.6	27 <sup>†</sup> , 38	36.6		

UTL = Upper Tolerance Limit; PCB = polychlorinated biphenyl; KM = Kaplan Meier; WH = Wilson Hilferty; HW = Hawkins Wixley.

Table 3-44. Continued

\* UTLs for normally distributed data were preferred over those derived from gamma distributed data. When the data were not normally distributed, the gamma distribution was used to estimate UTL values. Gamma UTLs were calculated two different ways, for which professional judgment can be used to select the value of interest.

† Potential outlier was based on professional judgment; all other outliers were based on statistical tests at the 5% significance level.

§ Both samples had the same concentration value, which was an outlier at the 5% significance level.

‡ The Kaplan-Meier method was used to determine means for 12 lake sediment samples with <80% nondetects, which were then multiplied by the number of congeners to yield estimated Total PCBs. For samples with >80% nondetects, the detected congener values and reporting limits for other congeners were summed and expressed as less than Total PCB values used in the UTL calculation.

## Metal PEC-Qs and mean PEC-Qs

### *Highlights:*

- The metal PEC-Qs and mean PEC-Qs were both significantly higher ( $p < 0.05$ ) in lake sediments from watersheds with developed land uses than those from each of the other three major land use classes (i.e., cultivated, forested, and lakes and wetlands). In addition, lake sediments in forested watersheds had significantly higher ( $p < 0.05$ ) metal PEC-Q and mean PEC-Q mean values than lakes dominated by cultivated watersheds.
- The metal PEC-Qs and mean PEC-Qs did not vary significantly ( $p > 0.05$ ) by lake surface area classes.
- For mean PEC-Qs, nearly 43% of sediment samples were less than the Level I SQT value (i.e., protective of benthic invertebrates), while 57.4% of sediment samples were between the Level I and Level II SQT values. No sediment samples exceeded the Level II SQT value, for which harmful effects on benthic invertebrates would be more likely to occur.
- UTL values were calculated for the metal PEC-Q and mean PEC-Q values.

## Background

Sediments often contain a mixture of contaminants, and it is useful to recognize this in a holistic way. The mean PEC-Qs provide a sediment assessment tool that distills data from a mixture of contaminants ( $\Sigma$ PAH<sub>13</sub>, Total PCBs, and 7 metals) into one unitless index (Crane and Hennes 2007). As such, the mean PEC-Qs provide a way to compare sediment quality over time and space (Long et al. 2006). The metal PEC-Qs represent those metals with reliable PECs that were adopted as Level II SQTs (i.e., arsenic, cadmium, chromium, copper, lead, nickel, and zinc; Crane et al. 2000, 2002).

The mean PEC-Qs are predictive of sediment toxicity. For matching sediment chemistry and toxicity test data conducted with amphipods and midges exposed to sediment from the St. Louis River AOC, the incidence of toxicity increased as the mean PEC-Q ranges increased (Crane et al. 2000, 2002). Similar comparisons were made for other areas around the Great Lakes and in North America (Ingersoll et al. 2001). These evaluations indicated the mean PEC-Qs provided a reliable basis for classifying sediments as toxic or not toxic in the St. Louis River AOC, in the larger geographic areas of the Great Lakes, and elsewhere in North America (Crane et al. 2000, 2002; Ingersoll et al. 2001).

An update of the predictive ability evaluation for the St. Louis River AOC was conducted in 2006 with a larger data set. This evaluation showed that the incidence of acute toxicity to amphipods and midges tended to be low (i.e., 4.3% and 2.1%, respectively) when the concentrations of sediment-associated contaminants were at or below the Level I SQT (i.e., mean PEC-Q  $\leq 0.1$ ; Crane 2006). In addition, the incidence of sediment toxicity in these sediments increased with increasing mean PEC-Q ranges in the 10-day amphipod and midge tests (Crane 2006).

## Summary statistics

Summary statistics for the metal PEC-Q and mean PEC-Q values are provided in Table 3-45. The metal PEC-Q data were more skewed and heavy-tailed (i.e., kurtosis) compared to a normal distribution than the mean PEC-Q data (Table 3-45). Additional summary statistics, percentiles, box plots, and Q-Q plots



Table 3-45. Summary Statistics for Metal PEC-Qs and Mean PEC-Qs

Parameter	N	Minimum	Maximum	Mean	SD	Skewness	Kurtosis
Metal PEC-Q	54	0.064	0.82	0.23	0.13	2.1	7.2
Mean PEC-Q	54	0.024	0.35	0.11	0.062	1.7	3.8

N = number of samples, SD = standard deviation; PEC-Q = probable effect concentration quotient.

(with outliers noted at the 5% significance level) are provided in Appendix I. Snail Lake (#38) was an outlier for both the metal PEC-Q and mean PEC-Q data sets due to high concentrations of arsenic in the sediment. As discussed in the Metals and Metalloids Section, this lake was treated numerous times with sodium arsenite to control algae and macrophyte growth. Thus, arsenic has accumulated in the surficial sediments of Snail Lake. Nokomis (#27) and Becoosin (#6) were additional statistical outliers of the mean PEC-Q data set. Both Nokomis (#27) and Snail (#38) were major outliers with the  $\Sigma$ PAH<sub>13</sub> and Total PCB (pesticide scan) data sets. Becoosin (#6) was a statistical outlier for copper and nickel due to natural enrichment of these metals in this BWCAW lake.

The metal PEC-Q and mean PEC-Q values were compared by land use categories to test the null hypothesis of no significant differences between land uses. For the mean values of both parameters, there were statistically significant differences ( $p < 0.001$ ) between land use categories (Table 3-46). The results of multiple pairwise comparisons for both parameters were the same, indicating the comparisons were influenced primarily by metals. Lakes in developed watersheds had significantly higher ( $p < 0.05$ ) metal PEC-Q and mean PEC-Q mean values than lakes in watersheds dominated by either cultivated, forested, or lakes and wetlands land uses (Table 3-47). In addition, lakes in forested watersheds had significantly higher ( $p < 0.05$ ) metal PEC-Q and mean PEC-Q mean values than lakes dominated by cultivated watersheds (Table 3-47). Several study lakes in forested watersheds were located in northeastern Minnesota where certain metals (e.g., copper, nickel) are naturally enriched in mineral deposits in these watersheds.

Table 3-46. Statistical Comparisons of PEC-Qs by Land Use Categories

Parameter	Transformation of Data	p-value
		One-Way ANOVA
Metal PEC-Q	natural log	<0.001*
Mean PEC-Q	natural log	<0.001*

PEC-Q = probable effect concentration quotient; ANOVA = analysis of variance.

\* Statistically significant ( $p < 0.05$ ).

The metal PEC-Q and mean PEC-Q values were also compared by lake surface area categories to test the null hypothesis of no significant differences between surface area categories. For both parameters, the null hypothesis was true (Table 3-48). Thus, the mean values of these parameters were not statistically different ( $p > 0.05$ ) among the five categories of lake surface areas.

### Comparisons to SQT values

The mean PEC-Qs were compared to the Level I and Level II SQT values (Table 3-49, Figure 3-41). Similar SQT ranges were also used to compare the metal PEC-Q values (Figure 3-42). The data were not

Table 3-47. Multiple Pairwise Comparisons of PEC-Qs by Land Use Categories. Pairs Shaded "Yes" are Significantly Different ( $p < 0.05$ ) from Each Other.

Parameter	$p < 0.05$					
	dev vs. cul	dev vs. wet	dev vs. for	for vs. cul	for vs. wet	wet vs. cul
Metal PEC-Q <sup>1,‡</sup>	Yes	Yes	Yes	Yes	No	No
Mean PEC-Q <sup>1,‡</sup>	Yes	Yes	Yes	Yes	No	No

PEC-Q = probable effect concentration quotient; dev = developed; cul = cultivated; for = forested; wet = lakes and wetlands.

<sup>1</sup> Based on natural log transformation of the data.

<sup>‡</sup> The Holm-Sidak method was used for these pairwise multiple comparisons.

Table 3-48. Statistical Comparisons of PEC-Qs by Lake Surface Area Categories

Parameter	Transformation of Data	p-value
		One-Way ANOVA
Metal PEC-Q	natural log	0.232 <sup>†</sup>
Mean PEC-Q	natural log	0.621

PEC-Q = probable effect concentration quotient; ANOVA = analysis of variance.

<sup>†</sup> The power of the performed test was below the desired power of 0.800, meaning less likelihood of detecting a difference when one actually exists.

Table 3-49. Comparison of Mean PEC-Q Data to the MPCA's Level I and Level II SQTs

PEC-Q	Percent of Samples (n = 54)		
	≤ Level I SQT	> Level I to ≤ Level II SQT	> Level II SQT
Mean PEC-Q	42.6	57.4	0

PEC-Q = probable effect concentration quotient; SQT = sediment quality target.

weighted to make general classifications for statewide lakes, although the study design could allow this to be done. Sediment quality was quite good for nearly 43% of the study lakes with mean PEC-Q values less than the Level I SQT value (Table 3-49); these lake sediments would be unlikely to cause harm to benthic invertebrates for the suite of contaminants incorporated into the mean PEC-Qs. The rest of the lake sediments were in-between the Level I and Level II SQT values (i.e., fair classification), and some of these lake sediments might show a small amount of toxicity to benthic invertebrates. This statement was based on previous work in the St. Louis River AOC, which showed that sediment toxicity increased as the mean PEC-Q ranges increased from  $\leq 0.1$ ,  $> 0.1$  to  $\leq 0.5$ , and three higher ranges (Crane et al. 2002). Other physical-chemical factors in sediments, such as particle size, TOC, acid volatile sulfide, and ammonia, can also influence the health of benthic invertebrates (Crane et al. 2000). For the metal PEC-Qs, higher values were always observed compared to the corresponding mean PEC-Qs for each lake (Figure 3-42). The inclusion of  $\Sigma\text{PAH}_{13}$  and total PCB data in the calculation of mean PEC-Qs reduced the contribution of metal PEC-Q values (Figure 3-41).

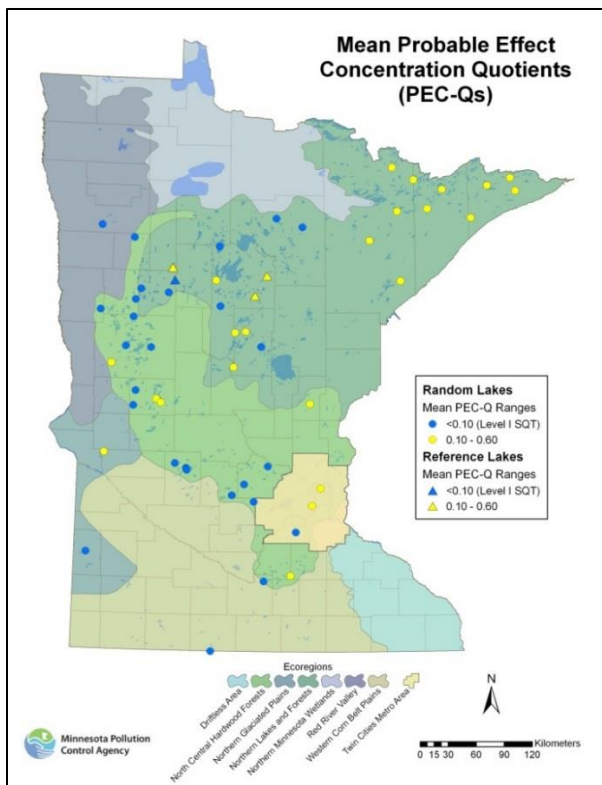


Figure 3-41. Comparison of mean PEC-Q ranges to Level I and Level II SQTs.

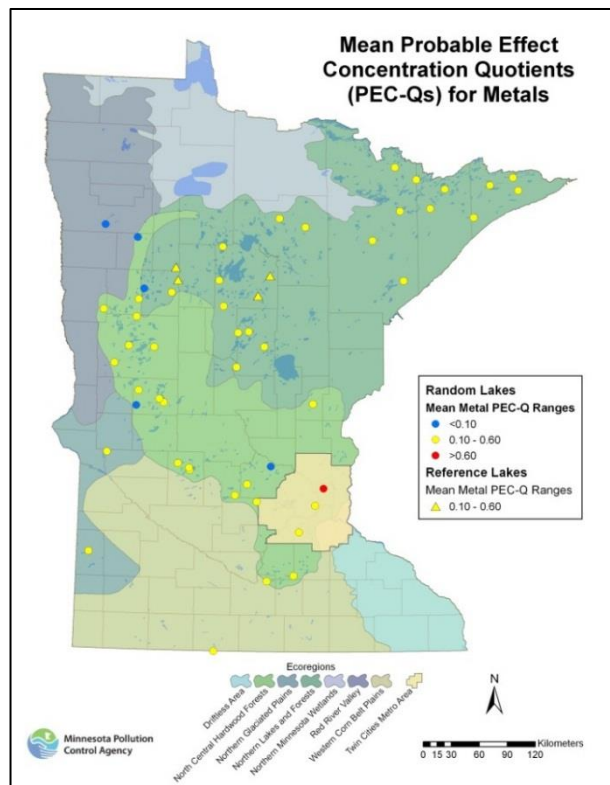


Figure 3-42. Metal PEC-Q ranges in NLAP lakes.

### UTL values

The UTL values for metal PEC-Qs and mean PEC-Qs are provided in Table 3-50. After removing Snail Lake (#38) as an outlier for the metal PEC-Qs, the only other lake that exceeded the UTL value for this parameter was Becosin (#6). As discussed previously, this lake is located in the BWCAW area where copper and nickel are naturally elevated in minerals found in the soil. After removing the outliers for mean PEC-Qs, the only study lake that exceeded the UTL value for this parameter was Elk (#51) due to a high arsenic concentration that exceeded the Level II SQT value. Elk (#51) was one of the *a priori* reference lakes added to this study, and the source of the high arsenic concentration is unknown.

Table 3-50. UTLs of Metal PEC-Qs and Mean PEC-Qs

Parameter	N	Potential Outliers Removed at 5% Significance Level (lake ID numbers)	Gamma Distribution*	
			95% Approximately Gamma UTL with 95% Coverage	
			WH	HW
Metal PEC-Q	53	38	0.48	0.48
Mean PEC-Q	51	6, 27, 38	0.21	0.22

N = number of samples; UTL = Upper Tolerance Limit; WH = Wilson Hilferty; HW = Hawkins Wixley; PEC-Q = probable effect concentration quotient.

\* UTLs for normally distributed data were preferred over those derived from gamma distributed data. When the data were not normally distributed, the gamma distribution was used to estimate UTL values. Gamma UTLs were calculated two ways, for which professional judgment can be used to select the value of interest.

## Legacy organochlorine pesticides

### Highlights:

- Eleven organochlorine pesticides and their metabolites were detected in sediments from over half of the NLAP lakes, even after some of them were banned 30 - 40 years ago.
- Total DDT and the metabolite p,p'-DDE were detected in all but one NLAP lake.
- Endrin, heptachlor epoxide, and toxaphene were not detected in any NLAP lakes.
- Lake #39 (South) had the highest number of organochlorine pesticides and metabolites detected (i.e., 19), while no such chemicals were detected in lake #36 (Red Rock).
- Mean values of Total DDT were significantly higher ( $p < 0.05$ ) in lakes dominated by developed land uses than those with either cultivated or forested land uses. For p,p'-DDE, a significantly higher ( $p < 0.05$ ) median concentration was observed in lakes from developed land uses than those in cultivated land uses.
- The concentrations of most pesticides were below their corresponding Level I SQT values.
- Sum DDD and sum DDE values had a small percentage of Level II SQT exceedances.
- UTLs were calculated for 21 pesticides and metabolites that had <80% nondetects after removing outliers. Some of these UTL values exceeded the corresponding Level I SQT values.

## Background

Organochlorine pesticides were first developed during World War II for use against insect-borne illnesses, such as malaria and typhoid, and later for control of insects in agricultural and urban environments (Bishop 2012). DDT was the first of these synthetic insecticides to be developed (<http://www.epa.gov/ingredients-used-pesticide-products/ddt-brief-history-and-status>; accessed 2/19/2016). The publication of Rachel Carson's book, *Silent Spring*, in 1962 exposed the environmental damage and harmful health effects resulting from the indiscriminate, widespread use of these pesticides in the U.S. In particular, she thoroughly described how DDT was harmful to birds and other animals, that insects developed resistance to organochlorine pesticides, and that these substances could accumulate in fat tissue and contribute to medical problems later on. Her book was a catalyst for government action, which ultimately resulted in restrictions and bans of numerous organochlorine pesticides (Table 3-51).

Although many of these organochlorine pesticides were banned in the 1970s and 1980s, these compounds have not gone away. Due to their hydrophobic and lipophilic properties, these compounds are resistant to degradation, persist in the environment, and accumulate in the lipids (i.e., fat) of organisms up the food chain. Like PCBs, these pesticides can travel far from their original source and cycle through the environment. The Arctic, in particular, has been contaminated by legacy organochlorine pesticides and currently used pesticides through atmospheric transport and ocean currents (Jantunen et al. 2015). For example, alpha- and beta- hexachlorocyclohexane (HCH) isomers bioaccumulate in biota and biomagnify in subsistence foods (e.g., caribou, seal, and whale), which are important to indigenous communities in Alaska and the circumpolar Arctic region ([http://archive.epa.gov/pesticides/reregistration/web/html/-lindane\\_isomers\\_fs.html](http://archive.epa.gov/pesticides/reregistration/web/html/-lindane_isomers_fs.html), accessed

Table 3-51. Information on Commonly Used Organochlorine Pesticides in the U.S. (adapted from USEPA 2000b)

Organochlorine Pesticide	EPA Health Classification	Action in U.S.		Prevalent Use by Watershed Type			Sources/Uses/Notes
		Discontinued or Phase Out Date	Ban Date	Agricultural	Suburban/Urban	Industrial	
Aldrin	B2	1974, 1985	1987	XX	X	XX	Used primarily on corn and citrus products, as well as for general crops and timber preservation. Also used for termite-proofing plywood, building boards, and for plastic and rubber coverings of electrical and telecommunication cables.
Chlordane	B2	1975, 1978	1988	XX	X	XX	Domestic termite control; pesticide manufacturing/-packaging/formulation sites. Includes cis (alpha)- and trans (gamma)-chlordane, cis- and trans-nonachlor, and oxychlordane.
DDT	B2	1972	1973	XX	X	XX	Broad spectrum pesticide use; pesticide manufacturing/-packaging/formulation sites. Includes total DDT and metabolites of DDD, DDE, and DDT.
Dieldrin	B2	1974, 1985	1987	XX	X	XX	Broad spectrum pesticide for termites/soil insects and for cotton, corn, and citrus; pesticide manufacturing/-packaging/formulation sites. Common degradate of aldrin.
Endosulfan	E	2010*	2016* (July 31)	XX		XX	Noncontact insecticide for seed and soil treatments; pesticide manufacturing/packaging/formulation sites. Includes alpha- and beta-endosulfan. Endosulfan sulfate is a major degradate product. The U.S. EPA negotiated a phase-out of all uses with the sole U.S. manufacturer, Makhteshim Agan, in June 2010.*
Endrin	D	1964 & 1979	1984	XX		XX	Broad spectrum pesticide; pesticide manufacturing/-packaging/formulation sites.
Heptachlor	B2	1974	1988	XX	X	XX	Used to protect corn, grain seeds, sorghum, pineapple, and other fruit crops from insect pests, and to control insects in the soil. Also used to protect homes and businesses from termite damage. One exception to ban is for commercial use to control fire ants in power transformers.

Table 3-51. Continued

Organochlorine Pesticide	EPA Health Classification	Action in U.S.		Prevalent Use by Watershed Type			Sources/Uses/Notes
		Discontinued or Phase Out Date	Ban Date	Agricultural	Suburban/Urban	Industrial	
Heptachlor epoxide	B2	1978	1987	XX	X	XX	Degradation product of heptachlor used as a contact and ingested soil insecticide for termites and household pesticide; also used with chlordane as a termiticide; pesticide manufacturing/packaging/formulation sites for heptachlor and chlordane.
Hexachlorobenzene	B2		1984	XX		XX	Fungicide used as a seed protectant, used as chemical intermediate in production of many other organochlorine pesticides; pesticide manufacturing/packaging/formulation sites for a wide variety of organochlorine pesticides.
Lindane (gamma-Hexachlorocyclohexane)	B2/C	1985	2006 <sup>†</sup>	XX	X	XX	Seed and soil treatments for tobacco; foliage applications for fruit and nut trees and vegetables; wood preservative; pesticide manufacturing/packaging/formulation sites. Includes a mixture of homologs of hexachlorocyclohexane whose major component is the gamma isomer. Pharmaceutical use still allowed for head lice and scabies. <sup>†</sup>
Mirex	B2	1975	1977	XX	X	XX	Used extensively in the southeast and Gulf Coast states against fire ants; used in fire retardants and plastic polymerizers; pesticide manufacturing/packaging/formulation sites (including in New York state); mirex is of concern in Great Lakes states.
Toxaphene	B2	1982	1990	XX		XX	Insecticide for cotton and sunflowers; piscicide for rough fish; pesticide manufacturing/packaging/formulation sites. Used in place of DDT for many years.

B2 = probable human carcinogen; C = possible human carcinogen; D = not classifiable as to human carcinogenicity; E = evidence of noncarcinogenicity in humans; X = analysis for target analyte should be considered if other sediment analysis results detect the target analyte or if historic or current use information provides evidence for the potential presence of this target analyte in the watershed; XX = analysis for target analyte is recommended for this land use type if historic or current use information provides evidence of the potential presence of this target analyte in the watershed; DDD = dichlorodiphenyldichloroethane; DDE = dichlorodiphenyldichloroethylene; DDT = dichlorodiphenyltrichloroethane; EPA = Environmental Protection Agency.

\*source: <http://archive.epa.gov/pesticides/reregistration/web/html/endosulfan-agreement.html>.

<sup>†</sup>source: [http://archive.epa.gov/pesticides/reregistration/web/html/lindane\\_isomers\\_fs.html](http://archive.epa.gov/pesticides/reregistration/web/html/lindane_isomers_fs.html).

2/22/2016). Contamination of these subsistence foods could pose an unacceptable risk to native populations. Legacy pesticides have been of worldwide concern. Nine organochlorine pesticides were included on the initial list of 12 POPs under the Stockholm Convention (<http://chm.pops.int/TheConvention/ThePOPs/The12InitialPOPs/tabid/296/Default.aspx>, accessed 2/22/2016). These pesticides included: aldrin, chlordane, DDT, dieldrin, heptachlor, hexachlorobenzene, mirex, and toxaphene. Pentachloroanisole, a metabolite of pentachlorophenol, was included in discussions of pentachlorophenol and its salts and esters at the seventh meeting of the POPs Review Committee of the Stockholm Convention in 2011, and this committee decided to continue to evaluate this group of chemicals (<http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC7/tabid/2240/mctl/ViewDetails/EventModID/871/EventID/142/xmid/7313/Default.aspx>, accessed 8/9/2016). Subsequent meetings under the Stockholm Convention listed additional POPs, including the following pesticides: alpha- and beta-HCH, chlordecone, lindane, pentachlorobenzene, pentachlorophenol and its salts and esters, and technical endosulfan and its related isomers (<http://chm.pops.int/TheConvention/ThePOPs/TheNewPOPs/tabid/2511/Default.aspx>, accessed 2/22/2016). Many of these organochlorine pesticides are probable or possible human carcinogens (Table 3-51).

The use and degradation of DDT in the environment has been well studied. Technical grade DDT was used historically for insecticide applications, and it contained two DDT isomers: 80% p,p'-DDT and 20% o,p'-DDT (Worthing and Walker 1987 as cited in Nowell et al. 1999). In addition, p,p'-DDD was formulated and applied as a pesticide on fruits and vegetables under the trade names TDE, Rothane, and Dilene (Nowell et al. 1999; ATSDR 2002b). DDT is slow to break down, and the metabolites it forms depend on environmental conditions. Under anaerobic conditions, DDD is the main metabolite formed, whereas under aerobic conditions, DDE is the predominant metabolite formed (Ricking and Schwarzbauer 2012). In the presence of sunlight, DDT may photodegrade to DDE (Pinkney and McGowan 2006). The o,p' or p,p'-substitutions at the aromatic rings remain the same during degradation. Thus, p,p'-DDT degrades to the p,p'-DDD and/or p,p'-DDE isomers, and o,p'-DDT degrades to the o,p'-DDD and/or o,p'-DDE isomers (Ricking and Schwarzbauer 2012). In turn, DDE can naturally degrade to 2,2-bis(chlorophenyl)-1-chloroethylene (DDMU) in the environment (Renner 1998; Wetterauer et al. 2012).

Linkages have been shown between DDT exposures and breast cancer. Women who were exposed to p,p'-DDT before they were 14 years old and who were mostly under 20 years as DDT use peaked, had a statistically significant 5-fold increased risk of breast cancer among women born after 1931 (Cohn et al. 2007). The women in this study took part in the Child Health and Development Studies in Oakland, CA during 1959-1967, and they were all mothers who provided blood samples 1 - 3 days after giving birth (Cohn et al. 2007). In a 54-year follow-up to this study, the 9300 daughters of this cohort were tracked to determine which ones had been diagnosed with breast cancer by age 52 years (Cohn et al. 2015). The daughters who were exposed to higher levels of o,p'-DDT in utero were nearly four times more likely to be diagnosed with breast cancer as adults than women who were exposed to lower levels before birth (Cohn et al. 2015). He et al. (2015) showed that estrogenic-like chiral compounds of o,p'-DDT can promote more cancer cell invasion in an in vitro breast tumor cell test using MCF-7 cells.

Legacy organochlorine pesticides have been replaced by less persistent organophosphate, carbamate, pyrethroid, and neonicotinoid pesticides, as well as with biopesticides. Biopesticides include naturally occurring substances (e.g., pheromones), microbes, and pesticidal substances produced by plants containing introduced genetic material (<http://www.epa.gov/pesticides/biopesticides>, accessed 2/23/2016). Like several of the legacy organochlorine pesticides, most of these replacement pesticides are neurotoxic (Kamel and Hoppin 2004; Costa et al. 2008) and several display endocrine disrupting

effects (Mnif et al. 2011; Zhang et al. 2016). It is beyond the scope of this report to address further environmental and human health concerns with these other synthetic pesticides.

The Minnesota Department of Agriculture (MDA) participated in Minnesota's component of the 2007 nationwide NLA project by analyzing surface water grab samples from 53 NLA lakes for 37 currently used agricultural pesticides and their degradates (VanRyswyk and Tollefson 2008). Thus, legacy organochlorine pesticides were excluded from their list. Pesticide and/or degradate detections were common in 91% of samples. Atrazine was detected most frequently in 87% of lakes. MDA also noted differences in major land uses. Lakes within watersheds dominated by cultivated land had substantially higher total pesticide concentrations than lakes in other watershed land uses. Urban and forest/water dominated watershed had similar concentrations of total pesticides, possibly due to atmospheric transport and deposition of these pesticides. The concentrations of pesticides were all below Minnesota aquatic life standards and other reference values used by MDA. The base neutral pesticides and chloroacetanilide degradates included in MDA's study were water soluble compounds that would not be expected to accumulate greatly in sediments.

## Summary statistics

The detection frequency of organochlorine pesticides and metabolites varied widely in the NLAP lake sediments (Table 3-52). Total DDT (which included all DDT metabolites) and three DDT metabolites (p,p'-DDE, p,p'-DDD, and o,p'-DDD) were detected the most frequently, ranging from 70.8 to 95.8% detects (Table 3-52). These DDT metabolites, along with o,p'-DDE, were also frequently detected in historical sediment cores from the Duluth-Superior Harbor (Schubauer-Berigan and Crane 1997). DDMU, a breakdown product of DDE, was detected in 66.7% of samples (Table 3-52). The DDT isomers (i.e., p,p'-DDT and o,p'-DDT) were detected less frequently (Table 3-52) due to degradation of these compounds to DDD and DDE metabolites. Sediment quality data on ambient DDT and DDT metabolite concentrations in freshwater, surficial sediments are lacking for much of the world (Ricking and Schwarzbauer 2012). A recent study of DDTs in Polish lake sediments also found p,p'-DDE in nearly all surficial samples (522 samples) followed by p,p'-DDD (502 samples); o,p'-DDT and o,p'-metabolites were not evaluated in this study (Bojakowska et al. 2014).

Endrin, heptachlor epoxide (a metabolite of heptachlor and chlordane), and toxaphene were not detected in any samples, although toxaphene had a high reporting limit exceeding the Level I SQT value. Both endrin and toxaphene were detected in longer sediment cores (0 - 30 cm) from a subset of sediment samples collected in the Duluth-Superior Harbor during 1993 (Schubauer-Berigan and Crane 1997), indicating there was historical use and/or airborne deposition of these pesticides in the St. Louis River watershed. Longer sediment cores from the NLAP lakes could have been used to assess historical inputs of legacy pesticides and metabolites. Aldrin was detected in only one lake (Table 3-52), and it is considered moderately persistent in the environment with a half-life of approximately 0.3 years in soil with 95% disappearance after three years (Freedman 1989). Dieldrin, which is also a common degradate of aldrin, is more persistent, and it was detected in nine lakes (Table 3-52). The half-life of dieldrin in temperate soils is about five years (ATSDR 2002c). The other organochlorine pesticides in Table 3-52 ranged from 29.2 to 87.5% nondetects in surficial sediments.

The number of pesticides and metabolites detected in the sediments of individual NLAP lakes varied from 0 to 19 compounds (Table 3-53). The highest number of pesticides and metabolites (19 or 63.3%) was detected in lake #39 (South; Table 3-53), which was located west of the Twin Cities metropolitan area in an agricultural watershed. Lake #20 (Long-Main Bay) had the next highest detection rate of 60.0% (Table 3-53); this lake is located in northcentral Minnesota, and its watershed is dominated by forests. The two developed lakes, #27 (Nokomis) and #38 (Snail), along with the forested reference lake



Table 3-52. Percentage of Detected and Nondetected Pesticides and Metabolites, Sorted from High to Low Detected Compounds

Pesticide or Metabolite	N	Number Detects	Number NDs	% Detects	% NDs
p,p'-DDE	24	23	1	95.8	4.2
Total DDT	24	23	1	95.8	4.2
p,p'-DDD	24	20	4	83.3	16.7
o,p'-DDD	24	17	7	70.8	29.2
Endosulfan sulfate	24	17	7	70.8	29.2
cis-Nonachlor	24	17	7	70.8	29.2
DDMU	24	16	8	66.7	33.3
Total Hexachlorocyclohexane	24	15	9	62.5	37.5
alpha-Endosulfan	24	14	10	58.3	41.7
beta-Hexachlorocyclohexane	24	14	10	58.3	41.7
trans-Nonachlor	24	13	11	54.2	45.8
Pentachloroanisole	24	12	12	50.0	50.0
o,p'-DDE	24	11	13	45.8	54.2
Mirex	24	11	13	45.8	54.2
gamma-Chlordane	24	9	15	37.5	62.5
p,p'-DDT	24	9	15	37.5	62.5
Dieldrin	24	9	15	37.5	62.5
beta-Endosulfan	24	8	16	33.3	66.7
alpha-Chlordane	24	7	17	29.2	70.8
Heptachlor	24	6	18	25.0	75.0
Hexachlorobenzene	24	6	18	25.0	75.0
Oxychlordane	24	5	19	20.8	79.2
alpha-Hexachlorocyclohexane	24	4	20	16.7	83.3
delta-Hexachlorocyclohexane	24	4	20	16.7	83.3
gamma-Hexachlorocyclohexane	24	3	21	12.5	87.5
o,p'-DDT	24	3	21	12.5	87.5
Aldrin	24	1	23	4.2	95.8
Endrin	24	0	24	0	100
Heptachlor epoxide	24	0	24	0	100
Toxaphene	24	0	24	0	100

N = number of samples; ND = nondetect; DDD = dichlorodiphenyldichloroethane; DDE = dichlorodiphenyl-dichloroethylene; DDT = dichlorodiphenyltrichloroethane; DDMU = 2,2-bis(chlorophenyl)-1-chloroethylene.

#53 (Island), all had 17 pesticides and metabolites detected (Table 3-53). However, there were some differences in the types of compounds detected in these three lakes. For example, beta-HCH and total HCH were detected in lake #38, but not #27; beta-HCH was not detected in #53, but it had total-HCH. Heptachlor and p,p'-DDT were detected in #27, but not #38; heptachlor was also not detected in #53, but it had p,p'-DDT. No pesticides were detected in lake #36 (Red Rock; Table 3-53); this lake tended to have very low concentrations of all contaminants due to its high sand content. The other lakes varied from 20.0 to 53.3% detected pesticides and metabolites (Table 3-53). Besides the two developed lakes

Table 3-53. Percentage of Pesticides and Metabolites (n = 30) Detected in NLAP Lake Sediments (n = 24), Sorted from High to Low Percentage of Detected Compounds

Lake ID #	Lake	Major Land Use	Total # Detects	% Detects
39	South	cul	19	63.3
20	Long (Main Bay)	for	18	60.0
27	Nokomis	dev	17	56.7
38	Snail	dev	17	56.7
53	Island	for	17	56.7
21	Lookout (Crocker)	for	16	53.3
37	Richey	for	15	50.0
50	Woodcock (W. Woodcock)	wet	15	50.0
33	Pelican	wet	13	43.3
41	Spring	cul	13	43.3
14	Fish	cul	12	40.0
32	Pebble	cul	12	40.0
42	Spring	for	12	40.0
45	Upper Hatch	for	12	40.0
52	Hungry Man	for	12	40.0
4	Aspen	for	11	36.7
5	August	for	11	36.7
15	Flat	for	11	36.7
7	Cass	wet	10	33.3
11	Eagle (North)	cul	10	33.3
1	Allen	cul	9	30.0
19	Long	cul	9	30.0
28	North Ash	cul	6	20.0
36	Red Rock	cul	0	0.0

cul = cultivated; dev = developed; for = forested; wet = lakes and wetlands.

that were clustered together, other major land use classifications and geography did not appear to correspond to the percentage of pesticides and metabolites observed in the other lakes. A larger sample size would be useful for examining these types of relationships in future sediment assessment projects.

For the 22 pesticides and metabolites with <80% nondetects, mean and SD values were estimated using the Kaplan-Meier method (Table 3-54). Total DDT had the highest mean concentration of 25.0 µg/kg dry wt. (Table 3-54). Total DDT ranged from <0.15 µg/kg dry wt. in lake #36 (Red Rock) to 226 µg/kg dry wt. in lake #38 (Snail). The DDT metabolites of p,p'-DDE, p,p'-DDD, and o,p'-DDD had the next highest mean concentrations, respectively, followed by DDMU (Table 3-54). For the other pesticides in Table 3-54, mean concentrations ranged from 0.079 – 0.67 µg/kg dry wt. Hexachlorobenzene had the lowest mean concentration, followed by dieldrin. The mean value of pentachloroanisole in the NLAP lake sediments (Table 3-54) was on the same order of magnitude as concentrations measured in surficial (0 - 1 cm) sediments from seven lakes in the Yukon Territory and northern British Columbia, Canada (Rawn et al. 2001). Other summary statistics, percentiles, box plots, and Q-Q plots with significant outliers noted are provided in Appendix J.

Table 3-54. Mean and Standard Deviation of Pesticide and Metabolite Data with <80% Nondetects, Sorted from High to Low Mean Concentrations

Pesticide or Metabolite	% NDs	KM Mean (µg/kg dry wt.)	KM SD (µg/kg dry wt.)
Total DDT	4.2	25.0	53.7
p,p'-DDE	4.2	12.5	24.8
p,p'-DDD	16.7	8.0	20.6
o,p'-DDD	29.2	2.2	5.8
DDMU	33.3	1.7	4.1
alpha-Endosulfan	41.7	0.67	1.7
gamma-Chlordane	62.5	0.38	0.91
p,p'-DDT	62.5	0.38	0.47
Total Hexachlorocyclohexane	37.5	0.38	0.38
alpha-Chlordane	70.8	0.36	0.63
o,p'-DDE	54.2	0.36	0.84
trans-Nonachlor	45.8	0.31	0.42
beta-Endosulfan	66.7	0.27	0.62
Endosulfan sulfate	29.2	0.27	0.25
Mirex	54.2	0.24	0.39
cis-Nonachlor	29.2	0.24	0.30
Pentachloroanisole	50.0	0.24	0.25
beta-Hexachlorocyclohexane	41.7	0.16	0.13
Heptachlor	75.0	0.12	0.21
Oxychlordane	79.2	0.12	0.17
Dieldrin	62.5	0.10	0.083
Hexachlorobenzene	75.0	0.079	0.049

ND = nondetect; KM = Kaplan-Meier; SD = standard deviation; DDD = dichlorodiphenyldichloroethane; DDE = dichlorodiphenyldichloroethylene; DDT = dichlorodiphenyltrichloroethane; DDMU = 2,2-bis(chlorophenyl)-1-chloroethylene.

Although pesticides and metabolites were only measured in a subset of the NLAP lakes, this limited data set was used to assess if any compounds with <5% nondetects differed by land use groups. Both Total DDT and p,p'-DDE fit this criterion with one nondetect value for Red Rock (#36), which was substituted at the reporting limit. A one-way ANOVA was run on the natural log transformed data for Total DDT, and the results were statistically significant ( $p < 0.05$ , Table 3-55). Transformations did not help normalize the p,p'-DDE data so a Kruskal-Wallis one-way ANOVA on ranks was conducted; this result was statistically significant ( $p < 0.05$ ), too (Table 3-55). Multiple pairwise tests showed that significant differences in mean concentrations were observed for Total DDT between lakes in developed watersheds and those in either cultivated or forested watersheds (Table 3-56). The median values of p,p'-DDE were significantly different ( $p < 0.05$ ) between lakes in developed versus cultivated watersheds (Table 3-56). For both compounds, higher concentrations were observed in the developed lakes.

DDT and its metabolite isomer ratios can be used to assess the environmental fate of these compounds (Ricking and Schwarzbauer 2012). While p,p'-DDE was detected in all but one lake (#36), p,p'-DDD was also commonly detected in all but four lakes (Table 3-52). Concentrations of p,p'-DDE were usually

Table 3-55. Statistical Comparisons of p,p'-DDE and Total DDT by Land Use Categories (n = 24 samples)

Parameter	Transformation of Data	p-value	
		One-Way ANOVA	Kruskal-Wallis One-Way ANOVA on Ranks
p,p'-DDE	none <sup>1</sup>		0.028*
Total DDT	natural log	0.002*	

DDE = dichlorodipenyldichloroethylene; DDT = dichlorodiphenyltrichloroethane; ANOVA = analysis of variance.

<sup>1</sup> Both the natural log and square root transformations did not pass the Shapiro-Wilk normality test so that a one-way ANOVA could be run.

\* Statistically significant (p<0.05).

Table 3-56. Multiple Pairwise Comparisons of p,p'-DDE and Total DDT by Land Use Categories. Pairs Shaded "Yes" are Significantly Different (p<0.05) from Each Other.

Parameter	p<0.05					
	dev vs. cul	dev vs. for	dev vs. wet	wet vs. cul	wet vs. for	for vs. cul
p,p'-DDE <sup>§</sup>	Yes	No	DNT	No	DNT	DNT
Total DDT <sup>‡</sup>	Yes	Yes	No	No	No	No

DDE = dichlorodipenyldichloroethylene; DDT = dichlorodiphenyltrichloroethane; dev = developed; cul= cultivated; for = forested; wet = lakes and wetlands; DNT = do not test.

<sup>1</sup> Based on the natural log transformation of the censored (i.e., one nondetect) and detected data.

<sup>§</sup> Dunn's method was used for these pairwise multiple comparisons.

<sup>‡</sup> The Holm-Sidak method was used for these pairwise multiple comparisons.

higher than p,p'-DDD for the same lake so most of the p,p'-DDD/p,p'-DDE ratios were below 1.0 (Table 3-57). There was probably a mix of aerobic and anaerobic conditions responsible for the distribution of these isomers in this subset of NLAP lake sediments, especially if the main source was from atmospheric deposition. The o,p'/p,p' ratios for detectable compounds of DDT, DDE, and DDD are provided in Table 3-57. For this small sample set, the p,p'-isomers of DDT and DDE exceeded the corresponding o,p'-isomer. The greatest range of o,p'/p,p' ratios was observed for DDD (0.098 – 4.8; Table 3-57), where the concentrations of o,p'-DDD exceeded those of p,p'-DDD for three lakes (#21, 39, and 50) and was equivalent for one lake (#20). These lakes may have had more anaerobic decomposition of p,p'-DDD than some of the other lakes based on ancillary information provided in Ricking and Schwarzbauer (2012).

If soil runoff was a major source for DDT and its metabolites, then these compounds would be expected to be associated with particle size and/or TOC. However, concentrations of Total DDT and p,p'-DDE were not significantly correlated to either the percentages of clay, sand, silt, or TOC (i.e., Spearman rho values >0.05; Table 3-58). The other DDT metabolites were not included in this analysis because of a higher percentage of nondetect values. Brown (1998) found that Total DDT was positively correlated to percent silt, but not TOC in surficial stream bed sediments from the Lower San Joaquin River, CA, which is a major agricultural area. Most of the nonurban NLAP sediment samples had low concentrations of Total DDT, which may be more indicative of ambient background from atmospheric deposition of DDT-related compounds, rather than inputs from eroded soil from the lake watersheds.

Table 3-57. Summary of Detectable DDT, DDE, and DDD Isomer Ratios

Lake ID	Lake	o,p'/p,p' Ratios			p,p'-DDD/p,p'-DDE Ratios
		DDT	DDE	DDD	
1	Allen				0.38
4	Aspen			0.65	0.61
5	August		0.020		0.85
7	Cass			0.098	0.92
14	Fish				0.20
19	Long			0.67	0.65
20	Long (Main Bay)	0.069		1.0	0.51
21	Lookout (Crocker)		0.054	1.8	0.20
27	Nokomis		0.039	0.24	0.43
32	Pebble		0.0096	0.24	0.21
33	Pelican		0.036	0.14	1.2
37	Richey				0.42
38	Snail		0.029	0.29	1.2
39	South		0.11	4.8	0.13
41	Spring			0.45	0.46
42	Spring	0.22	0.021	0.65	0.31
45	Upper Hatch			0.27	0.47
50	Woodcock (W. Woodcock)		0.043	3.3	0.089
52	Hungry Man		0.032		0.14
53	Island		0.023	0.15	1.0
Range		0.069 - 0.22	0.0096 - 0.11	0.098 - 4.8	0.089 - 1.2

DDD = dichlorodiphenyldichloroethane; DDE = dichlorodiphenyldichloroethylene; DDT = dichlorodiphenyltrichloroethane.

Table 3-58. Spearman Rank Order Correlation for Particle Size, TOC, p,p'-DDE, and Total DDT (n = 24 samples)

Parameter	Clay (%)	Silt (%)	Sand (%)	TOC (%)	p,p'-DDE
Silt (%)	-0.0139				
Sand (%)	<b>-0.451</b>	<b>-0.84</b>			
TOC (%)	0.190	<b>-0.437</b>	0.362		
p,p'-DDE	0.155	0.154	-0.143	0.0687	
Total DDT	0.221	0.150	-0.173	0.0722	<b>0.980</b>

TOC = total organic carbon; DDE = dichlorodiphenyldichloroethylene; DDT = dichlorodiphenyltrichloroethane.

Spearman Rho Values:

Black font: not statistically significant,  $p > 0.05$

Blue, bold, italic font: statistically significant,  $p < 0.05$  and  $> 0.001$

Orange, bold font: highly statistically significant,  $p < 0.001$

## Comparisons to SQT values

The NLAP pesticide and metabolite data were compared to available SQT values (Table 3-59). Except for Total DDTs, the majority of compounds were below the corresponding Level I SQT values. Total DDT had the highest percentage of samples (58.3%) between the Level I and Level II SQT values (Table 3-59,

Table 3-59. Comparison of Statewide Pesticide and Metabolite Data to the MPCA's Level I and Level II SQT Values

Pesticide or Metabolite	Percent of Samples (n = 24)		
	≤ Level I SQT	> Level I to ≤ Level II SQT	> Level II SQT
Chlordane*	91.7	8.3	0
Dieldrin	100	0	0
Sum DDD	75	16.7	8.3
Sum DDE	50	37.5	12.5
Sum DDT	100	0	0
Total DDT (measured)**	41.7	58.3	0
Endrin	100	0	0
Heptachlor Epoxide	100	0	0
gamma-Hexachloro-cyclohexane (Lindane)	100	0	0
Toxaphene†	100		0

SQT = sediment quality target; DDD = dichlorodiphenyldichloroethane; DDE = dichlorodiphenyldichloro-ethylene; DDT = dichlorodiphenyltrichloroethane.

\* Chlordane = cis-Nonachlor + trans-Nonachlor + alpha-Chlordane + gamma-Chlordane.

\*\* When Total DDT was calculated as Sum DDD + Sum DDE + Sum DDT, it yielded 45.8% of samples ≤ Level I SQT and 54.2% of samples > Level I to ≤ Level II SQT.

† The reporting limits for toxaphene exceeded the Level I SQT value of 0.1 µg/kg dry wt., but were less than the Level II SQT value of 32 µg/kg dry wt. Values can only be expressed as < Level II SQT.

Figure 3-43). Total DDTs are still a ubiquitous group of contaminants across the state. The developed lakes (#27 and 38) exceeded the Level II SQT values for Sum DDD and Sum DDE, as did lake #32 (Pebble) for Sum DDE. The surficial sediments in these lakes would be more likely to display harmful effects to sediment-dwelling organisms (Crane and Hennes 2007). Resuspension of these contaminated sediments could also impact downstream waters. Since these sediments encompassed the upper 15 cm, sampling of the upper 2 or 5 cm would provide a better estimate of current conditions to address whether these pesticides still exceeded the corresponding Level II SQT values. Unrelated to these data, the MPCA has recently included Total DDT on their second tier of priorities for updating human health-based water quality standards (Angela Preimesberger, MPCA, personal communication, 2/29/2016). Chlordane was the only other pesticide with values between the Level I and Level II SQTs, which occurred for the two developed lakes (#27 and 38; Table 3-59, Figure 3-44).

## UTL values

UTL values were calculated for pesticides and metabolites that had <80% nondetects after removing potential outliers (Table 3-60). Some UTL values exceeded the corresponding Level I SQT values. This included the sum of chlordane values, Total DDT, sum DDD isomers, and sum DDE isomers. The MPCA is lacking SQT values for several pesticides (e.g., heptachlor, mirex) so the UTL values are a useful benchmark to assess exceedances of ambient background concentrations.

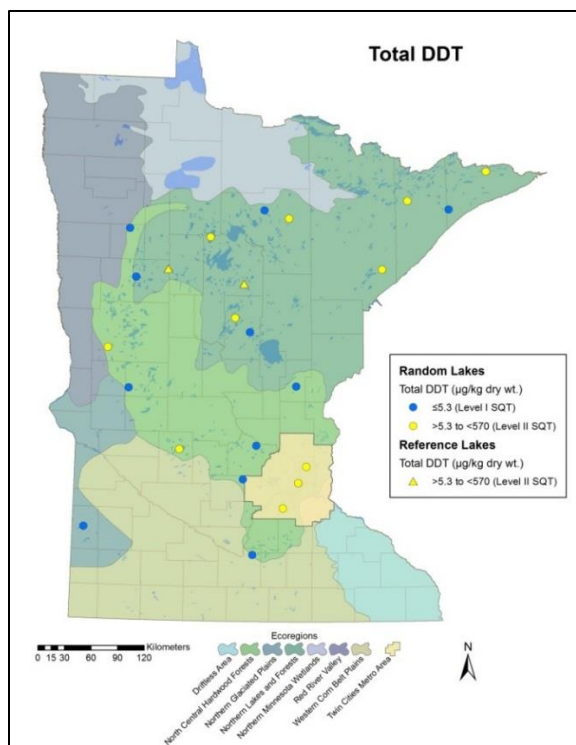


Figure 3-43. Comparison of measured Total DDT concentrations to the MPCA’s Level I and Level II SQT values.

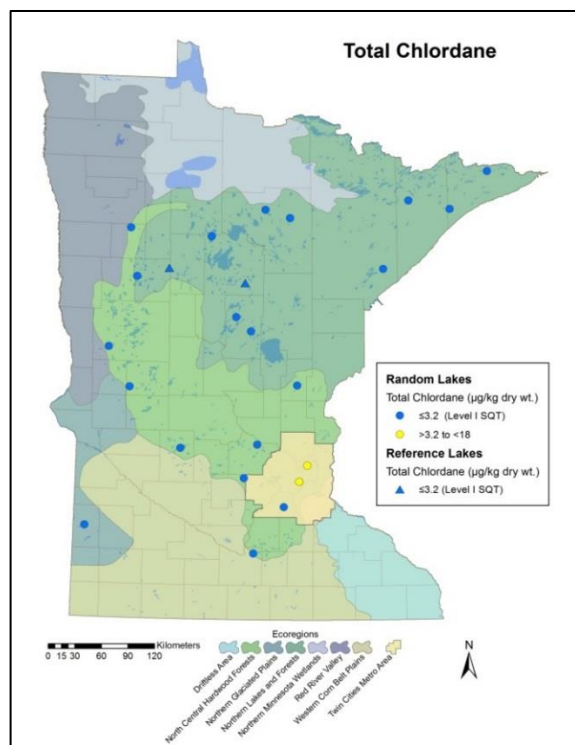


Figure 3-44. Comparison of chlordane concentrations to the MPCA’s Level I and Level II SQT values.

Table 3-60. UTLs of Detected and Censored Pesticide and Metabolite Data with Outliers Removed at the 5% Significance Level (UTL units in µg/kg dry wt.)

Pesticide or Metabolite	N (# detects after removing outliers)	% Nondetects	Potential Outliers Removed at 5% Significance Levels (lake ID numbers)	Normal Distribution and KM Estimates* 95% UTL with 95% Coverage	Gamma Distribution and KM Estimates*	
					95% Approx. Gamma UTL with 95% Coverage	
					WH	HW
alpha-Chlordane	24 (7)	70.8	-	1.8		
gamma-Chlordane	23 (8)	65.2	38		0.89	0.90
o,p'-DDD	22 (15)	31.8	27 <sup>†</sup> , 38	2.1		
o,p'-DDE	22 (9)	59.1	27, 38 <sup>†</sup>		0.36	0.36
p,p'-DDD	22 (18)	18.2	27 <sup>†</sup> , 38		13.9	15.9
p,p'-DDE	21 (20)	4.8	27, 32 <sup>†</sup> , 38 <sup>†</sup>	10.7		
p,p'-DDT	24 (9)	62.5	-	1.5		
Total DDT	21 (20)	4.8	27 <sup>†</sup> , 32 <sup>†</sup> , 38		30.8	35.0
DDMU	21 (13)	38.1	27 <sup>†</sup> , 32 <sup>†</sup> , 38	1.0		
Dieldrin	24 (9)	62.5	-	0.29		
alpha-Endosulfan	22 (12)	45.4	27 <sup>†</sup> , 41		0.97	1.0
beta-Endosulfan	23 (7)	69.6	27	0.73		
Endosulfan Sulfate	24 (17)	29.2	-		1.1	1.2
Heptachlor	23 (5)	78.3	39	0.29		
Hexachlorobenzene	24 (6)	75	-	0.19		
beta-Hexachlorocyclohexane	24 (14)	41.7	-	0.47		
Total Hexachlorocyclohexane	24 (15)	37.5	-	1.3		
Mirex	24 (11)	54.2	-		1.1	1.1
trans-Nonachlor	23 (12)	47.8	38	0.70		
cis-Nonachlor	22 (15)	31.8	27 <sup>†</sup> , 38	0.46		
Pentachloroanisole	24 (12)	50	-	0.81		

UTL = Upper Tolerance Limit; KM = Kaplan-Meier; WH = Wilson Hilferty; HW = Hawkins Wixley; DDD = dichlorodiphenyldichloroethane; DDE = dichlorodiphenyldichloroethylene; DDT = dichlorodiphenyltrichloroethane; DDMU = 2,2-bis(chlorophenyl)-1-chloroethylene.

\* UTLs for normally distributed data were preferred over those derived from gamma distributed data. When the data were not normally distributed, the gamma distribution was used to estimate UTL values. Gamma UTLs were calculated two different ways for which professional judgment can be used to select the value of interest.

† Potential outlier was based on professional judgment; all other outliers were based on statistical tests at the 5% significance level.



## PCDD/Fs

### *Highlights:*

- PCDD/F congeners and homolog groups were frequently detected at low concentrations throughout Minnesota.
- The highest  $\Sigma$ PCDD/F congener concentrations were observed in sediments from the developed lakes #27 (Nokomis) and #38 (Snail), while the lowest concentration was found in lake #36 (Red Rock).
- PCDD/F congeners and homologs were either significantly ( $p < 0.05$  and  $> 0.001$ ) or highly significantly ( $p < 0.001$ ) correlated with each other, except for PCD\_T4 (the four homolog series of PCDDs).
- Other sources, such as triclosan and chlorinated triclosan derivatives, may be contributing to PCD\_T4, but this requires further investigation.
- Most aquatic life PCDD/F TEQ values were between the Level I and Level II SQT values, which would not trigger further action.
- A general environmental forensic analysis of the data was conducted.
  - Ubiquitous combustion sources, like wood burning and automobile emissions, appear to be important.
  - In addition, burning of household garbage is likely another important source.
  - Land application of sewage sludge, with subsequent runoff into lakes, or WWTP effluent discharges could contribute PCDD/F congeners, too.
- UTLs were calculated for PCDD/F congeners, homolog groups, and  $\Sigma$ PCDD/F congeners, as well as for human health and aquatic life TEQs.

## Background

PCDD/Fs are a group of ubiquitous contaminants, which are found throughout the world at low concentrations. These compounds always occur in the environment as a mixture of PCDD/F congeners, for which there are 75 PCDD and 135 PCDF congeners (CCME 2001). These compounds are formed as an unintended by-product of human-based activities (e.g., industrial processing, combustion on a small and large scale, vehicle exhaust), as well as through natural events (e.g., forest fires; UNEP 1999; Hites 2011; USEPA 2013b; Augusto et al. 2016). Thus, PCDD/Fs are not produced for any commercial purposes and have no known use. PCDD/Fs are hydrophobic, persistent in the environment, lipophilic, bioaccumulative, and potentially toxic (Alcock and Jones 1996; ATSDR 2012). The 17 PCDD/F congeners that have chlorine atoms attached in at least the 2, 3, 7, and 8 lateral positions are the most toxic, best studied, and have a common mode of toxic action (CCME 2001). PCDD/Fs are classified as B2 probable human carcinogens (USEPA 1997), and 2,3,7,8-TCDD is the most potent animal carcinogen evaluated by the U.S. EPA (ATSDR 2012). In mammals, most of the toxic and biological effects of these compounds are mediated through the aryl hydrocarbon receptor (AhR; several references as cited in Van den Berg et al. 2006). PCDD/Fs were included in the original 12 POPs under the Stockholm Convention (<http://chm.pops.int/TheConvention/ThePOPs/The12InitialPOPs/tabid/296/Default.aspx>, accessed 2/4/2016).

The transport and fate of PCDD/Fs in the environment is similar to other hydrophobic organic contaminants, like PCBs, except that PCDD/Fs are more recalcitrant (i.e., resistant to degradation). These compounds have long atmospheric residence times and can undergo long-range atmospheric transport to remote areas like the Arctic (Lohmann and Jones 1998). As such, national and regional emission inventories of PCDD/Fs are important for tracking atmospheric releases of these compounds over time and developing strategies to reduce emissions. In the U.S., the efforts of the U.S. EPA and other stakeholders (e.g., industries, state governments) have resulted in a 75% reduction in quantifiable total dioxin emissions from 1987 levels (USEPA 2013b). In addition, emissions to air have been reduced by about 85% from 1987 levels in the U.S. (USEPA 2013b). Emission controls over the past two decades have also been successful in Europe as reflected in sharp downward trends in PCDD/F concentrations in sediment cores collected from the Rhone River basin, France (Van Metre et al. 2015). Atmospheric deposition and surface runoff of PCDD/Fs into waterways continues the environmental cycling of these compounds. These compounds preferentially sorb to organic matter on particles, which may settle to the bottom sediments or be consumed by fish and other aquatic organisms. PCDD/Fs are chemically stable in sediment and may accumulate and persist for a long period of time, resulting in long-term sources of these congeners to aquatic organisms (CCME 2001).

## Summary statistics

Of the 17 most toxic PCDD/F congeners analyzed in 23 NLAP lake sediments, some combination of congeners was found in every lake. The detection frequency of PCDD/F congeners (Table 3-61) was much higher than for PCB congeners (Table 3-41) or legacy organochlorine pesticides (Table 3-52). This was probably due to lower reporting limits for PCDD/F congeners, the recalcitrant physical/chemical properties of these congeners, and ongoing emissions of these compounds into the global airshed. The upper 15 cm depth interval of the sediment samples may reflect a greater time period than when national emissions of PCDD/Fs started to decrease. A shorter depth interval (e.g., 0 – 2 cm) would be more reflective of recent deposition of PCDD/Fs. Nine congeners and homolog groups of PCDD/Fs were detected in all lake sediment samples (Table 3-61). Most other congeners or homologs had only one or two nondetects [usually for Red Rock (#36)]. The most toxic compound, 2,3,7,8-TCDD (PCD2378), was not detected in 39% of lakes (Table 3-61). The highest percentage of nondetects (82.6%) occurred for 1,2,3,7,8,9-hexachlorodibenzofuran (PCF123789; Table 3-61). Table 3-61 provides the abbreviations for individual PCDD/F congeners and homolog groups, which will be referred to in the rest of this report.

Summary statistics for PCDD/F congeners and homologs with <80% censored values, as well as for  $\Sigma$ PCDD/F congeners are provided in Table 3-62. OCDD had the highest mean (SD) congener concentration of  $316.5 \pm 447.5$  ng/kg dry wt., while PCD2378 had the lowest congener concentration (SD) of  $0.39 \pm 0.72$  ng/kg dry wt. (Table 3-62). However, the low concentrations of PCD2378 should not be discounted since this congener is highly toxic. The TEF value for PCD2378 is 1.0, whereas the TEF for OCDD is 0.0001 (Appendix K). Multiplying the respective concentrations by their TEF value gives a lower TEQ for OCDD (i.e., 0.032) than PCD2378 (i.e., 0.39). Other summary statistics, percentiles, box plots, and Q-Q plots with significant outliers noted are provided in Appendix K.

A summary of the  $\Sigma$ PCDD/F congener concentrations for each lake is provided in Table 3-63. The highest total concentrations were observed in the developed lakes [#27 (Nokomis) and 38 (Snail)], while the lowest total concentration was found in lake #36 (Red Rock; Table 3-63). As observed in the Q-Q plot for  $\Sigma$ PCDD/F congeners (Appendix K), lake #27 was an outlier at the 5% significance level. In addition, lake #38 was an outlier based on professional judgment of the Q-Q plot. The mean  $\Sigma$ PCDD/F concentrations in the developed lakes ( $n = 2$ ) were statistically higher ( $p < 0.001$ ) than the mean  $\Sigma$ PCDD/F concentrations in the other lakes ( $n = 21$ ; Table 3-64). Other statistical comparisons by broader land use groups were not performed due to the smaller number of NLAP lakes targeted for PCDD/F analyses. For individual

Table 3-61. Percentage of Nondetects for PCDD/F Congeners and Homolog Groups, Sorted from Low to High Nondetects

Abbreviation	Parameter	N	Number Detects	Number NDs	% NDs
OCDD	1,2,3,4,6,7,8,9-Octachlorodibenzo- <i>p</i> -dioxin	23	23	0	0
PCD_T4	Dioxins, 4TCDD, total	23	23	0	0
PCD_T5	Dioxins, 5PeCDD, total	23	23	0	0
PCD_T6	Dioxins, 6HxCDD, total	23	23	0	0
PCD_T7	Dioxins, 7HpCDD, total	23	23	0	0
PCD123789	1,2,3,7,8,9-Hexachlorodibenzo- <i>p</i> -dioxin	23	23	0	0
PCD1234678	1,2,3,4,6,7,8-Heptachlorodibenzo- <i>p</i> -dioxin	23	23	0	0
PCF_T6	Furans, 6HxCDF, total	23	23	0	0
PCF1234678	1,2,3,4,6,7,8-Heptachlorodibenzofuran	23	23	0	0
PCD12378	1,2,3,7,8-Pentachlorodibenzo- <i>p</i> -dioxin	23	22	1	4.4
PCD123478	1,2,3,4,7,8-Hexachlorodibenzo- <i>p</i> -dioxin	23	22	1	4.4
PCD123678	1,2,3,6,7,8-Hexachlorodibenzo- <i>p</i> -dioxin	23	22	1	4.4
OCDF	1,2,3,4,6,7,8,9-Octachlorodibenzofuran	23	22	1	4.4
PCF_T4	Furans, 4TCDF, total	23	22	1	4.4
PCF_T5	Furans, 5PeCDF, total	23	22	1	4.4
PCF_T7	Furans, 7HpCDF, total	23	22	1	4.4
PCF12378	1,2,3,7,8-Pentachlorodibenzofuran	23	22	1	4.4
PCF23478	2,3,4,7,8-Pentachlorodibenzofuran	23	22	1	4.4
PCF123478	1,2,3,4,7,8-Hexachlorodibenzofuran	23	22	1	4.4
PCF123678	1,2,3,6,7,8-Hexachlorodibenzofuran	23	22	1	4.4
PCF234678	2,3,4,6,7,8-Hexachlorodibenzofuran	23	22	1	4.4
PCF2378	2,3,7,8-Tetrachlorodibenzofuran	23	21	2	8.7
PCF1234789	1,2,3,4,7,8,9-Heptachlorodibenzofuran	23	21	2	8.7
PCD2378	2,3,7,8-Tetrachlorodibenzo- <i>p</i> -dioxin	23	14	9	39.1
PCF123789	1,2,3,7,8,9-Hexachlorodibenzofuran	23	4	19	82.6

PCDD/F = polychlorinated dibenzo-*p*-dioxin/dibenzofuran; N = number of samples; ND = nondetect.

PCDD/F congeners and homolog groups with <5% nondetects (except PCD\_T4), the mean concentrations in the developed lakes were statistically greater ( $p < 0.05$ ) than the other lakes (Table 3-64). Only PCD\_T4 did not show statistically significant differences ( $p > 0.05$ ) between the median of the two developed lakes and the rest of the 21 lakes (Table 3-64).

Summary statistics for human health and aquatic life TEQs are provided in Table 3-65. The human health TEQs (HH\_TEQ) calculated using substitution of one-half the reporting limit overestimated the mean TEQs calculated using the Kaplan-Meier method (Table 3-65). Differences in the calculation method were less pronounced for the aquatic life TEQs (Table 3-65). The highest TEQ value, based on human health, was found in Snail Lake (#38) in the Twin Cities. It was the only TEQ value to exceed the MPCA's Tier 1 Soil Reference Value (SRV) for residential areas. That is, any sediment dredged from this lake could not be applied on residential land. Other summary statistics, percentiles, box plots, and Q-Q plots with significant outliers noted for the TEQs are provided in Appendix K.

Table 3-62. Mean and Standard Deviation of PCDD/F Congener and Homolog Data with <80% Censored Values, as well as  $\Sigma$ PCDD/F Congeners

Parameter	% NDs	Mean (ng/kg dry wt.)	SD (ng/kg dry wt.)
<b>Detected Data</b>			
OCDD	0	316.5	447.5
PCD_T4	0	9.0	11.8
PCD_T5	0	10.3	9.4
PCD_T6	0	32.2	28.5
PCD_T7	0	108.3	133.7
PCD1234678	0	51.3	60.8
PCD123789	0	3.6	3.0
PCF_T6	0	22.6	31.7
PCF1234678	0	11.6	15.3
$\Sigma$ PCDD/F Congeners	0	427.6	587.5
<b>Detected &amp; Censored Data*</b>			
OCDF	4.4	26.4	41.9
PCD123478	4.4	1.1	0.99
PCD123678	4.4	3.2	3.0
PCD12378	4.4	0.99	0.91
PCD2378	39.1	0.39	0.72
PCF_T4	4.4	33.1	39.9
PCF_T5	4.4	32.6	54.7
PCF_T7	4.4	25.0	39.7
PCF123478	4.4	2.2	1.9
PCF1234789	8.7	0.70	0.82
PCF123678	4.4	1.6	1.9
PCF12378	4.4	1.2	1.1
PCF234678	4.4	2.3	3.2
PCF23478	4.4	1.5	1.8
PCF2378	8.7	2.9	4.3

ND = nondetect; SD = standard deviation; see Table 3-61 for PCDD/F abbreviations.

\* The Kaplan-Meier method was used to estimate mean and standard deviation values for parameters with <80% censored data.

The relationship between particle size, TOC, and individual PCDD/F congeners and homologs with <5% nondetects, as well as  $\Sigma$ PCDD/F congeners was examined. The nondetect values were substituted with the reporting limits. Since the PCDD/F congeners, homologs, and  $\Sigma$ PCDD/F congener data failed normality, a Spearman rank order correlation was conducted (Table 3-66 and Appendix K). PCD\_T4 was significantly, positively correlated ( $p < 0.050$  and  $> 0.01$ ) with clay and silt and highly significantly negatively correlated ( $p < 0.001$ ) with sand (Table 3-66). No other PCDD/F congeners or homologs were significantly correlated ( $p > 0.05$ ) with particle size parameters. PCD\_T4 was also significantly negatively correlated ( $p < 0.050$  and  $> 0.001$ ) with TOC, whereas four other PCDD and five PCDF congeners were significantly positively correlated ( $p < 0.050$  and  $> 0.001$ ) with TOC (Table 3-66). The  $\Sigma$ PCDD/F congener concentrations were not significantly correlated ( $p > 0.05$ ) to either particle size parameters or TOC.

Table 3-63. Concentrations of  $\Sigma$ PCDD/F Congeners in Lake Sediment Samples

Lake ID	Lake	$\Sigma$ PCDD/F Congeners (ng/kg dry wt.)
1*	Allen	37.1
4*	Aspen	176
5*	August	93.2
7*	Cass	330
11*	Eagle (North)	137
14†	Fish	285
15*	Flat	41.8
20†	Long (Main Bay)	286
21*	Lookout (Crocker)	211
27†	Nokomis	2504
28*	North Ash	100
32*	Pebble	370
33*	Pelican	470
36*	Red Rock	4.6
37*	Richey	250
38*	Snail	1887
39*	South	175
41*	Spring	363
42*	Spring	651
45*	Upper Hatch	220
50*	Woodcock (W. Woodcock)	493
52†	Hungry Man	392
53*	Island	357

PCDD/F = polychlorinated dibenzo-*p*-dioxin/dibenzofuran.

\*Total calculated by multiplying the Kaplan-Meier mean by 17 (i.e., the number of PCDD/F congeners).

†Sum total of all detected PCDD/F congeners.

Similarly,  $\Sigma$ PCDD/F concentrations in flood-plain soil and sediment from the Tittabawassee River, MI were also not significantly correlated ( $p > 0.05$ ) with TOC in flood-plain soils and sediment, respectively (Hilscherova et al. 2003).  $\Sigma$ PCDD/F concentrations also did not correlate well with TOC in surficial sediment from the Willamette Basin, OR (Bonn 1998). PCD\_T4 was not significantly correlated ( $p > 0.05$ ) with any other PCDD/F congeners and homologs (Appendix K). This result seemed unusual since all the other PCDD/F congeners and homologs were either significantly ( $p < 0.05$  and  $> 0.001$ ) or highly significantly ( $p < 0.001$ ) correlated with each other (Appendix K). The data were double-checked against the laboratory results and were verified as matching the results. No other major QA/QC issues were brought up with these data to explain the differences in the distribution of PCD\_T4.

The lack of significant correlations between PCD\_T4 and the other PCDD/F congeners and homologs may be indicative of another source of congeners in this homolog series. One possible explanation may be dioxin photoproducts formed from triclosan and chlorinated triclosan derivatives, especially in any lakes that received WWTP discharges. Triclosan, an antimicrobial product added to numerous personal care and medical products during the past 50 years (Buth et al. 2010), is ultimately washed down the drain and released to WWTPs. It can photodegrade to 2,8-DCDD (Buth et al. 2010). Not all triclosan is

Table 3-64. Pairwise Statistical Comparisons Between Developed Lakes (n = 2) and the Other Lakes (n = 21)

Parameter	Transformation of Data	t-test (21 df)		Mann-Whitney Rank Sum Test	
		t statistic	one-tailed p-value	U statistic	p-value
PCD_T4	none <sup>1</sup>			5.00	0.091
PCD_T5	not needed	-8.2	<0.001*		
PCD_T6	not needed	-8.9	<0.001*		
PCD_T7	not needed	-12.4	<0.001*		
OCDD	square root	-7.4	<0.001*		
PCD12378	not needed	-7.2	<0.001*		
PCD123478	natural log	-2.8	0.0055*		
PCD123678	not needed	-8.9	<0.001*		
PCD123789	not needed	-6.8	<0.001*		
PCD1234678	not needed	-11.6	<0.001*		
PCF_T4	not needed	-16.2	<0.001*		
PCF_T5	square root	-7.8	<0.001*		
PCF_T6	square root	-7.1	<0.001*		
PCF_T7	square root	-8.7	<0.001*		
OCDF	not needed	-18.0	<0.001*		
PCF12378	not needed	-12.0	<0.001*		
PCF23478	not needed	-12.1	<0.001*		
PCF123478	not needed	-8.1	<0.001*		
PCF123678	square root	-6.3	<0.001*		
PCF234678	square root	-6.6	<0.001*		
PCF1234678	square root	-7.4	<0.001*		
∑PCDD/F Congeners	square root	-7.4	<0.001*		

df = degrees of freedom; PCDD/F = polychlorinated dibenzo-*p*-dioxin/dibenzofuran; see Table 3-61 for other PCDD/F abbreviations.

<sup>1</sup> Since the natural log and square root transformations also failed the Shapiro-Wilk normality test, a t-test could not be run.

\* Statistically significant (p<0.05).

removed during the WWTP process, and some chlorinated derivatives (CTDs) can form during wastewater chlorine disinfection. Photolysis of these compounds can form PCDDs, including 1,2,8-TricDD, 2,3,7-TricDD, and 1,2,3,8-TCDD (Buth et al. 2010). None of these triclosan or CTD-related PCDD congeners were analyzed in the NLAP lake sediments. Anger et al. (2013) collected sediment cores from wastewater-impacted Minnesota lakes, and they determined that triclosan and CTDs were the dominant source of the aforementioned (i.e., four) PCDD congeners after triclosan became available in 1965. They also collected sediment from a northern Minnesota reference lake with no wastewater input; low concentrations of the same four PCDD congeners were found in this lake, most likely due to atmospheric deposition (Anger et al. 2013). The potential contribution of 1,2,3,8-TCDD to the mass of PCD\_T4 observed in the NLAP lakes could contribute to the lack of significant correlations observed with other PCDD/F congeners and homologs. This is an issue that could be looked at further with these unique PCDD congeners to determine if any of the NLAP lakes were downstream of effluent discharges from WWTPs. Lakes in the BWCAW would be indicative of lakes receiving atmospheric deposition of PCDD/Fs. Other possible sources of PCD\_T4 could be investigated, as well.

Table 3-65. Summary Statistics for Human Health and Aquatic Life TEQs

Parameter	N	Minimum (ng TEQ/kg dry wt.)	Maximum (ng TEQ/kg dry wt.)	Mean (ng TEQ/kg dry wt.)	SD (ng TEQ/kg dry wt.)	Skewness	Kurtosis
<b>Human Health TEQ</b>							
HH_TEQ	23	3.8	24.5	9.3	5.1	1.8	3.3
HH_TEQ_KMDF	23	0.025	19.6	4.3	4.8	2.5	6.4
HH_TEQ_KMDFP	23	0.027	20.5	4.4	4.9	2.6	6.6
<b>Aquatic Life TEQ</b>							
W_TEQ	23	0.24	17.2	4.0	4.2	2.5	6.1
W_TEQ_KMDF	23	0.0038	17.0	3.8	4.1	2.5	6.2
W_TEQ_KMDFP	23	0.0038	17.1	3.8	4.2	2.5	6.2

TEQ = toxic equivalent; N = number of samples; SD = standard deviation; HH = human health; KMDF = Kaplan-Meier calculation of TEQs using polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/Fs); KMDFP = Kaplan-Meier calculation of TEQs using PCDD/Fs and coplanar polychlorinated biphenyls (PCBs); W = aquatic life.

## Comparisons to SQT values

The PCDD/F TEQ values for aquatic life were compared to the MPCA's Level I and II SQT values. Most TEQ values were between the Level I and Level II SQT values, which would not trigger further action (Table 3-67). No TEQ values exceeded the Level II SQT value. Three lakes, located in western Minnesota, were below the Level I SQT value (Figure 3-45). The comparisons to the Level I and II SQT values were the same, regardless of whether TEQs were calculated by substitution for nondetects or by Kaplan-Meier. It also made no difference whether coplanar PCBs were included in the TEQ calculations. These values were based on Van den Berg et al.'s (1998) TEF values for fish since there is insufficient information to determine TEFs for aquatic invertebrates. If such TEFs become available in the future for benthic invertebrates, then the SQT values will be reassessed.

The MPCA's human health SQT value of PCDD/F TEQs has changed over time. In 2000, the MPCA adopted a human health SQT value of 10 µg/kg OC for PCDD/F TEQs (Crane et al. 2000). This value was adopted from the New York State Department of Environmental Conservation (NYSDEC 1999). NYSDEC's criterion was intended to identify the maximum concentration of sediment-associated contaminants to prevent harmful levels of bioaccumulation in fish and other aquatic organisms that could adversely affect human health (NYSDEC 1999). In 2007, the SQT guidance was updated (Crane and Hennes 2007). In this update, the SQTs for the protection of human health in Crane et al. (2000) were superseded by human health screening values developed by MDH for the U.S. Steel Superfund site in the St. Louis River AOC (MDH 2005). This MDH guidance was deemed applicable throughout the State of Minnesota (Crane and Hennes 2007). MDH updated the human health screening values for the U.S. Steel Superfund site in 2013 (MDH 2013), and their current values supersede the 2005 values. MDH (2013) developed the following 2,3,7,8-TCDD TEQs human health-based sediment screening values of: 1) cancer-based: 0.02 ng/kg dry wt. and 2) non-cancer-based: 0.4 ng/kg dry wt. Fish consumption contributed 99% and 98% of the risk for the cancer and non-cancer exposure routes, respectively (MDH 2013). MDH assumed a consumption rate of a single fish meal per week, scaled over a reasonable lifetime, for their exposure estimates.

The MDH (2013) human health-based sediment screening values for TEQs were compared to the NLAP TEQ values for human health. The cancer-based sediment screening value was exceeded for all 23 NLAP sediment samples. The non-cancer sediment screening value was exceeded in most of this subgroup of

Table 3-66. Spearman Rank Order Correlation of Particle Size and TOC with Individual PCDD/F Congeners and Homolog Groups with <5% Nondetects, as well as with  $\Sigma$ PCDD/F Congeners

Parameter	Spearman Rho Values			
	Clay (%)	Sand (%)	Silt (%)	TOC (%)
Sand (%)	<b>-0.625</b>			
Silt (%)	0.108	<b>-0.818</b>		
TOC (%)	0.105	0.297	-0.381	
PCD_T4	<b>0.462</b>	<b>-0.703</b>	<b>0.549</b>	<b>-0.563</b>
PCD_T5	-0.0435	-0.201	0.323	-0.0840
PCD_T6	-0.0871	-0.0638	0.179	0.205
PCD_T7	-0.0524	-0.0810	0.171	0.291
OCDD	-0.0485	-0.0623	0.154	0.251
PCD12378	-0.158	0.141	-0.0247	<b>0.530</b>
PCD123478	-0.202	0.0909	0.0711	<b>0.469</b>
PCD123678	-0.120	0.0474	0.0632	<b>0.471</b>
PCD123789	-0.113	0.0781	0.0346	<b>0.486</b>
PCD1234678	-0.0668	-0.0598	0.161	0.310
PCF_T4	-0.00396	-0.222	0.361	0.232
PCF_T5	0.0470	-0.129	0.187	0.287
PCF_T6	-0.0168	-0.0889	0.162	0.310
PCF_T7	-0.0425	-0.0761	0.155	0.252
OCDF	-0.0475	0	0.0731	0.255
PCF12378	-0.0940	0.0356	0.0870	<b>0.464</b>
PCF23478	-0.145	0.0929	0.0356	<b>0.518</b>
PCF123478	-0.171	0.106	0.0237	<b>0.527</b>
PCF123678	-0.0979	0.0860	0.0138	<b>0.520</b>
PCF234678	-0.0831	0.0445	0.0425	<b>0.499</b>
PCF1234678	-0.0435	0.00593	0.0573	0.368
$\Sigma$ PCDD/F Congeners	-0.0445	-0.0632	0.150	0.256

TOC = total organic carbon; PCDD/F = polychlorinated dibenzo-*p*-dioxin/dibenzofuran; other PCDD/F congeners and homologs are identified in Table 3-61.

Spearman rho values:

Black font: not statistically significant,  $p > 0.05$

Blue, bold, italic font: statistically significant,  $p < 0.05$  and  $> 0.001$

Orange, bold font: highly statistically significant,  $p < 0.001$

NLAP lakes, except for lake #36 (Red Rock) when calculated using the Kaplan-Meier method. If the single sediment samples collected from each NLAP lake were representative of sediment quality throughout these lakes, then there could be a potential risk to people consuming fish from this group of lakes. Since the sediments were collected from the deepest part of each lake where sediment would be more likely to “focus,” then these TEQ concentrations may be representative of an upper bound estimate of risk. Information was not available on nearshore sediment concentrations of PCDD/Fs that people might come in contact with or measured PCDD/F concentrations in fish that people might consume from these lakes. In addition, not all people consume fish or consume fish from just one location. Thus, the MDH



Table 3-67. Comparison of NLAP Aquatic Life PCDD/F TEQs to the MPCA's Level I and Level II SQT Values

Parameter	Percent of Samples (n = 23)		
	≤ Level I SQT	> Level I to ≤ Level II SQT	> Level II SQT
PCDD/Fs TEQs	13.0	87.0	0

PCDD/F = polychlorinated dibenzo-*p*-dioxin/dibenzofuran; TEQ = toxic equivalent; SQT = sediment quality target.

human health screening values are conservative. Figure 3-46 provides a more general map of the human health TEQ results, for which the highest value was found in lake #38 (Snail).

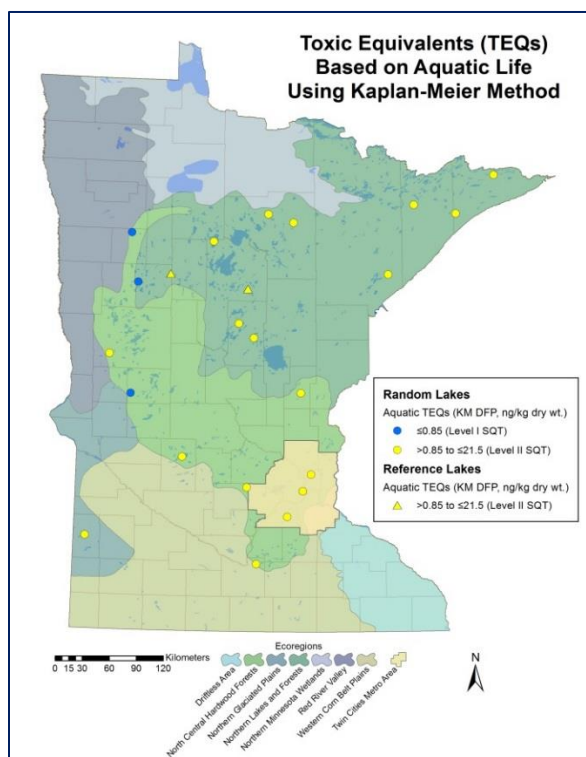


Figure 3-41. Aquatic life TEQs based on the Kaplan-Meier method. Values are based on 17 PCDD/Fs and coplanar PCBs.

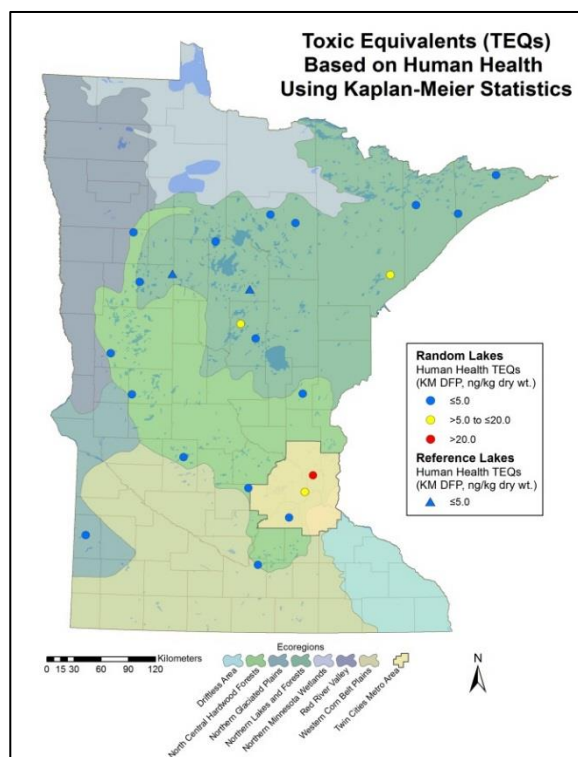


Figure 3-42. Human Health TEQs based on the Kaplan-Meier method. Values are based on 17 PCDD/Fs and coplanar PCBs.

## Environmental forensics

The weight percentage pattern of PCDD/F congeners and its homologs creates a unique “fingerprint” that can be used for environmental forensics work to identify sources of these compounds. The weight percentages of 17 PCDD/F congeners are plotted in Figure 3-47. OCDD comprised  $72.3 \pm 3.5\%$  of Total PCDD/F congeners followed by PCD1234678 at  $12.9 \pm 1.5\%$ . These two highly chlorinated congeners are indicative of ubiquitous combustion sources, such as wood fires and vehicle exhaust (Cleverly et al. 1997; Barabas et al. 2004; Shields et al. 2006; USEPA 2006b; Towey et al. 2012). These two congeners also dominated regional background sources in soils collected near the Tittabawassee River, MI; this river had been contaminated with PCDD/Fs from the Dow Chemical Company in Midland, MI (Towey et al. 2010). OCDD comprised 60 – 80% of Total PCDD/F concentrations in flood-plain soils and sediment of

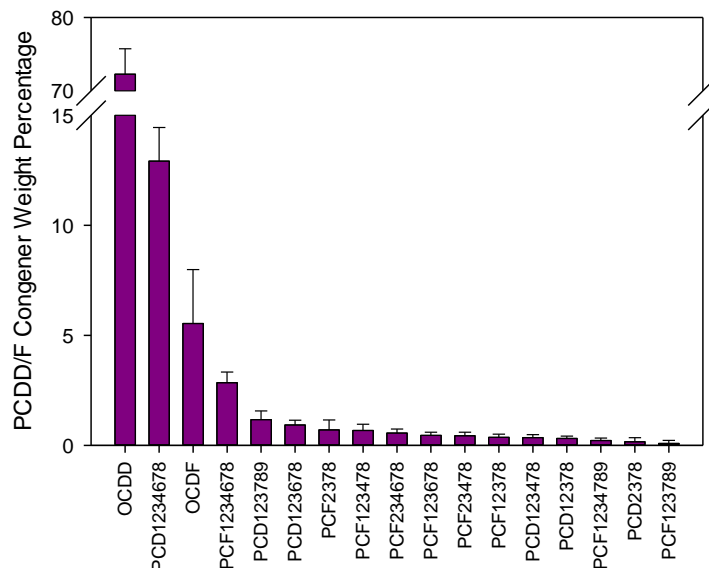


Figure 3-43. Mean (SD) weight percentages of PCDD/F congeners.

the Tittabawassee River upstream of Midland, MI and 30 - 60% in downstream samples (Hilscherova et al. 2003). Thus, the upstream percentages of OCDD in the Tittabawassee River flood-plain soils and sediments were consistent with the percentages of OCDD observed in the NLAP lake sediments. OCDF comprised the third highest weight percentage of PCDD/Fs in this subset of NLAP lakes (Figure 3-47) at  $5.5 \pm 2.5\%$ . OCDF is a common nonpoint source congener (Shields et al. 2006; USEPA 2006b; Towey et al. 2012). Because of these highly chlorinated ubiquitous congeners, some researchers (Towey et al. 2010; Quadri et al. 2015) suggest that the fractions of less chlorinated PCDD/F congeners are more useful for distinguishing unique sources in contaminant site investigations. The other PCDD/F congeners each comprised  $<3\%$  of the weight percentage of  $\Sigma$ PCDD/F congeners. Since only one sediment sample was collected from each lake over a wide geographic area in Minnesota, forensic use of less chlorinated PCDD/F congeners is more limited.

Another common forensic technique is to compare patterns in PCD2378 concentrations with PCD\_T4, as well as with ratios of these compounds. A plot of detected PCD2378 concentrations vs. PCD\_T4 concentrations is provided in Figure 3-48a. In this plot, the  $r^2$  value of 0.606 is driven by the high PCD2378 and PCD\_T4 concentrations in lake #38 (Snail) compared to the rest of the lakes. If this data point is removed, the  $r^2$  value decreases to 0.182. As indicated in the previous section, there appear to be other sources of congeners in the PCD\_T4 homolog group that could be contributing to poorer correlations with PCD2378. The ratio of detected PCD2378 to PCD\_T4 for individual lakes is provided in Figure 3-48b. The ratios ranged from 0.010 in lake #11 [Eagle (North)] to 0.21 in lake #37 (Richey). Ratios on the order of 0.06 or less may be indicative of wastewater and atmospheric sources (Chaky 2003). Quadri et al. (2015) noted high ratios between 0.6 and 1.0 in lower Passaic River, NJ sediments where 2,3,7,8-TCDD was a by-product of the 2,4,5-trichlorophenol manufacturing process. The ratios in the NLAP lakes were far below those observed in the lower Passaic River. PCDD/Fs emitted from residential burn barrels and open burning of yard waste is the number one source of these compounds in the U.S. EPA's national emissions inventory (USEPA 2006b). As such, the PCDD/F "fingerprint" can vary depending on the type of waste being burned (e.g., plastics and paper treated with chemicals, coatings,

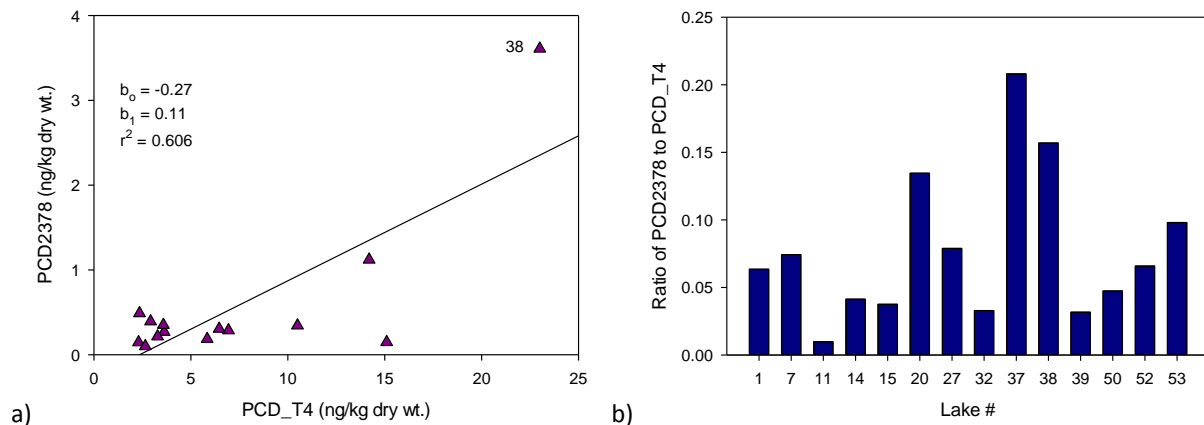


Figure 3-44. a) Detected PCD<sub>2378</sub> data compared to PCD<sub>T4</sub>, and b) the ratio of detected PCD<sub>2378</sub> concentrations to PCD<sub>T4</sub> plotted for each lake. For a),  $b_0$  = intercept,  $b_1$  = slope, and  $r^2$  = coefficient of determination.

and inks). Although most burning of household garbage is illegal in Minnesota, 45% of respondents in a Minnesota survey burned household wastes (<https://www.pca.state.mn.us/living-green/dont-burn-your-garbage>, accessed 3/17/2016). Thus, PCDD/Fs released into the air from burning household garbage could be transported long distances and be deposited to lake watersheds through wet and dry atmospheric deposition. The sediments could serve as a sink for these compounds.

The percent homolog patterns of PCDD/Fs provide another forensic technique. OCDD and OCDF were included in the homolog groups since there was not a separate homolog analysis of eight-chlorinated PCDD/F compounds. A fairly consistent source profile was observed for the mean weight percentages of PCDD/F homologs in 22 NLAP lakes, where  $OCDD > PCD_{T7} > PCD_{T6} > PCF_{T4} > PCF_{T5}$  (Figure 3-49). Interestingly, OCDD also dominated the PCDD/F homolog profile from residential and industrial areas in central South Africa (Nieuwoudt et al. 2009). Red Rock (#36) had very low PCDD/F homolog concentrations and a unique particle size distribution (i.e., very sandy) compared to the other study lakes. Red Rock had a higher percentage of lower and medium chlorinated PCDD homologs (i.e., PCD<sub>T5</sub>, PCD<sub>T4</sub>, and PCD<sub>T6</sub>), and a lower percentage of highly chlorinated PCDD homologs (i.e., PCD<sub>T7</sub> and OCDD) than the other NLAP lakes (Figure 3-49). For the PCDF data in Red Rock, only PCF<sub>T6</sub> had detectable concentrations, for which the homolog weight percentage was lower than in the other 22 lakes.

The homolog weight percentages for the 22 lakes were further divided into the developed lakes (#27 and 38) and the other 20 lakes (Figure 3-50). This was done because, based on a concentration basis, the developed lakes had significantly higher ( $p < 0.05$ ) concentrations for most PCDD/F congeners and homologs (except PCD<sub>T4</sub>; Table 3-64) than the other lakes. The results of either t-tests or Mann-Whitney rank sum tests showed that the weight percentages of only two PCDD/F homolog groups had statistically significant differences ( $p < 0.05$ ). The mean homolog weight percentages of PCD<sub>T6</sub> were significantly higher ( $p < 0.05$ ) in the other 20 lakes compared to the developed lakes, while the mean weight percentages of PCF<sub>T7</sub> were significantly higher ( $p < 0.05$ ) in the developed lakes than the other 20 lakes. These significant differences may be attributed to different sources. For example, residential trash burning (which could contribute PCD<sub>T6</sub>) should be less in the Twin Cities metropolitan area where residents have access to commercial trash haulers compared to outstate Minnesota where these services may be lacking. The Twin Cities metropolitan area also has more vehicle and commercial/industrial emissions than most outstate areas, which could contribute to higher weight percentages of PCF<sub>T7</sub>.

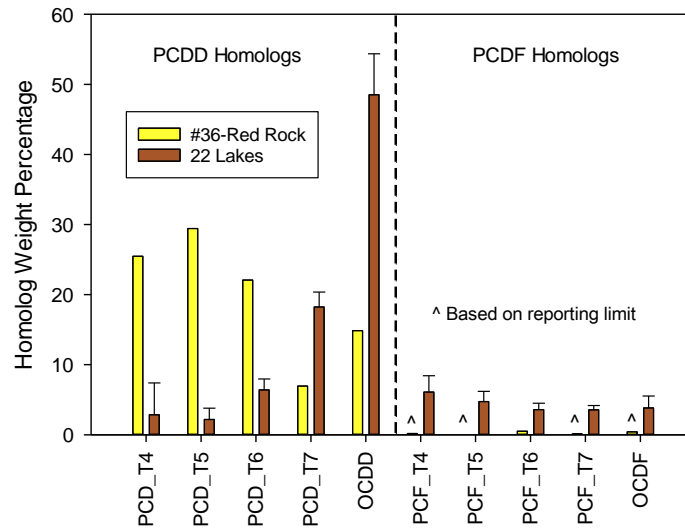


Figure 3-45. Mean weight percentages of PCDD/F homologs in lake #36 (Red Rock) and the other 22 NLAP lakes. Error bars represent 1 SD. The ^ symbol represents four nondetect PCDF homologs in lake #36.

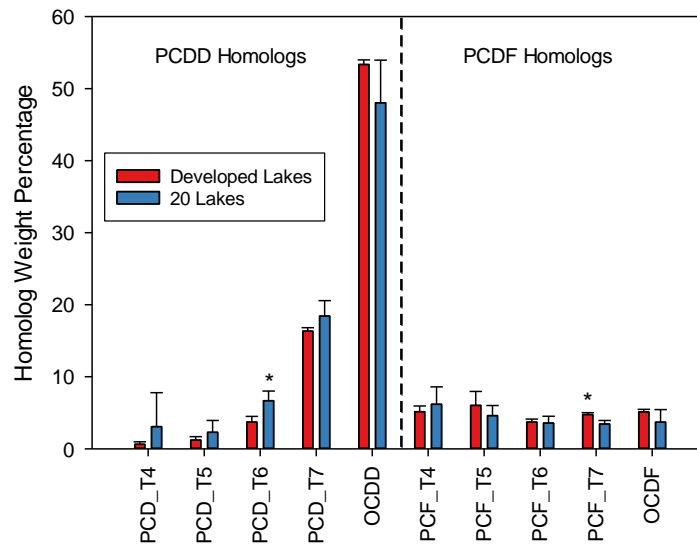


Figure 3-46. Mean weight percentages of PCDD/F homologs in developed lakes versus 20 other lakes (which excluded Lake #36—Red Rock). Error bars represent 1 SD. Statistically significant ( $p < 0.05$ ) differences are noted with an asterisk.

In summary, several different nonpoint sources may be contributing low concentrations of PCDD/F congeners to the subset of NLAP lake sediments sampled for PCDD/Fs. Atmospheric deposition of these congeners to the lakes and their watersheds (with subsequent runoff to the lakes) is probably the primary transport pathway. Ubiquitous combustion sources, like wood burning and automobile emissions, appear to be important. In addition, burning of household garbage is likely another important source in outstate areas. Land application of sewage sludge, with subsequent runoff into lakes, or WWTP effluent discharges could contribute PCDD/F congeners, too. Several other commercial (e.g.,

paper mills) and industrial sources could be a factor in some areas. However, it was beyond the scope of this document to do a thorough source apportionment of PCDD/F congeners in the study lakes.

## UTL values

UTLs were calculated for PCDD/F congeners and homolog groups,  $\Sigma$ PCDD/F congeners, and human health and aquatic life TEQs. The UTLs for detected PCDD/F values are provided in Table 3-68, whereas the UTLs for PCDD/F congeners and homologs groups containing detected and nondetect values are provided in Table 3-69. The UTLs for human health and aquatic life TEQs are listed in Table 3-70. The two developed lakes from the Twin Cities metropolitan area (i.e., #27 and 38) were the most frequently excluded outliers of this data set. Most of these data followed a normal distribution after excluding outliers, except for PCD\_T4, PCD2378, PCD12378, and PCD123478. These three congeners and homolog group followed a gamma distribution. Since these UTL values are based on a small number of samples, it will be beneficial to expand this analysis in the future as more randomly collected data are obtained from surficial sediments in Minnesota.

Table 3-68. UTLs of Detected PCDD/F Data with Outliers Removed at the 5% Significance Level (units in ng/kg dry wt.)

Parameter	N	Potential Outliers Removed at 5% Significance Level (lake ID numbers)	Normal Distribution* 95% UTL with 95% Coverage	Gamma Distribution*	
				95% Approximately Gamma UTL with 95% Coverage	
				WH	HW
OCDD	21	27, 38 <sup>†</sup>	486.9		
PCD_T4	20	4, 5 <sup>†</sup> , 38 <sup>†</sup>		17.1	17.8
PCD_T5	21	27 <sup>†</sup> , 38	18.6		
PCD_T6	21	27 <sup>†</sup> , 38	57.1		
PCD_T7	21	27, 38 <sup>†</sup>	175.3		
PCD1234678	21	27, 38 <sup>†</sup>	87.0		
PCD123789	21	27 <sup>†</sup> , 38	7.1		
PCF_T6	21	27, 38 <sup>†</sup>	33.4		
PCF1234678	21	27, 38 <sup>†</sup>	17.1		
$\Sigma$ PCDD/F Congeners	21	27, 38 <sup>†</sup>	654.6		

UTL = Upper Tolerance Limit; PCDD/F = polychlorinated dibenzo-*p*-dioxin/dibenzofuran; WH = Wilson Hilferty; HW = Hawkins Wixley; see Table 3-61 for a description of other PCDD/F abbreviations.

\* UTLs for normally distributed data were preferred over those derived from gamma distributed data. When the data were not normally distributed, the gamma distribution was used to estimate UTL values. Gamma UTLs were calculated two different ways, for which professional judgment can be used to select the value of interest.

<sup>†</sup> Potential outlier was based on professional judgment; all other outliers were based on statistical tests at the 5% significance level.

Table 3-69. UTLs of Detected and Censored PCDD/F Congeners and Homologs with Outliers Removed at the 5% Significance Level (units in ng/kg dry wt.)

Parameter	N (# detects)	% Nondetects	Potential Outliers Removed at 5% Significance Levels (lake ID numbers)	Normal Distribution and KM Estimates*	Gamma Distribution and KM Estimates*	
					95% Approx. Gamma UTL with 95% Coverage	
					WH	HW
OCDF	21 (20)	4.8	27, 38 <sup>†</sup>	36.6		
PCD123478	23 (22)	4.3	-		4.3	4.6
PCD123678	21 (20)	4.8	27 <sup>†</sup> , 38	5.8		
PCD12378	22 (21)	4.5	38		3.0	3.2
PCD2378	22 (13)	40.9	38		0.82	0.84
PCF_T4	21 (20)	4.8	27, 38 <sup>†</sup>	47.9		
PCF_T5	21 (20)	4.8	27, 38 <sup>†</sup>	41.1		
PCF_T7	21 (20)	4.8	27, 38 <sup>†</sup>	31.8		
PCF123478	21 (20)	4.8	27, 38 <sup>†</sup>	4.0		
PCF1234789	21 (19)	9.5	27, 38 <sup>†</sup>	1.1		
PCF123678	21 (20)	4.8	27, 38 <sup>†</sup>	2.6		
PCF12378	21 (20)	4.8	27, 38 <sup>†</sup>	1.8		
PCF234678	21 (20)	4.8	27, 38 <sup>†</sup>	3.4		
PCF23478	21 (20)	4.8	27, 38 <sup>†</sup>	2.4		
PCF2378	22 (20)	9.1	38		9.1	10.3

UTL = Upper Tolerance Limit; PCDD/F = polychlorinated dibenzo-*p*-dioxin/dibenzofuran; KM = Kaplan-Meier; WH = Wilson Hilferty; HW = Hawkins Wixley; see Table 3-61 for a description of other PCDD/F abbreviations.

\* UTLs for normally distributed data were preferred over those derived from gamma distributed data. When the data were not normally distributed, the gamma distribution was used to estimate UTL values. Gamma UTLs were calculated two different ways, for which professional judgment can be used to select the value of interest.

† Potential outlier was based on professional judgment; all other outliers were based on statistical tests at the 5% significance level.

Table 3-70. UTLs of Human Health and Aquatic Life TEQs with Outliers Removed at the 5% Significance Level (units in ng TEQ/kg dry wt.)

Parameter	N	Potential Outliers at 5% Significance Level (lake ID numbers)	Normal Distribution
			95% UTL with 95% Coverage
Human Health TEQs			
HH_TEQ*	21	27 <sup>†</sup> , 38	14.8
HH_TEQ_KMDF	21	27 <sup>†</sup> , 38	7.0
HH_TEQ_KMDFP	21	27 <sup>†</sup> , 38	7.0
Aquatic Life TEQs			
W_TEQ*	21	27 <sup>†</sup> , 38	6.5
W_TEQ_KMDF	21	27 <sup>†</sup> , 38	6.2
W_TEQ_KMDFP	21	27 <sup>†</sup> , 38	6.3

UTL = Upper Tolerance Limit; TEQ = toxic equivalent; HH = human health; KMDF = Kaplan-Meier calculation of TEQs using polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/Fs); KMDFP = Kaplan-Meier calculation of TEQs using PCDD/Fs and coplanar polychlorinated biphenyls (PCBs); W = aquatic life.

\* Calculated using substitution. Nondetect results were treated as one-half the reporting limit if there were a mix of nondetect and detected values. If all the reporting limits were nondetects, then the full reporting limits were used in the TEQ calculation.

† Potential outlier was based on professional judgment; the other outlier was based on Dixon's outlier test at the 5% significance level. This test can only select one outlier when there are <25 samples.

## PBDEs

### *Highlights:*

- Four BDE congeners were detected the most frequently in the sediment samples. BDE-209 was detected in 84% of samples, followed by BDEs-47, 206, and 99 in 33, 30, and 23% of samples, respectively.
- Total PBDEs were detected in 82.7% of sediment samples.
- PBDEs were analyzed in composite fish tissue samples collected from five NLAP lakes.
  - BDEs-47, 49, 99, and 100 were the most prevalent congeners. BDEs-47, 99, and 100 are also frequently found in humans, fish, and other biota.
  - For BDEs-47, 100, and 153, fish in the predator trophic group had significantly higher ( $p < 0.05$ ) mean lipid-normalized concentrations than those fish in the omnivore and benthic trophic groups.
  - For BDEs-47, 49, 99, 100, and 153, the mean lipid-normalized concentrations were not significantly different ( $p > 0.05$ ) for fish in the omnivore and benthic trophic groups.
- UTL values for BDEs-47, 99, 206, 209, and Total PBDEs were calculated for sediment samples.

## Background

PBDEs are organobromine compounds, similar to PCBs in their persistence, which have strong flame retardant properties. Commercial mixtures of PBDEs (i.e., pentaBDE, octaBDE, and decaBDE) have been commonly used in consumer and household products, such as sleepwear, furniture, electronics, and the interior of cars and trucks (USEPA 2009c). A review article on the history of PBDE use in the United States since the 1960s, environmental issues associated with its persistence and rapid accumulation in the environment, wildlife, and people, as well as policy changes resulting in the regulation of certain PBDE commercial mixtures is provided by Corder et al. (2013). PBDEs were considered as an emerging contaminant group at the time the 2007 NLAP sediment project was conducted.

The use of certain PBDE homologs has been restricted in Minnesota and nationwide. The Great Lakes Chemical Corporation was the sole U.S. manufacturer of pentaBDE and octaBDE until they voluntarily ceased production in 2004 (USEPA 2009c). In 2007, the Minnesota Legislature passed a law (effective January 1, 2008) prohibiting the manufacturing, processing, or distribution of products which contain more than 0.1% of pentaBDE or octaBDE (Minn. Stat. 2015 325E.385-325E.388; <https://www.revisor.mn.gov/statutes/?id=325e.385>; accessed 3/22/2016). The MPCA submitted a report on DecaBDE to the Minnesota Legislature in 2008 (Kovacevic and O'Dell 2008). MDH named decaBDE as a Minnesota Priority Chemical due to its persistence, pervasiveness, and potential to degrade into more toxic, lower brominated congeners (MDH 2011). The U.S. EPA negotiated with the two U.S. producers of decaBDE, Albemarle Corporation and Chemtura Corporation, along with the largest U.S. importer, ICL Industrial Products, Inc., to phase out this product by the end of 2013 (<https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/polybrominated-diphenyl-ethers-pbdes>; accessed 3/22/2016). In 2015, a new law was enacted in Minnesota to restrict the future use of four flame retardants, including: decaBDE, tris(1,3-dichloro-2-propyl)phosphate (TDCPP), tris(2-chloroethyl)phosphate (TCEP), and hexabromocyclododecane (HBCDD)



(<https://www.revisor.mn.gov/bills/bill.php?view=chrono&f=SF1215&y=2015&ssn=0&b=senate>; accessed 4/7/2016). Beginning on July 1, 2018, this law bans the manufacture or importation of children's products and residential upholstered furniture. In addition, a ban on the sale of such products in Minnesota takes effect on July 1, 2019.

PBDEs are of international concern. In May 2009, the following homolog PBDEs were added to Annex A of the Stockholm Convention: tetraBDE, pentaBDE, hexaBDE, and heptaBDE (UNEP 2012). These homologs are referred to as POP-PBDEs. HexaBDE and heptaBDE are the main components of commercial octaBDE. Higher brominated PBDE homologs (i.e., octaBDE, nonaBDE, and decaBDE) can degrade to POP-PBDEs by debromination (UNEP 2010a, b). However, the results of field experiments of sediment in a boreal lake in Canada suggest that the debromination of decaBDE occurs very slowly, if at all, in natural sediment (Orihel et al. 2016). The commercial mixture of decaBDE has recently been proposed for listing under the Stockholm Convention

(<http://chm.pops.int/TheConvention/ThePOPs/ChemicalsProposedforListing/tabid/2510/Default.aspx>; accessed 3/22/2016).

Dechlorane Plus has been proposed as an alternative to BDE-209, which is the major component of deca-BDE formulations. However, results of dietary exposures of Dechlorane Plus and BDE-209 in marine mussels suggest that Dechlorane Plus poses a greater genotoxic potential than BDE-209 and also shows a concentration-dependent bioaccumulation pattern not seen in BDE-209 (Barón et al. 2016). Therefore, replacement flame retardants for commercial mixtures of pentaBDE, octaBDE, and decaBDE may have adverse environmental effects, as well. In 2015, the Minnesota Legislature put the following restrictions on replacement flame retardant chemicals: "A manufacturer shall not replace a chemical whose use is prohibited under this section with a chemical identified on the basis of credible scientific evidence by a state, federal, or international agency as being known or suspected with a high degree of probability to:

1. Harm the normal development of a fetus or child or cause other developmental toxicity
2. Cause cancer, genetic damage, or reproductive harm
3. Disrupt the endocrine or hormone system
4. Damage the nervous system, immune system, or organs, or cause other systemic toxicity"

([https://www.revisor.mn.gov/bills/text.php?number=SF1215&version=3&session=ls89&session\\_year=2015&session\\_number=0](https://www.revisor.mn.gov/bills/text.php?number=SF1215&version=3&session=ls89&session_year=2015&session_number=0); accessed 4/7/2016)

## Summary statistics: sediments

Although a large number of BDE congeners were analyzed, only a few congeners were prevalent in surficial sediments from 52 NLAP lakes. BDE-209 was detected the most frequently in 84% of samples (Table 3-71). Next, BDEs-47, 206, and 99 were detected in 33, 30, and 23% of samples, respectively (Table 3-71). The other BDE compounds only had a few detections, if any (Table 3-71). Total PBDEs, as measured by the laboratory, had a detection frequency of 82.7% (Table 3-71). The Kaplan-Meier method was used to estimate summary statistics for the sediment data with <80% nondetects. BDE-209 had the highest mean concentration (19.3 µg/kg dry wt., Table 3-72), for which lake #41 (Spring) contributed an extremely high value of 513 µg/kg dry wt. This result increased the SD of the mean to 69.6 µg/kg dry wt. (Table 3-72). Lake #41, which is located north of the Twin Cities metropolitan area, should be sampled again in the future to verify this high value. The median value for BDE-209 was lower at 7.5 µg/kg dry wt. (Appendix L). Other summary statistics, percentiles, box plots, and Q-Q plots with significant outliers noted are provided in Appendix L.

BDE-209 was also the dominant BDE congener in two other MPCA sediment studies. One study was of PBDEs in the western Lake Superior watershed in which BDE-209 accounted for 78 to 99% of the Total

Table 3-71. Percentage of Nondetects for BDE Congeners and Total PBDEs, Sorted from Low to High Nondetects

BDE Congener	Homolog Group	N	Number Detects	Number NDs	% NDs
BDE-209	Decabromobiphenyl	52	44	8	15.4
Total PBDEs		52	43	9	17.3
BDE-47	Tetrabromobiphenyl	52	17	35	67.3
BDE-206	Nonabromobiphenyl	52	16	36	69.2
BDE-99	Pentabromobiphenyl	52	11	41	78.9
BDE-205	Octabromobiphenyl	52	10	42	80.8
BDE-75	Tetrabromobiphenyl	52	4	48	92.3
BDE-155	Hexabromobiphenyl	52	3	49	94.2
BDE-181	Heptabromobiphenyl	52	3	49	94.2
BDE-202	Octabromobiphenyl	52	3	49	94.2
BDE-207	Nonabromobiphenyl	52	3	49	94.2
BDE-25	Tribromobiphenyl	52	2	50	96.2
BDE-30	Tribromobiphenyl	52	1	51	98.1
BDE-49+71	Tetrabromobiphenyl	52	1	51	98.1
BDE-118	Pentabromobiphenyl	52	1	51	98.1
BDE-194	Octabromobiphenyl	52	1	51	98.1
BDE-198+199- +203+200	Octabromobiphenyl	52	1	51	98.1
BDE-208	Nonabromobiphenyl	52	1	51	98.1
BDE-1	Monobromo-	52	0	52	100
BDE-2	Monobromo-	52	0	52	100
BDE-3	Monobromo-	52	0	52	100
BDE-7	Dibromo-	52	0	52	100
BDE-8	Dibromo-	52	0	52	100
BDE-10	Dibromo-	52	0	52	100
BDE-11	Dibromo-	52	0	52	100
BDE-12	Dibromo-	52	0	52	100
BDE-13	Dibromo-	52	0	52	100
BDE-15	Dibromo-	52	0	52	100
BDE-17	Tribromobiphenyl	52	0	52	100
BDE-28	Tribromobiphenyl	52	0	52	100
BDE-32	Tribromobiphenyl	52	0	52	100
BDE-33	Tribromobiphenyl	52	0	52	100
BDE-35	Tribromobiphenyl	52	0	52	100
BDE-37	Tribromobiphenyl	52	0	52	100
BDE-66	Tetrabromobiphenyl	52	0	52	100
BDE-77	Tetrabromobiphenyl	52	0	52	100
BDE-85	Pentabromobiphenyl	52	0	52	100
BDE-100	Pentabromobiphenyl	52	0	52	100
BDE-116	Pentabromobiphenyl	52	0	52	100
BDE-119	Pentabromobiphenyl	52	0	52	100

Table 3-71. Continued

BDE Congener	Homolog Group	N	Number Detects	Number NDs	% NDs
BDE-126	Pentabromobiphenyl	52	0	52	100
BDE-138	Hexabromobiphenyl	52	0	52	100
BDE-153	Hexabromobiphenyl	52	0	52	100
BDE-154	Hexabromobiphenyl	52	0	52	100
BDE-166	Hexabromobiphenyl	52	0	52	100
BDE-183	Heptabromobiphenyl	52	0	52	100
BDE-190	Heptabromobiphenyl	52	0	52	100
BDE-195	Octabromobiphenyl	52	0	52	100
BDE-196	Octabromobiphenyl	52	0	52	100
BDE-197	Octabromobiphenyl	52	0	52	100
BDE-201	Octabromobiphenyl	52	0	52	100
BDE-204	Octabromobiphenyl	52	0	52	100

BDE = brominated diphenyl ether; PBDEs = polybrominated diphenyl ethers; N = number of samples; ND = nondetect value.

Table 3-72. Mean and SD Determined by the Kaplan-Meier Method for BDE Congeners and Total PBDEs with &lt;80% NDs in Sediment Samples

Parameter	% NDs	KM Mean ( $\mu\text{g}/\text{kg}$ dry wt.)	KM SD ( $\mu\text{g}/\text{kg}$ dry wt.)
BDE-47	67.3	0.93	0.49
BDE-99	78.9	1.1	0.48
BDE-206	69.2	4.6	8.3
BDE-209	15.4	19.3	69.6
Total PBDEs	17.3	32.7	82.9

BDE = brominated diphenyl ether; PBDEs = polybrominated diphenyl ethers; ND = nondetect value; KM = Kaplan-Meier; SD = standard deviation.

PBDEs present in sediment cores; BDE-209 concentrations in the upper 3 mm of sediment ranged from 1.9 to 6.2  $\mu\text{g}/\text{kg}$  dry wt. (MPCA 2006). A second MPCA study was of urban stormwater pond sediments from the Minneapolis-St. Paul metropolitan area (Crane and Hennes 2010a). BDE-209 was detected in all 15 stormwater ponds, which were located in watersheds dominated by residential, commercial, or industrial land uses. The highest value (647  $\mu\text{g}/\text{kg}$  dry wt.) occurred in a pond located in a commercial area draining a large shopping mall. The median concentration of BDE-209 in the NLAP lake sediments (7.5  $\mu\text{g}/\text{kg}$  dry wt.) was within the range of median values in stormwater pond sediments from residential (2.6  $\mu\text{g}/\text{kg}$  dry wt.) and commercial (11.0  $\mu\text{g}/\text{kg}$  dry wt.) land use areas (Crane and Hennes 2010a). The five stormwater ponds from industrial land use areas had a higher BDE-209 median concentration of 32.4  $\mu\text{g}/\text{kg}$  dry wt. (Crane and Hennes 2010a).

On a regional basis, BDE-209 is commonly detected in sediments from the Great Lakes watershed. BDE-209 was detected in 83% of sediment cores collected from depositional areas of all five Great lakes, ranging from 0.87 – 106  $\mu\text{g}/\text{kg}$  dry wt.; Lake Superior had the lowest concentration range of 0.87 – 7.1

µg/kg dry wt., and atmospheric deposition appeared to be the major source (Yang et al. 2012). This study also pointed out some of the analytical discrepancies that have arisen among researchers for analyzing BDE-209, particularly due to sample clean-up and instrument conditions (Yang et al. 2012). In another study from Lake Erie, BDE-209 dominated surficial sediments and was detected in 56% of samples, ranging from <0.3 to 12 µg/kg dry wt. (Lu et al. 2015); outflow from the Detroit River appeared to be a major source of PBDEs to Lake Erie. Stormwater runoff into urban rivers also appeared to be a major source of PBDEs in the Southern California Bight coastal area, where BDE-209 comprised 80% of the  $\Sigma$ PBDE<sub>13</sub> concentrations (Dodder et al. 2012). BDE-209 concentrations ranged from <1.65 to 513 µg/kg dry wt. in the NLAP lake sediments, for which all but the highest concentration sample were within the range of values observed in the Great Lakes.

## Comparisons to Environment Canada guidelines

The MPCA does not have any SQT values for BDE congeners or Total PBDEs. Environment Canada developed Federal Environmental Quality Guidelines (FEQGs) for BDE homologs as benchmark values, below which there is a low likelihood of adverse effects on the protected use (e.g., aquatic life or the wildlife that consume them; Environment Canada 2013). The FEQG for the decaBDE homolog is 19 µg/kg dry wt. (Environment Canada 2013), for which BDE-209 comprises most of this homolog. The following six NLAP lakes had BDE-209 concentrations that exceeded the FEQG for decaBDE: #12, 23, 24, 38, 41, and 47. Lake #47 (Vesper) is located in the BWCAW, and atmospheric deposition would have been the main transport pathway for PBDEs to enter that lake followed by subsequent settling to the bottom sediments. The FEQG for BDE-99 is 0.4 µg/kg dry wt. (Environment Canada 2013), and this value was below the reporting limits for BDE-99 congeners in the NLAP lakes. Thus, the FEQG is more restrictive than the analytical capabilities, at the time, to measure BDE-99 in these sediment samples. Although the FEQGs have not been adopted by the MPCA, they are useful as benchmark values for comparison purposes. In order for more jurisdictions to develop sediment quality guidelines (SQGs) for PBDEs, additional matching sediment chemistry and toxicity data will need to be collected. Alternatively, food web bioaccumulation models could be used to derive SQGs for certain classes of organisms, such as done in the marine environment off the coast of British Columbia, Canada for the protection of resident killer whales (Alava et al. 2016).

## Summary statistics: fish tissue

Two of the more commonly detected BDE congeners in sediment samples (i.e., BDEs-47 and 99) were also the dominant congeners in most composite fish tissue samples from five NLAP lakes (#5, 7, 16, 24, and 27). In addition, BDEs-49, 100, and 153 were commonly detected congeners in the fish tissue samples from different trophic groups. The median concentrations (pg/g wet wt.) were highest for BDE-47 followed by BDEs- 99, 100, 49, and 153 (Table 3-73). Interestingly, the wet weight concentrations of BDE-49 were greater than BDE-99 in the composite yellow perch samples from August (#5), Cass (#7), and Mayo (#24). The MPCA considered part of the sample results for BDEs-99 and 153 as estimated values due to the detection and quantification of these congeners in the procedural blanks (Appendix B). Two coeluting pairs of congeners (BDE-17/25 and BDE-28/33), as well as BDEs-66, 79, 154, and 155 were also detected in all of the composite samples. The MPCA considered four of the BDE-154 results and 10 of the BDE-155 results as estimated values (Appendix B).

The NLAP fish tissue data were comparable to other studies. BDEs-47, 49, 99, and 100 were also prevalent in the atmosphere over Lake Superior and showed a net flux into the lake near Duluth, MN during the summer of 2011 (Ruge et al. 2015); atmospheric deposition of these congeners to lakes, especially in the Lake Superior watershed, is a likely transport pathway to surface water by which they could accumulate in fish tissue or be bioaccumulated from benthic species. Similarly, BDEs-47 and 99

Table 3-73. Summary Statistics for Five BDE Congeners Detected in Composite Fish Tissues

Summary Statistics	Concentration (pg/g wet wt.)				
	BDE-47 <sup>†</sup>	BDE-49 <sup>†</sup>	BDE-99 <sup>†</sup>	BDE-100 <sup>†</sup>	BDE-153 <sup>†</sup>
All Trophic Data (n = 13*)					
Mean	798	187.5	313	160	33.1
SD	1137	315.5	461	235	39.4
Median	477	56.2	100	92.7	16.1
Minimum	87.7	13.2	28.7	18.7	4.8
Maximum	4210	1160	1350	887	128

BDE = brominated diphenyl ether; SD = standard deviation.

<sup>†</sup> The trophic guilds of fish were not significantly different ( $p > 0.05$ ) for each BDE congener.

\* A total of 13 composite samples were used, for which five fish comprised each composite sample. Benthic fish species were only collected from three of the five lakes.

(along with BDE-209) were also the most abundant congeners in water column samples from all five Great Lakes (Venier et al. 2014). The prevalence of BDEs-47, 99, and 100 in fish tissues from the NLAP lakes was consistent with other studies of fish tissues in western Lake Superior (MPCA 2006), Lake Michigan (Kuo et al. 2010), all five Great Lakes for lake trout (Crimmins et al. 2012), and in European high mountain lakes and Greenland for liver and muscle tissues of trout (Vives et al. 2004). Concentrations of BDE congeners in lake trout throughout the Great Lakes, in general, are declining as a result of the elimination of the commercial production of pentaBDE in the U.S. during 2004 (Crimmins et al. 2012).

The NLAP lakes varied in the concentrations of BDE congeners in different trophic levels of fish. Lake Nokomis (#27) in Minneapolis, MN had the highest concentrations of BDEs-47, 49, 99, and 100 in predator and omnivore species. Benthic fish species were not collected from Nokomis (#27) and Mayo (#24). BDE-47 is usually found more frequently than other BDE congeners in humans, fish, and other biota, followed by BDEs-99, 100, 153, and 154 (USEPA 2009c). BDE-209 was only detected in one composite fish tissue sample, for which a concentration of 575 pg/g wet wt. was observed in bluegills (an omnivore species) from Lake Nokomis (#27). Stapleton et al. (2006) showed that juvenile rainbow trout and common carp have a metabolic pathway for the debromination of BDE-209, particularly in fish tissue as opposed to the liver where it accumulates. The bluegill composite sample was based on skin-on whole fish with the scales removed so BDE-209 was likely accumulated in the liver of these fish; bluegills may also have a different efficiency for debrominating BDE-209 compared to other freshwater fish species. Some of the other fish species examined in this study were based on skin-on fillets or whole fish, and the fillets would be expected to have lower concentrations of BDE-209 based on the work of Stapleton et al. (2006). Kuo et al. (2010) also observed the concentration of BDE-209 decreased at higher trophic levels, whereas BDEs-47 and 100 biomagnified in a Lake Michigan food web of plankton, *Diporeia*, lake whitefish, lake trout, and Chinook salmon. Kuo et al. (2010) suggested that partial uptake or biotransformation of BDE-209 could explain their observations.

Wet weight concentrations of BDEs-47, 49, 99, 100, and 153 were examined for differences based on the trophic classification of fish samples. A natural log transformation of the wet weight data was performed, which allowed parametric one-way ANOVAs to be run. There were no statistically significant ( $p > 0.05$ ) differences in the mean values of each BDE congener between predator (n = 5 lakes), omnivore (n = 5 lakes), and benthic (n = 3 lakes) fish species. However, these congeners were elevated in an urban

lake (Nokomis--#27) for predator and omnivore fish species compared to other lakes that were dominated by other watershed land uses (i.e., forest, cultivated land, and lakes and wetlands).

The fish tissue wet weight results were compared to Environment Canada's (2013) FEQG values for BDE-99 and BDE-100. The FEQG value of 1000 pg/g wet wt. for BDE-99 was exceeded by both the predator (walleye) and omnivore (bluegill) fish species in Nokomis (#27). The composite BDE-99 value for walleye in Nokomis (1350 pg/g wet wt.) was 5.5 to 32.5 times larger than the composite BDE-99 values in the predator fish (all northern pike) from the other four lakes. The walleye in Nokomis were older (7 – 12 years) than the northern pike (3 – 6 years) from the other lakes (Appendix A). Thus, the walleye in Nokomis had a longer time period to accumulate BDEs in their diet from a lake system with higher concentrations of BDEs. Similarly, the composite BDE-99 value for bluegill in Nokomis (1280 pg/g wet wt.) was 8.1 to 40.5 times higher than the composite BDE-99 values in omnivore fish (i.e., bluegill and yellow perch) from the other four lakes. The bluegills in Nokomis were all younger (2 years) than the omnivore species (3 – 9 years) in the other lakes (Appendix A) so their environmental exposure to BDE-99 was apparently higher. Lake Nokomis has been classified as impaired by the MPCA since 1998 due to excess nutrients, as well as elevated mercury and PCB concentrations in fish tissue (Zadak et al. 2010). This lake has had many urban sources of pollutants over the years compared to the NLAP lakes in outstate Minnesota, and a total maximum daily load (TMDL) has been prepared for it (Zadak et al. 2010). The FEQG value of 1000 pg/g wet wt. for BDE-100 was not exceeded in any of the fish trophic groups.

The fish tissue data were normalized for percent lipids in each composite sample to enable all species to be treated similarly (Randall et al. 1998). For three trophic classes of fish, summary statistics were generated for the lipid-normalized concentrations of five BDE compounds (Table 3-74). For each congener, one-way ANOVAs were run of the lipid-normalized data for each trophic class of fish. A natural log transformation was needed for BDEs-47, 49, and 100 in order to pass the Shapiro-Wilk normality test prior to running the one-way ANOVA (Table 3-75). The statistical results were significant ( $p < 0.05$ ) for all five BDE congeners (Table 3-75), indicating the differences in the lipid-normalized mean values for the trophic groups were greater than would be expected by chance. Next, the Holm-Sidak method was used for all pairwise multiple comparisons. For BDEs-47, 100, and 153, there were significant differences ( $p < 0.05$ ) between the predator and omnivore trophic groups, as well as between the predator and benthic trophic groups (Table 3-76). In all cases, the corresponding lipid-normalized mean BDE concentrations were higher in the predator fish (Table 3-74). There was also a significant difference ( $p < 0.05$ ) between the predator and benthic trophic groups for BDE-49 (Table 3-76), where the mean value was higher in the predator fish (Table 3-74). All other pairwise comparisons were not significant ( $p > 0.05$ ), including the omnivore and benthic trophic group pairwise comparisons for all five lipid-normalized BDEs (Table 3-76).

Despite the small sample size of this study, useful results were obtained. A broader fish survey, with trophic samples from a greater number of lakes in different land use areas, would be helpful to provide greater statistical power than what was conducted here. Ruge et al. (2015) showed that BDE concentrations in the air and water of Lake Superior were highest near urban and populated areas, such as Duluth, MN. Thus, one could hypothesize that fish from urban lakes would be likely to have statistically higher concentrations of certain BDE congeners than fish from lakes dominated by other land uses.

## UTL values

UTL values were calculated for the four BDE congeners and total PBDEs with <80% nondetects in sediment samples (Table 3-77). BDEs-47 and 99 did not have any outliers, whereas the higher brominated BDEs (i.e., BDEs-206 and 209) and Total PBDEs had outliers removed before the UTL values

Table 3-74. Summary Statistics of Lipid-Normalized BDE Concentrations for Three Trophic Classes of Fish

BDE Congener and Fish Trophic Level	N	Concentration (pg/g lipid)				
		Mean	SD	Median	Minimum	Maximum
BDE-47						
Predator	5	889.3	635.0	792.3	282.9	1958.1
Omnivore	5	267.6	255.3	208.9	59.9	701.8
Benthic	3	140.7	43.6	138.2	98.4	185.5
BDE-49						
Predator	5	186.3	197.6	101.5	85.5	539.5
Omnivore	5	68.3	52.4	72.4	15.0	138.9
Benthic	3	16.9	10.7	21.9	4.6	24.2
BDE-99						
Predator	5	392.6	201.3	424.1	133.9	627.9
Omnivore	5	119.2	194.4	32.2	11.0	465.5
Benthic	3	71.7	59.7	89.6	5.1	120.4
BDE-100						
Predator	5	202.8	128.6	185.9	60.3	412.6
Omnivore	5	47.8	45.6	30.6	14.7	126.2
Benthic	3	29.8	13.5	29.3	16.6	43.5
BDE-153						
Predator	5	42.8	16.4	45.9	15.4	59.5
Omnivore	5	11.0	14.0	5.2	2.9	36.0
Benthic	3	9.6	6.9	8.6	3.3	16.9

BDE = brominated diphenyl ether; N = number of lakes for which fish species were collected for composite samples; SD = standard deviation.

Table 3-75. Statistical Comparisons of Lipid-Normalized BDE Congeners by Trophic Classes of Fish

BDE Congener	Transformation of Data	One-Way ANOVA (p-value)
BDE-47	natural log	0.018*
BDE-49	natural log	0.017*
BDE-99	not needed	0.049*
BDE-100	natural log	0.007*
BDE-153	not needed	0.008*

BDE = brominated diphenyl ether.

\* Statistically significant (p<0.05).

were calculated. Lake #41 (Spring) was a consistent outlier, and two other lakes in central Minnesota were also outliers for BDE-209 (lake #23) and Total PBDEs (lake #21). In the future, it would be useful to analyze a shorter depth interval (e.g., upper 5 cm) to better represent recent inputs and to assess possible reductions in PBDEs after statewide bans and national restrictions on some homolog groups.

Table 3-76. Multiple Pairwise Comparisons by Fish Trophic Classes for Lipid-Normalized BDEs with Significant One-Way ANOVA Results (Table 3-75). Pairs Shaded "Yes" are Significantly Different ( $p < 0.05$ ) from Each Other as Determined by the Holm-Sidak Method.

BDE Congener	p<0.05		
	Predator vs. Omnivore	Predator vs. Benthic	Omnivore vs. Benthic
BDE-47 <sup>1</sup>	Yes	Yes	No
BDE-49 <sup>1</sup>	No	Yes	No
BDE-99	No	No	No
BDE-100 <sup>1</sup>	Yes	Yes	No
BDE-153	Yes	Yes	No

BDE = brominated diphenyl ether; ANOVA = analysis of variance.

<sup>1</sup> Based on natural log transformation of the data.



Table 3-77. UTLs of Detected and Censored BDE Congener and Total PBDE Data in Sediment Samples with Outliers Removed at the 5% Significance Level (units in µg/kg dry wt.)

BDE Congener or Total PBDEs	N (# detects)	% Nondetects	Potential Outliers Removed at 5% Significance Levels (lake ID numbers)	Normal Distribution and KM Estimates*	Gamma Distribution and KM Estimates*	
					95% Approx. Gamma UTL with 95% Coverage	
				95% UTL with 95% Coverage	WH	HW
BDE-47	52 (17)	67.3	-	1.9		
BDE-99	52 (11)	78.8	-	2.1		
BDE-206	51 (15)	70.6	41		11.7	11.5
BDE-209	50 (42)	16.0	23, 41		27.9	29.3
Total PBDEs	50 (41)	18.0	21, 41		55.5	57.5

UTL = Upper Tolerance Limit; BDE = brominated diphenyl ether; PBDE = polybrominated diphenyl ethers; KM = Kaplan-Meier; WH = Wilson Hilferty; HW = Hawkins Wixley.

\* UTLs for normally distributed data were preferred over those derived from gamma distributed data. When the data were not normally distributed, the gamma distribution was used to estimate UTL values. Gamma UTLs were calculated two different ways, for which professional judgment can be used to select the value of interest.

## Compilation of NLAP data

### *Highlights:*

- Parametric and nonparametric correlation analyses showed that:
  - Individual PAH compounds tended to correlate most highly with other PAH compounds.
  - Metals tended to correlate most highly with other metals, except for lead which correlated most highly with two, six-ring PAH compounds.
  - Metalloids did not correlate well with other parameters.
  - Individual particle size classes had the highest correlations with other particle size classes.
  - TOC was most highly correlated with C1-dibenzothiophenes and zinc.
- Multivariate statistical analyses were run on two groups of analytical parameters. These analyses showed that:
  - Metals were the most important for distinguishing between NLAP lake sediments based on the PCA and HCA analyses of six common metals, mean PEC-Qs, and  $\Sigma\text{PAH}_{13}$ .
  - When biphenyl, particle size classes, and TOC were added to the above analyses, it resulted in particle size playing an important role in distinguishing between lakes.
  - With both analyses, the sediments of developed lakes (i.e., #27 and 38) differed significantly ( $p < 0.05$ ) from lakes in other major land use classes.

In order to examine the NLAP data in a holistic way, a variety of data were compiled together for statistical analyses. The analyte list was limited to parameters measured in all 54 sediment samples. Any censored data for individual analytes had to have <5% nondetects. The general analyte list included a number of metals and metalloids, individual PAHs,  $\Sigma\text{PAH}_{13}$ ,  $\Sigma\text{PAH}_{17}$ ,  $\Sigma\text{PAH}_{34}$ , biphenyl, particle size classes, and TOC. In addition, metal PEC-Qs and mean PEC-Qs were also included in the analyses.

For data that were normally distributed, a Pearson product-moment correlation was run on the data after removing outliers at the 5% significance level. This statistical method measures the strength of a linear relationship between paired data. The top two highest correlating analytes for each chemical or particle size parameter are provided in Table 3-78. Individual PAH compounds were usually highly significantly correlated with other PAH compounds. This finding was consistent with PAH compounds always occurring as a mixture in the environment. In particular, the six-ring PAH compounds of benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene had the highest Pearson  $r$  value of 0.993 (Table 3-78). These PAH compounds are more recalcitrant in the environment and do not readily break down. C1-naphthalenes were also highly correlated to individual alkylated methylnaphthalenes included in this general category of alkylated PAHs. Metals tended to correlate best with other metals. Aluminum had the highest correlations with vanadium ( $r = 0.886$ ) and nickel ( $r = 0.818$ ). This finding was consistent with other studies and is why aluminum and vanadium have been used to normalize other metal and metalloid concentrations; they are often reference elements in sediment samples (Carvalho et al. 2002). Lead was different than the other metals in that the two compounds that it had the highest correlations with were six-ring PAH compounds: indeno[1,2,3-cd]pyrene (Figure 3-51) and benzo[g,h,i]perylene. The

Table 3-78. Compilation of the Highest Pearson Product Moment Correlations (R) Based on Using ProUCL 5.0 Normality Designations. Outliers were Removed at the 5% Significance Limit.

Parameter	Highest R Value	Highest Correlating Parameter	Second Highest R Value	Second Highest Correlating Parameter
Benzo[g,h,i]perylene	<b>0.993</b>	Indeno[1,2,3-cd]pyrene	<b>0.911</b>	Dibenzo[a,h]anthracene
Indeno[1,2,3-cd]pyrene	<b>0.993</b>	Benzo[g,h,i]perylene	<b>0.906</b>	Dibenzo[a,h]anthracene
2-Methylnaphthalene	<b>0.992</b>	C1-Naphthalenes	<b>0.937</b>	1-Methylnaphthalene
C1-Naphthalenes	<b>0.992</b>	2-Methylnaphthalene	<b>0.968</b>	1-Methylnaphthalene
$\Sigma$ PAH <sub>13</sub>	<b>0.985</b>	$\Sigma$ PAH <sub>17</sub>	<b>0.872</b>	C1-Phenanthrenes/- Anthracenes
$\Sigma$ PAH <sub>17</sub>	<b>0.985</b>	$\Sigma$ PAH <sub>13</sub>	<b>0.909</b>	Chrysene
1-Methylnaphthalene	<b>0.968</b>	C1-Naphthalenes	<b>0.937</b>	2-Methylnaphthalene
Dibenzo[a,h]anthracene*	<b>0.911</b>	Benzo[g,h,i]perylene	<b>0.906</b>	Indeno[1,2,3-cd]pyrene
C1-Phenanthrenes/Anthracenes	<b>0.910</b>	Dibenzothiophene	<b>0.872</b>	$\Sigma$ PAH <sub>13</sub>
Dibenzothiophene*	<b>0.910</b>	C1-Phenanthrenes/- Anthracenes	<b>0.845</b>	$\Sigma$ PAH <sub>13</sub>
Chrysene	<b>0.909</b>	$\Sigma$ PAH <sub>17</sub>	<b>0.860</b>	$\Sigma$ PAH <sub>13</sub>
Naphthalene	<b>0.897</b>	C1-Naphthalenes	<b>0.894</b>	2-Methylnaphthalene
Aluminum	<b>0.886</b>	Vanadium	<b>0.818</b>	Nickel
Vanadium*	<b>0.886</b>	Aluminum	<b>0.824</b>	Nickel
Benzo[k]fluoranthene	<b>0.870</b>	Indeno[1,2,3-cd]pyrene	<b>0.860</b>	Benzo[g,h,i]perylene
Anthracene	<b>0.831</b>	Dibenzothiophene	<b>0.828</b>	$\Sigma$ PAH <sub>13</sub>
C3-Naphthalenes	<b>0.831</b>	C1-Phenanthrenes/- Anthracenes	<b>0.828</b>	$\Sigma$ PAH <sub>13</sub>
Nickel	<b>0.824</b>	Vanadium	<b>0.818</b>	Aluminum
C2-Phenanthrenes/Anthracenes*	<b>0.815</b>	$\Sigma$ PAH <sub>17</sub>	<b>0.812</b>	$\Sigma$ PAH <sub>13</sub>
Lead	<b>0.771</b>	Indeno[1,2,3-cd]pyrene	<b>0.767</b>	Benzo[g,h,i]perylene
Zinc	<b>0.761</b>	Nickel	<b>0.735</b>	Copper
C1-Dibenzothiophenes*	<b>0.750</b>	C3-Naphthalenes	<b>0.707</b>	TOC
Copper	<b>0.735</b>	Zinc	<b>0.668</b>	Nickel
$\Sigma$ PAH <sub>34</sub>	<b>0.729</b>	$\Sigma$ PAH <sub>17</sub>	<b>0.723</b>	Benzo[k]fluoranthene
TOC	<b>0.707</b>	C1-Dibenzothiophenes	<b>0.618</b>	Zinc
Barium	<b>0.662</b>	Manganese	<b>-0.447</b>	Lead
Manganese	<b>0.662</b>	Barium	<b>-0.368</b>	TOC
Sand	<b>-0.621</b>	Silt	<b>-0.531</b>	Clay
Silt	<b>-0.621</b>	Sand	<b>-0.475</b>	TOC
C1-Fluorenes	<b>0.619</b>	$\Sigma$ PAH <sub>13</sub>	<b>0.587</b>	$\Sigma$ PAH <sub>17</sub>

Table 3-78. Continued

Parameter	Highest R Value	Highest Correlating Parameter	Second Highest R Value	Second Highest Correlating Parameter
Fluorene	<b>0.55</b>	$\Sigma$ PAH <sub>13</sub>	<b>0.514</b>	C1-Fluorenes
Clay	<b>-0.531</b>	Sand	<b>0.389</b>	Dibenzo[a,h]anthracene
Selenium*	0.229	Anthracene	-0.212	C1-Fluorenes

\* These chemicals had a small number of censored values (1 to 3 samples), for which the full reporting limit was substituted.

Black font: not statistically significant,  $p > 0.05$

Blue, bold, italic font: statistically significant,  $p < 0.05$  and  $> 0.001$

Red, bold font: highly statistically significant,  $p < 0.001$

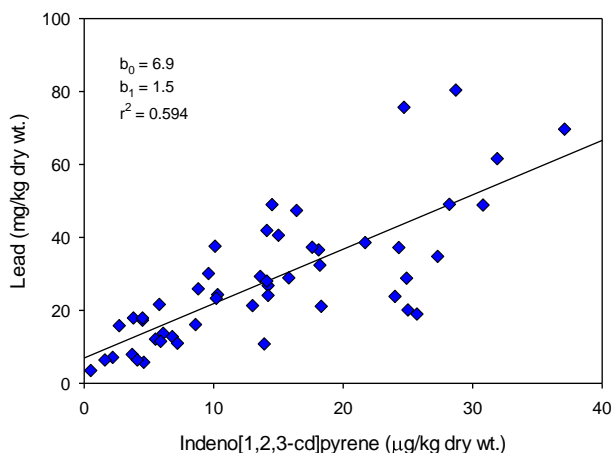


Figure 3-47. Scatter plot of lead vs. indeno[1,2,3-cd]pyrene. For the linear regression,  $b_0$  = intercept,  $b_1$  = slope, and  $r^2$  = coefficient of determination.

metalloid selenium did not have any statistically significant correlations with any other compounds. Individual particle size classes had the highest correlations with other particle size classes, and TOC was most highly correlated with C1-dibenzothiophenes ( $r = 0.707$ ) and zinc ( $r = 0.618$ ; Figures 3-52a, b).

The Spearman rank-order correlation is the nonparametric version of the Pearson product-moment correlation. It was run on the NLAP data measured in each sediment sample, including data that did not follow a normal distribution after removing outliers at the 5% significance level. Compilations of the two highest Spearman rho ( $\rho$ ) values for each parameter are provided in Table 3-79. Most of the analytes included in the Pearson product-moment correlation had a similar ranking of the highest correlating parameters in the Spearman rank-order correlations. Some exceptions to this finding included: C1-phenanthrenes/anthracenes, anthracene, C1-fluorenes, zinc, C3-naphthalenes,  $\Sigma$ PAH<sub>34</sub>, fluorine, and selenium (Table 3-79). The mean PEC-Qs had the highest Spearman rho values with metal PEC-Qs ( $\rho = 0.908$ ) and chromium ( $\rho = 0.776$ ), demonstrating that metals were more highly associated than PAHs in the mean PEC-Qs. This was because PAHs occurred at low concentrations in the NLAP lake sediments outside of the Twin Cities metropolitan area. Arsenic and selenium, both metalloids, had the lowest

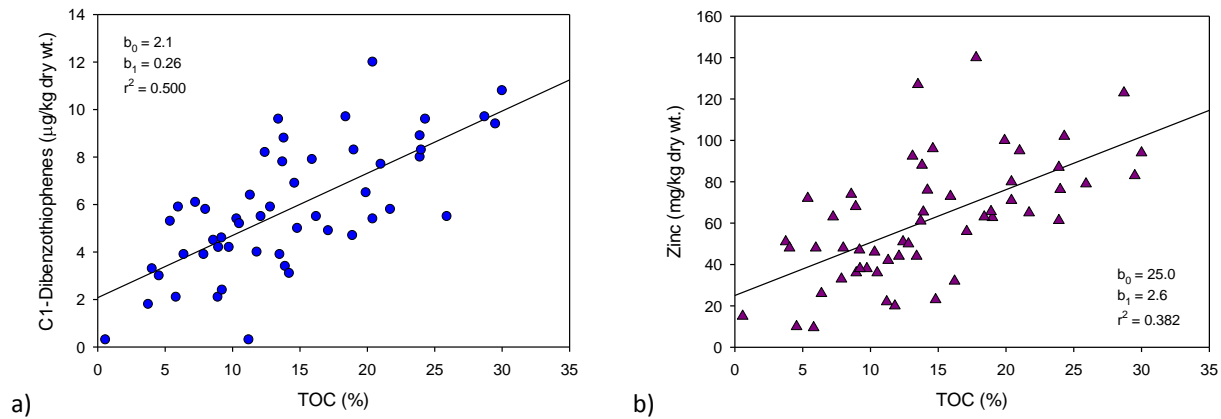


Figure 3-48. a) Scatter plot of C1-dibenzothiophene vs. TOC and b) zinc vs. TOC. For each graph,  $b_0$  = intercept,  $b_1$  = slope, and  $r^2$  = coefficient of determination.

“top” Spearman rho values of the analytes included in Table 3-79. Thus, the strength and direction of the association that existed between these metalloids and other parameters was weaker than those observed for the other analytes.

PCA analysis of the 54 lakes was performed with two different compilations of parameters. First, the PCA analysis was done for a subset of chemicals that also had SQT values, including: five metals (chromium, copper, lead, nickel, and zinc), the metalloid arsenic (hereafter lumped with the other metals),  $\Sigma$ PAH<sub>13</sub>, and mean PEC-Qs. The scree plot, component loading plots, and component score plots are provided in Appendix M. Three principal components accounted for 80.1% of the variance in the data. Each principal component is a linear combination of the original variables, after each original variable has been centered about its mean. The Eigenvectors in PC1 were highest for zinc, mean PEC-Qs, and lead, while nickel and arsenic contributed to PC2. Arsenic, copper, and zinc contributed the greatest Eigenvectors to PC3 (Appendix M). The unexplained variance ranged from 5.3% for mean PEC-Qs to 48.1% for chromium (Appendix M). Four significant outliers ( $p < 0.05$ ) were noted from the component scores, including: lakes #6 (Becoosin), 27 (Nokomis), 38 (Snail), and 51 (Elk; Figure 3-53; Appendix M). The groups on this plot were based on the HCA set-up with the paired group (UPGMA) algorithm and the Gower similarity index (Appendix M). Lakes #38 and 51 had the highest arsenic concentrations, respectively, noted in this study. However, the two developed lakes (#27 and #38) had more in common with each other from the HCA analysis (Appendix M) than any of the other lakes. The sediments in both developed lakes had the highest lead concentrations, and #27 also had the highest  $\Sigma$ PAH<sub>13</sub> concentration. The sediment of lake #6 had the highest copper concentration of the 54 lakes. In addition to the outliers previously noted, the northeastern Minnesota lakes of #3 (Arthur), 4 (Aspen), and 5 (August) clustered together. These lakes tended to have higher chromium and elevated nickel concentrations compared to the other lakes. All other lakes, encompassing cultivated, forested, and lakes and wetlands land uses, were clustered together in one group.

The second PCA analysis used the same parameters as the first PCA analysis with the addition of biphenyl, particle size parameters (i.e., clay, silt, and sand), and TOC (Figure 3-54). The scree plot, component loading plots, and component score plots are provided in Appendix M. Three principal components accounted for 69.6% of the variance in the data. The Eigenvectors in PC1 were highest for zinc, mean PEC-Qs, lead and TOC, while sand contributed to PC2. Clay, silt, and biphenyl contributed the greatest Eigenvectors to PC3 (Appendix M). The unexplained variance ranged from 5.6% for sand to 78.1% for arsenic (Appendix M). Two significant outliers ( $p < 0.05$ ) were noted from the component

Table 3-79. Compilation of the Highest Spearman Rho Values for Selected Chemical Parameters. Outliers were Removed at the 5% Significance Level.

Parameter	Highest Rho Value	Highest Correlating Parameter	Second Highest Rho Value	Second Highest Correlating Parameter
2-Methylnaphthalene	<b>0.995</b>	C1-Naphthalenes	<b>0.949</b>	1-Methylnaphthalene
C1-Naphthalenes	<b>0.995</b>	2-Methylnaphthalene	<b>0.966</b>	1-Methylnaphthalene
Benzo[g,h,i]perylene	<b>0.991</b>	Indeno[1,2,3-cd]pyrene	<b>0.923</b>	Benzo[b]fluoranthene
Indeno[1,2,3-cd]pyrene	<b>0.991</b>	Benzo[g,h,i]perylene	<b>0.932</b>	Benzo[b]fluoranthene
ΣPAH <sub>13</sub>	<b>0.984</b>	ΣPAH <sub>17</sub>	<b>0.938</b>	Fluoranthene
ΣPAH <sub>17</sub>	<b>0.984</b>	ΣPAH <sub>13</sub>	<b>0.952</b>	Fluoranthene
Fluoranthene	<b>0.969</b>	Pyrene	<b>0.952</b>	ΣPAH <sub>17</sub>
Pyrene	<b>0.969</b>	Fluoranthene	<b>0.949</b>	C1-Fluoranthenes/Pyrenes
1-Methylnaphthalene	<b>0.966</b>	C1-Naphthalenes	<b>0.949</b>	2-Methylnaphthalene
2,6-Dimethylnaphthalene	<b>0.963</b>	C2-Naphthalenes	<b>0.608</b>	C1-Dibenzothiophenes
C2-Naphthalenes	<b>0.963</b>	2,6-Dimethylnaphthalene	<b>0.688</b>	C1-Dibenzothiophenes
C1-Fluoranthenes/Pyrenes	<b>0.951</b>	Fluoranthene	<b>0.949</b>	Pyrene
C1-Phenanthrenes/-Anthracenes	<b>0.940</b>	Phenanthrene	<b>0.925</b>	1-Methylphenanthrene
Naphthalene	<b>0.940</b>	C1-Naphthalenes	<b>0.931</b>	2-Methylnaphthalene
Phenanthrene	<b>0.940</b>	C1-Phenanthrenes/-Anthracenes	<b>0.911</b>	Dibenzothiophene
Benzo[b]fluoranthene	<b>0.932</b>	Indeno[1,2,3-cd]pyrene	<b>0.930</b>	Benzo[a]pyrene
Benzo[a]pyrene	<b>0.930</b>	Benzo[b]fluoranthene	<b>0.903</b>	Benzo[k]fluoranthene
1-Methylphenanthrene	<b>0.925</b>	C1-Phenanthrenes/-Anthracenes	<b>0.879</b>	Phenanthrene
Benzo[a]anthracene	<b>0.923</b>	Pyrene	<b>0.903</b>	Chrysene
Dibenzo[a,h]anthracene*	<b>0.922</b>	Benzo[g,h,i]perylene	<b>0.913</b>	Indeno[1,2,3-cd]pyrene
Dibenzothiophene*	<b>0.914</b>	C1-Phenanthrenes/-Anthracenes	<b>0.911</b>	Phenanthrene
Mean PEC-Q	<b>0.908</b>	Metal PEC-Q	<b>0.776</b>	Chromium
Metal PEC-Q	<b>0.908</b>	Mean PEC-Q	<b>0.83</b>	Zinc
Benzo[k]fluoranthene	<b>0.903</b>	Benzo[a]pyrene	<b>0.886</b>	Indeno[1,2,3-cd]pyrene
Chrysene	<b>0.903</b>	Benzo[a]anthracene or ΣPAH <sub>17</sub>	<b>0.88</b>	ΣPAH <sub>13</sub>
Anthracene	<b>0.893</b>	Phenanthrene	<b>0.891</b>	C1-Phenanthrenes/-Anthracenes
Aluminum	<b>0.889</b>	Vanadium	<b>0.849</b>	Nickel
Vanadium*	<b>0.889</b>	Aluminum	<b>0.817</b>	Nickel
Cobalt	<b>0.887</b>	Nickel	<b>0.857</b>	Zinc

Table 3-79. Continued

Parameter	Highest Rho Value	Highest Correlating Parameter	Second Highest Rho Value	Second Highest Correlating Parameter
Nickel	<b>0.887</b>	Cobalt	<b>0.849</b>	Aluminum
Biphenyl	<b>0.882</b>	Naphthalene	<b>0.794</b>	C1-Naphthalenes
Acenaphthene	<b>0.871</b>	C1-Fluorenes	<b>0.698</b>	C1-Chrysenes
C1-Fluorenes	<b>0.871</b>	Acenaphthene	<b>0.733</b>	C1-Chrysenes
Zinc	<b>0.857</b>	Cobalt	<b>0.83</b>	Metal PEC-Q
Acenaphthylene	<b>0.849</b>	$\Sigma$ PAH <sub>13</sub>	<b>0.847</b>	$\Sigma$ PAH <sub>17</sub>
C2-Phenanthrenes/-Anthracenes*	<b>0.836</b>	C1-Fluoranthenes/-Pyrenes	<b>0.785</b>	$\Sigma$ PAH <sub>17</sub>
Benzo[e]pyrene	<b>0.835</b>	Dibenzo[a,h]anthracene	<b>0.828</b>	C1-Chrysenes
C1-Chrysenes*	<b>0.828</b>	Benzo[e]pyrene	<b>0.779</b>	Chrysene
Chromium	<b>0.825</b>	Metal PEC-Q	<b>0.798</b>	Cobalt
C3-Naphthalenes	<b>0.804</b>	1-Methylnaphthalene	<b>0.798</b>	Acenaphthylene
Lead	<b>0.785</b>	Indeno[1,2,3-cd]pyrene	<b>0.784</b>	Benzo[g,h,i]perylene
Copper	<b>0.782</b>	Chromium	<b>0.774</b>	Zinc
$\Sigma$ PAH <sub>34</sub>	<b>0.772</b>	C1-Fluoranthenes/-Pyrenes	<b>0.755</b>	Benzo[e]pyrene
Barium	<b>0.732</b>	Manganese	<b>-0.443</b>	TOC
Manganese	<b>0.732</b>	Barium	<b>-0.429</b>	TOC
C2-Fluorenes*	<b>0.731</b>	C1-Fluorenes	<b>0.587</b>	Acenaphthene
C1-Dibenzothiophenes*	<b>0.725</b>	C3-Naphthalenes	<b>0.688</b>	C2-Naphthalenes or TOC
TOC	<b>0.688</b>	C1-Dibenzothiophenes	<b>0.64</b>	Zinc
1,6,7-Trimethylnaphthalene	<b>0.661</b>	C3-Naphthalenes	<b>0.626</b>	C2-Naphthalenes
Perylene	<b>0.659</b>	$\Sigma$ PAH <sub>34</sub>	<b>0.539</b>	Benzo[k]fluoranthene
Sand	<b>-0.644</b>	Silt	<b>-0.512</b>	Clay
Silt	<b>-0.644</b>	Sand	<b>-0.508</b>	TOC
Fluorene	<b>0.583</b>	Phenanthrene	<b>0.562</b>	$\Sigma$ PAH <sub>13</sub>
Clay	<b>-0.512</b>	Sand	<b>0.382</b>	Aluminum
Arsenic	<b>0.452</b>	2,6-Dimethylnaphthalene	<b>0.418</b>	Acenaphthylene
Selenium*	<b>0.331</b>	2,6-Dimethylnaphthalene	<b>0.302</b>	Arsenic

\* These chemicals had a small number of censored values (1 to 3 samples), for which the full reporting limit was substituted.

Blue, bold, italic font: statistically significant,  $p < 0.05$  and  $> 0.001$

Red, bold font: highly statistically significant,  $p < 0.001$

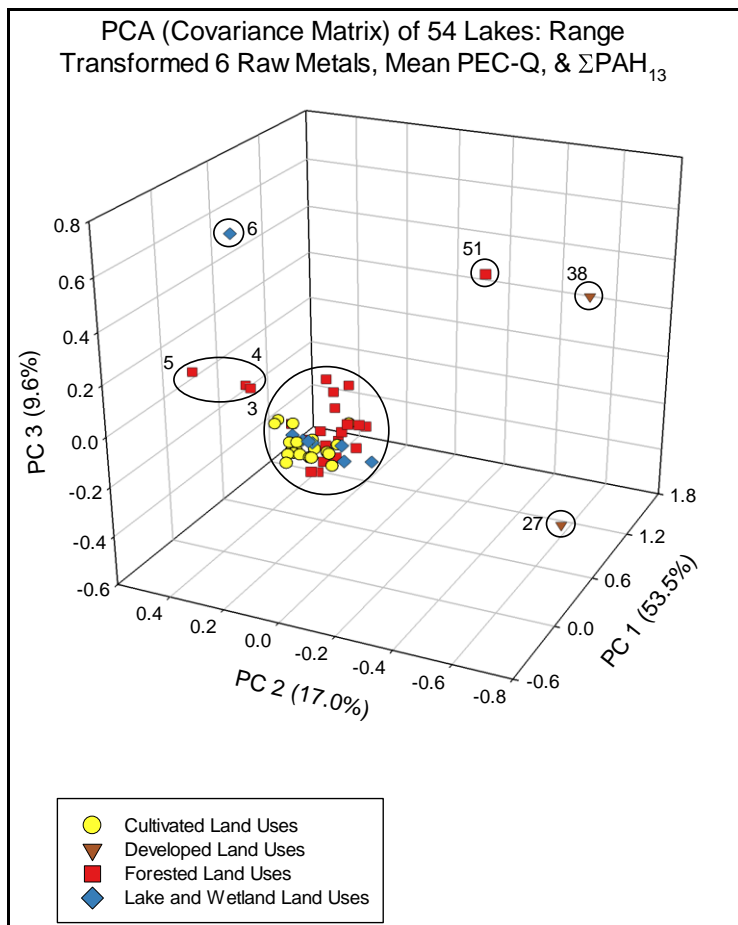


Figure 3-49. PCA plot of three principal components for the metals, mean PEC-Q, and  $\Sigma\text{PAH}_{13}$  parameters that also have SQT values. The significant outliers ( $p < 0.05$ ) identified in the PCA analysis included lakes #6, 27, 38, and 51.

scores, including the developed lakes of #27 (Nokomis) and 38 (Snail; Figure 3-54; Appendix M). The groups on this plot were based on the HCA set-up with the paired group (UPGMA) algorithm and the Gower similarity index (Appendix M). Similar to the first PCA analysis, the developed lakes had more in common with each other than the other lakes according to the HCA analysis (Appendix M). For this second PCA analysis, particle size had a major impact on the PC2 and PC3 Eigenvectors. If one was only interested in chemical parameters that had corresponding SQT values, then the first PCA analysis would provide a better multivariate assessment of the data. Nevertheless, both PCA plots clearly demonstrated that the developed lakes (#27 and 38) differed significantly ( $p < 0.05$ ) from the other NLAP lakes encompassed by other major land uses.



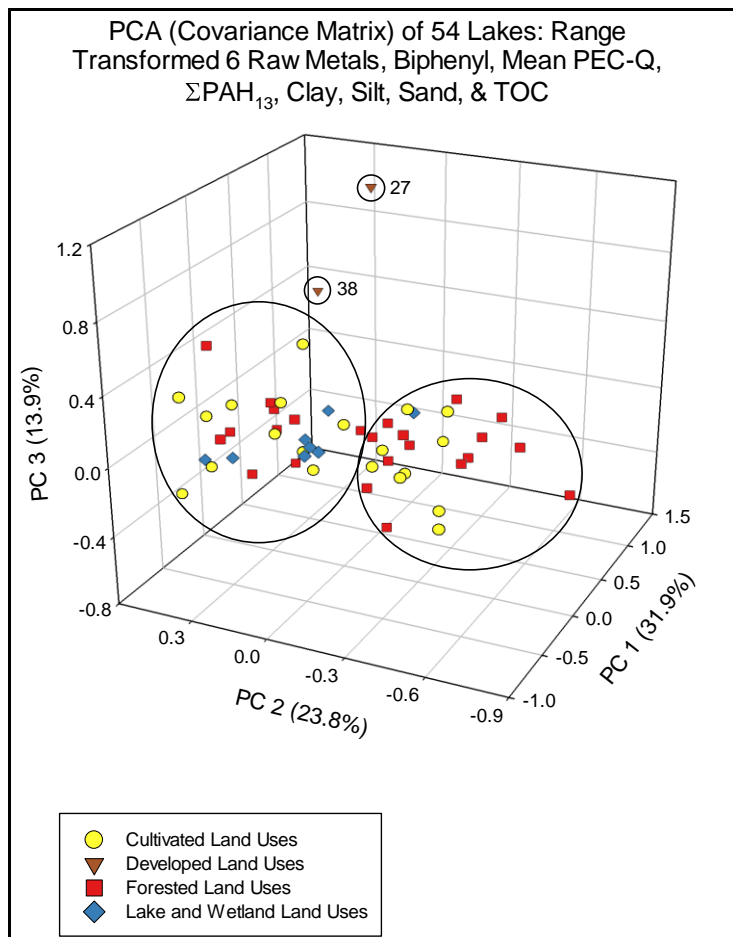


Figure 3-50. PCA plot of three principal components for the parameters in Figure 3-53 plus particle size fractions, TOC, and biphenyl. The significant outliers ( $p < 0.05$ ) identified in the PCA analysis included lakes #27 and 38.

## Section 4: Comparisons of wetland and St. Louis River AOC sediment quality to NLAP sediment quality

---

### *Highlights:*

- Elevated chloride concentrations were found in both urban and agricultural wetland sediments. Possible sources are discussed.
- The wetland and St. Louis River AOC data had a small percentage of samples likely to cause harmful effects to benthic invertebrates (i.e., parameters > Level II SQT values).
- The St. Louis River AOC samples tended to have a higher percentage of samples between the Level I and Level II SQTs than the wetland samples.
- For the wetland data, the highest exceedances of the NLAP UTL values occurred for beryllium > silver > selenium > vanadium.
- For the St. Louis River AOC data, the highest exceedances of the NLAP UTL values occurred for  $\Sigma\text{PAH}_{13}$  > aquatic life PCDD/F TEQs (W\_TEQ\_KMDF) > copper > nickel.
- Compilation Q-Q plots were used to show differences and similarities between the NLAP, wetland, and St. Louis River AOC data sets.

The NLAP sediment quality data provided a valuable, random data set to compare to other study data collected from Minnesota waterways. In particular, sediment chemistry data from a wetland survey and newer data from the St. Louis River AOC were selected for this comparison.

### Summary of wetland data

The wetland sediment chemistry data were analyzed using ProUCL 5.0 software. A compilation of the summary statistics, percentiles, box plots, and individual Q-Q plots for metals, metalloids, metal PEC-Qs, and chloride are provided in Appendix N. Outlier tests were also run in ProUCL 5.0, but only the number of outliers (rather than specific site IDs) was provided alongside the Q-Q plots. These statistical analyses included 27 samples that were excluded from further data comparisons and GIS work due to spurious GIS coordinates measured in 1999; the spurious sites comprised Site ID's 86, 87, and 89 – 113. The quality of the analytical results for these 27 samples appeared acceptable. In addition, Site ID #224 (DURice) was included in these ProUCL 5.0 statistical analyses, but excluded from further data comparisons based on the recommendation of Mark Gernes (MPCA). Site ID #224 was located by a suspected contaminated site, and it had high copper (226 mg/kg dry wt.) and zinc (829 mg/kg dry wt.) concentrations.

The wetland data set included eight unique chemical parameters that were not measured in the NLAP lake sediments. These parameters included chloride and the following metals: boron, iron, lithium, rubidium, silicon, strontium, and titanium. Strontium was not detected in any of the wetland sediments, and lithium and boron had 52.2% and 12.4% nondetects, respectively (Appendix N). All other metals and metalloids analyzed in the NLAP lake sediments were also analyzed in the wetland sediments, except for mercury. Comparisons of the metal, metalloid, and metal PEC-Q values to benchmark values and NLAP

data will be provided in subsequent sections. TOC was measured in the wetland sediments, but was not included in the initial data request. Gernes and Helgen (1999) reported TOC values ranging from 2.1 – 31.2% in 26 wetlands from reference, agricultural, and stormwater-influenced sites. In comparison, TOC values ranged from 0.57 – 30.0% in the NLAP lake sediments. Thus, the TOC ranges were comparable between data sets.

Since chloride does not have any sediment benchmark values, the wetland results will be presented in this section. Chloride is of concern because it can make surface water and groundwater more saline, resulting in adverse ecological and drinking water impacts. It can also cause density stratification in small lakes. Once surface water is contaminated, chloride can only be removed by expensive reverse osmosis technology (MPCA 2011). The MPCA, with the assistance of numerous partner agencies and groups, developed a draft chloride management plan for the Twin Cities metropolitan area (MPCA 2016b). The main purpose of this plan is to reduce the usage of salt, particularly for deicing roads, parking lots, and sidewalks, as well as for residential water softening. While this plan considered surface water and groundwater concentrations of chloride, the role of sediments in the transport and fate of chloride in the metro area was not considered. This was probably because chloride containing compounds are highly soluble in water; once they dissociate, the chloride ion is highly mobile (CCME 2011). There is also a paucity of chloride data in freshwater sediments. Chloride was measured in Lake Ontario sediments in an older study, which showed the amount of chloride accumulated in the upper 30 cm of sediments was on the order of 1-2% of the amount of chloride in lake water (Lerman and Weiler 1970). Figure 4-1 shows the concentration ranges of chloride in surficial wetland sediments. Over 25 sites were sampled within the Twin Cities metropolitan area, with most sites showing elevated chloride concentrations. Deicing salt was the most likely source of chloride to these metro wetlands, several of which received stormwater drainage. Sediments may be a repository for some chloride compounds, which can subsequently disassociate to pore water and overlying surface water. Brand et al. (2010) found that elevated amounts of chloride leached from stormwater pond sediments into the overlying water of treatment microcosms, resulting in decreased survival of gray treefrog (*Hyla versicolor*) embryos. This type of amphibian is commonly found in Minnesota ([http://www.dnr.state.mn.us/reptiles\\_amphibians/frogs\\_toads/treefrogs/gray.html](http://www.dnr.state.mn.us/reptiles_amphibians/frogs_toads/treefrogs/gray.html), accessed 1/19/2016). The agency should consider including sediment-associated chloride in future chloride management plans.

The highest concentration of chloride (i.e., 5821 mg/kg dry wt.) was observed at Site #131 (Henry) in Alexandria, MN (Figure 4-1). This amount was three times higher than the next most contaminated site located in Hennepin County (Twin Cities metropolitan area). Lake Henry is part of a chain of lakes in Alexandria. It is connected to Lake Agnes, which receives outflow water from Lake Winona. The Alexandria Lakes Area Sanitary District WWTP discharges into the south end of Lake Winona (AECOM, Inc. 2009). Treated wastewater can be an important source of chloride to some water systems, such as in Illinois (Table 4-1). Most of the land use inputs to Lake Henry are due to low to medium density residential development, for which roads, parking lots, and sidewalks comprise 25%, 1.0%, and 5.0%, respectively, of the total acreage (AECOM, Inc. 2009). Further work is needed to verify the high chloride value in Henry Lake, assess chloride concentrations in connecting lake sediments and water column samples, and to determine sources of chloride to this lake and wetland system.

Agricultural areas of Minnesota, particularly in southwest Minnesota, displayed elevated concentrations of chloride in wetland sediments (Figure 4-1). The extent to which these elevated concentrations could be due to natural sources of chloride is not known. For areas with shallow water tables, dissolved salts can precipitate and accumulate as groundwater is discharged through the soil surface (Seelig 2000). Eroded soils and dust can then be transported in surface runoff or by wind to adjacent waterbodies.

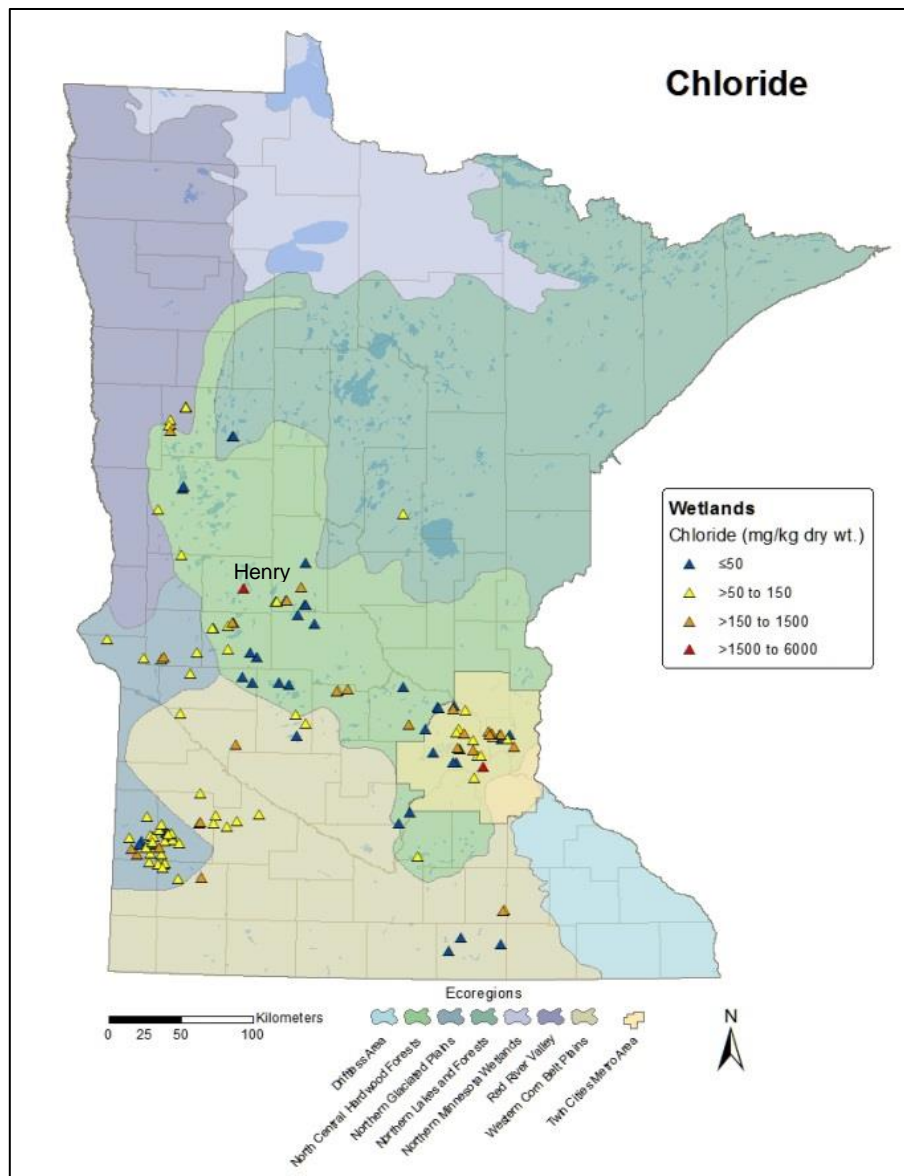


Figure 4-1. Concentration ranges of chloride in wetland sediments.

Eastern North Dakota has high saline soils and thus increased soluble salts in the tile effluent below farm fields, particularly for sulfate salts (Johnson 2010). The northern Red River Valley in North Dakota has widespread areas of saline soils that have high amounts of chloride salts (Seelig 2000). No information could be found about the presence of saline soils in Minnesota, although areas bordering North Dakota, particularly in the Red River Valley, would be a likely area to investigate. No wetlands were sampled in the Red River Valley of northwestern Minnesota for this data set. Salinization can also occur as a result of irrigation and wetland drainage if water is not managed properly (Seelig 2000). However, in 2012, only 2.8% of cultivated cropland was irrigated in Minnesota (U.S. Department of Agriculture 2015). If the amount of irrigated cropland acreage increases in the future, then salinization of soils may become a more important issue in Minnesota.

Fertilizer applications of potassium chloride (KCl) to row crops of corn, soybeans, and wheat is a possible source of chloride to Minnesota's agricultural wetlands. Fertilizer (KCl) was the second highest contributor of chloride fluxes in Illinois waters (Table 4-1; Kelly et al. 2012). For the latest available data,

Table 4-1. Annual Chloride Fluxes in Illinois (Kelly et al. 2012)

Source	Flux (metric tons)
Treated Wastewater	
MWRDGC	175,000
Remainder of Illinois	125,000
Atmospheric	18,000
Road Salt	471,000
Water Conditioning Salt	135,000
Fertilizer (KCl)	373,000
Livestock	139,000
Lake Michigan Withdrawals	34,000
Groundwater Withdrawals	
Public Supply Wells	12,500
Industrial/Commercial	5,300
Irrigation	10,000
Oil-Field Brines	23,000

MWRDGC = Metropolitan Water Reclamation District of Greater Chicago; KCl = potassium chloride.

the U.S. Department of Agriculture (USDA) indicates potash (mostly KCl) was used on 68% of corn acreage in Minnesota during 2010, 16% of soybean acreage in 2006, and 56% of wheat acreage in 2009 (<http://www.ers.usda.gov/data-products/fertilizer-use-and-price.aspx> accessed 1/6/2016). Row crop farming has also expanded in central Minnesota during the past decade due to higher crop prices (Figure 4-2). During 2008 to 2012, nearly 400 square miles of land was converted to row crops, including 13,742 acres of forest; this was the second highest amount in the nation (Lark et al. 2015). Minnesota ranked highest in the conversion of wetlands to cropland (25,659 acres) during 2008 - 2012 (Lark et al. 2015). These changes increase runoff and nutrients, which degrades the quality and quantity of water resources. In turn, these changes could result in higher costs to provide clean drinking water to river communities (Lark et al. 2015).

Some chloride compounds are included in agricultural products as inert ingredients. Very small quantities (10 ppm) of rare earth chlorides are used as tagging agents in herbicide and fungicide formulations to distinguish one company's formulation from another (Rosenblatt 2005). Rare earth chlorides may also be used in some fertilizers. The U.S. EPA reassessed the exemptions of seven rare earth chlorides in 2005 and determined the tolerance exemptions of these inert ingredients should be maintained (Rosenblatt 2005). This finding was based on the U.S. EPA's finding that small amounts of cerous chloride, dysprosium chloride, europic chloride, lanthanum chloride, scandium chloride, ytterbium chloride, and yttrium chloride were not expected to pose a hazard to humans or the environment (Ward 2005). These compounds are naturally present in background concentrations of agricultural soils. Therefore, it seems unlikely these compounds would contribute substantially to chloride concentrations observed in wetland sediments collected from agricultural areas.

Livestock waste is another potential source of chloride to surface water and ground water (Table 4-1; Kelly et al. 2012). Panno et al. (2006) measured chloride concentrations as high as 1980 mg/L in swine waste from Illinois farms. In 2007, Minnesota was ranked 8<sup>th</sup> in the country for the number of livestock (i.e., cattle, swine, and poultry) animal units (AUs), which comprised 3,268,570 AUs (USEPA 2013c). This amount was about 58.5% of the AUs in Iowa (rank #2), and slightly greater than the number of AUs in



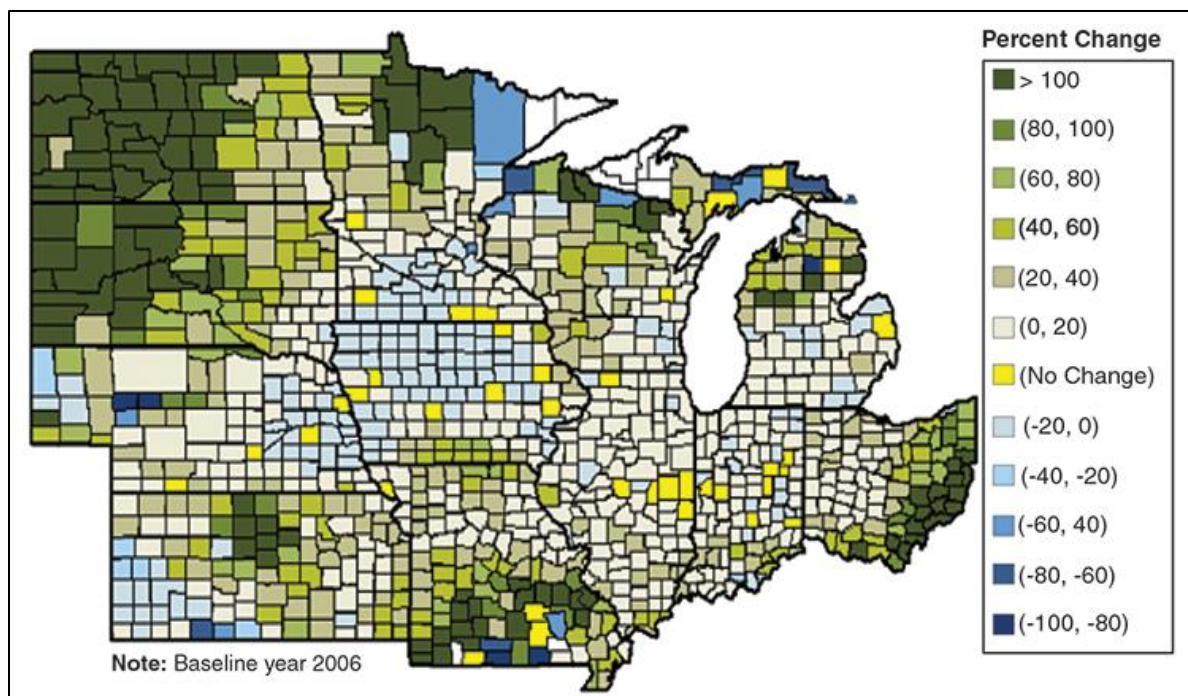


Figure 4-2. Corn and soybean acreage percentage changes from 2006 to 2014 using Cropland Data Layer (CDL) results (Gonzalez-Ramirez and Ji 2015).

Wisconsin (rank #9) and South Dakota (rank #10) during 2007 (USEPA 2013c). These Minnesota AUs produced 39,816,914 tons of manure, which was the 9<sup>th</sup> highest in the U.S. (USEPA 2013c). Although the production of livestock and poultry in the U.S. has more than doubled since the 1950s, the number of farm operations has decreased by 80% (USEPA 2013c). This decrease is due to a greater percentage of farms comprising small, medium, and large concentrated animal feeding operations (CAFOs). The large CAFOs present greater challenges for managing livestock waste, and greater risks to water quality in case of spills or other failures.

Additional work is needed to elucidate sources of chloride to wetlands in Minnesota. Frequent pulses of chloride to these waterways may lead to accumulation of chloride in sediments that had previously been unrecognized as an issue. Incorporation of BMPs would be helpful to reduce chloride loads to waterways. In addition, further study of chloride in the water column, pore water, and sediments of lakes and rivers would also be helpful to conduct.

## Summary of St. Louis River AOC data

The St. Louis River AOC data were analyzed using ProUCL 5.0 software. A compilation of the summary statistics, percentiles, box plots, and individual Q-Q plots for particle size, TOC, metals, metalloids, metal PEC-Qs,  $\Sigma$ PAH<sub>13</sub>, Total PCBs, mean PEC-Qs, and PCDD/F TEQs are provided in Appendix O. Outlier tests were also run in ProUCL 5.0, but only the number of outliers (rather than specific site IDs) were provided alongside the Q-Q plots.

The St. Louis River AOC data differed from the NLAP lake sediment data for a few parameters. Iron was measured in the AOC sediment samples, but not the NLAP samples. In addition, beryllium and molybdenum were not measured in the AOC sediment samples, but were included in the NLAP suite of metals. All other AOC sediment parameters matched the NLAP analytes.

## Comparisons to sediment benchmarks and NLAP data

### SQT and NLAP UTL comparisons

The wetland and St. Louis River AOC data were compared to two types of sediment benchmarks. First, the data were compared to the MPCA's Level I and Level II SQTs (Crane and Hennes 2007; Table 4-2). Second, the data were compared to the UTL values derived from the NLAP data set (Table 4-3). GIS maps were developed for chemicals that exceeded the Level II SQTs and had higher exceedances of the NLAP UTL values (Figures 4-3 to 4-15). An interactive Tableau workbook of selected wetland data was prepared, and it is available at: <http://tableau/#/views/WetlandMetals/Dashboard?iid=3>.

Exceedances of the Level II SQTs were low for most of the wetland and St. Louis River AOC chemical parameters (Table 4-2). This meant that a small percentage of samples had chemical values likely to cause harmful effects to benthic invertebrates. For the wetland samples, lead, copper, nickel, zinc, and metal PEC-Qs exceeded the corresponding Level II SQTs in <4% of samples. Most of these wetland samples were located in the Twin Cities metropolitan area and received stormwater runoff. PCDD/F TEQs (W\_TEQ\_KMDF) had the highest exceedance of the Level II SQTs for 6.8% of the St. Louis River AOC samples. Less than 1.5% of the AOC samples exceeded the corresponding Level II SQTs for cadmium, copper, lead, nickel, metal PEC-Qs, and  $\Sigma$ PAH<sub>13</sub>. The St. Louis River AOC samples tended to have a higher

Table 4-2. Comparison of Wetland and St. Louis River AOC Data to the Level I and Level II SQTs

Parameter	Wetland Data (%)			SLRAOC Data (%)		
	≤ Level I SQT	> Level I SQT and ≤ Level II SQT	> Level II SQT	≤ Level I SQT	> Level I SQT and ≤ Level II SQT	> Level II SQT
Metals & Metalloids						
Arsenic	94.0	6.0	0	100.0	0	0
Cadmium	92.7	7.3	0	64.3	35.3	0.3
Chromium	95.3	4.7	0	92.7	7.3	0
Copper	91.3	8.0	0.7	76.6	22.7	0.7
Lead	87.3	9.3	3.3	76.6	22.0	1.4
Mercury	N/A	N/A	N/A	76.6	23.4	0
Nickel	78.7	20.7	0.7	65.0	34.6	0.4
Zinc	89.3	10.0	0.7	73.8	26.2	0
Organics						
$\Sigma$ PAH <sub>13</sub>	N/A	N/A	N/A	71.8	27.7	0.4
Total PCBs	N/A	N/A	N/A	94.7	5.3	0
W_TEQ_KMDF	N/A	N/A	N/A	27.6	65.8	6.6
PEC-Qs						
Metal PEC-Qs	22.0	76.0	2.0	22.3	76.9	0.8
Mean PEC-Qs	22.0	76.0	2.0	66.4	33.6	0

AOC = Area of Concern; SLRAOC = St. Louis River Area of Concern; SQT = sediment quality target; N/A = not applicable (parameter not measured); PAH = polycyclic aromatic hydrocarbon; PCBs = polychlorinated biphenyls; W\_TEQ\_KMDF = aquatic life (W) toxic equivalents (TEQ) calculated by Kaplan-Meier (KM) for polychlorinated dibenzo-*p*-dioxins/dibenzo-furans (DF); PEC-Q = probable effect concentration.

percentage of samples between the Level I and Level II SQTs than the wetland samples. For metal PEC-Qs, the percentages in each SQT range were about the same for the wetland and AOC samples.

Comparison of the wetland and St. Louis River AOC data to the NLAP UTLs provided a more interesting comparison to a wider suite of chemicals and particle size. The highest exceedances of the UTLs in the wetland data set occurred for beryllium > silver > selenium > vanadium (Table 4-3). The wetland data had a higher number of samples in southwest Minnesota, where most of these exceedances occurred, than the NLAP data. Thus, there may have been more regional geological differences in these data or else more anthropogenic sources of these metals and metalloids. Beryllium, selenium, and vanadium can all be released from the combustion of fossil fuels. The only wetland metals that did not exceed the NLAP UTL values were barium and chromium. For the St. Louis River AOC, the highest exceedances of the NLAP UTLs were for  $\Sigma\text{PAH}_{13}$  > PCDD/F TEQs (W\_TEQ\_KMDF) > copper > nickel (Table 4-3). PAHs are widespread contaminants of potential concern in the lower St. Louis River estuary, particularly starting at the U.S. Steel Superfund site and progressing downstream along past industrial operations (Crane 2006; Figure 4-14). Current sources of PAHs to surficial sediments include: transport and deposition of resuspended PAH-contaminated sediments from elsewhere in the AOC, WWTP discharges, stormwater transport and discharge into the AOC (e.g., vehicle emission particles, abraded coal tar-based sealant runoff from parking lots and driveways, oil and fuel spills), and atmospheric deposition of coal combustion, vehicle emission, and wood combustion particles. Historical paper mills, located near Cloquet, MN, were the main source of 2,3,7,8-TCDD to the upper St. Louis River and reservoirs (Schubauer-Berigan and Crane 1996; Figure 4-15). PCDD/Fs are also constituents of interest at the U.S. Steel Superfund site (Barr 2013). Copper and nickel are constituents of interest at the Wire Mill delta of the U.S. Steel Superfund site (Barr 2013), which could contribute to downstream exceedances of these metals.

Copper is also a common contaminant in waterways from abraded brake linings in cars and trucks (TDC Environmental 2004). The states of California and Washington passed laws reducing the use of copper and other toxic compounds in automotive brake pads and shoes. In January 2015, brake manufacturers signed a memorandum of agreement with the U.S. EPA and the Environmental Council of the States to adopt standards based on Washington and California's brake laws (<http://www.ecy.wa.gov/programs/hwtr/betterbrakes.html>; accessed 1/20/2016). Copper will be phased-out of brake pads over the next decade to <0.5% by 2025. Although copper and nickel are naturally high in some areas of northeastern Minnesota, the exceedances in the lower St. Louis River AOC appear to be from anthropogenic sources since the upper St. Louis River had few exceedances (Figures 4-7 and 4-10, respectively). The only St. Louis River AOC metals and metalloids that did not exceed the NLAP UTLs were aluminum, arsenic, manganese, and vanadium (Table 4-3).

Sediment quality data from some of the large depressional wetland sites were used to compare to IBI values as part of the original studies. The IBIs are comprised of several metrics of the benthic invertebrate community, for which the composite scores should show a strong response to the degree of disturbance to the wetland (Helgen 2002). Invertebrate IBI scores for 44 large depressional wetlands had significant Pearson correlation coefficients with the log of surficial sediment concentrations of copper ( $p = 0.007$ ), nickel ( $p = 0.045$ ), and zinc ( $p = 0.040$ ) (Gernes and Helgen 2002). These metals were also significantly correlated to wetland plant IBI values from the same group of 44 wetlands (Gernes and Helgen 2002). In an earlier study of 25 depressional wetlands, log copper was also significantly correlated to the wetland vegetation IBI (Gernes and Helgen 1999). The wetlands from these two studies were included with the other wetland data evaluated for this report. These studies showed the value of comparing sediment chemistry parameters to wetland IBI values. These types of analyses with sediment chemistry were discontinued by agency wetland staff after 2002, but it may be useful to


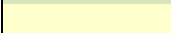





Table 4-3. Comparisons of Wetland and St. Louis River AOC Data to NLAP UTL Values

Parameter	Wetland Data			SLRAOC Data		
	Percent <UTL	Indeterminate*	Percent ≥UTL	Percent <UTL	Indeterminate*	Percent ≥UTL
Particle Size						
Clay	N/A		N/A	100		0
Silt	N/A		N/A	98.8		1.2
Sand	N/A		N/A	83.1		16.9
TOC	N/A		N/A	98.5		1.5
Metals & Metalloids						
Aluminum	88.7		11.3	100		0
Arsenic	99.3		0.7	100		0
Barium	100		0	98.3		1.7
Beryllium	62.0		38.0	N/A		N/A
Cadmium	97.3		2.7	80.4		19.6
Chromium	100		0	99.7		0.3
Cobalt	95.3		4.7	71.4	2.6	26.0
Copper	88.7		11.3	69.2		30.8
Lead	94.0		6.0	91.3		8.7
Manganese	99.3		0.7	100		0
Mercury	N/A		N/A	85	0.3	14.7
Molybdenum	81.4		18.6	N/A		N/A
Nickel	86.0		14.0	69.6		30.4
Selenium	76.3		23.7	89.2	9.4	1.4
Silver	52.7	22.6	24.7	53.1	25.9	21.0
Vanadium	76.7		23.3	100		0
Zinc	89.3		10.7	73.8		26.2
Organics						
ΣPAH <sub>13</sub>	N/A		N/A	58.4	0.4	41.2
Total PCBs	N/A		N/A	90.7		9.3
W_TEQ_KMDF	N/A		N/A	62.5		37.5
PEC-Qs						
Metal PEC-Qs	96.0		4.0	97.1		2.9
Mean PEC-Qs	96.0		4.0	89.9		10.1

SLRAOC = St. Louis River Area of Concern; NLAP = National Lake Assessment Project; UTL = upper tolerance limit; TOC = total organic carbon; N/A = not applicable; PAH = polycyclic aromatic hydrocarbon; PCBs = polychlorinated biphenyls; W\_TEQ\_KMDF = aquatic life (W) toxic equivalents (TEQ) calculated by Kaplan-Meier (KM) for polychlorinated dibenzo-p-dioxins/dibenzofurans (DF); PEC-Q = probable effect concentration quotient.

\* Indeterminate results were for nondetect values in which the reporting limits exceeded the corresponding UTL value.

Values ≥ UTL	Shading
>0 to ≤10%	
>10 to ≤20%	
>20 to ≤30%	
>30 to ≤40%	
>40 to ≤50%	

incorporate sediment chemistry in future wetland studies. More rigorous statistical techniques could be applied as multivariate statistical tools have become more accessible.

More recent wetland surveys have been conducted in Minnesota for status and trends work. A 2012 assessment of depressional wetlands in the temperate plains and mixed wood plains ecoregions showed varying degrees of degradation from vegetation and macroinvertebrate invertebrate IBIs (Genet 2015). The IBI results revealed a higher percentage of macroinvertebrate communities in good condition (43%) compared to the plant communities (17%; Genet 2015). Conversely, the plant communities had a higher percentage of wetlands rated in poor condition (56%) than the macroinvertebrates (29%; Genet 2015). A broader vegetation study, representing all wetland types statewide, showed that wetlands in the north central and northeast regions of Minnesota continue to thrive (Bourdagh et al. 2015). These areas of the state have less development and more natural land uses, which is beneficial to 75% of the state wetlands located there. Most of the wetlands located in the rest of the state have degraded floristic quality, primarily from invasive plant species (Bourdagh et al. 2015).

### **Compilation Q-Q plots**

The compilation Q-Q plots allow for quick comparisons between the NLAP, St. Louis River AOC, and wetland sediment data sets (Figures 4-16 to 4-44). Data that approximate a straight line represent a normal distribution. Data that exhibits a curve in the plot (e.g., bowing upward) represents skewed data. As previously discussed for the individual Q-Q plots of each data set, these types of plots can also be used for identifying possible outliers (which was confirmed with statistical outlier tests) and separate populations of data.

Taken together, the compilation Q-Q plots show the differences and similarities between a statewide, random data set (i.e., NLAP) with a focused geographic area (i.e., St. Louis River AOC) and a wider, nonrandom geographic area of about half of the state (i.e., wetland data). The scales on the plots differed for most chemical and particle size parameters, which can affect visual interpretation of these sediment data sets. The NLAP sediment samples tended to have a higher percentage of clay than the St. Louis River AOC samples (Figure 4-16), and less silt and sand for part of the samples (Figures 4-17 and 4-18, respectively). TOC was usually higher in the NLAP sediment samples than the St. Louis River AOC samples (Figure 4-19). The metals and metalloids data showed a variety of relationships. The NLAP and wetland Q-Q plots tended to be more similar for cadmium (Figure 4-25), cobalt (Figure 4-27), molybdenum (Figure 4-33), selenium (part of distribution; Figure 4-35), silver (Figure 4-36), and thallium (Figure 4-37). The St. Louis River AOC and wetlands tended to have similar Q-Q plots for chromium (Figure 4-26) and manganese (Figure 4-31). All three data sets were similar for copper (Figure 4-28), except the higher ranges. The metal PEC-Q and mean PEC-Q plots were similar for most the NLAP and St. Louis River AOC data (Figures 4-40 and 4-41, respectively). The St. Louis River AOC Q-Q plots were higher for part of the hydrophobic organic parameters than the NLAP data (Figures 4-42 to 4-44); this was due to more anthropogenic contamination sources in this AOC.

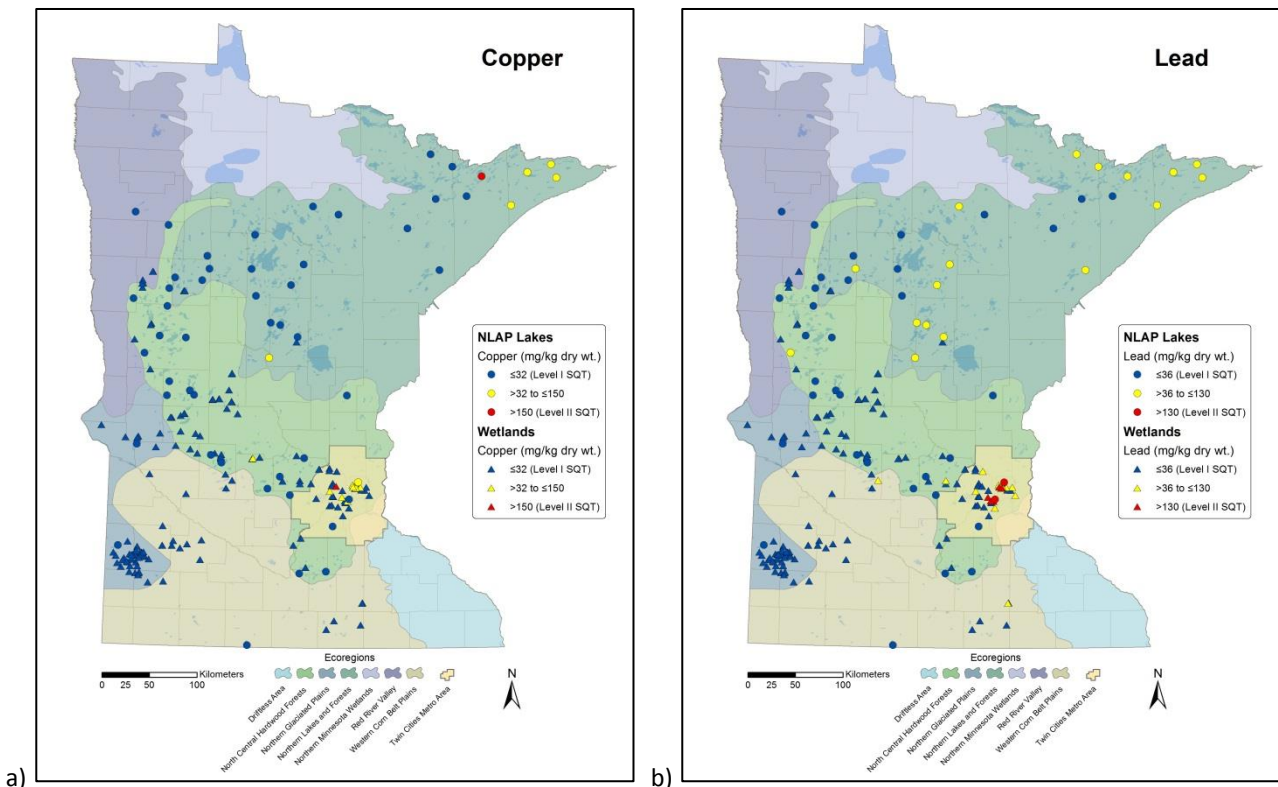


Figure 4-3. Concentration ranges of copper (a) and lead (b) in NLAP lakes and MPCA wetland sediments.

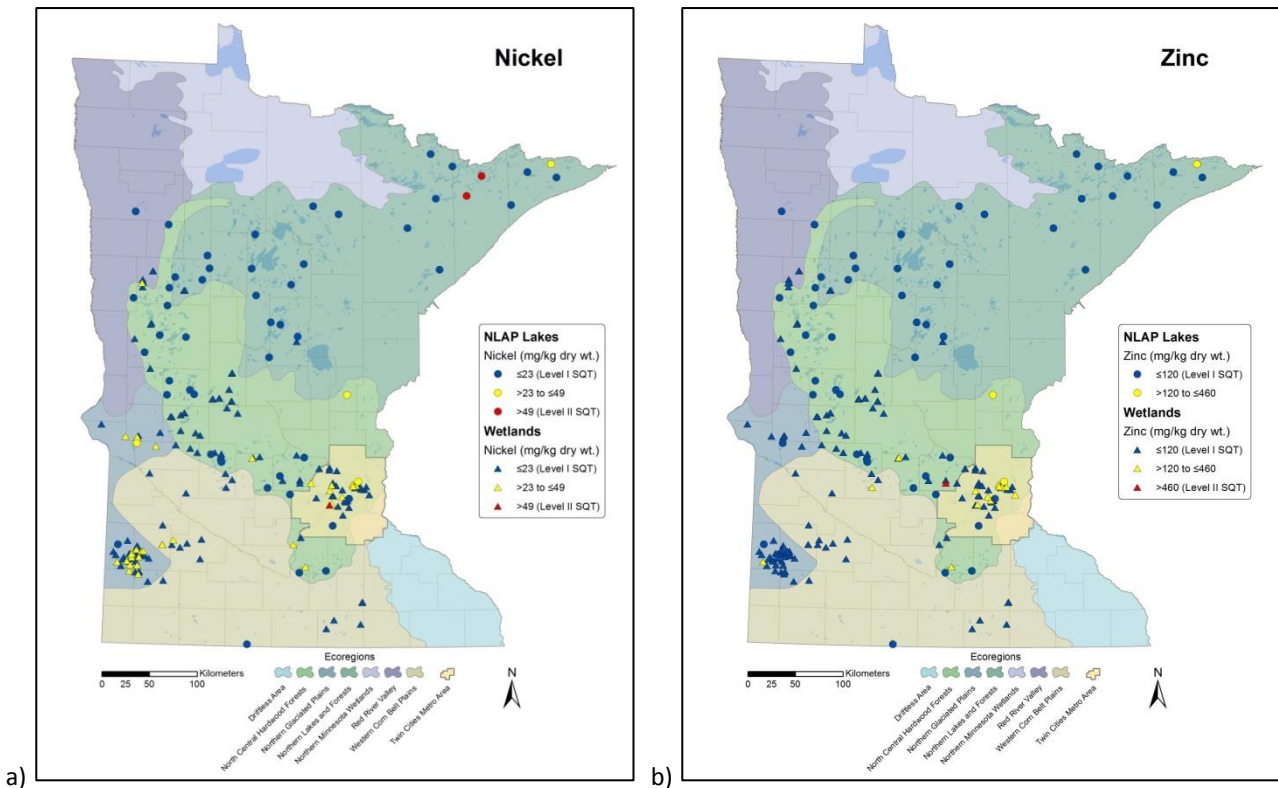


Figure 4-4. Concentration ranges of nickel (a) and zinc (b) in NLAP lakes and MPCA wetland sediments.

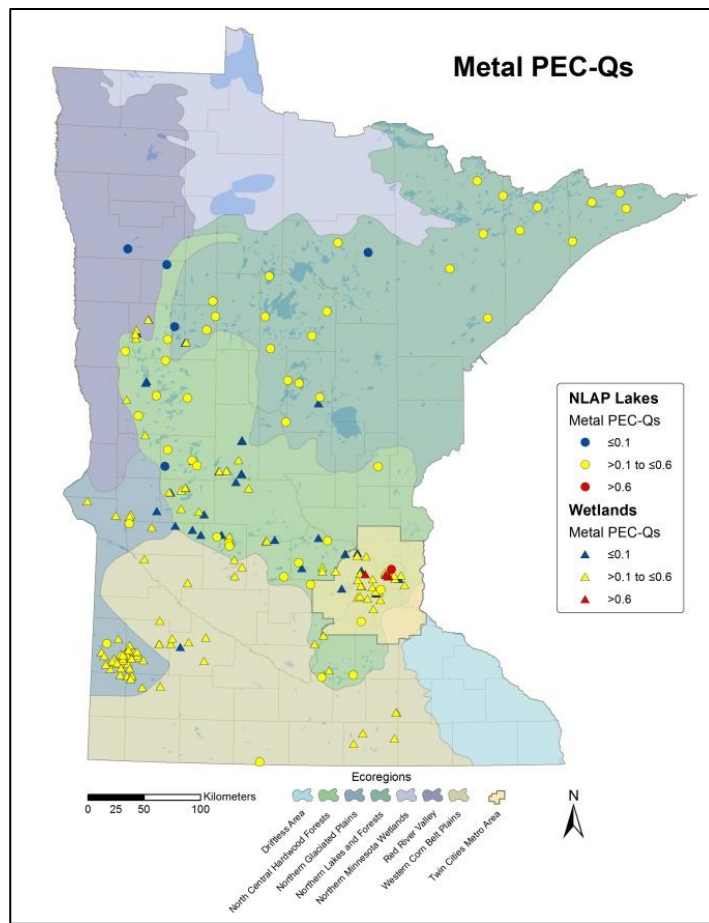


Figure 4-5. Concentration ranges of metal PEC-Qs in NLAP lake and MPCA wetland sediments.

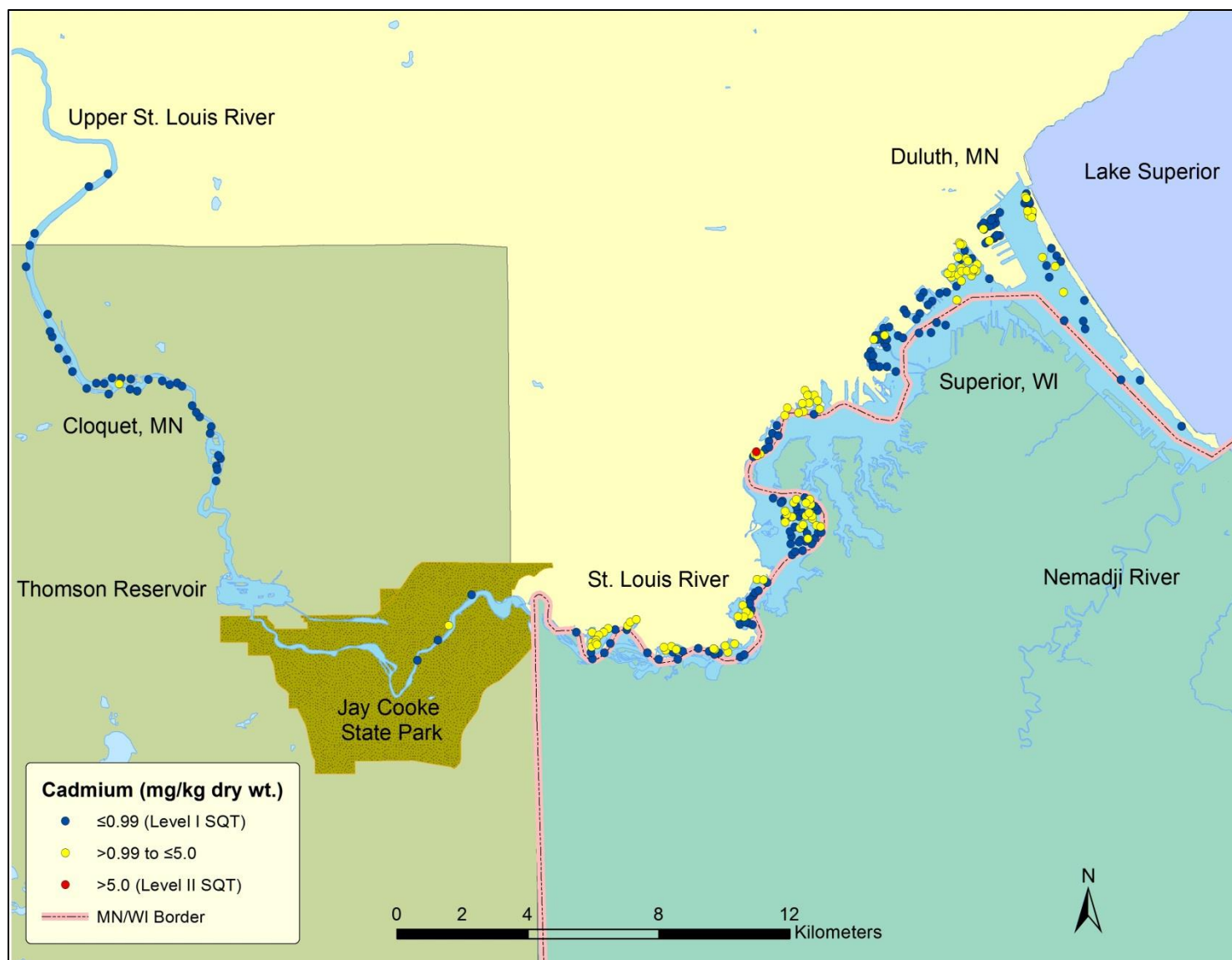


Figure 4-6. Concentration ranges of cadmium in surficial sediments from designated sites in the St. Louis River AOC. Values are compared to the Level I and Level II SQTs for cadmium.

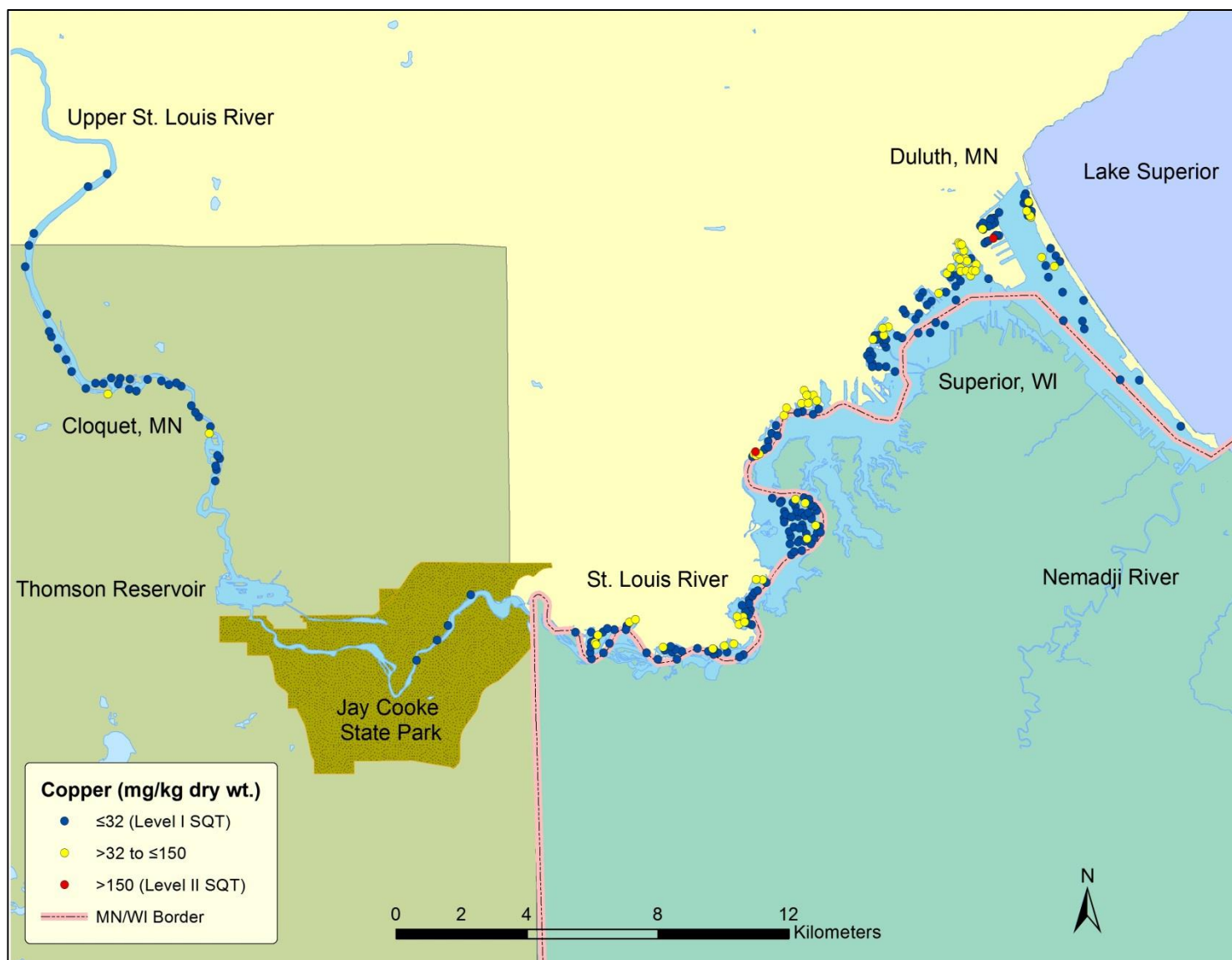


Figure 4-7. Concentration ranges of copper in surficial sediments from designated sites in the St. Louis River AOC. Values are compared to the Level I and Level II SQTs for copper.



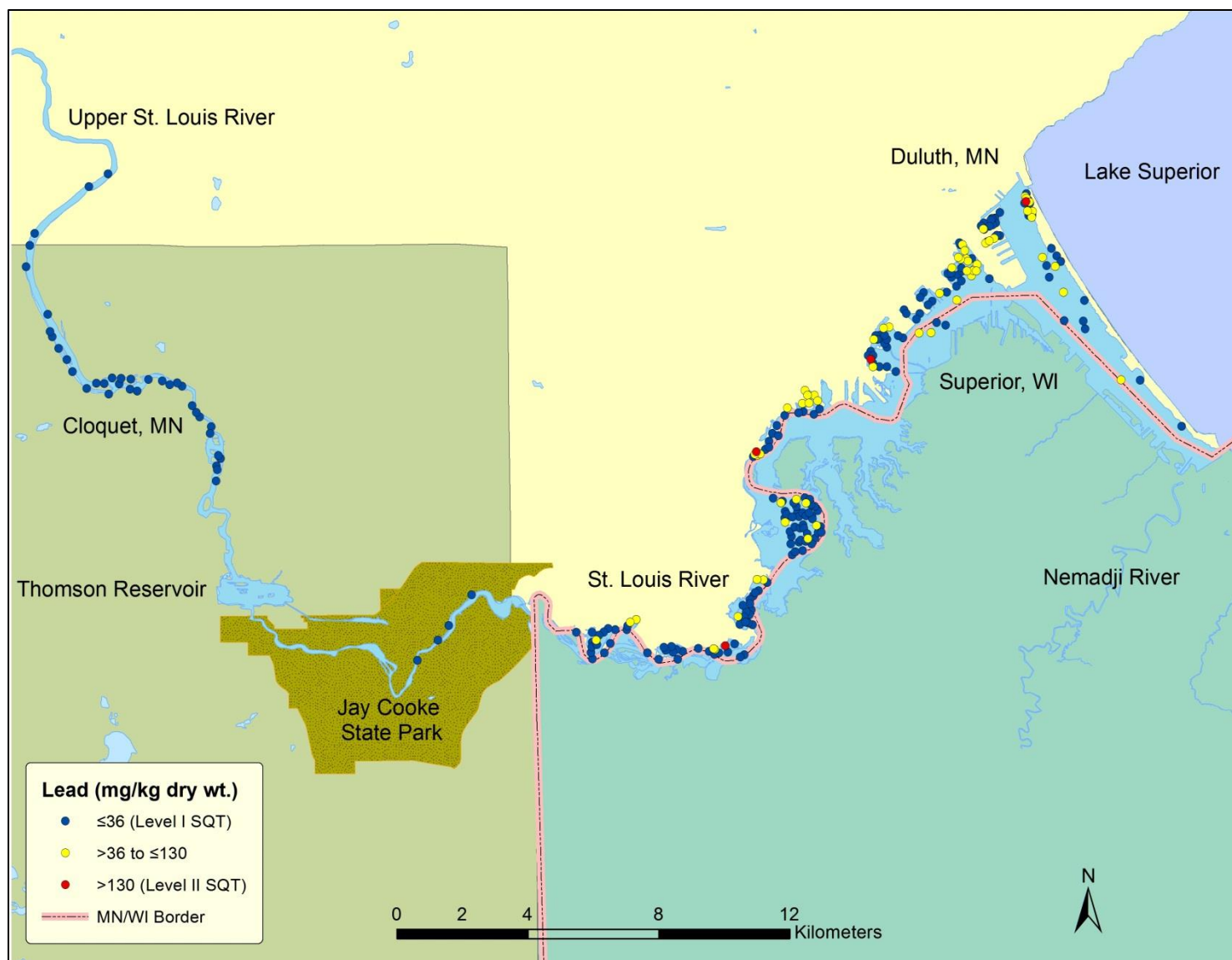


Figure 4-8. Concentration ranges of lead in surficial sediments from designated sites in the St. Louis River AOC. Values are compared to the Level I and Level II SQTs for lead.

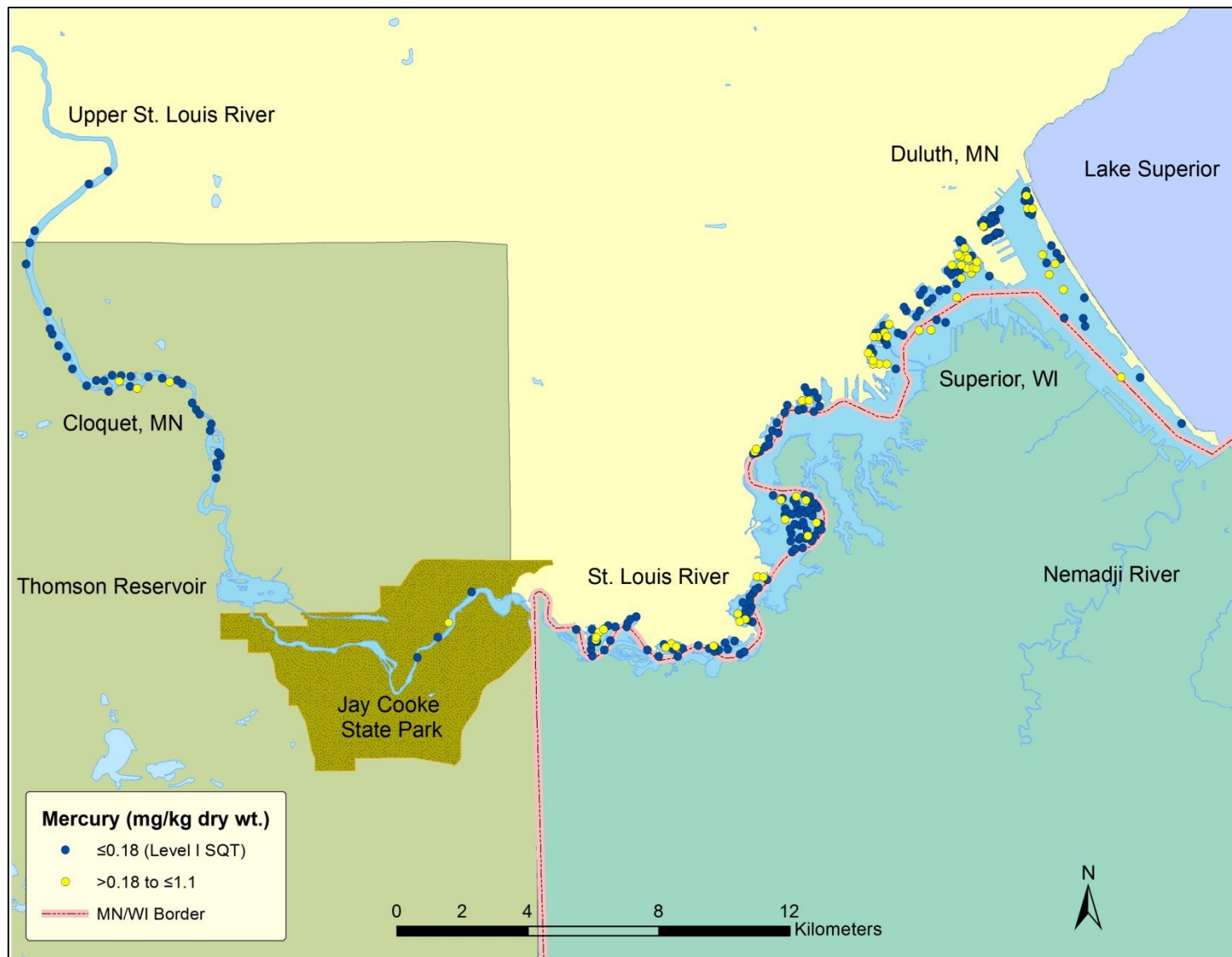


Figure 4-9. Concentration ranges of mercury in surficial sediments from designated sites in the St. Louis River AOC. Values are compared to the Level I and Level II SQTs for mercury.



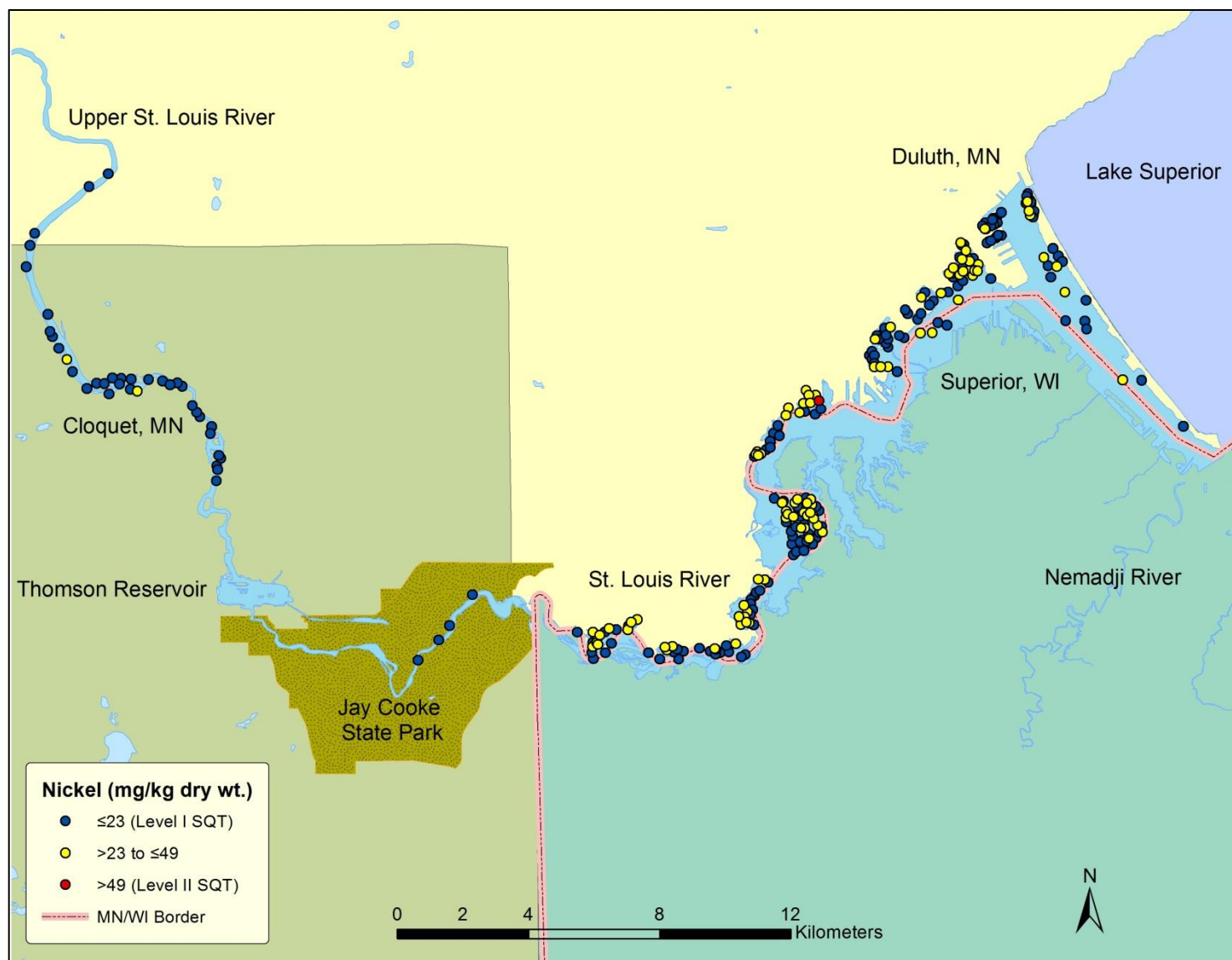


Figure 4-10. Concentration ranges of nickel in surficial sediments from designated sites in the St. Louis River AOC. Values are compared to the Level I and Level II SQTs for nickel.

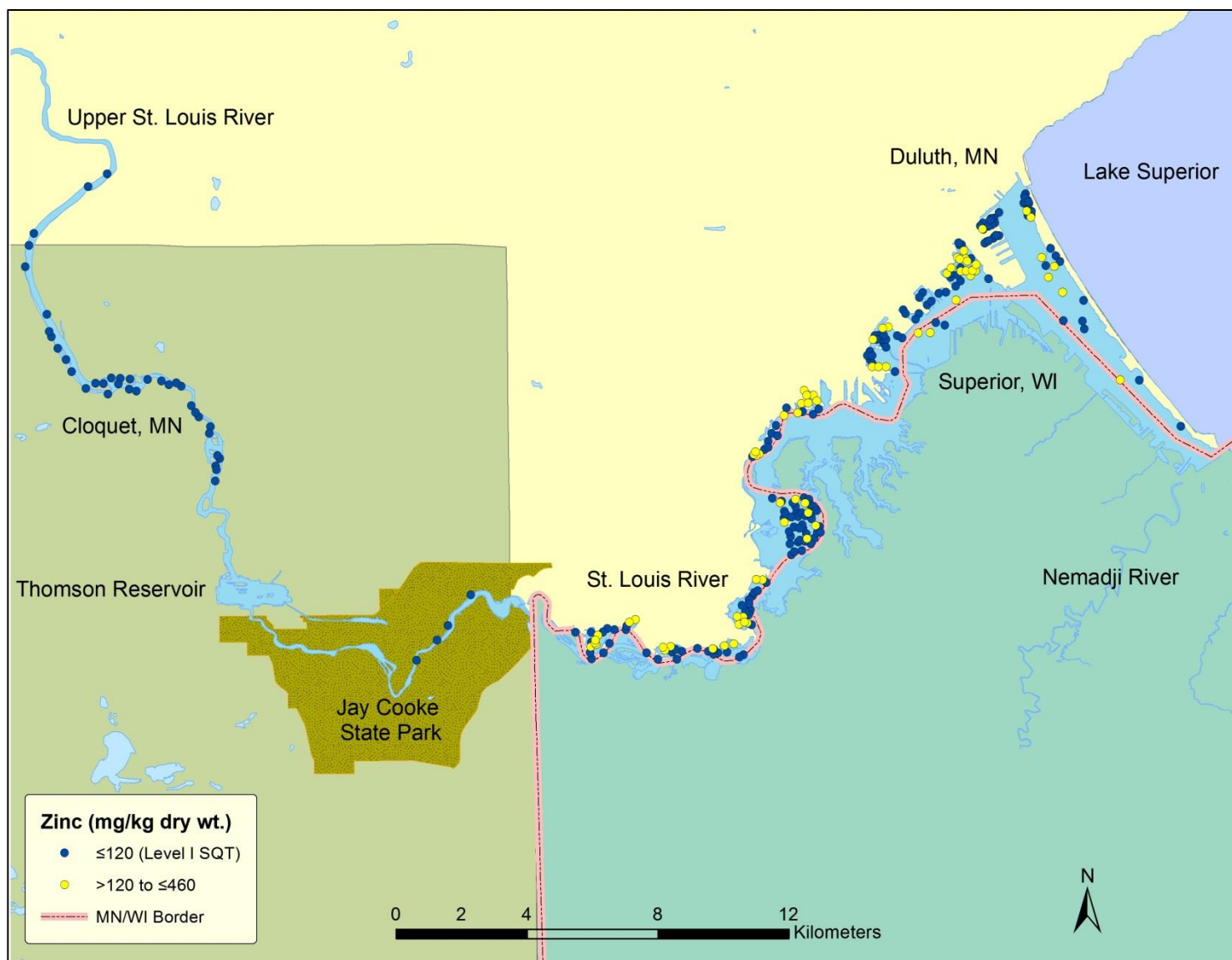


Figure 4-11. Concentration ranges of zinc in surficial sediments from designated sites in the St. Louis River AOC. Values are compared to the Level I and Level II SQTs for zinc.

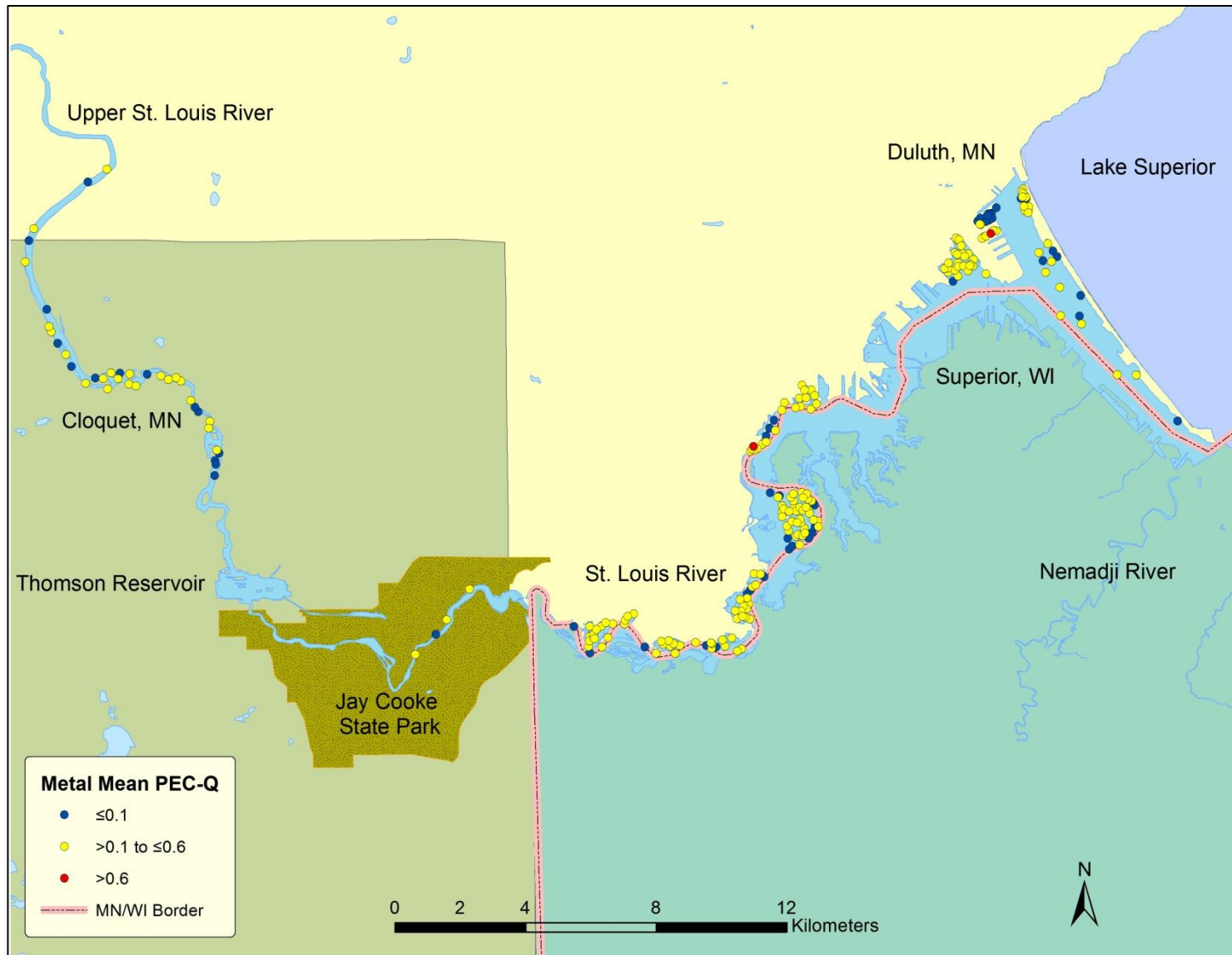


Figure 4-12. Concentration ranges of metal mean PEC-Qs in surficial sediments from designated sites in the St. Louis River AOC.

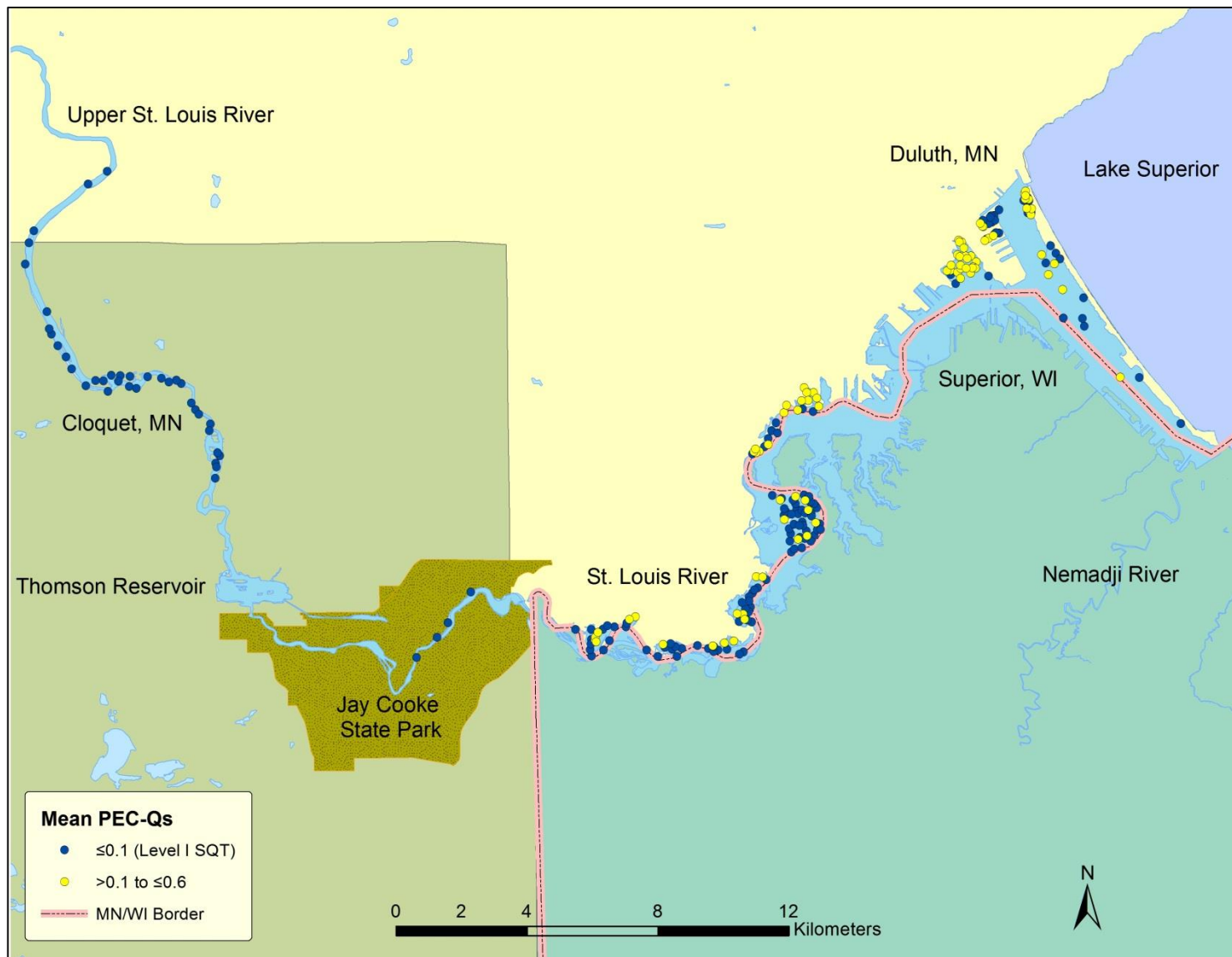


Figure 4-13. Concentration ranges of mean PEC-Qs in surficial sediments from designated sites in the St. Louis River AOC. Values are compared to the Level I and Level II SQTs for mean PEC-Qs.

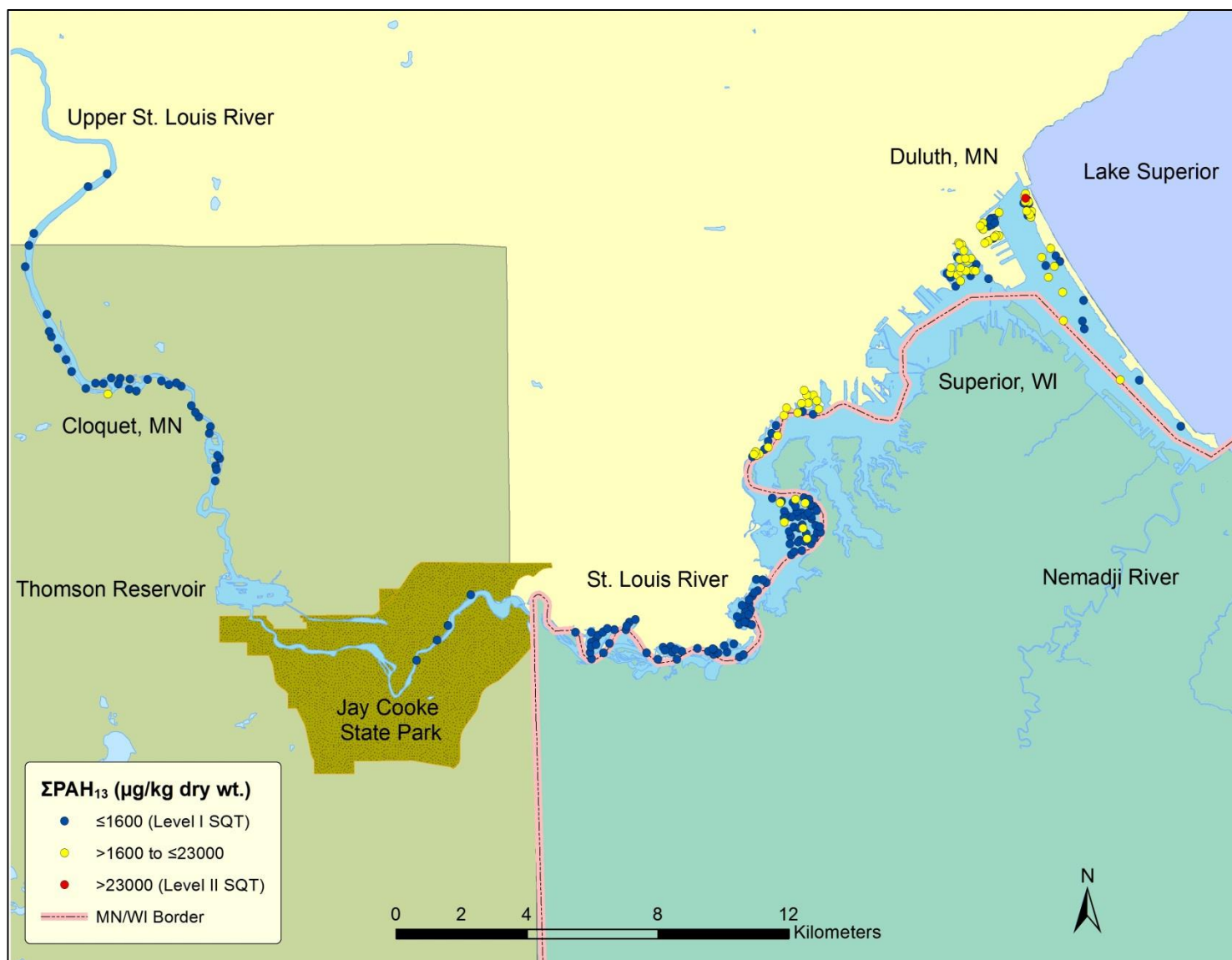


Figure 4-14. Concentration ranges of  $\Sigma\text{PAH}_{13}$  in surficial sediments from designated sites in the St. Louis River AOC. Values are compared to the Level I and Level II SQTs for  $\Sigma\text{PAH}_{13}$ .



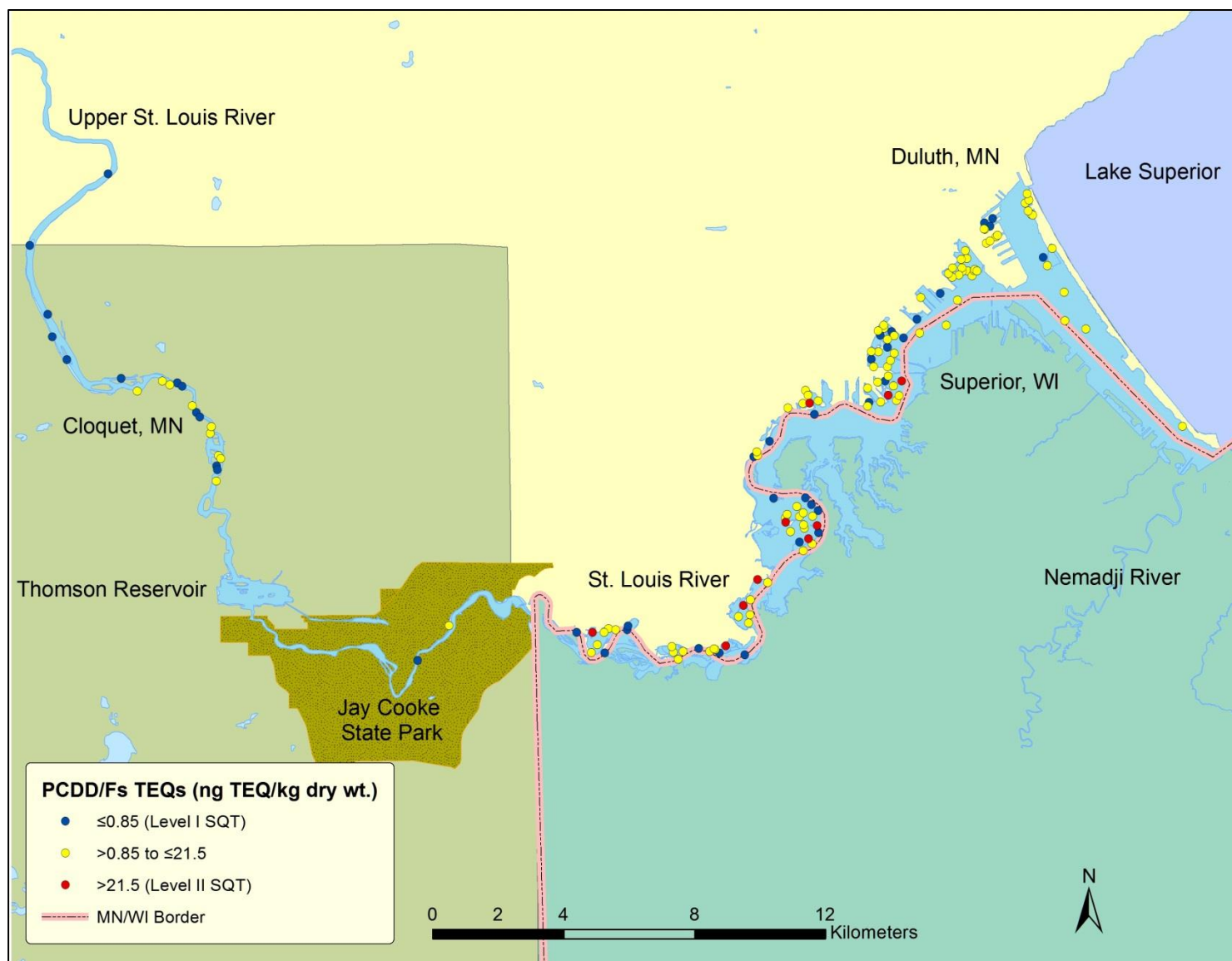


Figure 4-15. Concentration ranges of aquatic life PCDD/F TEQs (W\_TEQ\_KMDF) in surficial sediments from designated sites in the St. Louis River AOC. Values are compared to the Level I and Level II SQTs for PCDD/Fs TEQs.

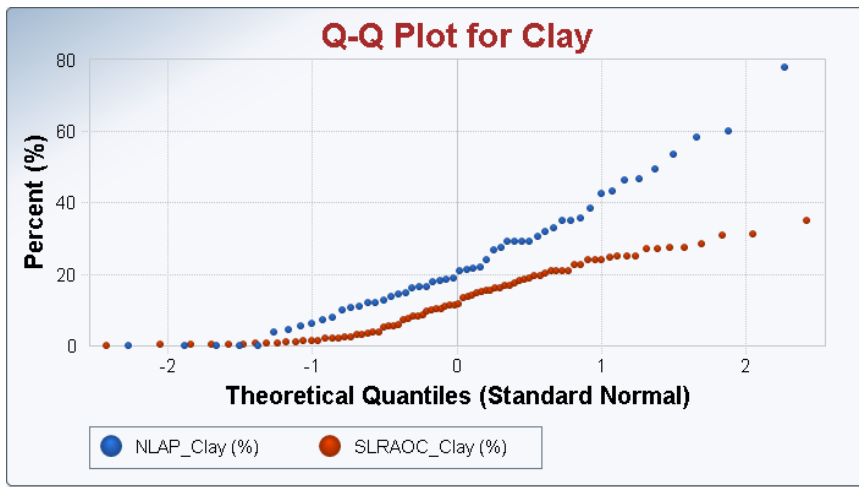


Figure 4-16. Compilation Q-Q plot for clay (%).

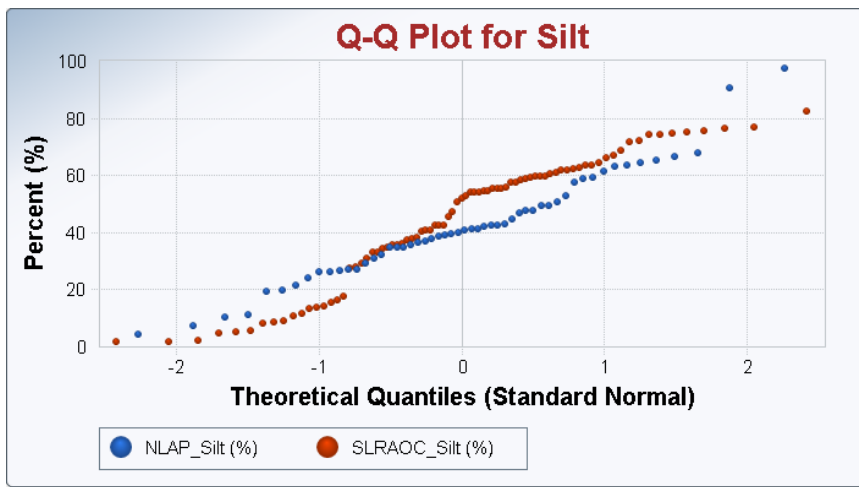


Figure 4-17. Compilation Q-Q plot for silt.

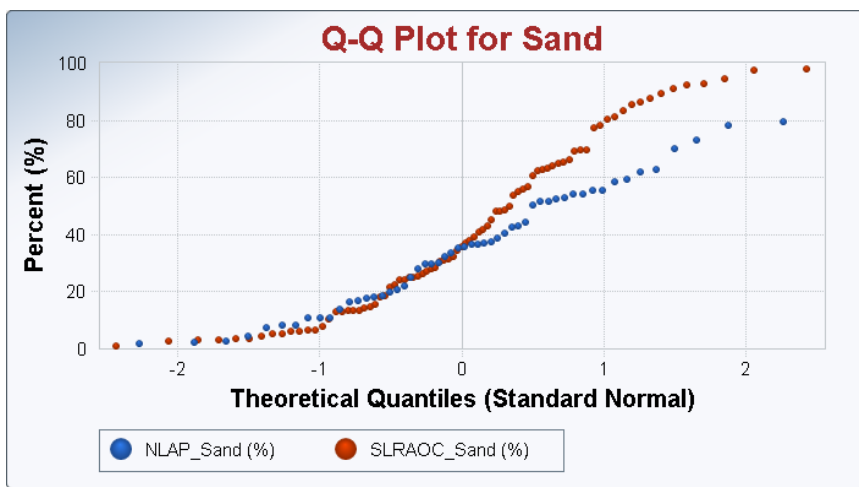


Figure 4-18. Compilation Q-Q plot for sand.

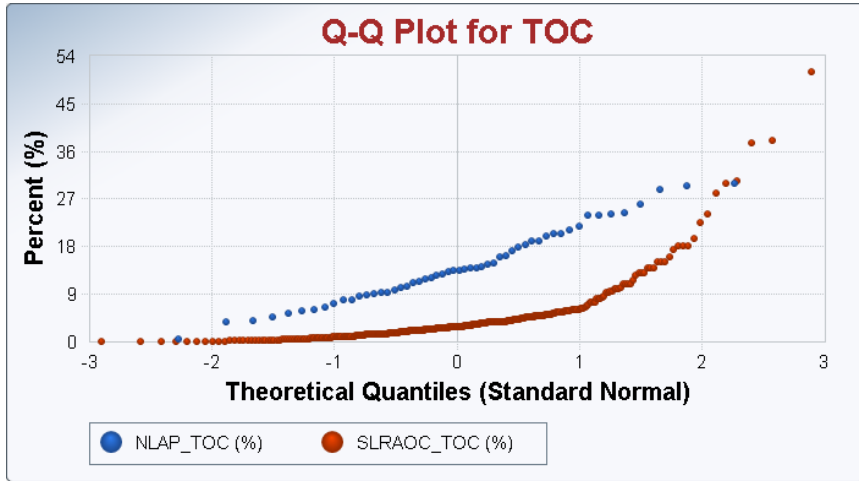


Figure 4-19. Compilation Q-Q plot for TOC.

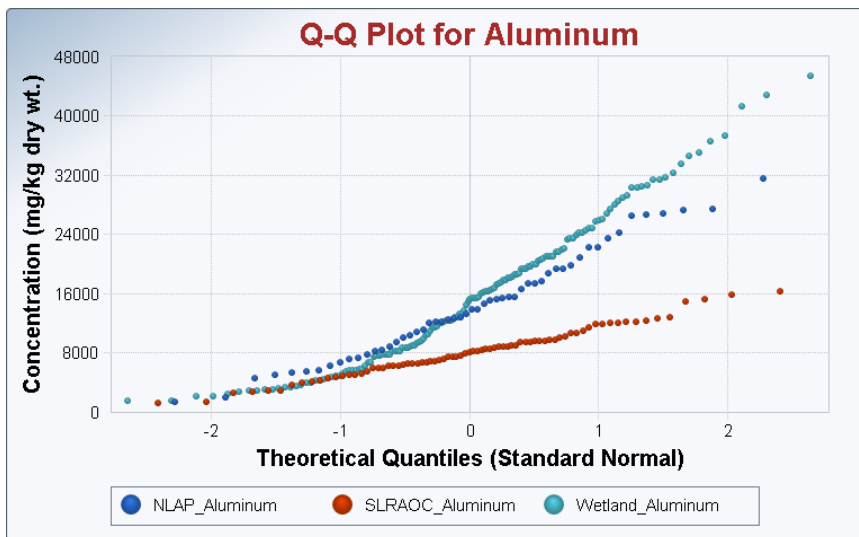


Figure 4-20. Compilation Q-Q plot for aluminum.

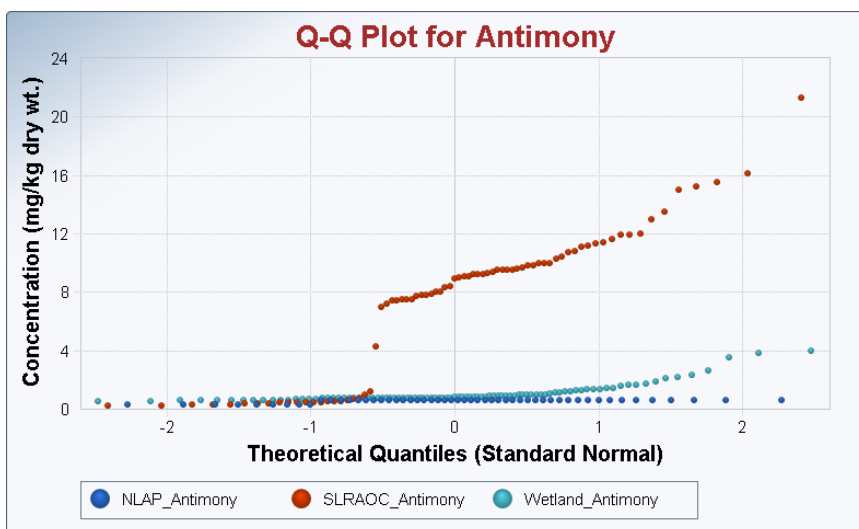


Figure 4-21. Compilation Q-Q plot for antimony.



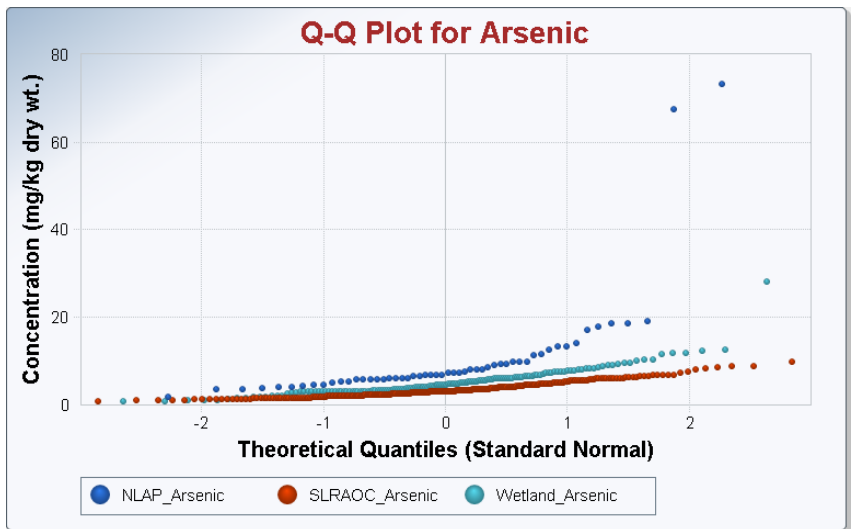


Figure 4-22. Compilation Q-Q plot for arsenic.

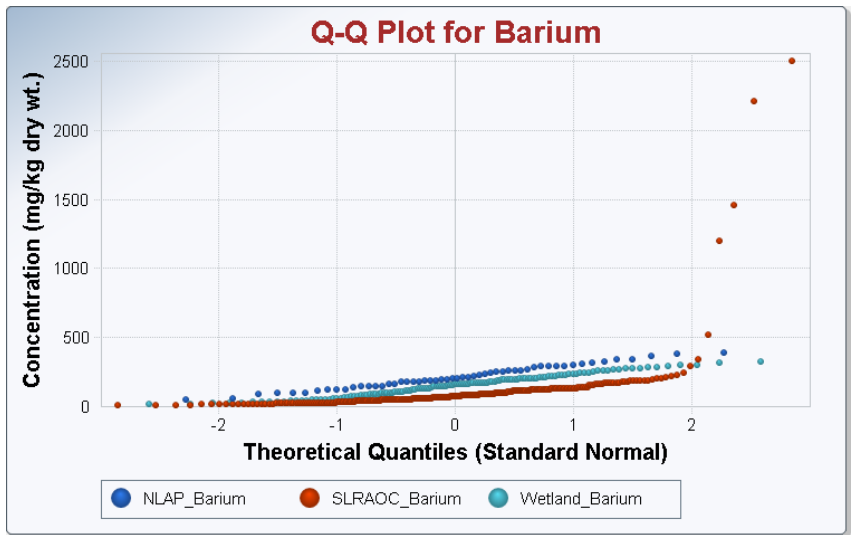


Figure 4-23. Compilation Q-Q plot for barium.

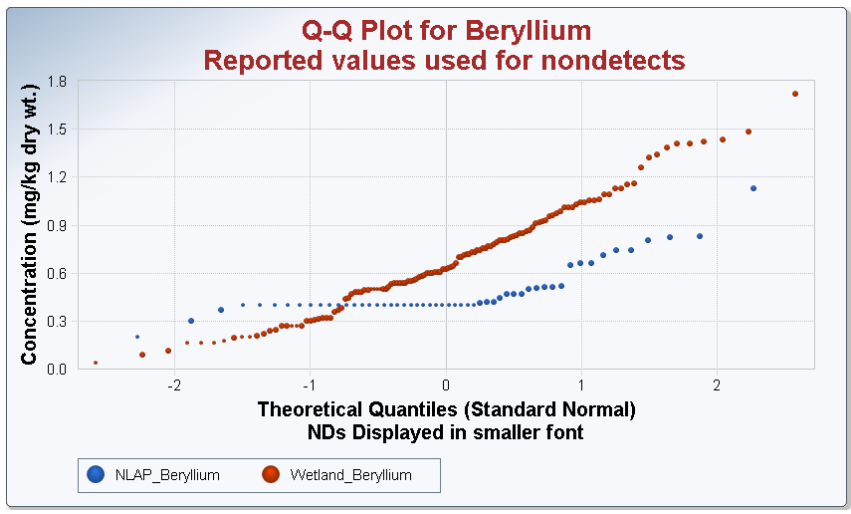


Figure 4-24. Compilation Q-Q plot for beryllium.

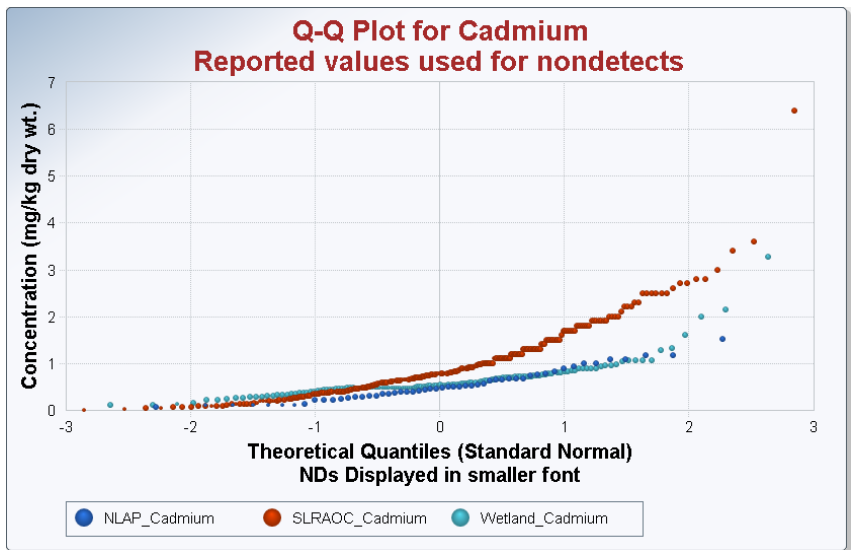


Figure 4-25. Compilation Q-Q plot for cadmium.

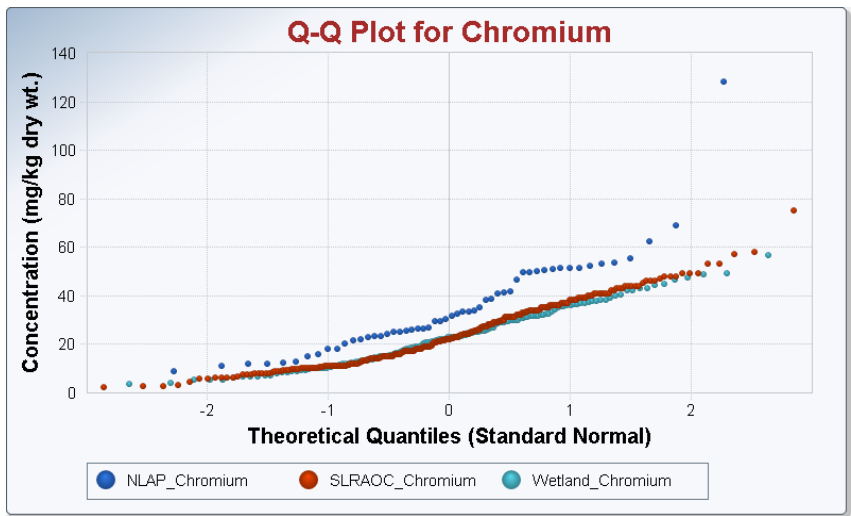


Figure 4-26. Compilation Q-Q plot for chromium.

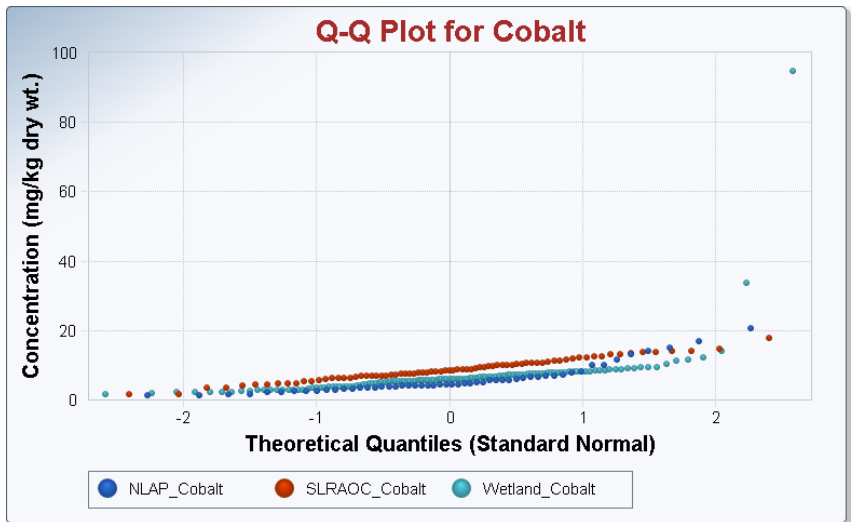


Figure 4-27. Compilation Q-Q plot for cobalt.

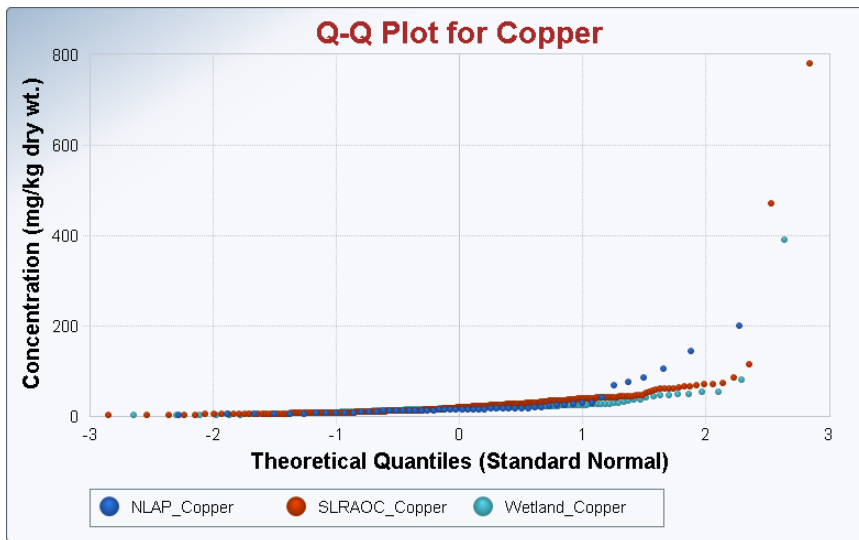


Figure 4-28. Compilation Q-Q plot for copper.

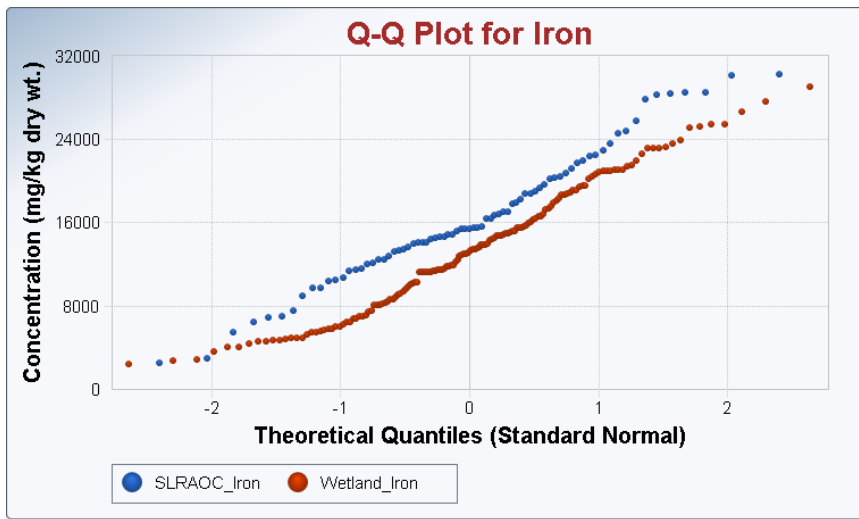


Figure 4-29. Compilation Q-Q plot for iron.

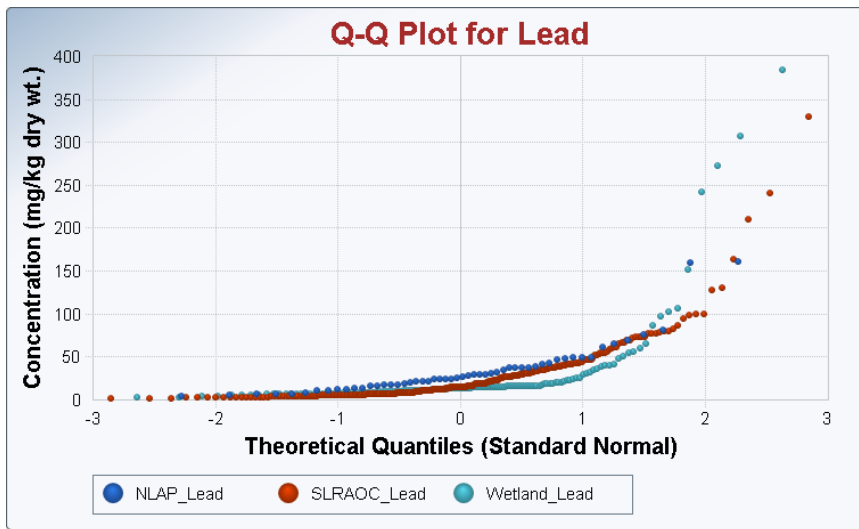


Figure 4-30. Compilation Q-Q plot for lead.

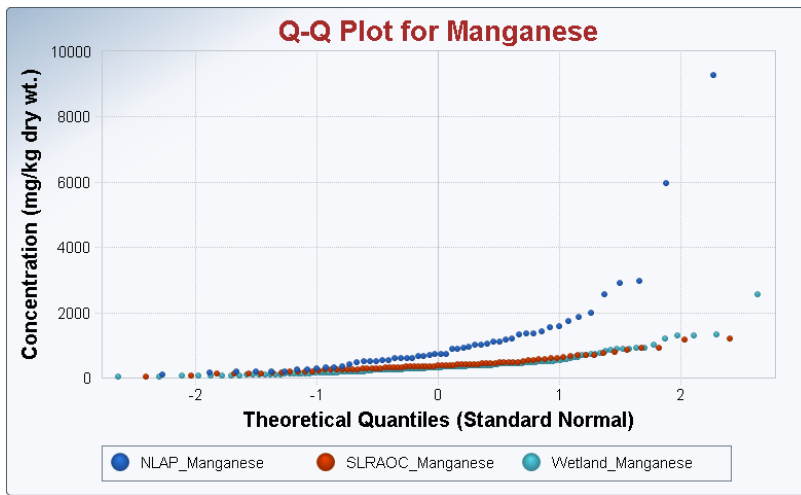


Figure 4-31. Compilation Q-Q plot for manganese.

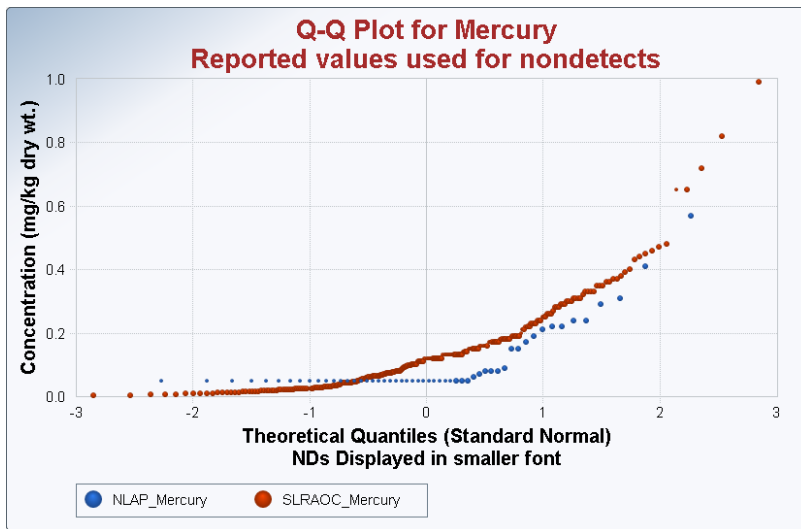


Figure 4-32. Compilation Q-Q plot for mercury.

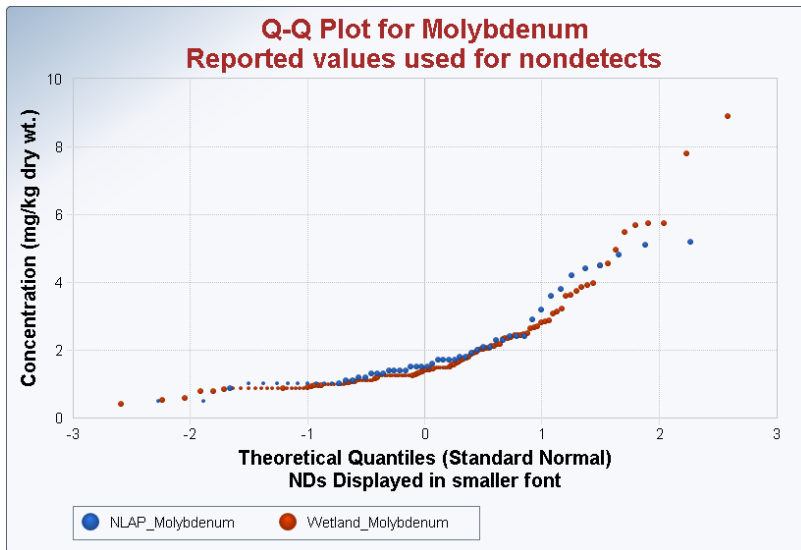


Figure 4-33. Compilation Q-Q plot for molybdenum.

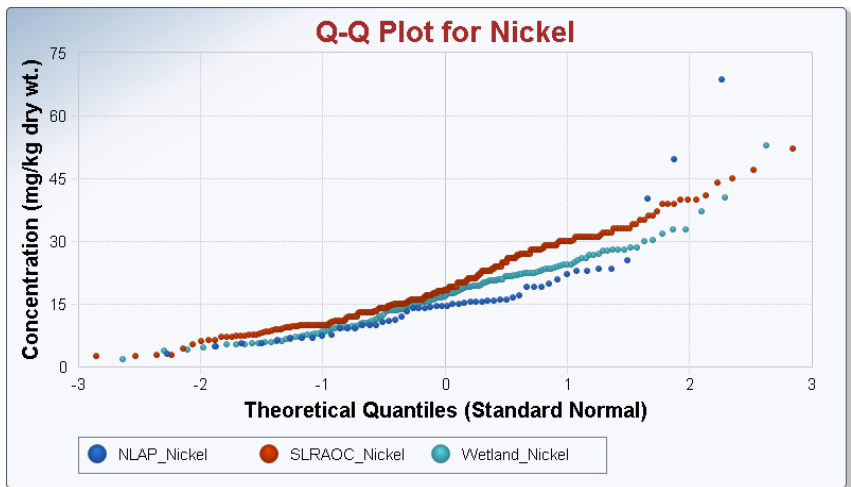


Figure 4-34. Compilation Q-Q plot for nickel.

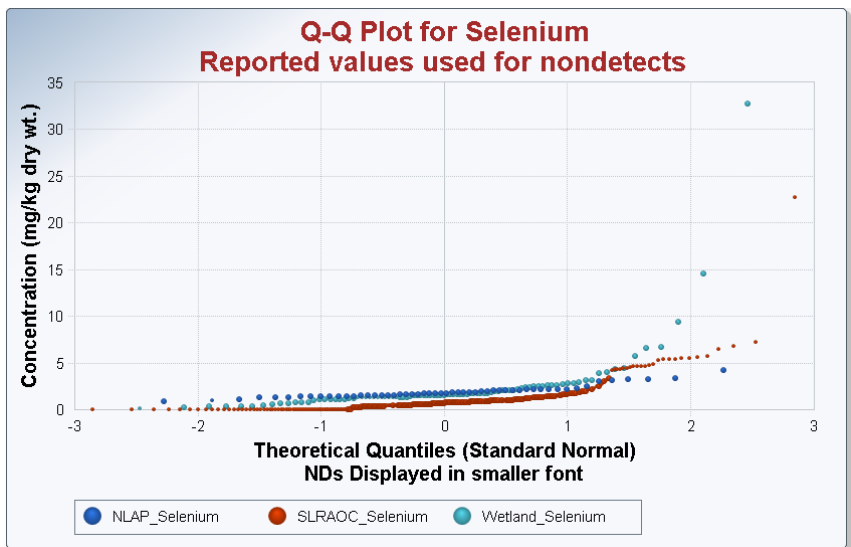


Figure 4-35. Compilation Q-Q plot for selenium.

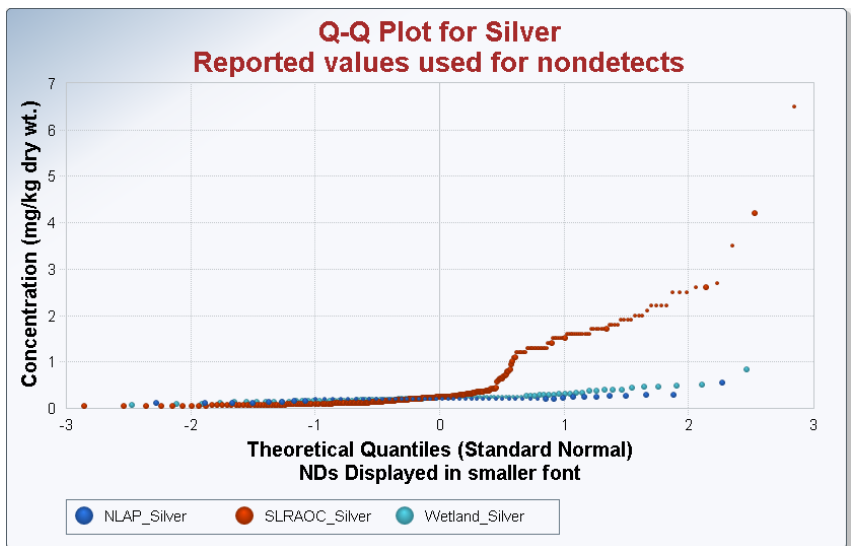


Figure 4-36. Compilation Q-Q plot for silver.

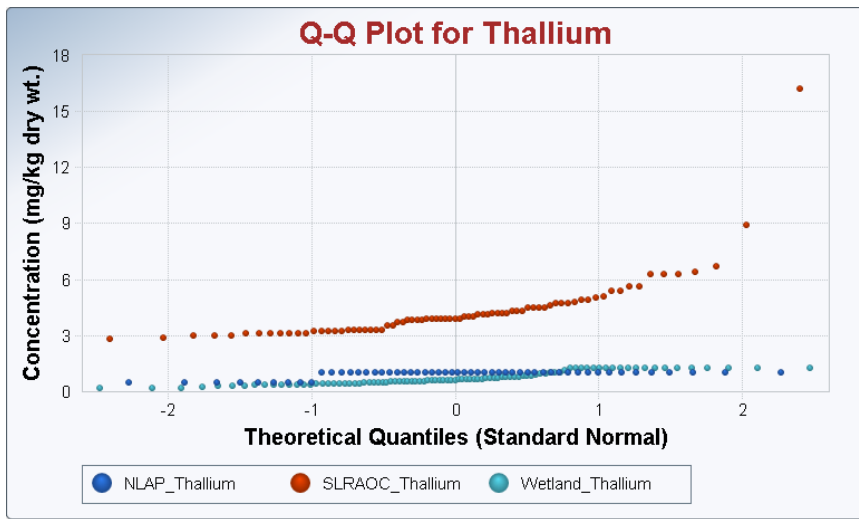


Figure 4-37. Compilation Q-Q plot for thallium.

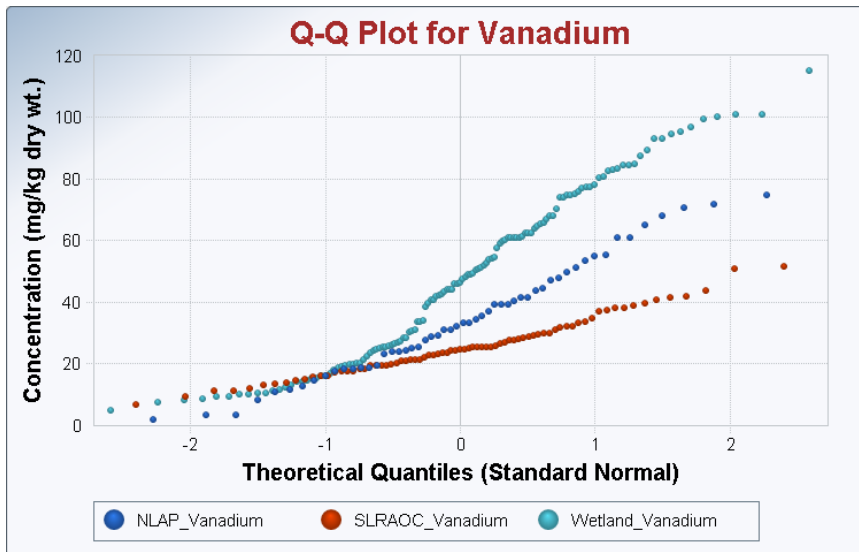


Figure 4-38. Compilation Q-Q plot for vanadium.

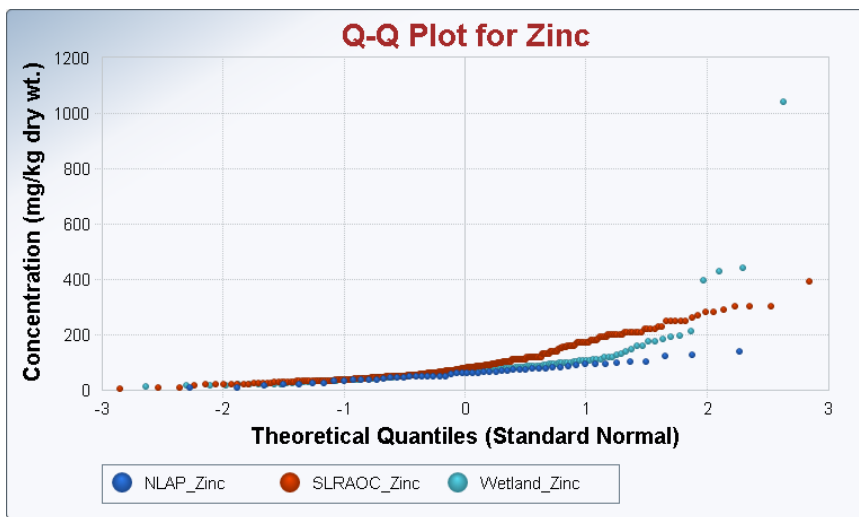


Figure 4-39. Compilation Q-Q plot for zinc.

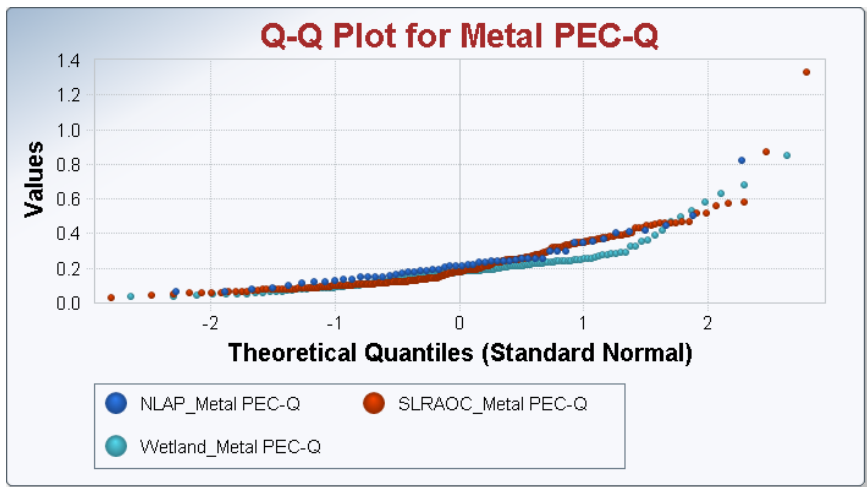


Figure 4-40. Compilation Q-Q plot for metal PEC-Qs.

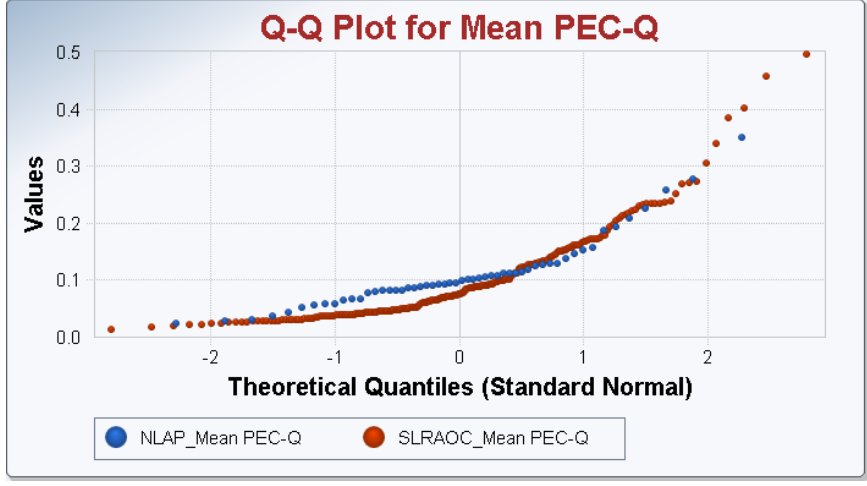


Figure 4-41. Compilation Q-Q plot for mean PEC-Qs.

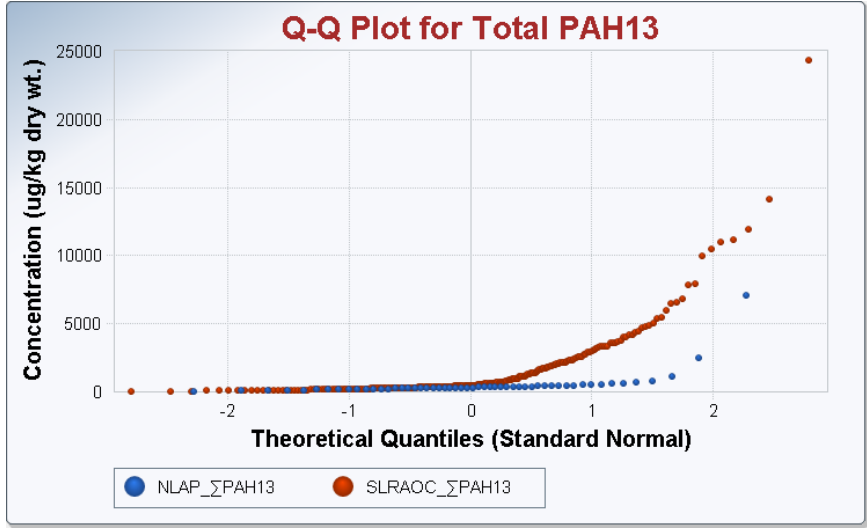


Figure 4-42. Compilation Q-Q plot for ΣPAH<sub>13</sub>.

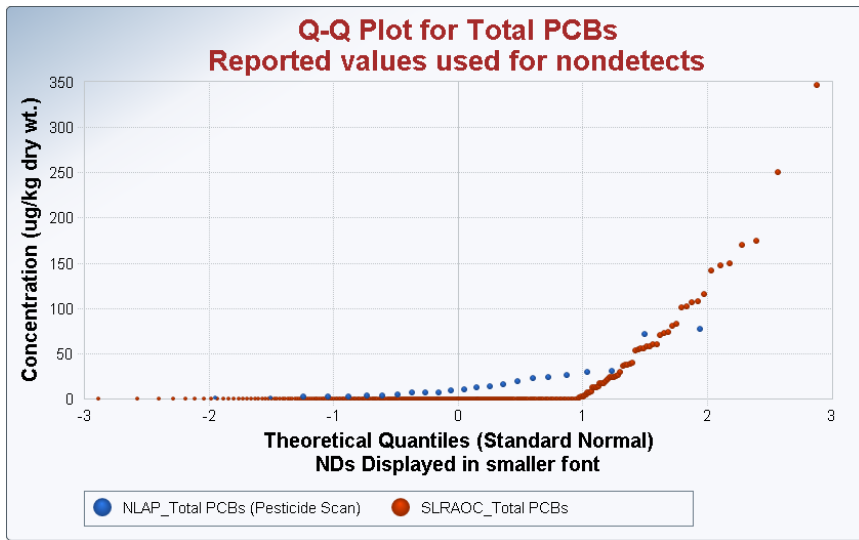


Figure 4-43. Compilation Q-Q plot for Total PCBs.

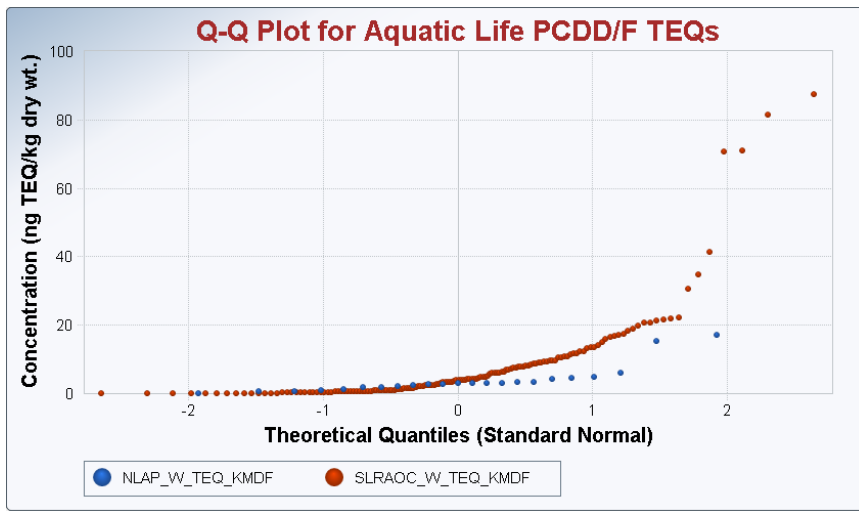


Figure 4-44. Compilation Q-Q plot for aquatic life PCDD/F TEQs (W\_TEQ\_KMDF).



## Section 5: Recommendations

---

Based on the results of this report, we offer the following recommendations for additional sediment assessment work. In addition, other items are described for further consideration.

### Status and trends monitoring

- The 2007 NLAP sediment data could be re-examined to weight the data so that the results could be extrapolated to other Minnesota lakes with surface areas >4 ha.
- Future “NLA-like” projects should consider collecting the upper 5 cm, instead of upper 15 cm, of sediment to obtain a better assessment of recent contaminant deposition. For the first time, the U.S. EPA will add sediment chemistry and physical parameters to the next round of national NLA sampling in 2017. For this effort, the U.S. EPA has proposed collecting one composite sample of the upper 5 cm for the analysis of TOC, particle size (% clay, silt, sand), 16 metals and metalloids, 21 PCB congeners, 27 legacy pesticides, 24 PAHs, and biphenyl. Unlike the 2007 NLA lakes survey, which were limited to >4 ha in size, the surface areas of the 2017 lakes will be >1 ha. The MPCA will expand the random draw of 42 lakes in Minnesota with an additional eight lakes so that sediment samples will be collected from 50 randomly selected lakes in 2017. The deepest part of each lake will be sampled for sediments. This additional sampling will allow the UTLs to be updated for chemicals included in both the 2007 and 2017 sampling efforts. These data will be merged to determine if they represent one population group, excluding outliers. If the deeper sediment sections from the 2007 samples represent a separate population of chemical and particle size analytes, then UTLs will be developed separately for the 2017 samples. In addition, further statistical analyses will be done using weight values determined for each lake, based on surface area and the frequency of each lake in the lake sample population within an ecoregion. Thus, the 50 lakes to be sampled in 2017 will be considered representative of the final lake sample population in Minnesota, because they will all meet the site criteria of adequate size, depth, and surface area.
- Conduct other status and trends monitoring of sediment quality at randomly selected waterbodies (e.g., lakes, streams, rivers, harbors, wetlands) throughout Minnesota. One option is to develop separate monitoring needs for waterbodies by land uses (e.g., urban versus non-urban) and/or ecoregions (e.g., Northern Lakes and Forests ecoregion in northeastern Minnesota where some metals are naturally high compared to other ecoregions). Sediment sampling for a suite of contaminants and particle size could be added to regular watershed sampling. At this time, the addition of sediment toxicity tests and/or benthic invertebrate community surveys would probably not be warranted for this type of broad assessment, unless there was historical information pertaining to contaminant sources at the study sites.
- Conduct status and trends sediment sampling of chemicals that have been banned (e.g., some PBDEs, legacy PCBs, legacy organochlorine pesticides and their degradation products) or of chemicals in products that have been banned (e.g., ban of coal tar-based sealants in 2014 due to PAH contamination). Doing so would help address the effectiveness of bans and the amount of time before reductions of contaminants are achieved at a safe level in surficial sediments (and potentially fish tissue, too, if bioaccumulation modeling was done). This type of project could also demonstrate the recalcitrant nature of some hydrophobic organic contaminants that continue to cycle in the environment. Thus, there could be the need for bans of certain chemicals worldwide due to long-range atmospheric transport to Minnesota. For this type of project, deeper sediment

cores would need to be collected for radioisotope dating and chemical analysis of discrete core sections to obtain a record of pre- and post-ban concentrations over time.

- Integrate sediment and water quality data with habitat information for more comprehensive status and trends work. For example, the Michigan Department of Environmental Quality (MDEQ) developed a strategy in 1997 to describe the watershed monitoring activities that are necessary for a comprehensive assessment of water quality in their surface waters (see [http://www.michigan.gov/deq/0,4561,7-135-3313\\_3681\\_3686\\_3728-32365--,00.html](http://www.michigan.gov/deq/0,4561,7-135-3313_3681_3686_3728-32365--,00.html)). They monitored sediment chemistry (through grants to Michigan State University to collect and analyze sediment cores), conducted aquatic life community evaluations, implemented fish and wildlife contaminant studies, and measured water chemistry within the framework of a five-year permitting cycle. The objectives of their sediment chemistry monitoring (which ended in 2010) were to:
  - Determine the chemical character of sediments in waters of the state and to assess temporal differences in contaminant levels
  - Identify priority locations for sediment remediation activities in Michigan
  - Determine background sediment chemical character of waters of the state
  - Determine whether new chemicals are accumulating in sediment
  - Evaluate the overall effectiveness of the National Pollutant Discharge Elimination System (NPDES) permit program in reducing contaminant levels in sediments
  - Determine the contaminant anthropogenic sediment burden in inland lakes
  - Investigate the relationships among contaminant accumulation trends and anthropogenic and natural processes including changes in land use

Michigan State University collected sediment cores from the deepest location of each lake, which were analyzed at discrete intervals for chemical parameters and radioisotope dating. Contaminant flux rates were determined from these data. Pore water sampling was done, too, for the analysis of metals. A total of 44 lakes were monitored over the course of the program, of which 10 lakes were sampled twice. This type of sampling program is more expensive to run than NLA-type sampling. An evaluation of MDEQs program could be made to determine if such sampling would be beneficial to the MPCA.

## Other sediment investigations

- Chloride-related investigations:
  - Further work is needed to verify the high chloride value in Henry Lake (Alexandria, MN), to assess chloride concentrations in connecting lake sediments and water column samples, and to determine sources of chloride to this lake/wetland system.
  - Chloride should be included as a parameter in more sediment assessments, especially in urban and agricultural areas and near major roadways. The role of sediments should be considered in any updates of the Twin Cities metropolitan area chloride management plan (MPCA 2016b), as well as for any future statewide chloride management plan.
  - The MPCA, or its partners, could investigate whether chloride in sediment promotes the release of phosphorus into the water column. A limited laboratory experiment of estuarine sediment from China indicated that chloride improved phosphorus adsorption on sediment at first, but that the complexes were unstable and easily released phosphorus under disturbed conditions (Jin et al. 2013). Thus, this situation could result in a flux of phosphorus from the sediment to the overlying water. However, it is unclear if

similar results would be observed in the natural environment under freshwater conditions.

- Conduct more focused sediment sampling of lakes in regions that are naturally enriched in certain metals to develop separate ambient background threshold values (e.g., UTLs) for those regions. Sediment toxicity tests on split, surficial sediment samples would be prudent to conduct in order to obtain matching sediment chemistry and toxicity testing results.
- Conduct further reviews of MDNR historical records for uses of sodium arsenate, sodium arsenite, arsenic trioxide, and/or copper sulfate in Minnesota lakes and analyze those lake sediments for arsenic and copper. Sediment toxicity tests on split, surficial sediment samples would be prudent in order to obtain matching sediment chemistry and toxicity testing results.
- Recommend including nonlegacy PCB congeners (e.g., PCB 11) in surficial sediment, water, and fish tissue monitoring, in addition to a regular suite of legacy PCB congeners. This type of project would provide valuable information on the emerging issue of nonlegacy PCB congeners that are inadvertently produced in some household paint pigments and other pigments used in a variety of consumer products.
- Suggest coordinating future pesticide monitoring of sediments with MDA for pesticides of interest. For example, pyrethroids and pyrethrins were analyzed in metro-area stormwater pond sediments for a MPCA study (Crane and Hennes 2010b), and MDA is developing their analytical capabilities for analyzing these compounds in sediments. Previously, MDAs analysis of pesticides was limited to water samples. Pyrethroids and pyrethrins are being used as a substitute for organophosphate pesticides throughout the U.S. Bifenthrin and total permethrin comprised 48.6 and 39.8%, respectively, of all pyrethroid and pyrethrin compounds sold in Minnesota during 2009 (MDA sales information). Ninety-five percent of bifenthrin sales in Minnesota are for crop chemicals, and additional research is needed to assess environmental impacts in agricultural areas. Pyrethroids could be assessed in sediments from agricultural areas and urban areas. Pyrethroid compounds are used more widely on agricultural crops than in urban areas in Minnesota, which is the opposite of California where more research has been done on this class of compounds. These compounds are also more toxic at colder temperatures, and the toxicity of these compounds in Minnesota sediments has not been adequately assessed. The inclusion of sediment toxicity tests with the amphipod *Hyalella azteca*, which tend to be more sensitive to pyrethroids, would be useful. There could also be a tie-in with the implementation of buffer strips along waterways in agricultural areas to determine if it is reducing contaminant inputs.
- Conduct sediment quality studies pertaining to small dam removals in Minnesota per coordination with the MDNR. More than 85% of U.S. dams will exceed their 50-year engineered life expectancies by 2020 (Bennett et al. 2013). Small dam removals are becoming more popular as the cost of maintaining old dams becomes prohibitive. More than 1000 U.S. dams were removed between 1975 and 2015 (Evans 2015). While these removal efforts can have the ecological advantage of restoring rivers to their free-flowing state, they have the potential disadvantage of releasing significant quantities of contaminated sediments behind the dams and from reservoirs. There are also concerns that the release of phosphorus from sediments resuspended from dam removals could promote downstream blooms of toxic algae (e.g., *Microcystis*; Evans 2015). The MDNR has prepared guidance on removing dams to enhance fish passage, but potential contaminated sediment issues are only briefly mentioned (Aadland 2010).
- Further consider bioavailability and bioaccessibility of sediment contaminants to ecological receptors and human health (e.g., role of black carbon in reducing bioavailability of hydrophobic organic contaminants).
- Further consider biogeochemical factors in contaminant fate (e.g., methylation of mercury in sediment).

- Consider the use of passive samplers for pore water measurements of contaminants to provide a better indication of freely available contaminants in sediment pore water.
- Conduct a broader fish survey for PBDEs to provide greater statistical power to the study design than what was presented in this report (i.e., include more lakes from different watershed land uses for the trophic classes of fish collected).
- Evaluate the distribution of emerging contaminants, such as persistent pharmaceuticals and personal care products (e.g., musks) in sediments from a random selection of waterbodies. An analogous study was conducted on water column samples collected as an internal add-on to Minnesota’s 2012 NLA lakes (Ferrey et al. 2015). However, the percentages of detected compounds were generally low (i.e., 2 – 48%; Ferrey et al. 2015), and some compounds would be more likely to accumulate in sediments (e.g., 4-nonylphenol) than the water column. Such a sediment study would provide a more complete assessment of the distribution of emerging chemicals (that are less water soluble) in a random selection of lakes. For lakes in remote areas, companion air sampling could elucidate the role of atmospheric transport and deposition of these contaminants in lake watersheds.
- Incorporate new types of indicators in the “-omics” field of environmental science in sediment assessments, particularly for benthic invertebrates or bottom-dwelling fish. Metabolomics is being used to assess chemical stress on metabolites in organisms resulting from biochemical pathways known or predicted to be connected to chemical stress. Other “-omics” technologies include whole transcriptome and proteome sequencing, as well as epigenetic studies to look at genetic changes passed on to offspring from the parents’ exposure to contaminants. Van Aggelen et al. (2010) commented that “-omics” technologies are useful for elucidating modes of action of toxicants and can contribute to other data used in risk assessments, but there are several challenges for incorporating the results in regulatory programs. The use of “-omics” technologies continues to be a developing field that should be watched for potential applications to agency activities involving sediment.
- Consider emerging issues such as microplastics and nanomaterials in sediment in regards to biological impacts and the fate and transport of hydrophobic organic contaminants that partition to these materials (Driedger et al. 2015; Sanchís et al. 2016).

## Data analysis and interpretation methods

- The UTL calculations for some metals could be revised by pooling other reference lake sediment data (Heiskary 1996; King 2000) with the NLAP data for metals that did not have significant differences ( $p > 0.05$ ) between study groups (e.g., chromium).
- Multivariate statistical methods for censored data (e.g., PCA analysis on ranks; Helsel 2012) could be utilized for broader analysis of data sets containing censored data.
- Alternative ways of determining outliers or “separate” populations of data could be examined. Such techniques would benefit from larger sample sizes. For nondetect data, statistical outlier tests for censored data could be tried, rather than having to replace one-half the reporting limit or excluding nondetects as done in the EPA’s ProUCL 5.0 software.
- For areas of the state that have data gaps, could consider looking at neighboring states for data from similar watershed types and geology (e.g., agricultural areas in southwest MN could compare to northwest Iowa if data were available).
- Heat maps could be prepared in RStudio to visually compare the suite of 54 NLAP lakes for all chemicals that have Level I and Level II SQT values. Such a grid map would provide a quick color representation of how the chemical data compares to the matching SQT values in each lake. For example, concentrations  $\leq$  Level I SQT values could appear green, concentrations  $>$  Level I SQT to

≤Level II SQT values could appear yellow, concentrations >Level II SQT values could appear red, and samples lacking chemical data could appear white. Lakes that have the most exceedances of SQT values would be easy to discern from a heat map due to the hotter colors used to represent these data.

- Bayesian networks (a type of probabilistic statistical model) could be used for incorporating uncertainty in sediment assessments.

## Guidance and agency recommendations

- Provide updated guidance on how to use sediment quality data to protect and restore beneficial uses. This would be particularly important in such projects as small dam removals.
- Provide a recommendation on whether to normalize chemical concentrations to TOC. Support efforts to collect TOC data and give the option of providing both dry weight and organic carbon-normalized values.
- The MPCA's SQT guidance (Crane and Hennes 2007) should be updated if the MPCA adopts SQT values for other chemicals.
- In consultation with the MPCA's Stormwater Program, discuss the merits of recommending frequent street sweeping or use of other BMPs to continue to reduce the load of contaminants entering urban waterways.
- The MPCA should consider how to handle water quality standard exceedances of Total PCBs if nonlegacy PCB congeners (e.g., PCB 11) are included in monitoring efforts. This could be a particular problem with WWTP discharges.

## Data management

- Develop a consistent sediment quality database for the entire state (e.g., EQUIS) that can encompass sediment chemistry, physical parameters, sediment toxicity, benthic invertebrate community, tissue residue, pore water, and “-omics” data.

## Potential new developments

- Suggest using adaptive management principles for sediment assessment and restoration activities that may be affected by climate change. For example, lower water levels resulting from climate change will expose former sediment as upland soil. In particular, lakes across the world are warming faster than ocean and air temperatures based on rapid increases in summer surface water temperatures (global mean = 0.34 °C per decade) between 1985 and 2009 (O'Reilly et al. 2015). In addition, the magnitude of lake warming is not consistent across regions (O'Reilly et al. 2015). These changes will impact aquatic biota, water resources, contaminant cycling, and sediment quality.
- Future ecotoxicology work with sediments may want to consider using an adverse outcome pathway framework to improve predictions of chronic toxicity. This approach uses data generated by non-traditional toxicity testing (e.g., “-omics” testing) and high throughput screening technologies based on small organisms or *in vitro* systems. These data are then used in models to extrapolate effects to higher levels of organisms as part of the chemical hazard evaluations (Groh et al. 2015). This concept has applications for quantitative chemical and site-specific risk assessments, as well as for extrapolations across species in the future.

Implementation of the aforementioned recommendations will depend on MPCA management priorities and the availability of funding and staff to conduct such work. Opportunities for more collaborative work between local, state, federal, and tribal agencies, as well as with nonprofit organizations and academic institutions would be constructive. Any type of project work would benefit from consultation with a variety of stakeholders early on in the development of the project and on an ongoing basis during the project. Results should be communicated in a timely manner.

# References

---

- Aadland, L.P. 2010. Reconnecting rivers: Natural channel design in dam removals and fish passage. First Edition. Ecological Resources Division, Minnesota Department of Natural Resources, Fergus Falls, MN. ([http://www.dnr.state.mn.us/eco/streamhab/reconnecting\\_rivers.html](http://www.dnr.state.mn.us/eco/streamhab/reconnecting_rivers.html))
- Abramowicz, D.A. 1990. Aerobic and anaerobic biodegradation of PCBs: A review. *Critical Rev. Biotech.* 10:241-251.
- Achten, C. and J.T. Andersson. 2015. Overview of polycyclic aromatic compounds (PAC). *Polycycl. Aromat. Compd.* 35:177-186.
- AECOM, Inc. 2009. Draft Lake Winona TMDL. AECOM, Inc., Minneapolis, MN. Prepared for Minnesota Pollution Control Agency, St. Paul, MN. (<http://alexandrialakeareasanitarydistrict.com/Files/Lk%20Winona%20Draft%20TMDL%20Nov09.pdf>)
- Akcha, F., T. Burgeot, J-F. Narbonne, and P. Garrigues. 2003. Metabolic activation of PAHs: Role of DNA adduct formation in induced carcinogenesis. In: P.E.T. Douben (Ed.). *PAHs: An Ecotoxicological Perspective*. John Wiley & Sons Ltd.: West Sussex, England. pp. 65-79.
- Alava, J.J., P.S. Ross, and F.A.P.C. Gobas. 2016. Food web bioaccumulation model for resident killer whales from the northeastern Pacific Ocean as a tool for the derivation of PBDE-sediment quality guidelines. *Arch. Environ. Contam. Toxicol.* 70:155-168.
- Alcock, R.E. and K.C. Jones. 1996. Dioxins in the environment: A review of trend data. *Environ. Sci. Technol.* 30:3133-3143.
- Alexander, M. 2000. Aging, bioavailability, and overestimation of risk from environmental pollutants. *Environ. Sci. Technol.* 34:4259-4265.
- Altenburger, R., H. Segner, and R. Van Der Oost. 2003. Biomarkers and PAHs – Prospects for the assessment of exposure and effects in aquatic systems. In: P.E.T. Douben (Ed.). *PAHs: An Ecotoxicological Perspective*. John Wiley & Sons Ltd.: West Sussex, England. pp. 297-328.
- Anderson, J.L., J.C. Bell, T.H. Cooper, and D.F. Grigal. 2001. Tillage: Soils and landscapes of Minnesota. University of Minnesota Extension, Minneapolis, MN. (<http://www.extension.umn.edu/agriculture/tillage/soils-and-landscapes-of-minnesota/>)
- Anger, C.T., C. Sueper, D.J. Blumentritt, K. McNeill, D.R. Engstrom, and W.A. Arnold. 2013. Quantification of triclosan, chlorinated triclosan derivatives, and their dioxin photoproducts in lacustrine sediment cores. *Environ. Sci. Technol.* 47:1833-1843.
- Ankley, G.T., L.P. Burkhard, P.M. Cook, S.A. Diamond, R.J. Erickson, and D.R. Mount. 2003. Assessing risks from photoactivated toxicity of PAHs to aquatic organisms. In: P.E.T. Douben (Ed.). *PAHs: An Ecotoxicological Perspective*. John Wiley & Sons Ltd.: West Sussex, England. pp. 275-296.
- ATSDR. 1995. Toxicology profile for polycyclic aromatic hydrocarbons. Agency for Toxic Substances and Disease Registry, Public Health Services, U.S. Department of Health and Human Services, Atlanta, GA. (<http://www.atsdr.cdc.gov/toxprofiles/tp69.pdf>)
- ATSDR. 2002a. Toxicological profile for wood creosote, coal tar creosote, coal tar, coal tar pitch, and coal tar pitch volatiles. Agency for Toxic Substances and Disease Registry, Atlanta, GA. (<http://www.atsdr.cdc.gov/toxprofiles/tp85.pdf>)
- ATSDR. 2002b. Toxicological profile for DDT, DDE, and DDD. Agency for Toxic Substances and Disease Registry, Atlanta, GA. (<http://www.atsdr.cdc.gov/toxprofiles/tp35.pdf>)

- ATSDR. 2002c. Toxicological profile for aldrin/dieldrin. Agency for Toxic Substances and Disease Registry, Atlanta, GA. (<http://www.atsdr.cdc.gov/toxprofiles/tp1.pdf>)
- ATSDR. 2012. Addendum to the toxicological profile for chlorinated dibenzo-p-dioxins (CDDs). Agency for Toxic Substances and Disease Registry, Atlanta, GA. ([http://www.atsdr.cdc.gov/toxprofiles/cdds\\_addendum.pdf](http://www.atsdr.cdc.gov/toxprofiles/cdds_addendum.pdf))
- Augusto, S., P. Pinho, A. Santos, M.J. Botelho, J. Palma-Oliveira, and C. Branquinho. 2016. Tracking the spatial fate of PCDD/F emissions from a cement plant by using lichens as environmental biomonitors. *Environ. Sci. Technol.* 50:2434-2441.
- Authman, M.M.N., M.S. Zaki, E.A. Khallaf, and H.H. Abbas. 2015. Use of fish as bio-indicator of the effects of heavy metals pollution. *J. Aquac. Res. Development* 6: 328. doi:10.4172/2155-9546.1000328.
- Bakhtiari, A.R., M.P. Zakaria, M.I. Yaziz, M.N.H. Lajis, X. Bi, and M.C.A. Rahim. 2009. Vertical distribution and source identification of polycyclic aromatic hydrocarbons in anoxic sediment cores of Chini Lake, Malaysia: Perylene as indicator of land plant-derived hydrocarbons. *Appl. Geochem.* 24:1777-1787.
- Ballschmiter, K and M. Zell. 1980. Analysis of polychlorinated biphenyls (PCB) by glass capillary gas chromatography. *Fresenius Z. Anal. Chem.* 302:20-31.
- Barabas, N., P. Goovaerts, and P. Adriaens. 2004. Modified polytopic vector analysis to identify and quantify a dioxin dechlorination signature in sediments. 2. Application to the Passaic River. *Environ. Sci. Technol.* 38:1821-1827.
- Barón, E., A. Dissanayake, J. Vilà-Cano, C. Crowther, J.W. Readman, A.N. Jha, E. Eljarrat, and D. Barceló. 2016. Evaluation of the genotoxic and physiological effects of decabromodiphenyl ether (BDE-209) and Dechlorane Plus (DP) flame retardants in marine mussels (*Mytilus galloprovincialis*). *Environ. Sci. Technol.* 50:2700-2708.
- Barr. 2013. Sediment remedial investigation report. Volume I. Great Lakes Legacy Act project, Spirit Lake sediment site, former U. S. Steel Duluth Works, Saint Louis River, Duluth, Minnesota. Prepared for U.S. Steel and U.S. EPA Great Lakes National Program Office by Barr, Duluth, MN. c-s3-06ac. (<https://www.pca.state.mn.us/sites/default/files/c-s3-06ac.pdf>)
- Barrett, P.T. and P. Kline. 1981. The observation to variable ratio in factor analysis. *Personality Study and Group Behaviour* 1:23-33.
- Battelle Memorial Institute, Earth Tech, Inc., and NewFields, Inc. 2003. Guidance for environmental background analysis. Volume II: Sediment. Appendix A: Chemical fingerprinting of PAHs in sediments—recognizing the contribution of urban background. Prepared by Battelle Memorial Institute, Columbus, OH, Earth Tech, Inc., Honolulu, HI, and NewFields, Inc., Atlanta, GA for Naval Facilities Engineering Service Center, Port Hueneme, CA. UG-2054-ENV. ([http://www.navfac.navy.mil/content/dam/navfac/Specialty%20Centers/Engineering%20and%20Expeditionary%20Warfare%20Center/Environmental/Restoration/er\\_pdfs/gpr/navfacesc-ev-ug-2054-env-bkgrd-seds-200304.pdf](http://www.navfac.navy.mil/content/dam/navfac/Specialty%20Centers/Engineering%20and%20Expeditionary%20Warfare%20Center/Environmental/Restoration/er_pdfs/gpr/navfacesc-ev-ug-2054-env-bkgrd-seds-200304.pdf))
- Beauvais, S.L., J.G. Wiener, and G.J. Atchison. 1995. Cadmium and mercury in sediment and burrowing mayfly nymphs (*Hexagenia*) in the upper Mississippi River, USA. *Arch. Environ. Contam. Toxicol.* 28:178-183.
- Bennett, S.J., J.A. Dunbar, F.E. Rhoton, P.M. Allen, J.M. Bigham, G.R. Davidson, and D.G. Wren. 2013. Assessing sedimentation issues within aging flood-control reservoirs. *Rev. Eng. Geol.* 21:25-44.



- Bishop, R. 2012. The legacy of Rachel Carson's Silent Spring. American Chemical Society National Historic Chemical Landmarks, Washington, DC.  
(<http://www.acs.org/content/dam/acsorg/education/whatischemistry/landmarks/rachel-carson-silent-spring/rachel-carsons-silent-spring-historical-resource.pdf>)
- Boehm, P.D. 2006. Polycyclic aromatic hydrocarbons (PAHs). In: Morrison, R.D. and Murphy, B.L. (eds.) Environmental Forensics: Contaminant Specific Guide. Elsevier: New York. pp. 313-337.
- Bojakowska, I., M. Stasiuk, J. Gasior, and W. Wolkowicz. 2014. Assessment of DDT, HCH and PCB pollution of lake sediments in Poland. *Limnol. Rev.* 14:63-74.
- Bonn, B.A. 1998. Dioxins and furans in bed sediment and fish tissue of the Willamette Basin, Oregon, 1992-95. National Water-Quality Assessment Program, U.S. Geological Survey, Portland, OR. Water-Resources Investigations Report 97-4082-D.  
(<https://pubs.er.usgs.gov/publication/wri974082D>)
- Bourdaghs, M., J. Genet, M. Gernes, and E. Peters. 2015. Status and trends of wetlands in Minnesota: Vegetation quality baseline. Minnesota Pollution Control Agency, St. Paul, MN. MPCA Document Number wq-bwm-1-09. (<https://www.pca.state.mn.us/sites/default/files/wq-bwm1-09.pdf>)
- Brand, A.B., J.W. Snodgrass, M.T. Gallagher, R.E. Casey, and R. Van Meter. 2010. Lethal and sublethal effects of embryonic and larval exposure of *Hyla versicolor* to stormwater pond sediments. *Arch. Environ. Contam. Toxicol.* 58:325-331.
- Breneman, D., C. Richards, and S. Lozano. 2000. Environmental influences on benthic community structure in a Great Lakes embayment. *J. Great Lakes Res.* 26:287-304.
- Brown, L.R. 1998. Concentrations of chlorinated organic compounds in biota and bed sediment in streams of the Lower San Joaquin River drainage, California. U.S. Geological Survey, Sacramento, CA. Open-File Report 98-171. (<http://pubs.usgs.gov/of/1998/0171/report.pdf>)
- Budzinski, H., I. Jones, J. Bellocq, C. Piérard, and P. Garrigues. 1997. Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde estuary. *Mar. Chem.* 58:85-97.
- Burgess, R.M. 2009. Evaluating ecological risk to invertebrate receptors from PAHs in sediments at hazardous waste sites. U.S. Environmental Protection Agency, Ecological Risk Assessment Support Center, Cincinnati, OH. EPA/600/R-06/162F.  
(<https://cfpub.epa.gov/ncea/risk/recordisplay.cfm?deid=214715>)
- Burgess, R.M., M.J. Ahrens, C.W. Hickey, P.J. Den Besten, D. Ten Hulscher, B. Van Hattum, J.P. Meador, and P.E.T. Douben. 2003. An overview of the partitioning and bioavailability of PAHs in sediments and soils. In: P.E.T. Douben (Ed.). PAHs: An Ecotoxicological Perspective. John Wiley & Sons Ltd.: West Sussex, England. pp. 99-126.
- Buth, J.M., P.O. Steen, C. Sueper, D. Blumentritt, P.J. Vikesland, W.A. Arnold, and K. McNeill. 2010. Dioxin photoproducts of triclosan and its chlorinated derivatives in sediment cores. *Environ. Sci. Technol.* 44: 4545-4551.
- Callender, E. and P.C. Van Metre. 1997. Reservoir sediment cores show U.S. lead declines. *Environ. Sci. Technol.* 31:424A-428A.
- Carvalho, A., S.J. Schropp, G.M. Sloane, T.P. Biernacki, and T.L. Seal. 2002. Development of an interpretive tool for assessment of metal enrichment in Florida freshwater sediment. Taylor Engineering, Inc., Jacksonville, FL and Florida Department of Environmental Protection, Tallahassee, FL. Report # C2001-022.  
([http://www.dep.state.fl.us/water/monitoring/docs/seds/FFW\\_Metals\\_Report\\_Final.pdf](http://www.dep.state.fl.us/water/monitoring/docs/seds/FFW_Metals_Report_Final.pdf))

- CCME. 1999. Canadian environmental quality guidelines. Guidelines and Standards Division, Environment Canada, Winnipeg, Manitoba.
- CCME. 2001. Canadian sediment quality guidelines for the protection of aquatic life. Canadian Council of Ministers of the Environment, Winnipeg, Manitoba. (<http://cegg-rcqe.ccme.ca/download/en/245>)
- CCME. 2011. Canadian water quality guidelines for the protection of aquatic life: Chloride. Canadian Council of Ministers of the Environment, Winnipeg, Manitoba. (<http://cegg-rcqe.ccme.ca/download/en/337>)
- Chaky, D.A. 2003. Polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins and furans in the New York metropolitan area: Interpreting atmospheric deposition and sediment chronologies. Ph.D. Dissertation, Rensselaer Polytechnic Institute, Troy, NY. 431 pp. ([http://digitool.rpi.edu:8881/R/TL4XXQ1X6A1ISXT1MFG9TNRJY7UF5135P49DYPVB5GH1JEGS8A-00444?func=dbin-jump-full&object\\_id=15897&local\\_base=GEN01&pds\\_handle=GUEST](http://digitool.rpi.edu:8881/R/TL4XXQ1X6A1ISXT1MFG9TNRJY7UF5135P49DYPVB5GH1JEGS8A-00444?func=dbin-jump-full&object_id=15897&local_base=GEN01&pds_handle=GUEST))
- Chapman, P.M., F. Wang, W.J. Adams, and A. Green. 1999. Appropriate applications of sediment quality values for metals and metalloids. *Environ. Sci. Technol.* 33:3937-3941.
- Chapman, P.M., W.J. Adams, M.L. Brooks, C.G. Delos, S.N. Luoma, W.A. Maher, H.M. Ohlendorf, T.S. Presser, and D.P. Shaw. 2010. Chapter 2. Executive summary. In: P.M. Chapman et al. (Eds.). *Ecological Assessment of Selenium in the Aquatic Environment*. CRC Press: Boca Raton, FL. pp. 5-6.
- Christensen, G.N., V. Savinov, T. Savinova, L. Alexeeva, A. Kochetkov, A. Konoplev, D. Samsonov, V.A. Dauvalter, N.A. Kashulin, and S.S. Sandimirov. 2007. Screening studies of POP levels in bottom sediments from selected lakes in the Paz watercourse. *Akvaplan-niva*, Tromsø, Norway. Report number 3665.01 (<https://helda.helsinki.fi/handle/10138/38236>)
- Cleverly, D., J. Schaum, G. Schweer, J. Becker, and D. Winters. 1997. The congener profiles of anthropogenic sources of chlorinated dibenzo-*p*-dioxins and chlorinated dibenzofurans in the United States. *Organohalogen Comp.* 32:430-435.
- Cohn, B.A., M.S. Wolff, P.M. Cirillo, and R.I. Sholtz. 2007. DDT and breast cancer in young women: New data on the significance of age at exposure. *Environ. Health Persp.* 115:1406-1414.
- Cohn, B.A., M. La Merrill, N.Y. Krigbaum, G. Yeh, J.S. Park, L. Zimmermann, and P.M. Cirillo. 2015. DDT exposure in utero and breast cancer. *J. Clin. Endocrinol. Metab.* 100:2865-2872.
- Cordner, A., M. Mulcahy, and P. Brown. 2013. Chemical regulation on fire: Rapid policy advances on flame retardants. *Environ. Sci. Technol.* 47:7067-7076.
- Cornelissen, G., O. Gustafsson, T.D. Bucheli, M.T.O. Jonker, A.A. Koelmans, and P.C.M. van Noort. 2005. Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: Mechanisms and consequences for distribution, bioaccumulation, and biodegradation. *Environ. Sci. Technol.* 39:6881-6895.
- Costa, L.G., G. Giordano, M. Guizzetti, and A. Vitalone. 2008. Neurotoxicity of pesticides: A brief review. *Frontiers Biosci.* 13:1240-1249.
- Coulter, C.T. 2004. EPA-CMB8.2 users manual. United States Environmental Protection Agency, Research Triangle Park, NC. EPA-452/R-04-011. <http://www.epa.gov/scram001/models/receptor/EPA-CMB82Manual.pdf>.
- Councell, T.B., K.U. Dickenfield, E.R. Landa, and E. Callender. 2004. Tire-wear particles as a source of zinc to the environment. *Environ. Sci. Technol.* 38:4206-4214.

- Crane, J.L. 1999. Assessment of contaminated sediments in Slip C, Duluth Harbor, Minnesota. Environmental Outcomes Division, Minnesota Pollution Control Agency, St. Paul, MN. EPA-905-R-99-007. (<https://www.pca.state.mn.us/sites/default/files/slipc.pdf>)
- Crane, J.L. 2006. Phase IV GIS-based sediment quality database for the St. Louis River Area of Concern—Wisconsin focus. Overview of sediment quality conditions in the St. Louis River Area of Concern. Minnesota Pollution Control Agency, Environmental Analysis and Outcomes Division, St. Paul, MN. MPCA Document Number tdr-fg06-04. (<https://www.pca.state.mn.us/sites/default/files/tdr-fg06-04a.pdf>, <http://www.pca.state.mn.us/publications/tdr-fg06-04b.pdf>, <http://www.pca.state.mn.us/publications/tdr-fg06-04c.pdf>, <http://www.pca.state.mn.us/publications/tdr-fg06-04d.pdf>, and <http://www.pca.state.mn.us/publications/tdr-fg06-04e.pdf>)
- Crane, J.L. 2014. Source apportionment and distribution of polycyclic aromatic hydrocarbons, risk considerations, and management implications for urban stormwater pond sediments in Minnesota, USA. Arch. Environ. Contam. Toxicol. 66:176-200.
- Crane, J.L. and S. Hennes. 2007. Guidance for the use and application of sediment quality targets for the protection of sediment-dwelling organisms in Minnesota. Minnesota Pollution Control Agency, St. Paul, MN. tdr-gl-04. (<http://www.pca.state.mn.us/index.php/view-document.html?gid=9163>)
- Crane, J.L. and S. Hennes. 2010a. Regional variation in the distribution of PBDEs in Minnesota lake sediments and fish tissues contrasted with local urban sediments. Poster presentation given at the 31<sup>st</sup> Annual Meeting of the Society of Environmental Toxicology and Chemistry, November 7-11, 2010, Portland, OR.
- Crane, J.L. and S. Hennes. 2010b. Effect of land use on the distribution of conventional and emerging contaminants in urban stormwater pond sediments from a major metropolitan area. Poster presentation given at the 31<sup>st</sup> Annual Meeting of the Society of Environmental Toxicology and Chemistry, November 7-11, 2010, Portland, OR.
- Crane, J.L. and D.D. MacDonald. 2003. Applications of numerical sediment quality targets for assessing sediment quality conditions in a US Great Lakes Area of Concern. Environ. Manage. 32:128-140.
- Crane, J.L. and P.L. Myre. 2006. Phase IV GIS-based sediment quality database for the St. Louis River Area of Concern—Wisconsin focus. Supplement to the Phase II/III help sections for database users. Minnesota Pollution Control Agency, Environmental Analysis and Outcomes Division, St. Paul, MN. MPCA Document Number tdr-fg06-02. (<https://www.pca.state.mn.us/sites/default/files/tdr-fg06-02.pdf>)
- Crane, J.L., K. Grosenheider, and C.B. Wilson. 2010. Contamination of stormwater pond sediments by polycyclic aromatic hydrocarbons (PAHs) in Minnesota. Minnesota Pollution Control Agency, St. Paul, MN. MPCA Document Number tdr-g1-07. (<https://www.pca.state.mn.us/sites/default/files/tdr-g1-07.pdf>)
- Crane, J.L., C. Richards, D. Breneman, S. Lozano, and J.A. Schuldt. 2005. Evaluating methods for assessing sediment quality in a Great Lakes embayment. Aquatic Ecosystem Health Manage. 8:323-349.
- Crane, J.L., D.D. MacDonald, C.G. Ingersoll, D.E. Smorong, R.A. Lindskoog, C.G. Severn, T.A. Berger, and L.J. Field. 2000. Development of a framework for evaluating numerical sediment quality targets and sediment contamination in the St. Louis River Area of Concern. Great Lakes National Program Office, United States Environmental Protection Agency, Chicago, IL. EPA 905-R-00-008. (<https://www.pca.state.mn.us/sites/default/files/sqt-slraoc.pdf>)

- Crane, J.L., D.D. MacDonald, C.G. Ingersoll, D.E. Smorong, R.A. Lindskoog, C.G. Severn, T.A. Berger, and L.J. Field. 2002. Evaluation of numerical sediment quality targets for the St. Louis River Area of Concern. *Arch. Environ. Contam. Toxicol.* 43:1-10.
- Crimmins, B.S., J.J. Pagano, X. Xia, P.K. Hopke, M.S. Milligan, and T.M. Holsen. 2012. Polybrominated diphenyl ethers (PBDEs): Turning the corner in Great Lakes trout 1980-2009. *Environ. Sci. Technol.* 46:9890-9897.
- Danish EPA. 2015. Survey of biphenyl (CAS no. 92-52-4). Danish Ministry of the Environment, Environmental Protection Agency, Copenhagen, Denmark. ISBN no. 978-87-93352-35-3. (<http://www2.mst.dk/Udgiv/publications/2015/06/978-87-93352-35-3.pdf>).
- Daskalakis, K.D. and T.P. O'Connor. 1995. Normalization and elemental sediment contamination in the coastal United States. *Environ. Sci. Technol.* 29:470-477.
- De Boo, W. 1990. Cadmium in agriculture. *Toxicol. Environ. Chem.* 27:55-63.
- de Castro-Català, N., M. Kuzmanovic, N. Roig, J. Sierra, A. Ginebreda, D. Barceló, S. Pérez, M. Petrovic, Y. Picó, M. Schuhmacher, and I. Muñoz. 2016. Ecotoxicity of sediments in rivers: Invertebrate community, toxicity bioassays and the toxic unit approach as complementary assessment tools. *Science Total Environ.* 540:297-306.
- Di Toro, D.M., C.S. Zarba, D.J. Hansen, W.J. Berry, R.C. Swartz, C.E. Cowan, S.P. Pavlou, H.E. Allen, N.A. Thomas, and P.R. Paquin. 1991. Technical basis for establishing sediment quality criteria for non-ionic organic chemicals using equilibrium partitioning. *Environ. Toxicol. Chem.* 10:1541-1583.
- Diamond, S.A., N.J. Milroy, V.R. Mattson, L.J. Heinis, and D.R. Mount. 2003. Photoactivated toxicity in amphipods collected from polycyclic aromatic hydrocarbon-contaminated sites. *Environ. Toxicol. Chem.* 22:2752-2760.
- Diamond, S.A., D.R. Mount, L.P. Burkhard, G.T. Ankley, E.A. Makynen, and E.N. Leonard. 2000. Effect of irradiance spectra on the photoinduced toxicity of three polycyclic aromatic hydrocarbons. *Environ. Toxicol. Chem.* 19:1389-1396.
- Dickhut, R.M., E.A. Canuel, K.E. Gustafson, K. Liu, K.M. Arzayus, S.E. Walker et al. 2000. Automotive sources of carcinogenic polycyclic aromatic hydrocarbons associated with particulate matter in the Chesapeake Bay region. *Environ. Sci. Technol.* 34:4635-4640.
- Dodder, N.G., K.A. Maruya, G.G. Lauenstein, J. Ramirez, K.J. Ritter, and K.C. Schiff. 2012. Distribution and sources of polybrominated diphenyl ethers in the Southern California Bight. *Environ. Toxicol. Chem.* 31:2239-2245.
- Douben, P.E.T. 2003. Introduction. In P.E.T. Douben (Ed.). *PAHs: An Ecotoxicological Perspective*. John Wiley & Sons Ltd.: West Sussex, England. pp. 3-6.
- Driedger, A.G.J., H.H. Dürr, K. Mitchell, and P. Van Cappellen. 2015. Plastic debris in the Laurentian Great Lakes: A review. *J. Great Lakes Res.* 41:9-19.
- Duffus, J.H. 2002. "Heavy metals"—a meaningless term? *Pure Appl. Chem.* 74:793-807.
- Engstrom, D.R., S.J. Balogh, E.B. Swain. 2007. History of mercury inputs to Minnesota lakes: Influences of watershed disturbance and localized atmospheric deposition. *Limnol. Oceanogr.* 52:2467-2483.
- Environment Canada. 2013. Canadian Environmental Protection Act, 1999. Federal environmental quality guidelines. Polybrominated diphenyl ethers (PBDEs). Environment Canada. ([https://www.ec.gc.ca/ese-ees/05DF7A37-60FF-403F-BB37-0CC697DBD9A3/FEQG\\_PBDE\\_EN.pdf](https://www.ec.gc.ca/ese-ees/05DF7A37-60FF-403F-BB37-0CC697DBD9A3/FEQG_PBDE_EN.pdf))

- Environment Canada and Health Canada. 2014. Screening assessment 1,1'-Biphenyl, Chemical Abstracts Service Registry Number 92-52-4. Environment Canada and Health Canada. (<http://www.ec.gc.ca/ese-ees/default.asp?lang=En&n=70D7175D-1>)
- Era, B. and D. Serdar. 2001. Reassessment of toxicity of Lake Roosevelt sediments. Environmental Assessment Program, Washington State Department of Ecology, Olympia, WA. Publication No. 01-03-043. (<https://fortress.wa.gov/ecy/publications/documents/0103043.pdf>)
- Evans, J.E. 2015. Contaminated sediment and dam removals: Problem or opportunity? EOS 96, doi:10.1029/2015EO036385. (<https://eos.org/features/contaminated-sediment-and-dam-removals-problem-or-opportunity-2>)
- Ferrey, M.L., S. Heiskary, R. Grace, M.C. Hamilton, and A. Lueck. 2015. Pharmaceuticals and other anthropogenic tracers in surface water: A randomized survey of 50 Minnesota lakes. Environ. Toxicol. Chem. 34:2475-2488.
- Förstner, U. 1976. Lake sediments as indicators of heavy-metal pollution. The Science of Nature 63:465-470.
- Freedman, B. 1989. Environmental Ecology: The Impacts of Pollution and Other Stresses on Ecosystem Structure and Function. Academic Press, Inc.: San Diego, CA.
- Gao, S., C. Sun, and A. Zhang. 2007. Pollution of polycyclic aromatic hydrocarbons in China. In: A. Li, S. Tanabe, G. Jiang, J.P. Giesy, and P.S.K. Lam (Eds.) Persistent Organic Pollutants in Asia: Sources, Distributions, Transport and Fate, Vol. 7. Elsevier: Amsterdam. pp. 237-287.
- Genet, J. 2015. Status and trends of wetlands in Minnesota: Depressional wetland quality assessment (2007-2012). Minnesota Pollution Control Agency, St. Paul, MN. MPCA Document Number sq-bwm1-08. (<https://www.pca.state.mn.us/sites/default/files/wq-bwm1-08.pdf>)
- Gernes, M.C. and J.C. Helgen. 1999. Indexes of biotic integrity (IBI) for wetlands: Vegetation and invertebrate IBIs. Minnesota Pollution Control Agency, St. Paul, MN. MPCA Document Number wq-bwm6-06.
- Gernes, M.C. and J.C. Helgen. 2002. Indexes of biological integrity (IBI) for large depressional wetlands in Minnesota. Minnesota Pollution Control Agency, St. Paul, MN. (<https://www.pca.state.mn.us/sites/default/files/wet-report-largewetland.pdf>)
- Gonzalez-Ramirez, J. and Y. Ji. 2015. Agricultural land use change in the corn belt. Iowa State University, Ames, IA. Agricultural Policy Review, Spring 2015. ([http://www.card.iastate.edu/ag\\_policy\\_review/pdf/spring-2015.pdf](http://www.card.iastate.edu/ag_policy_review/pdf/spring-2015.pdf))
- Groh, K.J., R.N. Carvalho, J.K. Chipman, N.D. Denslow, M. Halder, C.A. Murphy, D. Roelofs, A. Rolaki, K. Schirmer, and K.H. Watanabe. 2015. Development and application of the adverse outcome pathway framework for understanding and predicting chronic toxicity: I. Challenges and research needs in ecotoxicology. Chemosphere 120:764-777.
- Grossman, E. 2013. Nonlegacy PCBs. Pigment manufacturing by-products get a second look. Environ. Health Perspect. 121:A86-A93.
- Hall, R.I., B.B. Wolfe, J.A. Wiklund, T.W.D. Edwards, A.J. Farwell, and D.G. Dixon. 2012. Has Alberta oil sands development altered delivery of polycyclic aromatic compounds to the Peace-Athabasca Delta? PLOS One 7: 1-17.
- Han, Y.M., C. Wei, B.A.M. Bandowe, W. Wilcke, J.J. Cao, B.Q. Xu, S.P. Gao, X.X. Tie, G.H. Li, Z.D. Jin, and Z.S. An. 2015. Elemental carbon and polycyclic aromatic compounds in a 150-year sediment core from Lake Qinghai, Tibetan Plateau, China: Influence of regional and local sources and transport pathways. Environ. Sci. Technol. 49:4176-4183.

- Hanson, P.J., D.W. Evans, D.R. Colby, and V.S. Zdanowicz. 1993. Assessment of elemental contamination in estuarine and coastal environments based on geochemical and statistical modeling of sediments. *Mar. Environ. Res.* 36:237-266.
- Hawthorne, S.B., D.J. Miller, and J.P. Kreitinger. 2006. Measurement of total polycyclic aromatic hydrocarbon concentrations in sediments and toxic units used for estimating risk to benthic invertebrates at manufactured gas plant sites. *Environ. Toxicol. Chem.* 25:287-296.
- He, X., X. Dong, D. Zou, Y. Yu, Q. Fang, Q. Zhang, and M. Zhao. 2015. Enantioselective effects of o,p'-DDT on cell invasion and adhesion of breast cancer cells: Chirality in cancer development. *Environ. Sci. Technol.* 49:10028-10037.
- Heiskary, S. 1996. Lake sediment contaminant levels in Minnesota. Water Quality Division, Minnesota Pollution Control Agency, St. Paul, MN.
- Heiskary, S. and M. Lindon. 2010. Minnesota National Lakes Assessment Project: An overview of water chemistry in Minnesota lakes. Minnesota Pollution Control Agency, St. Paul, MN. MPCA Document Number wq-nlap1-05. (<https://www.pca.state.mn.us/sites/default/files/wq-nlap1-05.pdf>)
- Helgen, J. 2002. Method for evaluating wetland condition. #9 Developing an invertebrate index of biological integrity for wetlands. Office of Water, U.S. Environmental Protection Agency, Washington, DC. EPA-822-R-02-019. ([http://www.epa.gov/sites/production/files/documents/wetlands\\_9invertebrate.pdf](http://www.epa.gov/sites/production/files/documents/wetlands_9invertebrate.pdf))
- Helsel, D.R. 2010. Summing nondetects: Incorporating low-level contaminants in risk assessment. *Integr. Environ. Assess. Manag.* 6:361-366.
- Helsel, D.R. 2012. *Statistics for Censored Environmental Data Using Minitab® and R*. Second Edition. John Wiley & Sons, Inc.: Hoboken, NJ.
- Herlihy, A.T., J.B. Sobota, T.C. McDonnell, T.J. Sullivan, S. Lehmann, and E. Tarquinio. 2013. An a priori process for selecting candidate reference lakes for a national survey. *Freshwat. Sci.* 32:385-396.
- Hilscherova, K., K. Kannan, H. Nakata, N. Hanari, N. Yamashita, P.W. Bradley, J.M. McCabe, A.B. Taylor, and J.P. Giesy. 2003. Polychlorinated dibenzo-*p*-dioxin and dibenzofuran concentration profiles in sediment and flood-plain soils of the Tittabawassee River, Michigan. *Environ. Sci. Technol.* 37:468-474.
- Hites, R.A. 2011. Dioxins: An overview and history. *Environ. Sci. Technol.* 45:16-20.
- Hsu-Kim, H., K.H. Kucharzyk, T. Zhang, and M.A. Deshusses. 2013. Mechanisms regulating mercury bioavailability for methylating microorganisms in the aquatic environment: A critical review. *Environ. Sci. Technol.* 47:2441-2456.
- Hu, D. and K.C. Hornbuckle. 2010. Inadvertent polychlorinated biphenyls in commercial paint pigments. *Environ. Sci. Technol.* 44:2822-2827.
- Hu, D., A. Martinez, and K.C. Hornbuckle. 2011. Sedimentary records of non-Aroclor and Aroclor PCB mixtures in the Great Lakes. *J. Great Lakes Res.* 37:359-364.
- Ingersoll, C.G., D.D. MacDonald, N. Wang, J.L. Crane, L.J. Field, P.S. Haverland, N.E. Kemble, R.A. Lindscoog, C. Severn, and D.E. Smorong. 2001. Predictions of sediment toxicity using consensus-based freshwater sediment quality guidelines. *Arch. Environ. Contam. Toxicol.* 41:8-21.
- Jantunen, L.M., F. Wong, A. Gawor, H. Kylin, P.A. Helm, G.A. Stern, W.M.J. Strachan, D.A. Burniston, and T.F. Bidleman. 2015. 20 years of air-water gas exchange observations for pesticides in the western Arctic Ocean. *Environ. Sci. Technol.* 49:13844-13852.



- Jautzy, J.J., J.M.E. Ahad, R.I. Hall, J.A. Wiklund, B.B. Wolfe, C. Gobeil, and M.M. Savard. 2015. Source apportionment of background PAHs in the Peace-Athabasca Delta (Alberta, Canada) using molecular level radiocarbon analysis. *Environ. Sci. Technol.* 49:9056-9063.
- Jin, X., Y. He, B. Zhang, Y. Hassan, and K. George. 2013. Impact of sulfate and chloride on sediment phosphorus release in the Yangtze Estuary Reservoir, China. *Water Sci. Technol.* 67:1748-1756.
- Johnson, A., M. Friese, J. Roland, C. Gruenenfelder, B. Dowling, A. Fernandez, and T. Hamlin. 2011. Background characterization for metals and organic compounds in northeast Washington lakes. Part 1: Bottom sediments. Washington Department of Ecology, Olympia, WA. Publication No. 11-03-035. (<https://fortress.wa.gov/ecy/publications/SummaryPages/1103035.html>)
- Johnson, G.W., R. Ehrlich, and W. Full. 2004. Principal components analysis and receptor models in environmental forensics. In: Murphy, B.L. and R.D. Morrison (eds). *Introduction to environmental forensics*. Elsevier Academic Press: Burlington. pp. 461-515.
- Johnson, G.W., J.F. Quensen, III, J.R. Chiarenzelli, and M.C. Hamilton. 2006. Polychlorinated biphenyls. In: Morrison, R.D. and Murphy, B.L. (eds) *Environmental forensics: Contaminant specific guide*. Elsevier: New York. pp. 187-225.
- Johnson, R. 2010. Red River Valley tile drainage water quality assessment. Phase I final report. North Dakota State University, Fargo, ND. (available from <https://www.ag.ndsu.edu/>).
- Juracek, K.E. and A.C. Ziegler. 2006. The legacy of leaded gasoline in bottom sediment of small rural reservoirs. *J. Environ. Qual.* 35:2092-2102.
- Kahn, L. 1988. Determination of total organic carbon in sediment (Lloyd Kahn method). U.S. Environmental Protection Agency, Region II Environmental Services Division, Edison, NJ. (<http://www.nj.gov/dep/srp/guidance/rs/lloydkahn.pdf>)
- Kamel, F. and J.A. Hoppin. 2004. Association of pesticide exposure with neurologic dysfunction and disease. *Environ. Health Perspect.* 112:950-958.
- Katsoyiannis, A., A.J. Sweetman, and K.C. Jones. 2011. PAH molecular diagnostic ratios applied to atmospheric sources: A critical evaluation using two decades of source inventory and air concentration data from the UK. *Environ. Sci. Technol.* 45:8897-8906.
- Keiser, L., G.S. Soreghan, and Y.J. Joo. 2014. Effects of drying techniques on grain-size analyses of fine-grained sediment. *J. Sedimentary Res.* 84:893-896.
- Kelly, W.R., S.V. Panno, and K. Hackley. 2012. The sources, distribution, and trends of chloride in the waters of Illinois. Illinois State Water Survey, Prairie Research Institute, University of Illinois at Urbana-Champaign, Champaign, IL. Bulletin B-74. (<http://www.isws.illinois.edu/pubdoc/b/iswsb-74.pdf>)
- Khairy, M., D. Muir, C. Teixeira, and R. Lohmann. 2015. Spatial distribution, air-water fugacity ratios and source apportionment of polychlorinated biphenyls in the lower Great Lakes basin. *Environ. Sci. Technol.* 49:13787-13797.
- King, P. 2000. Trace metal concentrations in surface sediments of nine Minnesota northern lakes and forests ecoregion reference lakes. Minnesota Pollution Control Agency, St. Paul, MN.
- Klosterhaus, S., L.J. McKee, D. Yee, J.M. Kass, and A. Wong. 2014. Polychlorinated biphenyls in the exterior caulk of San Francisco Bay area buildings, California, USA. *Environ. Internat.* 66:38-43.
- Kovacevic, A. and C. O'Dell. 2008. Decabromodiphenyl ether (Deca-BDE). Minnesota Pollution Control Agency, St. Paul, MN. MPCA Document Number Irp-ei-2sy08. (<https://www.pca.state.mn.us/sites/default/files/lrp-ei-2sy08.pdf>)

- Kuo, Y-M., M.S. Sepúlveda, I. Hua, H.G. Ochoa-Acuña, and T.M. Sutton. 2010. Bioaccumulation and biomagnification of polybrominated diphenyl ethers in a food web of Lake Michigan. *Ecotoxicol.* 19:623-634.
- Lark, T.J., J.M. Salmon, and H.K. Gibbs. 2015. Cropland expansion outpaces agricultural and biofuel policies in the United States. *Environ. Res. Lett.* 10: 044003. doi: 10.1088/1748-9326/10/4/044003.
- Lemaire, P., A. Mathieu, S. Carriere, P. Draï, J. Giudicelli, and M. Lafaurie. 1990. The uptake metabolism and biological half-life of benzo[a]pyrene in different tissues of sea bass, *Dicentrarchus labrax*. *Ecotoxicol. Environ. Safety* 20:223-233.
- Lerman, A. and R.R. Weiler. 1970. Diffusion and accumulation of chloride and sodium in Lake Ontario sediment. *Earth Planetary Sci. Lett.* 10:150-156.
- Li, A., J-K. Jang, and P.A. Scheff. 2003. Application of EPA CMB8.2 model for source apportionment of sediment PAHs in Lake Calumet, Chicago. *Environ. Sci. Technol.* 37:2958-2965.
- Lima, A.L.C., J.W. Farrington, and C.M. Reddy. 2005. Combustion-derived polycyclic aromatic hydrocarbons in the environment—A review. *Environ. Forensics* 6:109-131.
- LimnoTech. 2013a. St. Louis River Area of Concern implementation framework: Roadmap to delisting (remedial action plan update). LimnoTech (with input from multiple stakeholders). wq-ws4-02a. (<http://www.pca.state.mn.us/index.php/view-document.html?gid=19677>)
- LimnoTech. 2013b. St. Louis River Area of Concern sediment characterization. LimnoTech, Ann Arbor, MI. Prepared for the Minnesota Pollution Control Agency, Duluth, MN. ([https://www.pca.state.mn.us/sites/default/files/20130711\\_final\\_slraoc\\_sediment\\_characterization\\_report.pdf](https://www.pca.state.mn.us/sites/default/files/20130711_final_slraoc_sediment_characterization_report.pdf))
- Lohmann, R. and K.C. Jones. 1998. Dioxins and furans in air and deposition: A review of levels, behaviour and processes. *Science Total Environ.* 219:53-81.
- Lombi, E. and P.E. Holm. 2010. Chapter 3. Metalloids, soil chemistry and the environment. In: T.P. Jahn and G.P. Bienert (Eds.). *MIPs and Their Role in the Exchange of Metalloids*. Springer: New York, NY. pp. 33-44.
- Long, E.R., C.G. Ingersoll, and D.D. MacDonald. 2006. Calculation and uses of mean sediment quality guideline quotients: A critical review. *Environ. Sci. Technol.* 40:1726-1736.
- Lu, Z., R.J. Letcher, S. Chu, J.J.H. Ciborowski, G.D. Haffner, K.G. Drouillard, S.L. MacLeod, and C.H. Marvin. 2015. Spatial distributions of polychlorinated biphenyls, polybrominated diphenyl ethers, tetrabromobisphenol A and bisphenol A in Lake Erie sediment. *J. Great Lakes Res.* 41:808-817.
- Luch, A. 2005. *The Carcinogenic Effects of Polycyclic Aromatic Hydrocarbons*. Imperial College Press: London, UK.
- MacDonald, D.D., C.G. Ingersoll, and T.A. Berger. 2000. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *Arch. Environ. Contam. Toxicol.* 39:20-31.
- Macksasitorn, S., J. Janssen, and K.A. Gray. 2015. PCBs refocused: Correlation of PCB concentrations in Green Bay legacy sediments with adjacent lithophilic, invasive biota. *J. Great Lakes Res.* 41:215-221.
- Mahler, B.J., P.C. Van Metre, J.L. Crane, A.W. Watts, M. Scoggins, and E.S. Williams. 2012. Coal-tar-based pavement sealcoat and PAHs: Implications for the environment, human health, and stormwater management. *Environ. Sci. Technol.* 46:3039-3045.



- Mahler, B.J., P.C. Van Metre, J.T. Wilson, M. Musgrove, T.L. Burbank, T.E. Ennis, and T.J. Bashara. 2010. Coal-tar-based parking lot sealcoat: An unrecognized source of PAH to settled house dust. *Environ. Sci. Technol.* 44:894-900.
- Mason, R.P. 2013. *Trace Metals in Aquatic Systems*. First Edition. Wiley-Blackwell: West Sussex, UK. 440 pp.
- MDH. 1999. Screening evaluation of arsenic, cadmium, and lead levels in Minnesota fertilizer products. Minnesota Department of Health, St. Paul, MN. (<http://www.health.state.mn.us/divs/eh/risk/studies/fertrpt.pdf>)
- MDH. 2005. Human health screening values for St. Louis River sediments: U.S. Steel site. Minnesota Department of Health, Environmental Health Division, St. Paul, MN. (<http://www.health.state.mn.us/divs/eh/hazardous/sites/stlouis/ussteelmemo1005.pdf>)
- MDH. 2011. C. Decabromodiphenyl ether. Site Assessment and Consultation Unit, Minnesota Department of Health, St. Paul, MN. (<http://www.health.state.mn.us/divs/eh/hazardous/topics/toxfreekids/pclist/decabde.pdf>)
- MDH. 2013. Public health consultation. Updated human health screening values for St. Louis River sediments: US Steel site. Minnesota Department of Health, St. Paul, MN.
- MDH. 2016. Guidance for evaluating the cancer potency of polycyclic aromatic hydrocarbon (PAH) mixtures in environmental samples. Environmental Health Division, Minnesota Department of Health, St. Paul, MN. (<http://www.health.state.mn.us/divs/eh/risk/guidance/pahguidance.pdf>)
- Meador, J.P. 2003. Bioaccumulation of PAHs in marine invertebrates. In: P.E.T. Douben (ed.). *PAHs: An Ecotoxicological Perspective*. John Wiley & Sons Ltd.: West Sussex, England. pp. 147-171.
- Meijer, S.N., W.A. Ockenden, A. Sweetman, K. Breivik, J.O. Grimalt, and K.C. Jones. 2003. Global distribution and budget of PCBs and HCB in background surface soils: Implications for sources and environmental processes. *Environ. Sci. Technol.* 37:667-672.
- Minnesota Conservation Department. 1959. A summary of aquatic nuisance control in Minnesota. Division of Game and Fish, Minnesota Conservation Department, St. Paul, MN.
- Mnif, W., A.I.H. Hassine, A. Bouaziz, A. Bartegi, O. Thomas, and B. Roig. 2011. Effect of endocrine disrupter pesticides: A review. *Int. J. Environ. Res. Public Health* 8:2265-2303.
- Moll, A. 1982. Economic analysis for the final rule to exclude closed and controlled processes from the PCB (polychlorinated biphenyls) ban rule. Office of Pesticides and Toxic Substances, U.S. Environmental Protection Agency, Washington, DC. PB83-159731. (<http://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=9100B9O9.txt>)
- Monson, B. and S. Heiskary. 2008. Minnesota National Lakes Assessment Project: Water mercury concentrations in Minnesota lakes. Minnesota Pollution Control Agency, St. Paul, MN. wq-nlap-02. (<https://www.pca.state.mn.us/sites/default/files/wq-nlap1-02.pdf>)
- MPCA. 2006. Polybrominated diphenyl ethers: The emerging contaminants in the Lake Superior watershed (GL2002-184). Environmental Outcomes Division, Minnesota Pollution Control Agency, St. Paul, MN. MPCA Document Number tdr-g1-14.
- MPCA. 2009. Implementation plan for Minnesota's statewide mercury total maximum daily load. Minnesota Pollution Control Agency, St. Paul, MN. MPCA Document Number wq-iw4-01p. (<https://www.pca.state.mn.us/sites/default/files/wq-iw4-01p.pdf>)

- MPCA. 2011. Twin Cities metropolitan area chloride project phase 2. 2011 work plan summary. Minnesota Pollution Control Agency, St. Paul, MN. MPCA Document Number wq-iw11-06s. (<https://www.pca.state.mn.us/sites/default/files/wq-iw11-06s.pdf>)
- MPCA. 2013. Sources of mercury pollution and methylmercury contamination of fish in Minnesota. Minnesota Pollution Control Agency, St. Paul, MN. MPCA Document Number p-p2s4-06. (<https://www.pca.state.mn.us/sites/default/files/p-p2s4-06.pdf>)
- MPCA. 2016a. Actions to restrict or discontinue the use of coal tar-based sealants in the United States. Minnesota Pollution Control Agency, St. Paul, MN. MPCA Document Number tdr-g1-12. (<https://www.pca.state.mn.us/sites/default/files/tdr-g1-12.pdf>)
- MPCA. 2016b. Twin Cities metropolitan area chloride management plan. Minnesota Pollution Control Agency, St. Paul, MN. MPCA Document Number wq-iw11-06ff. (<https://www.pca.state.mn.us/sites/default/files/wq-iw11-06ff.pdf>)
- Muller, P. 2002. Potential for occupational and environmental exposure to ten carcinogens in Toronto. Prepared by ToxProbe Inc., Toronto, ON for Toronto Public Health, Toronto, ON. ([http://www1.toronto.ca/City%20of%20Toronto/Toronto%20Public%20Health/Healthy%20Public%20Policy/PDF%20Reports%20Repository/cr\\_technicalreport.pdf](http://www1.toronto.ca/City%20of%20Toronto/Toronto%20Public%20Health/Healthy%20Public%20Policy/PDF%20Reports%20Repository/cr_technicalreport.pdf))
- Myers, J. and K. Thorbjornsen. 2004. Identifying metals contamination in soil: A geochemical approach. *Soil Sed. Contam.* 1:1-16.
- Neff, J.M. 1979. Polycyclic Aromatic Hydrocarbons in the Aquatic Environment. Applied Science Publishers Ltd.: London, England.
- Nieuwoudt, C., L.P. Quinn, R. Pieters, I. Jordaan, M. Visser, H. Kylin, A.R. Borgen, J.P. Giesy, and H. Bouwman. 2009. Dioxin-like chemicals in soil and sediment from residential and industrial areas in central South Africa. *Chemosphere* 76:774-783.
- Nowell, L.H, P.D. Capel, and P.D. Dileanis. 1999. Pesticides in Stream Sediment and Aquatic Biota. Distribution, Trends, and Governing Factors. Lewis Publishers: New York, NY. 1001 pp.
- NYSDEC. 1999. Technical guidance for screening contaminated sediments. Division of Fish, Wildlife and Marine Resources, New York State Department of Environmental Conservation, Albany, NY. 39 pp.
- O'Hara, K., S. Heiskary, R. Valley, and M. Habrat. 2011. Sentinel lake assessment report. Elk Lake (15-0010). Clearwater County, Minnesota. Water Monitoring Section, Minnesota Pollution Control Agency, St. Paul, MN and Section of Fisheries, Minnesota Department of Natural Resources, St. Paul, MN. MPCA Document Number wq-2slice15-0010. (<https://www.pca.state.mn.us/sites/default/files/wq-2slice15-0010.pdf>)
- O'Reilly, C.M., S. Sharma, D.K. Gray, S.E. Hampton, and 60 co-authors. 2015. Rapid and highly variable warming of lake surface waters around the globe. *Geophys. Res. Lett.* DOI: 10.1002/2015GLO66235.
- Orihel, D.M., T. Bisbicos, C.T.R. Darling, A.P. Dupuis, M. Williamson, and D.C.G. Muir. 2016. Probing the debromination of the flame retardant decabromodiphenyl ether in sediments of a boreal lake. *Environ. Toxicol. Chem.* 35:573-583.
- Osborne JW, Costello AB. 2004. Sample size and subject to item ratio in principal components analysis. [cited 2012 March 12]. Available from: <http://pareonline.net/getvn.asp?v=9&n=11>. *Pract. Assess. Res. Eval.* 9(11).

- Page, A.L., A.C. Chang, and M. El-Amamy. 1987. Chapter 10. Cadmium levels in soils and crops in the United States. In: T.C. Hutchinson and K.M. Meema (Eds.). Lead, Mercury, Cadmium and Arsenic in the Environment. John Wiley & Sons Ltd. pp. 119-145.
- Panno, S.V., K.C. Hackley, H.H. Hwang, S. Greenberg, I.G. Krapac, S. Landsberger and D.J. O'Kelly. 2006. Characterization and identification of the sources of Na-Cl in ground water. *Ground Water* 44:176-187.
- Pavlowsky, R.T. 2012. Baseline study of PAH sources and concentrations in pond and stream sediments, Springfield, Missouri. Ozarks Environmental and Water Resources Institute, Missouri State University, Springfield, MO. OEWRI EDR-12-002.  
(<http://oewri.missouristate.edu/assets/OEWRI/PAH.pdf>)
- Payne, J.F., A. Mathieu, and T.K. Collier. 2003. Ecotoxicological studies focusing on marine and freshwater fish. In: P.E.T. Douben (Ed.). PAHs: An Ecotoxicological Perspective. John Wiley & Sons Ltd.: West Sussex, England. pp. 191-224.
- Peterson, G.S., R.P. Axler, K.B. Lodge, J.A. Schuldt, and J.L. Crane. 2002. Evaluation of a fluorometric screening method for predicting total PAH concentrations in contaminated sediments. *Environ. Monit. Assess.* 78:111-129.
- Pinkney, A.E. and P.C. McGowan. 2006. Use of the p,p'-DDD: p,p'-DDE concentration ratio to trace contaminant migration from a hazardous waste site. *Environ. Monit. Assess.* 120:559-574.
- Pluta, B. 2006. Freshwater sediment screening benchmarks. U.S. EPA Region III BTAG.  
(<http://www.epa.gov/risk/freshwater-sediment-screening-benchmarks> and  
[http://www.epa.gov/sites/production/files/2015-09/documents/r3\\_btag\\_fw\\_sediment\\_benchmarks\\_8-06.pdf](http://www.epa.gov/sites/production/files/2015-09/documents/r3_btag_fw_sediment_benchmarks_8-06.pdf))
- Prairie Research Institute. 2015. An updated look at PCBs. Prairie Research Institute, University of Illinois at Urbana-Champaign, Champaign, IL. ([http://prairie.illinois.edu/pdf-files/PCBreport\\_PrairieResearchInstitute\\_2015.pdf](http://prairie.illinois.edu/pdf-files/PCBreport_PrairieResearchInstitute_2015.pdf))
- Press Trust of India. 2015. Govt to ban manufacturing, import & export of toxic PCBs. *Business Standard*, New Delhi, India, September 15, 2015. ([http://www.business-standard.com/article/pti-stories/govt-to-ban-manufacturing-import-export-of-toxic-pcbs-115091500275\\_1.html](http://www.business-standard.com/article/pti-stories/govt-to-ban-manufacturing-import-export-of-toxic-pcbs-115091500275_1.html))
- Quadrini, J.D., W. Ku, J.P. Connolly, D.A. Chiavelli, and P.H. Israelsson. 2015. Fingerprinting 2,3,7,8-tetrachlorodibenzodioxin contamination within the Lower Passaic River. *Environ. Toxicol. Chem.* 34:1485-1498.
- Randall, R.C., D.R. Young, H. Lee II, and S.F. Echols. 1998. Lipid methodology and pollutant normalization relationships for neutral nonpolar organic pollutants. *Environ. Toxicol. Chem.* 17:788-791.
- Rawn, D.F.K., W.L. Lockhart, P. Wilkinson, D.A. Savoie, G.B. Rosenberg, and D.C.G. Muir. 2001. Historical contamination of Yukon Lake sediments by PCBs and organochlorine pesticides: Influence of local sources and watershed characteristics. *Sci. Total Environ.* 280:17-37.
- Renner, R. 1998. "Natural" remediation of DDT, PCBs debated. *Environ. Sci. Technol.* 32:360A-363A.
- Ricking, M. and J. Schwarzbauer. 2012. DDT isomers and metabolites in the environment: An overview. *Environ. Chem. Lett.* 10:317-323.
- Rockne, K.J., L.M. Shor, L.Y. Yong, G.L. Taghon, and D.S. Kosson. 2002. Distributed sequestration and release of PAHs in weathered sediment: The role of sediment structure and organic carbon properties. *Environ. Sci. Technol.* 36:2636-2644.

- Rodenburg, L.A., J. Guo, S. Du, and G.J. Cavallo. 2010. Evidence for unique and ubiquitous environmental sources of 3,3'-dichlorobiphenyl (PCB 11). *Environ. Sci. Technol.* 44:2816-2821.
- Rogge, W.F., L.M. Hildemann, M.A. Mazurek, and G.R. Cass. 1998. Sources of fine organic aerosol. 9. Pine, oak, and synthetic log combustion in residential fireplaces. *Environ. Sci. Technol.* 32:13-22.
- Rosenblatt, D. 2005. Action memorandum to Lois A. Rossi, Director, Registration Division. May 6, 2005. Minor Use, Inerts, and Emergency Response Branch, U.S. Environmental Protection Agency, Washington, DC. (<http://www.epa.gov/sites/production/files/2015-04/documents/chloride.pdf>)
- Rudnick, R.L. and S. Gao. 2003. Chapter 3.01. Composition of the continental crust. pp. 1-64 in H.D. Holland and K.K. Turekian (Eds.) *Treatise on Geochemistry*, Volume 3. Elsevier Ltd.
- Ruge, Z., D. Muir, P. Helm, and R. Lohmann. 2015. Concentrations, trends, and air-water exchange of PAHs and PBDEs derived from passive samplers in Lake Superior in 2011. *Environ. Sci. Technol.* 49:13777-13786.
- Sanchís, J., M. Olmos, P. Vincent, M. Farré, and D. Barceló. 2016. New insights on the influence of organic co-contaminants on the aquatic toxicology of carbon nanomaterials. *Environ. Sci. Technol.* 50:961-969.
- Sanders, M., S. Sivertsen, and G. Scott. 2002. Origin and distribution of polycyclic aromatic hydrocarbons in surficial sediments from the Savannah River. *Arch. Environ. Contam. Toxicol.* 43:438-448.
- Schauer, J.J., M.J. Kleeman, G.R. Cass, and B.R.T. Simoneit. 2001. Measurement of emissions from air pollution sources. 3. C<sub>1</sub>-C<sub>29</sub> organic compounds from fireplace combustion of wood. *Environ. Sci. Technol.* 35:1716-1728.
- Schubauer-Berigan, M. and J.L. Crane. 1996. Preliminary contaminant assessment of the Thomson, Forbay, and Fond du Lac reservoirs. Minnesota Pollution Control Agency, St. Paul, MN. (<https://www.pca.state.mn.us/sites/default/files/cloquet.pdf>)
- Schubauer-Berigan, M. and J.L. Crane. 1997. Survey of sediment quality in the Duluth/Superior Harbor: 1993 sampling results. Minnesota Pollution Control Agency, St. Paul, MN. EPA 905-R97-005. (<https://www.pca.state.mn.us/sites/default/files/93mud.pdf>)
- Seelig, B.D. 2000. Salinity and sodicity in North Dakota soils. NDSU Extension Service, North Dakota State University, Fargo, ND. ([https://www.ndsu.edu/soilhealth/wp-content/uploads/2014/07/ND-saline-sodic-soils\\_20001.pdf](https://www.ndsu.edu/soilhealth/wp-content/uploads/2014/07/ND-saline-sodic-soils_20001.pdf))
- Shields, W.J., Y. Tondeur, L. Benton, and M.E. Edwards. 2006. Dioxins and furans. In: Morrison, R.D. and Murphy, B.L. (eds) *Environmental Forensics: Contaminant Specific Guide*. Elsevier: New York. pp. 293-312.
- Shine, J.P., R.V. Ika, and T.E. Ford. 1995. Multivariate statistical examination of spatial and temporal patterns of heavy metal contamination in New Bedford Harbor marine sediments. *Environ. Sci. Technol.* 29:1781-1788.
- Siami, M., C.D. McNabb, T.R. Batterson, and R.P. Glandon. 1987. Arsenic sedimentation along the slope of a lake basin. *Environ. Toxicol. Chem.* 6:595-605.
- Silliman, J.E., P.A. Meyers, B.J. Eadie, and J.V. Klump. 2001. A hypothesis for the origin of perylene based on its low abundance in sediments of Green Bay, Wisconsin. *Chem. Geol.* 177:309-322.
- Silliman, J.E., P.A. Meyers, P.H. Ostrom, N.E. Ostrom, and B.J. Eadie. 2000. Insights into the origin of perylene from isotopic analyses of sediments from Saanich Inlet, British Columbia. *Org. Geochem.* 31:1133-1142.

- Simcik, M.F., S.J. Eisenreich, K.A. Golden, S-P. Liu, E. Lipiatou, D.L. Swackhamer, and D.T. Long. 1996. Atmospheric loading of polycyclic aromatic hydrocarbons to Lake Michigan as recorded in the sediments. *Environ. Sci. Technol.* 30:3039-3046.
- Singh, A. and A.K. Singh. 2013. ProUCL Version 5.0.00 Technical Guide. Statistical software for environmental applications for data sets with and without nondetect observations. U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC. EPA/600/R-07/041 ([http://www2.epa.gov/sites/production/files/2015-03/documents/proucl\\_v5.0\\_tech.pdf](http://www2.epa.gov/sites/production/files/2015-03/documents/proucl_v5.0_tech.pdf))
- Siver, P.A. and J.A. Wozniak. 2001. Lead analysis of sediment cores from seven Connecticut lakes. *J. Paleolimnol.* 26:1-10.
- Slater, G.F., A.A. Benson, C. Marvin, and D. Muir. 2013. PAH fluxes to Siskiwit revisited: Trends in fluxes and sources of pyrogenic PAH and perylene constrained via radiocarbon analysis. *Environ. Sci. Technol.* 47:5066-5073.
- Somat Engineering. 2012a. Sediment investigation report. St. Louis River, Duluth Harbor. Duluth, St. Louis County, Minnesota. Somat Engineering, Inc., Detroit, MI. Prepared for the U.S. Army Corps of Engineers, Detroit, MI and Minnesota Pollution Control Agency, Duluth, MN. (<https://www.pca.state.mn.us/sites/default/files/c-rem5-01.pdf>)
- Somat Engineering. 2012b. Sediment investigation report. Lower St. Louis River, Fond du Lac dam to Kingsbury Bay. Duluth, St. Louis County, Minnesota. Somat Engineering, Inc., Detroit, MI. Prepared for the U.S. Army Corps of Engineers, Detroit, MI and Minnesota Pollution Control Agency, Duluth, MN. (<https://www.pca.state.mn.us/sites/default/files/c-rem5-02.pdf>)
- Stapleton, H.M., B. Brazil, R.D. Holbrook, C.L. Mitchelmore, R. Benedict, A. Konstantinov, and D. Potter. 2006. In vivo and in vitro debromination of decabromodiphenyl ether (BDE 209) by juvenile rainbow trout and common carp. *Environ. Sci. Technol.* 40:4653-4658.
- Tanner, C.C. and J.S. Clayton. 1990. Persistence of arsenic 24 years after sodium arsenite herbicide application to Lake Rotoroa, Hamilton, New Zealand. *NZ J. Marine Freshwater Res.* 24:173-179.
- Tchounwou, P.B., C.G. Yedjou, A.K. Patlolla, and D.J. Sutton. 2012. Heavy metals toxicity and the environment. In: A. Luch (Ed.), *Molecular, Clinical and Environmental Toxicology, Experientia Supplementum* 101:133-164.
- TDC Environmental. 2004. Copper sources in urban runoff and shoreline activities. TDC Environmental, LLC, San Mateo, CA. Prepared for Clean Estuary Partnership. (<http://www.cdpr.ca.gov/docs/emon/surfwtr/copper1104.pdf>)
- TDI – Brooks International, Inc. 2009. Analytical results report. TDI – Brooks International, Inc., College Station, TX. Catalog Number 3080058. MPCA Document Number tdr-gl-19b. (<https://www.pca.state.mn.us/sites/default/files/tdr-gl-19b.pdf>)
- Thijssen, M. 1997. Body burdens of PAH's in benthic invertebrates from the Duluth-Superior Harbor. University of Utrecht, The Netherlands.
- Titaley, I.A., A. Chlebowski, L. Truong, R.L. Tanguay, and S.L.M. Simonich. 2016. Identification and toxicological evaluation of unsubstituted PAHs and novel PAH derivatives in pavement sealcoat products. *Environ. Sci. Tech. Lett.* 3:234-242.
- Towey, T.P., N. Barabas, A. Demond, A. Franzblau, D.H. Garabrant, B.W. Gillespie, J. Lepkowski, and P. Adriaens. 2012. Polytopic vector analysis of soil, dust, and serum samples to evaluate exposure sources of PCDD/Fs. *Environ. Toxicol. Chem.* 31:2191:2200.

- Towey, T.P., S-C. Chang, A. Demond, D. Wright, N. Barabás, A. Franzblau, D.H. Garabrant, B.W. Gillespie, J. Lepkowski, W. Luksemburg, and P. Adriaens. 2010. Hierarchical cluster analysis of polychlorinated dioxins and furans in Michigan, USA soils: Evaluation of industrial and background congener profiles. *Environ. Toxicol. Chem.* 29:64-72.
- UNEP. 1999. Dioxin and furan inventories. National and regional emissions of PCDD/PCDF. United Nations Environment Programme, Geneva, Switzerland.  
([http://www.unep.org/chemicalsandwaste/Portals/9/POPs/Toolkit-Inventories/Dioxin%20and%20Furan%20Inventories\\_May%201999.pdf](http://www.unep.org/chemicalsandwaste/Portals/9/POPs/Toolkit-Inventories/Dioxin%20and%20Furan%20Inventories_May%201999.pdf))
- UNEP. 2010a. Technical review of the implications of recycling commercial penta and octabromodiphenyl ethers. Annexes. Stockholm Convention document for 6<sup>th</sup> POP Reviewing Committee Meeting (UNEP/POPS/POPRC.6/INF/6). Geneva, Switzerland, 11-15, October 2010.
- UNEP. 2010b. Technical review of the implications of recycling commercial pentabromodiphenyl ether and commercial octabromodiphenyl ether. Draft. Stockholm Convention document for 6<sup>th</sup> POP Reviewing Committee Meeting (UNEP/POPS/POPRC.6/2). Geneva, Switzerland, 11-15, October 2010.
- UNEP. 2012. Guidance for the inventory of polybrominated diphenyl ethers (PBDEs) listed under the Stockholm Convention on Persistent Organic Pollutants. United Nations Environment Programme, Geneva, Switzerland.  
([https://www.unido.org/fileadmin/user\\_media/Services/Environmental\\_Management/Stockholm\\_Convention/Guidance\\_Docs/UNEP-POPS-GUID-NIP-2012-PBDEs-Inventory.En.pdf](https://www.unido.org/fileadmin/user_media/Services/Environmental_Management/Stockholm_Convention/Guidance_Docs/UNEP-POPS-GUID-NIP-2012-PBDEs-Inventory.En.pdf))
- U.S. Army. 2004. Tier II ecological risk assessment report, Twin Cities Army Ammunition Plant, Arden Hills, Minnesota. Final Report, December, 2004. U.S. Army Center for Health Promotion and Preventive Medicine.
- U.S. Department of Agriculture. 2015. Summary report: 2012 national resources inventory. Natural Resources Conservation Service, Washington, DC and Center for Survey Statistics and Methodology, Iowa State University, Ames, IA.  
([http://www.nrcs.usda.gov/Internet/FSE\\_DOCUMENTS/nrcseprd396218.pdf](http://www.nrcs.usda.gov/Internet/FSE_DOCUMENTS/nrcseprd396218.pdf))
- USEPA. 1994a. Method 6020: Inductively coupled plasma – mass spectrometry. Revision 0. U.S. Environmental Protection Agency. (<http://servicio.us.es/sgiaus/Nuevo-Sia/Metodos/EPA6020.pdf>)
- USEPA. 1994b. Method 7471A: Mercury in solid or semisolid waste (manual cold-vapor technique). Revision 1. U.S. Environmental Protection Agency.  
(<http://www.greencouncil.org/doc/ResourcesCentre/7471a.pdf>)
- USEPA. 1994c. Method 1613: Tetra- through octa- chlorinated dioxins and furans by isotope dilution HRGC/HRMS. Revision B. U.S. Environmental Protection Agency, Office of Water, Washington, DC. EPA 821-B-94-005.  
(<https://nepis.epa.gov/Exe/ZyPDF.cgi/20002GR6.PDF?Dockey=20002GR6.PDF>)
- USEPA. 1997. Health effects assessment summary tables. FY 1997 update. U.S. Environmental Protection Agency, Solid Waste and Emergency Response, Washington, DC. EPA 540/R-97-036.  
(<https://cfpub.epa.gov/ncea/risk/recordisplay.cfm?deid=2877&CFID=60845252&CFTOKEN=13787379>)
- USEPA. 1999. Integrated Risk Information System (IRIS) on polycyclic organic matter. U.S. Environmental Protection Agency, National Center for Environmental Assessment, Office of Research and Development, Washington, DC.



- USEPA. 2000a. Prediction of sediment toxicity using consensus-based freshwater sediment quality guidelines. U.S. Environmental Protection Agency, Great Lakes National Program Office, Chicago, IL. EPA 905/R-00/007. (<http://www.cerc.usgs.gov/pubs/center/pdfdocs/91126.pdf>)
- USEPA. 2000b. Guidance for assessing chemical contaminant data for use in fish advisories. Volume 1. Fish sampling and analysis. Third edition. U.S. Environmental Protection Agency, Office of Water, Washington, DC. EPA 823-B-00-007. (<https://www.epa.gov/sites/production/files/2015-06/documents/volume1.pdf>)
- USEPA. 2003. Procedures for the derivation of equilibrium partitioning sediment benchmarks (ESBs) for the protection of benthic organisms: PAH mixtures. U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC. EPA/600/R-02/013. (<https://clu.in.org/conf/tio/porewater1/resources/EPA-ESB-Procedures-PAH-mixtures.pdf>)
- USEPA. 2006a. Survey of the nation's lakes. Quality assurance project plan. Draft. U.S. Environmental Protection Agency, Office of Water and Office of Environmental Information, Washington, DC.
- USEPA. 2006b. An inventory of sources and environmental releases of dioxin-like compounds in the United States for the years 1987, 1995, and 2000. U.S. Environmental Protection Agency, Washington, DC. EPA 600/P-03/002. (<https://cfpub.epa.gov/ncea/risk/recordisplay.cfm?deid=159286&CFID=57378536&CFTOKEN=69449246>)
- USEPA. 2007a. Survey of the nation's lakes. Field operations manual. Draft (Revision No. 1, March 2007). U.S. Environmental Protection Agency, Washington, DC. EPA/841-B-07-004. (<http://www.in.gov/dnr/fishwild/files/finaldraftfieldops0307.pdf>)
- USEPA. 2007b. Method 3051A: Microwave assisted acid digestion of sediments, sludges, soils, and oils. U.S. Environmental Protection Agency. (<https://www.epa.gov/sites/production/files/2015-12/documents/3051a.pdf>)
- USEPA. 2007c. Method 1614. Brominated diphenyl ethers in water soil, sediment and tissue by HRGC/HRMS. U.S. Environmental Protection Agency, Office of Water and Office of Science and Technology, Washington, DC. EPA-821-R-07-005. (<http://nepis.epa.gov/Exe/ZyPDF.cgi/P10070D4.PDF?Dockey=P10070D4.PDF>)
- USEPA. 2009a (Final). Survey of the nation's lakes: Quality assurance project plan. U.S. Environmental Protection Agency, Office of Water and Office of Research and Development, Washington, DC. EPA/841-B-07-003. ([https://www.epa.gov/sites/production/files/2013-11/documents/2009\\_12\\_31\\_lakes-lakessurvey\\_pdf\\_qualityassuranceplan.pdf](https://www.epa.gov/sites/production/files/2013-11/documents/2009_12_31_lakes-lakessurvey_pdf_qualityassuranceplan.pdf))
- USEPA. 2009b. National lakes assessment: A collaborative survey of the nation's lakes. U.S. Environmental Protection Agency, Office of Water and Office of Research and Development, Washington, DC. EPA/841-R-09-001. ([https://www.epa.gov/sites/production/files/2013-11/documents/nla\\_newlowres\\_fullrpt.pdf](https://www.epa.gov/sites/production/files/2013-11/documents/nla_newlowres_fullrpt.pdf))
- USEPA. 2009c. Polybrominated diphenyl ethers (PBDEs) action plan. U.S. Environmental Protection Agency. ([https://www.epa.gov/sites/production/files/2015-09/documents/pbdes\\_ap\\_2009\\_1230\\_final.pdf](https://www.epa.gov/sites/production/files/2015-09/documents/pbdes_ap_2009_1230_final.pdf))
- USEPA. 2013a. 2011 National listing of fish advisories. U.S. Environmental Protection Agency. EPA-820-F-13-058. (<http://www.epa.gov/sites/production/files/2015-06/documents/technical-factsheet-2011.pdf>)

- USEPA. 2013b (External Review Draft). Update to an inventory of sources and environmental releases of dioxin-like compounds in the United States for the years 1987, 1995, and 2000. U.S. Environmental Protection Agency, Washington, DC. EPA/600/R-11/005A. (<https://cfpub.epa.gov/ncea/risk/recordisplay.cfm?deid=235432&CFID=60847107&CFTOKEN=93683293>)
- USEPA. 2013c. Literature review of contaminants in livestock and poultry manure and implications for water quality. Office of Water, U.S. Environmental Protection Agency, Washington, DC. EPA 820-R-13-002. (<http://nepis.epa.gov/Exe/ZyPDF.cgi/P100H2NI.PDF?Dockey=P100H2NI.PDF>).
- Valdez Domingos, F.X., C.A. Oliveira Ribeiro, É. Pelletier, and C. Rouleau. 2011. Tissue distribution and depuration kinetics of waterborne <sup>14</sup>C-labeled light PAHs in mummichog (*Fundulus heteroclitus*). Environ. Sci. Technol. 45:2684-2690.
- Van Aggelen, G. et al. (32 co-authors). 2010. Integrating omic technologies into aquatic ecological risk assessment and environmental monitoring: Hurdles, achievements, and future outlook. Environ. Health Perspect. 118:1-5.
- Van Brummelen, T.A., B. Van Hattum, T. Crommentuijn, and D.F. Kalf. 1998. Bioavailability and ecotoxicity of PAHs. In: A. Neilson and O. Hutzinger (Eds.). PAHs and Related Compounds. The Handbook of Environmental Chemistry, vol. 3, Part J. Springer-Verlag: Berlin, Germany. pp. 203-263.
- Van den Berg, M., L. Birnbaum, A.T.C. Bosveld, B. Brunström, P. Cook, M. Feeley, J.P. Giesy, A. Hanberg, R. Hasegawa, S.W. Kennedy, T. Kubiak, J.C. Larsen, F.X. Rolaf van Leeuwen, A.K.D. Liem, C. Nolt, R.E. Peterson, L. Poellinger, S. Safe, D. Schrenk, D. Tillitt, M. Tysklind, M. Younes, F. Waern, and T. Zacharewski. 1998. Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. Environ. Health Perspectives 106:775:792.
- Van den Berg, M., L.S. Birnbaum, M. Denison, M. De Vito, W. Farland, M. Feeley, H. Fiedler, H. Hakansson, A. Hanberg, L. Haws, M. Rose, S. Safe, D. Schrenk, C. Tohyama, A. Tritscher, J. Tuomisto, M. Tysklind, N. Walker, and R.E. Peterson. 2006. The 2005 World Health Organization reevaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. Toxicol. Sci. 93: 223-241.
- van der Oost, R., J. Beyer, and N.P.E. Vermeulen. 2003. Fish bioaccumulation and biomarkers in environmental risk assessment: A review. Environ. Toxicol. Pharm. 13:57-149.
- Van Metre, P.C. and B.J. Mahler. 2010. Contribution of PAHs from coal-tar pavement sealcoat and other sources to 40 U.S. lakes. Sci. Total Environ. 409:334-344.
- Van Metre, P.C., B.J. Mahler, J.T. Wilson, and T.L. Burbank. 2008. Collection and analysis of samples for polycyclic aromatic hydrocarbons in dust and other solids related to sealed and unsealed pavement from 10 cities across the United States, 2005-07. United States Geological Survey, Austin, TX. Data Series 361. (<http://pubs.usgs.gov/ds/361>)
- Van Metre, P.C., M. Babut, B. Mourier, B.J. Mahler, G. Roux, and M. Desmet. 2015. Declining dioxin concentrations in the Rhone River basin, France, attest to the effectiveness of emissions controls. Environ. Sci. Technol. 49:12723-12730.
- Van Metre, P.C., M.S. Majewski, B.J. Mahler, W.T. Foreman, C.L. Braun, J.T. Wilson, and T.L. Burbank. 2012a. PAH volatilization following application of coal-tar-based pavement sealant. Atm. Environ. 51:108-115.
- Van Metre, P.C., M.S. Majewski, B.J. Mahler, W.T. Foreman, C.L. Braun, J.T. Wilson, and T.L. Burbank. 2012b. Volatilization of polycyclic aromatic hydrocarbons from coal-tar-sealed pavement. Chemosphere 88:1-7.



- VanRyswyk, B. and D. Tollefson. 2008. Minnesota National Lakes Assessment Project: Pesticides in Minnesota lakes. Minnesota Department of Agriculture, St. Paul, MN. Document no. MAU-08-102.  
(<http://www.mda.state.mn.us/chemicals/pesticides/~media/Files/chemicals/pesticidesinmnlakes.ashx>)
- Venier, M., A. Dove, K. Romanak, S. Backus, and R. Hites. 2014. Flame retardants and legacy chemicals in Great Lakes' water. *Environ. Sci. Technol.* 48:9563-9572.
- Villanacci, J.F. and R.A. Beauchamp. 2003. Health consultation. Barton Springs Pool, Austin, Travis County, Texas. Prepared by Bureau of Epidemiology and Toxicology Division, Texas Department of Health under Cooperative Agreement with the Agency for Toxic Substances and Disease Registry. (<http://www.atsdr.cdc.gov/hac/pha/pha.asp?docid=59&pg=0>)
- Vives, I., J.O. Grimalt, S. Lacorte, M. Guillamón, and D. Barceló. 2004. Polybrominated ether flame retardants in fish from lakes in European high mountains and Greenland. *Environ. Sci. Technol.* 38:2338-2344.
- Volkerling, F. and A.M. Breure. 2003. Biodegradation and general aspects of bioavailability. In: P.E.T. Douben (Ed.). *PAHs: An Ecotoxicological Perspective*. John Wiley & Sons Ltd.: West Sussex, England. pp. 81-96.
- Ward, T. 2005. Memorandum through Pauline Wagner, Inerts Team Coordinator to Dan Rosenblatt, Chief. May 6, 2005. Minor Use, Inerts, and Emergency Response Branch, U.S. Environmental Protection Agency, Washington, DC. (<http://www.epa.gov/sites/production/files/2015-04/documents/chloride.pdf>)
- Wentz, D.A., M.E. Brigham, L.C. Chasar, M.A. Lutz, and D.P. Krabbenhoft. 2014. Mercury in the nation's streams—levels, trends, and implications. U.S. Geological Survey, Reston, VA. Circular 1395. (<http://dx.doi.org/10.3133/cir1395>)
- Weston Solutions, Inc. 2012a. Sediment assessment report – Revision 1. St. Louis Bay – St. Louis River Area of Concern. Duluth, St. Louis County, Minnesota. Weston Solutions, Inc., Chicago, IL. Prepared for the U.S. Environmental Protection Agency's Great Lakes National Program Office, Chicago, IL. (<https://www.pca.state.mn.us/sites/default/files/c-rem5-03.pdf>)
- Weston Solutions, Inc. 2012b. Sediment assessment report. Upper St. Louis River – St. Louis River AOC. Cloquet, Carlton and St. Louis County, Minnesota. Weston Solutions, Inc., Chicago, IL. Prepared for the U.S. Environmental Protection Agency's Great Lakes National Program Office, Chicago, IL. (<https://www.pca.state.mn.us/sites/default/files/c-rem5-04.pdf>)
- Wetterauer, B., M. Ricking, J.C. Otte, A.V. Hallare, A. Rastall, L. Erdinger, J. Schwarzbauer, T. Braunbeck, and H. Hollert. 2012. Toxicity, dioxin-like activities, and endocrine effects of DDT metabolites—DDA, DDMU, DDMS, and DDCN. *Environ. Sci. Pollut. Res.* 19:403-415.
- Windom, H.L., S.J. Schropp, F.D. Calder, J.D. Ryan, R.G. Smith Jr., L.C. Burney, F.G. Lewis, and C.H. Rawlinson. 1989. Natural trace metal concentrations in estuarine and coastal marine sediments of the southeastern United States. *Environ. Sci. Technol.* 23:314-320.
- World Health Organization. 1999. Concise International Chemical Assessment Document 6. Biphenyl. United Nations Environment Programme, the International Labour Organisation, and the World Health Organization, Geneva, Switzerland. 31 pp.  
(<http://www.who.int/ipcs/publications/cicad/en/cicad06.pdf>)
- Yang, R., H. Wei, J. Guo, and A. Li. 2012. Emerging brominated flame retardants in the sediment of the Great Lakes. *Environ. Sci. Technol.* 46:3119-3126.

- Zadak, C., N. Kale, M. Wyatt, A. Plevan, and J. Olson. 2010 (Draft). MCWD lakes TMDL--Lake Nokomis, Parley Lake, Lake Virginia, and Wassermann Lake. Minnesota Pollution Control Agency, Minnehaha Creek Watershed District, and Emmons & Olivier Resources, Inc. MPCA Document Number wq-iw11-09b. (<https://www.pca.state.mn.us/sites/default/files/wq-iw11-09b.pdf>)
- Zhang, J., J. Zhang, R. Liu, J. Gan, J. Liu, and W. Liu. 2016. Endocrine-disrupting effects of pesticides through interference with human glucocorticoid receptor. *Environ. Sci. Technol.* 50:435-443.