

# Annual Pollution Report

# To the Legislature

April 2004



Tom Clark, Patricia Engelking and Kari Palmer of the Monitoring and Reporting Section of the Environmental Outcomes Division prepared this report, with assistance from other staff in the Majors and Remediation, Regional Environmental Management and the Environmental Outcomes divisions.

Cost to prepare this report: Total staff hours: 243 Salary and fringe costs: \$7696 Production costs: \$1351

An electronic version of this report can be found on the MPCA web site at <a href="http://www.pca.state.mn.us/hot/legislature/reports/index.html">http://www.pca.state.mn.us/hot/legislature/reports/index.html</a>

This report can be made available in other formats, including Braille, large type, or audiotape upon request.

This report is printed on paper with at least 30 percent post-consumer recycled paper.

# **Table of Contents**

Forewordii
List of Tables and Figures iv
Introduction and Summary1
Chapter 1: Air Pollutant Emissions Overview
Criteria Air Pollutant Emissions6
Air Quality Index (AQI)8
Particulate Matter10
Ozone
Nitrogen Oxides17
Volatile Organic Compounds19
Carbon Monoxide21
Sulfur Dioxide23
Lead25
Carbon Dioxide27
Mercury
Air Toxics
Chapter 2: Water Pollutant Discharges Overview
Major Water Discharge Parameters and Trends
Total Suspended Solids
Biological Oxygen Demand (BOD) and Carbonaceous BOD
Total Phosphorus
Nitrogen
Nonpoint Source Pollution
Other Contaminants of Concern in Minnesota

# Foreword

The Annual Pollution Report statute requires the Minnesota Pollution Control Agency (MPCA) to estimate to the best of its ability the total amounts of air and water pollution emitted in the state during the most recent calendar year for which data are available. The statute further directs the MPCA to estimate the percentage increase or decrease over the previous calendar year, and to estimate the relative contributions of the various sources of these emissions and discharges to the environment.

The MPCA has prepared this report since 1996. It has evolved to include new kinds of information, such as discharges of toxic air pollutants, greenhouse gas emissions, and emerging contaminants of concern as these kinds of data have become available. The following observations of some strengths and shortcomings of the current reporting process are presented for interested parties to help determine if and how the report should be changed.

#### Strengths

- The Annual Pollution Report is the only MPCA report that specifically asks for an accounting of emissions and discharges. Such inventories are inherently important, as understanding emission amounts and sources is fundamental in protecting the environment and human health.
- The report attempts to track trends year to year, which is valuable if data are reliable.
- The report covers both air and water pollutants in one document, instead of separate reports, reminding readers of the potential for cross-media impacts.
- The report shows relative contributions of various pollution sources to the total.

#### Minn. Statutes 116.011 Annual pollution report.

A goal of the pollution control agency is to reduce the amount of pollution that is emitted in the state. By April 1 of each year, the pollution control agency shall report the best estimate of the agency of the total volume of water and air pollution that was emitted in the state in the previous calendar year for which data are available. The agency shall report its findings for both water and air pollution:

(1) in gross amounts, including the percentage increase or decrease over the previous calendar year; and

(2) in a manner which will demonstrate the magnitude of the various sources of water and air pollution.

HIST: 1995 c 247 art 1 s 36; 2001 c 187 s 3

Copyright 2001 by the Office of Revisor of Statutes, State of Minnesota.

#### Shortcomings

- Aggregating data into total volumes lacks the important context of relative risk. Pollutants emitted in smaller volumes can have a greater impact than some emitted in tremendously larger volumes. The volume figures also do not convey whether such emissions and discharges are acceptable or unacceptable from a risk perspective.
- The most current pollutant emissions and discharge data is usually at least two years behind real time, sometimes more, depending on the type of pollutants. Air emission estimates are frequently revised as industrial output models and factors used to estimate emissions are refined. Year-to-year comparisons are not always reliable, as methodologies for estimating emissions are still evolving.

#### Shortcomings, cont.

• There is currently no reliable way to quantify the volumes of water pollutants released by nonpoint sources in the form of polluted runoff, such as city streets, construction sites and farm fields. This is a major gap in inventorying pollutants discharged, for a category highly culpable for water quality impairments.

#### New this year

In attempting to overcome some of these difficulties, the report presents some of the information differently. For example:

- Air pollution estimates for point source emissions are based on the Minnesota emission inventory, instead of on estimates supplied by the U.S. Environmental Protection Agency. These estimates are based on the most recent inventories compiled by the MPCA, and should be more timely and representative of actual Minnesota emissions. Initially, this will make it more difficult to compare emissions in this report to those from previous years. Over time, however, these comparisons will become more reliable and meaningful as Minnesota emission inventory numbers are used from this year forward.
- Nonpoint source water pollutant estimates are being highlighted in basin-loading studies, which attempt to quantify the amounts of specific pollutants entering a given watershed from specific sources, both point and nonpoint. While this falls short of being able to quantify nonpoint source discharges statewide, it represents an important first step to better understanding the relative contributions of point and nonpoint sources to specific watersheds, which in turn can guide local and state officials in planning for water quality improvements.

The examples noted above are presented to help the reader get a sense for the dilemmas the MPCA faces in attempting to deliver accurate, timely and useful information about what is discharged into Minnesota's air and water.

Toward that end, the MPCA proposes that this edition of the report be the last paper version, as the emission and discharge inventories will be available on the MPCA Environmental Data Access website in October 2004. The MPCA would continue to conduct trend analysis approximately every three years.

The MPCA welcomes suggestions from interested parties for upgrading the current reporting process to better meet its intended purposes envisioned in the statute.

# **List of Tables**

Table 1:	Minnesota Air Pollution Emission Estimates, 1999-2001	. 2
Table 2:	Minnesota Water Pollution Discharge Estimates from Major Point Sources, 1998-2002	.3
Table 3:	1999 Minnesota Air Toxics Emissions Inventory Statewide Summary	32
Table 4:	Point Source P % Contribution (Theor.) of the Total P Load at Rockford USGS site	46
Table 5:	Crow River Percent of Mississippi River Loads at Anoka (Calendar Year Basis)	17

# List of Figures

AQI Days by AQI Category and Region in Minnesota, 20039
PM <sub>2.5</sub> Composition at Three Minnesota Sites12
Sources of PM <sub>10</sub> Emissions in Minnesota, 200114
PM <sub>10</sub> Point Source Emission Trends by Sector in Minnesota, 1997-2001
Sources of Nitrogen Oxide Emissions in Minnesota, 200117
Nitrogen Oxide Point Source Emission Trends by Sector in Minnesota, 1997-200118
Sources of Volatile Organic Compounds in Minnesota, 200119
Volatile Organic Compound Point Source Emission Trends by Sector in Minnesota, 1997-200120
Sources of Carbon Monoxide Emissions in Minnesota, 200121
Carbon Monoxide Point Source Emissions Trends by Sector in Minnesota, 1997-200122
Sources of Sulfur Dioxide Emissions in Minnesota, 2001
Sulfur Dioxide Point Source Emission Trends by Sector in Minnesota, 1997-200124
Sources of Lead Emissions in Minnesota, 2001
Lead Point Source Emission Trends by Sector in Minnesota, 1997-2001
Sources of Carbon Dioxide Emissions from Fossil Fuel Burning in Minnesota, 200127
Carbon Dioxide Emission Trends from Fossil Fuel Burning in Minnesota, 1997-200128
Sources of Atmospheric Mercury Deposition to Minnesota
Trends in Minnesota Mercury Emissions from Human Activities
Contribution of Principal Source Categories to 1999 Air Toxics Emissions in Minnesota
Contribution of Major Categories to 1999 Point Source Air Toxics Emissions in Minnesota
Contribution of Major Categories to 1999 Area Source Air Toxics Emissions in Minnesota
Contribution of Major Categories to 1999 Mobile Source Air Toxics Emissions in Minnesota 37
Total Suspended Solids Discharges from Major Point Sources, 2002
Biological Oxygen Demand Discharges from Major Point Sources, 2002
Total Phosphorus Discharges from Major Point Sources, 2002
Ammonia Discharges from Major Point Sources, 2002
North and South Fork of the Crow River Site Overview45

# Introduction and Summary

The Minnesota Pollution Control Agency (MPCA) is required by Minnesota Statutes, Chapter 116.011 to submit to the Legislature an annual report of the volume of pollution emitted or discharged to the state's air and water resources. In addition to gross amounts, the MPCA must report the annual percentage increase or decrease of pollutants for the most recent year for which data are available. The report must also demonstrate the magnitude of the various sources of air and water pollution. The basis of the MPCA's 2004 Annual Pollution Report is 1999 and 2001 Minnesota Criteria Pollutant Emission Inventory, the 1999 Air Toxics Emission Inventory and the 2001 Water Quality National Pollutant Discharge Elimination System (NPDES) Discharge Monitoring Reports, which are part of the U.S. Environmental Protection Agency's (EPA) Permit Compliance System.

Annual emission and discharge estimates are one important component of tracking progress on air and water pollution, and for tracking performance and relative contributions of pollution sources. The MPCA also regularly prepares reports on the physical, chemical and biological conditions measured in the environment, and on pollutants of special concern to human health and the environment. These reports and others are available on the Internet and are referenced throughout this document for readers who would like additional context and information.

### **Air Emissions**

In past reports, the MPCA has used data from the EPA's Air Emissions Inventory. Starting this year, the MPCA will report data from its own Minnesota Criteria Pollutant Emission Inventory, using data generated in the state, for more accurate and timely results. The major air pollutants summarized in this report include carbon monoxide (CO), nitrogen oxides (NO<sub>x</sub>), sulfur dioxide (SO<sub>2</sub>), volatile organic compounds (VOCs), particulate matter (PM) and lead. These are known as the criteria pollutants. The most recent emissions data available from large facilities for these pollutants are from 2001.

#### **About Emission Inventories**

Completing air pollutant emission inventories is a time-intensive process. For example, to develop the Criteria Pollutant Emission Inventory for the year 2001, facilities with MPCA permits have until April 1, 2002 to submit their 2001 emissions estimates to the MPCA. Agency staff then compile these emission estimates into a draft Criteria Pollutant Emission Inventory, which is sent back to the facilities for review in December 2002. Facilities complete their review by February 1, 2003. MPCA staff then review the changes and complete the inventory for 2001 in March 2003.

The Minnesota Air Toxics Emission Inventory is completed once every three years to coincide with the three-year cycle of the U.S. EPA's National Emission Inventory. MPCA staff develop emissions estimates for the Air Toxics Emission Inventory based upon the completed Criteria Pollutant Emission Inventory, the assistance of permittees, and statistical information from other state and federal agencies.

Global climate change is a continuing concern worldwide. Therefore, Minnesota emissions of the principal greenhouse gas, carbon dioxide ( $CO_2$ ), are included again for 2001. The statewide emissions were calculated using a variety of fuel use data sources.

The Minnesota Air Toxics Emission Inventory estimates emissions of air toxics including compounds such as benzene and formaldehyde. There may be some overlap between the Minnesota Air Toxics Emission Inventory and the estimates for VOCs because many air toxics are also VOCs. Air toxics emission inventories are not generated every year. The most recent complete inventory of air toxics emissions is from 1999.

The MPCA releases a complete emission inventory including criteria pollutants and air toxics every three years. Emissions of criteria pollutants from large facilities are estimated every year. Therefore, the 2001 emissions include 2001 criteria emissions from large facilities. The 1999, 2000 and 2001 numbers all include 1999 data from smaller area and mobile sources. Next year, updated 2002 emissions from area and mobile sources will be available. The air toxics emission inventory will also be updated at that time.

Table 1 lists the total statewide emissions of the major air pollutants from 1999 to 2001. The percent change from 2000 to 2001 is given in the final column. It is possible to look at emission trends between these years. However, it is important not to place undue emphasis on a yearly change. Trends should be viewed over several years of data. In addition, emission estimates fluctuate as a result of changes and improvements in the inventory.

Pollutant	1999	2000	2001	2000 to 2001
				% Change
Carbon monoxide (CO)	2503	2505	2503	-0.08%
Sulfur dioxide (SO <sub>2</sub> )	154	156	150	-4.0%
Oxides of nitrogen (NO <sub>x</sub> )	478	482	466	-3.4%
Volatile organic compounds (VOCs)	396	395	393	-0.5%
Particulate matter (PM <sub>10</sub> )**	858	862	850	-1.4%
Total	4389	4400	4362	-0.9%

# Table 1: Minnesota Air Pollution Emission Estimates, 1999-2001<br/>(thousand short tons)\*

\*1999 mobile and area emission estimates are used in all years. Differences between years are attributable to changes in point source emissions.

\*\*PM<sub>10</sub> emissions represent only primary formation; secondary formation is not included.

There may be differences in the total emission figures for a given year discussed in this report versus previous emission reports the MPCA has published because MPCA data is being used instead of EPA data. Differences in methodology exist between the two inventories. In addition, data may be updated in MPCA's emission inventory due to corrections or changes in methodology.

It should also be noted that despite the importance of the secondary formation of particulate matter, estimated air emissions data in this report are only based on direct releases from sources into the atmosphere. Secondary formation occurs when emissions of volatile gases combine and form fine particulates. These particles are not directly emitted but are formed downwind of the emission source. Although EPA-approved models to predict the secondary formation of fine particulates do not currently exist, work is underway to develop these models. Ammonia and fine particulate matter ( $PM_{2.5}$ ) are not currently included in the Minnesota Criteria Pollutant Emission Inventory. The MPCA plans to add these pollutants to the 2002 inventory which should be available for inclusion in next year's report.

All pollutants showed a slight decrease from 2000 to 2001. All of the decrease was attributable to point sources, since only 1999 emissions are available for area and mobile sources. This coincides with the

national economic downturn. The total emissions of  $CO_2$  in 2001 were 106 million short tons. This represents a 2.6 percent decrease from 2000. The 1999 air toxics emissions are given in the body of the report.

An important development this year was the completion of an agreement with XCel Energy to significantly reduce emissions from three of its older Twin Cities coal-fired power plants. The agreement, known as the Metropolitan Emissions Reduction Project, will beginning in 2007 convert the High Bridge plant in St. Paul and the Riverside plant in Minneapolis from coal to natural gas, and apply advanced scrubbing technology to the Allan S. King plant in Stillwater. While these emission reductions are still a number of years off, these projects will result in the following percentage reductions of Minnesota's total emissions: for SO<sub>2</sub>, 17 percent; NO<sub>x</sub>, 4 percent; and mercury, 12 percent. Significant particle emission reductions also are anticipated.

# Water Discharges

Owners or operators of any disposal system or point source are required by Minnesota Statutes, Chapter 115.03(7) to maintain records and make reports of any discharges to waters of the state. These selfmonitoring reports submitted to MPCA are commonly referred to as Discharge Monitoring Reports (DMRs). These data, in addition to those contained in Effluent Discharge Mass Loading Reports, which can be generated from EPA's Permit Compliance Tracking System (maintained by MPCA data specialists), are the basis for the point source discharge summary (Table 2) for the last five years for which data are available. The 2002 figures represent the combined loading from 58 municipal and 24 industrial discharges (82 major facilities each discharging more than one million gallons per day to waters of the state). These major facilities represent approximately 85% of the total volume of discharge to waters of the state from point sources. The remaining 15% comes from many smaller municipal and industrial facilities. Although discharges from these facilities are small, they can have significant impacts on individual lake and stream segments.

Pollutant	1998	1999	2000	2001	2002	2001-2002 % change
						, e en en ge
Total suspended solids (TSS)	8,000	6,069	5,119	8,552	8,852	3.40%
Biological oxygen demand						
(BOD)	5,397	4,264	3,471	4,920	5,828	15.6%
Phosphorus	1,652	1,405	1,441	1,374	1,289	-6.20%
Ammonia	1,415	1,219	1,283	1,023	1,127	9.20%
Nitrate	4,703	4,701	4,684	4,276	4,234	10%
Total	21,167	17,658	15,998	20,145	21,330	5.6%

# Table 2: Minnesota Water Pollution Discharge Estimates from<br/>Major Point Sources, 1998-2002 (thousand kilograms)

In 2001, major point source discharges of total suspended solids (TSS) and biological oxygen demand (BOD) showed significant increases, a departure from the steady year-to-year downward trend shown by these parameters beginning in 1996. Statewide, total suspended solids increased by about 40 percent, while biological oxygen demand was up by nearly 30 percent over 2000. Much of this increase was attributed to rapid snowmelt, heavy spring rains and high runoff rates in especially the southern half of the state. For example, the Mississippi River at St. Paul was above flood stage for 33 straight days during the

spring of 2001. For more discussion of this unusual occurrence, see the April 2003 Annual Pollution Report at: <u>http://www.pca.state.mn.us/publications/reports/lr-air-water-pollution-sy03.pdf</u>

It was therefore somewhat unexpected to see a continued increase in both TSS (3.4%) and BOD (15.6%) from 2001 to 2002. However, 2002 turned out to be the wettest year ever recorded in parts of Minnesota and the number of high-intensity rainfall events across the state was unprecedented. The State Climatologist's Office evaluated and reported on 12 separate rainfall events that occurred between June 9 and September 6, 2002 where six inches of rain or more in a 24-hour period were reported, meeting the criteria for a 100-year storm. Yearly precipitation totals exceeded historical averages by more that eight inches across many areas of Minnesota and in much of Wright County, the exceedance was 16 inches! (Minnesota Department of Natural Resources, 2001-2002 Water Year Data Summary, published May 2003).

With the 2001 and 2002 discharge monitoring data from the state's major treatment facilities, we see the effects of back-to-back years of unusual climatic events on waters of the state, at least with regard to TSS and BOD, and probably to some extent, ammonia. Prolonged periods of high flows and increased infiltration of precipitation carrying sediment and BOD load may have reduced treatment plant performance by decreasing residence time; these factors may have contributed to increases in levels of TSS and BOD over what would have been expected. As reported in 2003, a total of 16 of the 85 major treatment facilities more than doubled their discharge of TSS to waters of the state in 2001 compared to 2000. In 2002, 22 facilities showed an increase in reported discharges of TSS, while 57 showed a decrease. In addition, three facilities more than doubled their TSS load in 2002 compared to 2001. A similar trend was noted for biological oxygen demand, also a likely reflection of high flows, intense rainfall events and in some cases, flooding conditions. Although some increase in discharges could be expected as a result of increased loadings due to population growth and economic expansion, it will be telling to examine the 2003 TSS, BOD and ammonia data in next year's report, since 2003 was a very dry year compared to 2001 and 2002, with drought conditions even being reported in parts of the state during the second half of the year.

Phosphorus and nitrate discharges were down again in 2002, continuing the decrease reported in 2001 and reversing the slight increase for both parameters noted in 1999 and 2000. Treatment advances combined with continued progress in removal of phosphorus and nitrogen from the waste stream likely contributed to these declines. Dilution caused by high flows may also have been partly responsible for the declines. Nitrate discharges showed a 0.1% decline in 2001, continuing a trend begun in 1998. Statewide, nitrate discharges have declined almost 10% since 1998, from 4,703 thousand kilograms down to 4,234 thousand kilograms in 2002. This is encouraging, since nitrate is a major contributor to the problem of hypoxia in the Gulf of Mexico.

However, point source contributions of nitrate and phosphorus to waters of the state are still small compared to nonpoint contributions of these pollutants from sources such as agricultural and urban runoff. Point sources tend to have greatest impact during periods of low precipitation and stream flow, while nonpoint sources are most significant during periods of high precipitation and stream flow, both of which were a factor during 2001 and 2002. Unfortunately, it is difficult to directly measure the effects of nonpoint pollution on Minnesota's lakes, rivers and ground water. Although MPCA is investigating better ways to do this, nonpoint source monitoring is expensive and often requires a more complex, labor-intensive (and therefore more costly) monitoring network than measuring volume and quality of discharge from pipes. Later in Chapter 2, the report includes the results of a recent loading study the MPCA has conducted on the Crow River basin in central Minnesota. Accounting for municipal and industrial discharges to a river reach using data from the DMRs and measuring actual concentrations of a pollutant (such as phosphorus) in the same reach enables the MPCA to estimate indirectly the contribution of nonpoint pollution to that reach.

# Chapter 1: Air Pollutant Emissions Overview

Thousands of chemicals are emitted into the air. Many of these are air pollutants that can directly or indirectly affect human health, reduce visibility, cause property damage and harm the environment. For these reasons, the MPCA attempts to reduce the amount of air pollutants released into the air. In order to understand how much pollution is released and to track the success of reduction strategies, the MPCA estimates the emissions of certain air pollutants released in Minnesota.

#### Criteria Pollutants

The 1970 Clean Air Act identified six major air pollutants that were present in high concentrations throughout the United States called "criteria pollutants." These air pollutants are particulate matter  $(PM_{10})$ , sulfur dioxide  $(SO_2)$ , nitrogen oxides  $(NO_x)$ , ozone  $(O_3)$ , carbon monoxide (CO) and lead (Pb). Fine particulate matter  $(PM_{2.5})$  was later added as an additional criteria pollutant. The Minnesota Criteria Pollutant Emission Inventory estimates emissions of five criteria pollutants  $(PM_{10}, SO_2, NO_x, CO)$  and Pb). Ozone is not directly emitted, so a group of ozone precursors called volatile organic compounds (VOCs) is included instead.  $PM_{2.5}$  will be included in the 2002 inventory. To provide some additional details about ozone and  $PM_{2.5}$  for this year's report, the Criteria Pollutant Emissions section contains information about ozone, sources of fine particulates in Minnesota and a summary of the MPCA's Air Quality Index (AQI) data for 2003. The AQI provides a simple way to report daily air quality conditions.

#### Greenhouse Gases

Although greenhouse gases do not necessarily directly harm human health, their increase in concentration can lead to global climate change. The principal greenhouse gas emitted is carbon dioxide ( $CO_2$ ), which the MPCA tracks in Minnesota.

#### Air Toxics

Many other chemicals are released in smaller amounts than the criteria pollutants, but are still toxic. The EPA refers to chemicals that cause serious health and environmental hazards as hazardous air pollutants or air toxics. Air toxics include chemicals such as benzene, formaldehyde, acrolein, mercury and polycyclic organic matter. Minnesota data come from the 1999 Minnesota Air Toxics Emission Inventory.

This report is limited to a summary and discussion of emissions of various air pollutants in Minnesota. However, the MPCA has prepared several other reports that discuss air pollution trends and emissions in more detail. Please reference the following reports for more information regarding air pollution.

Air Quality in Minnesota: Into the Future—2003 Legislative Report <u>http://www.pca.state.mn.us/publications/reports/lr-airqualityreport-2003.html</u> Air Quality in Minnesota: Problems and Approaches—2001 Legislative Report <u>http://www.pca.state.mn.us/hot/legislature/reports/2001/airquality.html</u> Air Toxics Monitoring in the Twin Cities Metropolitan Area Preliminary Report <u>http://www.pca.state.mn.us/hot/legislature/reports/2003/lr-airtoxmonitoring-1sy03.pdf</u>

# **Criteria Air Pollutant Emissions**

<u>Minnesota's Emission Inventory Rule</u> requires all facilities in Minnesota that have an air emissions permit to submit an annual emission inventory report to the Minnesota Pollution Control Agency (MPCA). The report quantifies emissions of the regulated pollutants listed below:

- carbon monoxide (CO)
- nitrogen oxides (NO<sub>x</sub>)
- lead (Pb)
- particulate matter (PM)
- particulate matter less than 10 microns in diameter ( $PM_{10}$ )
- sulfur dioxides (SO<sub>2</sub>)
- volatile organic compounds (VOC)

The emission inventory is used to track the actual pollutant emissions of each facility and to determine the type and quantity of pollutants being emitted into the atmosphere. Ozone is a criteria pollutant that is not directly emitted, so a group of ozone precursors called volatile organic compounds (VOCs) is included instead. The data is then used to calculate an annual emission fee for each facility.

The Minnesota Criteria Pollutant Emission Inventory estimates emissions from these large facilities every year in order to fulfill the Minnesota rule. In addition, every three years, the MPCA estimates emissions from two other principal source categories: area sources and mobile sources. Overall, the Minnesota Criteria Pollution Emission Inventory includes emissions from three principal source categories.

- 1. **Point Sources**: Typically large, stationary sources with relatively high emissions, such as electric power plants and refineries. A "major" source emits a threshold amount (or more) of at least one criteria pollutant, and must be inventoried and reported.
- 2. Area Sources: Typically stationary sources, but generally smaller sources of emissions than point sources. Examples include dry cleaners, gasoline service stations and residential wood combustion. Area sources may also include a diffuse stationary source, such as wildfires or agricultural tilling. These sources do not individually produce sufficient emissions to qualify as point sources. For example, a single gas station typically will not qualify as a point source, but collectively the emissions from many gas stations may be significant.
- 3. **Mobile Sources**: Mobile sources are broken up into two categories; on-road vehicles and nonroad sources. On-road vehicles include vehicles operated on highways, streets and roads. Nonroad sources include lawn and garden equipment, construction equipment, aircraft and locomotives.

Criteria pollutant emission inventories for the State of Minnesota are available for all three principal source categories in 1999 and for point sources from 1990-2001. This report presents trend data for point sources from 1997-2001.

With each new inventory, improvements are made in terms of pollutants covered, source categories included, and the accuracy of emission estimates. Therefore, changes in the way emissions are calculated may affect trends, even if there was no real increase or decrease in emissions.

The reader may note differences in the total emission figures for a given year discussed in this report versus previous emission reports the MPCA has published because MPCA data is being used instead of EPA data. Differences in methodology exist between the two inventories. Data may be also updated in past year emissions inventories due to corrections or changes in methodology.

In addition, despite the importance of secondary formation for some pollutants (e.g.  $PM_{10}$ ), estimated air emissions data in this report are only based on direct releases from sources into the atmosphere. Secondary formation of pollutants is not included in the estimates, because there is currently no reliable way to estimate their quantity. However, models to predict secondary formation of particulates are under development.

Find more information on the Minnesota Criteria Pollutant Emission Inventory:

http://www.pca.state.mn.us/air/emissions.html

http://www.pca.state.mn.us/air/emissions/emissearch.cfm

Find more information on criteria air pollutants in the following EPA web site:

http://www.epa.gov/air/urbanair/index.html

See the EPA AIRData web site to download criteria pollutant emissions data:

http://www.epa.gov/air/data/index.html

# Air Quality Index (AQI)

The Air Quality Index (AQI) was developed by the EPA to provide a simple, uniform way to report daily air quality conditions.

In Minnesota, four criteria pollutants are used to calculate the AQI: ground-level ozone, sulfur dioxide, carbon monoxide and fine particles ( $PM_{2.5}$ ). The AQI is currently calculated for Duluth, Ely, Mille Lacs area, Rochester, St. Cloud, and the Twin Cities area. Not all pollutants are monitored at each location.

The AQI translates each pollutant measurement to a common index, with an index of 100 set to reflect where health effects might be expected in sensitive populations. The pollutant with the highest index value is used to determine the overall AQI. The table below shows the different AQI categories along with the corresponding index range.

#### **AQI Color Legend:**

Good	0-50
Moderate	51-100
Unhealthy for Sensitive Groups	101-150
Unhealthy	151-200
Very Unhealthy	201-300

The AQI in Minnesota cities rarely reaches the Unhealthy range; however, many citizens are affected by air quality in the Unhealthy for Sensitive Groups category.

The following chart displays the number of Good, Moderate, and Unhealthy for Sensitive Groups days in Minnesota. Days are categorized by the highest AQI level calculated at anytime during that day. The EPA may report different AQI summary totals for Minnesota because the MPCA and EPA use different methods to calculate the AQI. In general, the MPCA believes its AQI numbers to be more accurate and protective of human health, because they better account for particles present in liquid and gaseous form.



#### AQI Days by AQI Category and Region in Minnesota, 2003

The Twin Cities had 161 Good air quality days, 191 Moderate air quality days and 13 days that were considered Unhealthy for Sensitive Groups. The Twin Cities in 2003 had more days falling in the Moderate and Unhealthy for Sensitive Groups categories than in the Good category.

Since not all pollutants are monitored at each location, some regions do not show a total of 365 days being reported for the year. For instance, the Ely and Mille Lacs locations are only monitored for ozone. Ozone is only a problem in warm weather and is monitored from April through September. Many of the monitors located in areas outside the Twin Cities were added throughout 2003 and had varying degrees of AQI coverage.

This explains in part why the Twin Cities had significantly more Moderate and Unhealthy for Sensitive Group days than the other locations. High AQI days in Minnesota are usually the result of elevated levels of ozone and  $PM_{2.5}$ . Only the Twin Cities area was monitored for  $PM_{2.5}$  for all of 2003.

#### References/Web Links

For more information on the AQI, see the following web sites:

http://aqi.pca.state.mn.us/hourly/ http://www.epa.gov/airnow/

http://www.epa.gov/airnow/aqibroch/

### **Particulate Matter**

Particulate matter is the general term for particles found in the air, including dust, dirt, soot, smoke, and liquid droplets. Some particles are seen as soot or smoke. Others are so small that they can only be detected with an electron microscope. Particles less than or equal to 2.5 micrometers ( $\mu$ m) in diameter, or PM<sub>2.5</sub>, are known as "fine" particles. Those larger than 2.5  $\mu$ m but less than or equal to 10  $\mu$ m are known as "coarse" particles. PM<sub>10</sub> refers to all particles less than or equal to 10  $\mu$ m in diameter.

Both coarse and fine particles can be inhaled into the lungs. These particles then accumulate in the respiratory system and are associated with numerous adverse health effects, which are briefly described in the following sections.

Particulate matter also causes adverse impacts to the environment. Fine particulates are the major cause of reduced visibility in parts of the United States. In addition, when particles containing nitrogen and sulfur deposit onto land or water bodies, they may affect nutrient balances and acidity. This can result in the depletion of nutrients in the soil, damage to sensitive forests and farm crops, and diversity changes in ecosystems. Particulate matter also causes soiling and erosion damage to materials and buildings.

### **PM**<sub>2.5</sub>

Fine particles can be inhaled deeply into the lung. These particles then accumulate in the respiratory system and are linked with a number of serious health effects such as increased cardiovascular and respiratory hospital admissions and deaths. Studies indicate that peaks in  $PM_{2.5}$  may aggravate respiratory conditions such as asthma and chronic bronchitis.

For 10 days in 2003, levels of fine particulate matter were high enough in the Twin Cities area to lead to air alerts for people in sensitive groups. These groups include people with respiratory or heart disease, the elderly and children.  $PM_{2.5}$  was also responsible for the majority of moderate air quality days. The number of moderate days is significant because recent evidence suggests some people may suffer health effects at the high end of the moderate air quality range.

#### **Emissions Data and Sources**

Fine particles can be directly released during combustion processes, for example, when coal, gasoline, diesel, other fossil fuels and wood are burned. Many particles are also formed secondarily in the atmosphere from chemical reactions involving gaseous pollutants such as nitrogen oxides, sulfur oxides, some volatile organic compounds and ammonia. Major sources of fine particles are cars, trucks, buses, diesel construction equipment, coal-fired power plants, biomass (wood, vegetation, etc.) burning and agriculture.

Because they are tiny and light, fine particles can be carried by the wind for hundreds of miles, making exposure to these pollutants a regional problem. Unlike ozone, which is typically elevated in the hot summer months, fine particles can be a problem throughout the year.

The Minnesota Criteria Pollutant Emission Inventory did not estimate 2001 emissions of  $PM_{2.5}$ . Therefore, emission estimates cannot be provided in this report. Direct source emissions of  $PM_{2.5}$  will be included in the 2002 inventory. However, secondarily formed particles which are not directly emitted, but are formed downwind of the emissions source will not be included because this formation cannot be accurately quantified at this time. Work is underway to develop models to predict secondary formation. This is significant because secondary particles are a major component of the mass of ambient  $PM_{2.5}$ .

While emissions data is not available, the MPCA has three fine particle monitors in St. Paul, Minneapolis and Rochester, which are set up to help determine the source of particles in urban areas. The figure on the next page shows the results of a preliminary analysis of the major  $PM_{2.5}$  components from these monitors.



#### PM<sub>2.5</sub> Composition at Three Minnesota Sites, October 2001-September 2002

The concentrations of the different fractions of  $PM_{2.5}$  are very similar across the three monitors. The largest fraction is organic carbon, followed by sulfate and nitrate. Getting a sense of the composition of fine particles in Minnesota can help to pinpoint the sources of these particles.

**Organic carbon particles:** These can be either primary particles or can be formed secondarily from the reaction of some volatile organic compounds. They can result from human activities (fossil fuel consumption, prescribed fires, cooking) or biogenic activities (vegetative material, biogenic gases, naturally occurring forest fires). Scientists are unsure at this point whether the majority of organic carbon particles are of primary or secondary origin. See the VOC section of this report for Minnesota's 2001 VOC emissions associated with human activities.

**Fine sulfate particles**: These result from the oxidation of sulfur dioxide, forming sulfuric acid, which can then react with ammonia. Most sulfur dioxide emissions result from human sources including coalfired power plants and other industrial sources such as smelters, industrial boilers and oil refineries. See the SO<sub>2</sub> section of this report for Minnesota's 2001 SO<sub>2</sub> emissions.

**Nitrate particles:** These particles form from the oxidation of nitrogen oxides. Nitrogen oxide gases are released from virtually all combustion activities, especially those involving cars, trucks, buses, off-road sources (e.g., construction equipment, lawn mowers and boats), coal-fired power plants and other industrial sources. See the  $NO_x$  section of this report for Minnesota's 2001  $NO_x$  emissions.

**Elemental carbon particles:** These particles are commonly called soot. They are smaller than most particles and tend to absorb rather than scatter light. These particles are emitted into the air from virtually all combustion activity, but are especially prevalent in diesel exhaust and smoke from the burning of wood and wastes.

**Ammonia:** Most of the ammonia emitted in Minnesota is generated from livestock waste management and fertilizer production. The MPCA plans to include ammonia in its 2002 emissions inventory.

Soil Fraction: This fraction consists of primary particles that are eroded from the landscape.

#### References/Web Links

For more information on PM<sub>2.5</sub>, see the following web sites:

http://www.epa.gov/air/urbanair/pm/index.html http://www.epa.gov/airnow/aqguidepart.html http://www.epa.gov/airtrends/

# Particulate Matter (PM<sub>10</sub>)

Exposure to  $PM_{10}$  particles is primarily associated with the aggravation of respiratory conditions such as asthma.  $PM_{10}$  has also been linked to cardiovascular mortality and related health effects, but many studies indicate a stronger association between  $PM_{2.5}$  and these health effects.

Coarse particles are generally emitted from sources such as vehicles traveling on unpaved roads, materials handling, and crushing and grinding operations, and windblown dust. Coarse particles can settle rapidly from the atmosphere within hours, and their spatial impact is typically limited (compared to  $PM_{2.5}$ ) because they tend to fall out of the air in the downwind area near their emissions point

#### **Emissions Data and Sources**

The MPCA estimate for statewide direct emissions of PM<sub>10</sub> in 2001 is 850,499 tons.

The figure below shows estimated sources of 2001 PM<sub>10</sub> direct emissions.



#### Sources of PM<sub>10</sub> Emissions in Minnesota, 2001

Emissions of naturally occurring and secondarily formed  $PM_{10}$  are not accounted for in these pie charts and graphs. Area sources contribute 94 percent of  $PM_{10}$  emissions. The majority of area source emissions come from dust from unpaved roads (54 percent) and agriculture production (33 percent). Fugitive dust from paved roads and construction and combustion sources make up the remainder of the area source contribution.

Point sources account for 4 percent of  $PM_{10}$  emissions. These emissions come from the mining, manufacturing and utility sectors. On-road vehicles and non-road sources make up about 2 percent of total  $PM_{10}$ .

Although most of the mass of  $PM_{10}$  emissions come from fugitive dust sources, these sources tend to be located away from people and tend to be coarser particles, which are of less concern from a human health perspective. Particles emitted from non-fugitive dust sources such as cars, wood stoves, and industrial and commercial combustion are smaller, more toxic and more often released in populated areas.

#### Trends

Point sources contribute 4 percent to the total state  $PM_{10}$  emissions. Emissions from the mining sector decreased significantly in 2001. This decrease in mining emissions of  $PM_{10}$  was due primarily to the closing of LTV Steel Company.



#### PM<sub>10</sub> Point Source Emission Trends by Sector in Minnesota, 1997-2001

#### References/Web Links

For more information on PM<sub>10</sub>, see the following web sites:

http://www.epa.gov/oar/urbanair/pm/index.html http://www.epa.gov/airtrends/

# Ozone

Ozone is an odorless, colorless gas composed of three atoms of oxygen. Naturally occurring ozone in the upper atmosphere helps protect the earth's surface from ultraviolet radiation. However, at elevated concentrations, ground-level ozone can irritate the respiratory system, reduce lung function, aggravate and potentially cause asthma, and cause other lung effects. Children, active adults, and people with respiratory diseases are particularly sensitive to ozone. Ozone was responsible for three AQI unhealthy for sensitive groups days in the Twin Cities and one in Mille Lacs in 2003.

#### **Emissions Data and Sources**

Emissions of ozone are not reported because ozone is not normally emitted directly into the air. Instead, it is created when "ozone precursors" such as nitrogen oxides  $(NO_x)$  and volatile organic compounds (VOCs) react in a hot stagnant atmosphere. Since heat and sunlight are needed for ozone to be produced, elevated levels of ozone in Minnesota are normally seen on very hot summer afternoons.

Ozone precursors come from a variety of sources.  $NO_x$  can form when fuels are burned at high temperatures. The major  $NO_x$  sources are combustion processes from automobiles and power plants. VOCs are emitted from a variety of sources, including industrial sources, motor vehicles and consumer products.  $NO_x$  and VOCs are also emitted by naturally occurring sources such as soil and vegetation. See the  $NO_x$  and VOC sections of this report for more information regarding 2001 emissions of ozone precursors.

#### **References/Web Links**

For more information on ozone, see the following web sites:

http://www.epa.gov/air/urbanair/ozone/index.html http://www.epa.gov/airnow/consumer.html http://www.epa.gov/airtrends/ http://www.pca.state.mn.us/air/ozonestudy.html

# **Nitrogen Oxides**

Nitrogen oxides  $(NO_x)$  is the generic term for a group of highly reactive gases, all of which contain nitrogen and oxygen in varying amounts. The two primary constituents are nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>). NO is a colorless, odorless gas that is readily oxidized in the atmosphere to NO<sub>2</sub>. NO<sub>2</sub> exists as a brown gas that gives photochemical smog its yellowish-brown color. NO<sub>x</sub> is reported because NO and NO<sub>2</sub> continuously cycle between the two species. NO<sub>x</sub> form when fuel is burned at high temperatures. NO is the principal oxide of nitrogen produced in combustion processes.

 $NO_x$  contributes to a wide range of human health effects.  $NO_2$  can irritate the lungs and lower resistance to respiratory infection (such as influenza). More importantly,  $NO_x$  are a major precursor both to ozone and to particulate matter (PM). As discussed in the ozone and PM sections of this report, exposure to these pollutants is associated with serious adverse health effects.

High  $NO_x$  concentrations also have serious environmental impacts. Deposition of nitrogen can lead to fertilization, eutrophication, or acidification of terrestrial, wetland and aquatic systems. This can result in changes in species number and composition such as the reduction of fish and shellfish populations. In addition, nitrous oxide (N<sub>2</sub>O), another component of NO<sub>x</sub>, is a greenhouse gas that contributes to global warming.

#### **Emissions Data and Sources**

The MPCA estimate for statewide emissions of  $NO_x$  in 2001 is 466,358 tons.

The figure below shows sources of 2001 NO<sub>x</sub> emissions.



#### Sources of Nitrogen Oxide Emissions in Minnesota, 2001

The majority of  $NO_x$  emissions come from the transportation sector, which consists of on-road vehicles and non-road sources. On-road vehicles contribute 37 percent of total statewide  $NO_x$  emissions, while non-road sources contribute 27 percent of total  $NO_x$  emissions. Gasoline engines contribute the majority of emissions from the transportation sector. Thirty percent of  $NO_x$  emissions come from point sources, primarily from the utility and mining sectors. Area sources are responsible for the remaining 6 percent of  $NO_x$  emissions. Residential and small industrial and commercial combustion makes up the majority of area source emissions.

#### Trends

Point sources contribute 30 percent of the  $NO_x$  emissions in the state. In Minnesota,  $NO_x$  emission estimates from point sources have gradually decreased since 1997. All categories have decreased from 2000 levels, however mining and utilities have decreased the most significantly. The decrease in mining emissions of  $NO_x$  was in part due to the closing of LTV Steel Company.



#### Nitrogen Oxide Point Source Emission Trends by Sector in Minnesota, 1997-2001

#### References/Web Links

For more information on nitrogen oxides, see the following web sites:

http://www.epa.gov/air/urbanair/nox/index.html http://www.epa.gov/airtrends/

# **Volatile Organic Compounds**

Volatile organic compounds (VOCs) are compounds containing the elements carbon and hydrogen that exist in the atmosphere primarily as gases because of their low vapor pressure. VOCs are defined in federal rules as chemicals that participate in forming ozone. Therefore, only gaseous hydrocarbons that are photochemically reactive and participate in the chemical and physical atmospheric reactions that form ozone and other photochemical oxidants are considered VOCs.

Many VOCs are also air toxics and can have harmful effects on human health and the environment. However, VOCs are regulated as a criteria pollutant because they are precursors to ozone. See the sections on ozone and air toxics for related human health and environmental effects.

#### **Emissions Data and Sources**

The MPCA estimate for statewide emissions of VOCs in 2001 is 392,918 tons.

VOCs are emitted from a variety of sources: including industrial sources, motor vehicles, consumer products and natural sources such as soils and vegetation. The figure below shows only manmade Minnesota sources of VOCs in 2001.



Sources of Volatile Organic Compounds in Minnesota, 2001

Over half of the emissions come from the transportation sector, which consists of on-road vehicles and non-road sources. Twenty-seven percent of emissions come from on-road vehicles and 26 percent come from non-road sources. Non-road sources include recreational equipment, pleasure boats, and lawn and garden equipment as well as other agricultural and commercial equipment. Area sources contribute 40 percent of VOC emissions, primarily from residential wood burning, gasoline service stations, commercial and consumer solvent usage, and petroleum bulk stations and terminals. The final 7 percent of emissions come from point sources such as the manufacturing sector, pulp and paper operations, and refineries.

#### Trends

Point sources contribute 7 percent of the VOC emissions in the state. VOC point source emission estimates have gradually decreased in Minnesota since 1999. All categories except refineries have decreased from 2000 levels.



#### Volatile Organic Compound Point Source Emission Trends by Sector in Minnesota, 1997-2001

#### References/Web Links

For more information on volatile organic compounds, see the following web site:

http://www.epa.gov/airtrends/

# **Carbon Monoxide**

Carbon monoxide (CO) is a colorless and odorless toxic gas formed in high concentrations when carbon in fuels is not burned completely.

CO enters the bloodstream and reduces the delivery of oxygen to the body's organs and tissues. The health threat from CO is most serious for those who suffer from cardiovascular disease. At higher concentrations it also affects healthy individuals. Exposure to elevated CO levels is associated with impaired visual perception, work capacity, manual dexterity, learning ability and performance of complex tasks. Prolonged exposure to high levels can lead to death.

At concentrations commonly found in the ambient air, CO does not appear to have adverse effects on plants, wildlife or materials. However, CO is oxidized to form carbon dioxide  $(CO_2)$ , a contributor to global warming.

#### **Emissions Data and Sources**

The MPCA estimate for statewide emissions of CO in 2001 is 2,502,920 tons.

The figure below shows sources of 2001 CO emissions.



#### Sources of Carbon Monoxide Emissions in Minnesota, 2001

The majority of CO emissions come from the transportation sector, which consists of on-road vehicles and non-road sources. On-road vehicles contribute 59 percent of total statewide CO emissions, while non-road sources contribute 23 percent of total CO emissions. Non-road emissions come primarily from gasoline consumption by lawn and garden, recreational and commercial equipment.

The remaining 18 percent of emissions come from point and area sources. Area source emissions are primarily from prescribed burning, residential wood burning, forest fires and waste disposal through open burning. Major point source contributors to CO emissions are from the manufacturing and utility sectors.

#### Trends

Point sources contribute only 1 percent to the total state CO emissions. Emissions from point sources have remained relatively constant since 1998. The decrease in emissions from 1997 to 1998 was the result of a change in estimation methodology from Marathon Ashland Petroleum. The new methodology is similar to that used by other major refineries in the state.



#### Carbon Monoxide Point Source Emission Trends by Sector in Minnesota, 1997-2001

#### References/Web Links

For more information on carbon monoxide, see the following web sites:

http://www.epa.gov/air/urbanair/co/index.html http://www.epa.gov/airtrends/

# **Sulfur Dioxide**

Sulfur dioxide  $(SO_2)$  belongs to the family of sulfur oxide gases. It is a colorless gas that can be detected by taste and odor at concentrations as low as 0.3 ppm. Sulfur oxide gases are formed when fuel containing sulfur (mainly coal and oil) is burned and during metal smelting and other industrial processes.

 $SO_2$  reacts with other chemicals in the air to form tiny sulfate particles. In fact, sulfate aerosols make up the largest single component of fine particulate matter. It is difficult to distinguish between health effects due to  $SO_2$  exposure and those due to fine particulate exposure. The major health effects of concern associated with exposures to high concentrations of  $SO_2$ , sulfate aerosols and fine particulates include impaired breathing, respiratory illness, alterations in the lung's defenses, aggravation of existing respiratory and cardiovascular disease, and mortality. Children, asthmatics and the elderly may be particularly sensitive.

 $SO_2$  also causes significant environmental damage.  $SO_2$  reacts with other substances in the air to form acids, which fall to earth as rain, fog, snow, or dry particles. Acid rain damages forests and crops, changes the makeup of soil, and makes lakes and streams acidic and unsuitable for fish. Continued exposure changes the number and variety of plants and animals in an ecosystem. In addition,  $SO_2$  accelerates the decay of buildings and monuments and is a major cause of reduced visibility due to haze in Minnesota.

#### **Emissions Data and Sources**

The MPCA estimate for statewide emissions of  $SO_2$  in 2001 is 149,747 tons. The figure below shows sources of 2001  $SO_2$  emissions.



#### Sources of Sulfur Dioxide Emissions in Minnesota, 2001

More than 80 percent of  $SO_2$  emissions come from point sources. Electric utilities and industrial facilities burning coal emit the majority of  $SO_2$  attributed to point sources. Non-road sources emit 9 percent of  $SO_2$ . Non-road source emissions come primarily from agricultural equipment, marine vessels, trains and construction and mining equipment. On-road vehicles contribute 4 percent of the emissions. These emissions are divided between gasoline-powered cars, trucks and motorcycles, and diesel vehicles.

The remaining four percent of area emissions of  $SO_2$  result from fuel combustion by small industrial and commercial facilities and residences.

#### Trends

Point sources contribute 83 percent to the total state  $SO_2$  emissions. Emissions from point sources have remained relatively constant since 1997. Coal-burning utilities are the greatest emitters of  $SO_2$ . Estimated emissions have decreased from all categories except refineries since 2000.



Sulfur Dioxide Point Source Emission Trends by Sector in Minnesota, 1997-2001

#### References/Web Links

For more information on sulfur dioxide, see the following web sites:

http://www.epa.gov/oar/urbanair/so2/index.html http://www.epa.gov/airtrends/

### Lead

Lead (Pb) is a metal found naturally in the environment as well as in manufactured products. In the past, the major sources of lead emissions were motor vehicles and industrial sources. Since lead in gasoline was phased out, metals processing (lead and other metals smelters) and aircraft using leaded fuel became the primary sources of lead emissions.

Lead causes damage to organs such as the kidneys and liver and may lead to high blood pressure and increased heart disease. In addition, exposure to lead may contribute to osteoporosis and reproductive disorders. Most importantly, lead exposure causes brain and nerve damage to fetuses and young children, resulting in seizures, behavioral disorders, memory problems, mood changes, learning deficits and lowered IQ.

Elevated lead levels are also detrimental to animals and to the environment. Wild and domestic animals experience the same kind of effects as people exposed to lead. Elevated levels of lead in the water can cause reproductive damage in some aquatic life and cause blood and neurological changes in fish.

#### **Emissions Data and Sources**

The MPCA estimate for statewide emissions of lead in 2001 is 79 tons. The total mass of lead emitted is much less than the other criteria pollutants. However, it takes only a small amount of lead to cause serious and permanent health problems. Therefore, even relatively low lead emissions are a concern. The figure below shows sources of 2001 lead emissions.





Non-road sources (primarily airplanes using leaded fuels) contribute 66 percent of Minnesota's lead emissions. Point sources such as utilities and metal processing (including lead and other metal smelters) add an additional 29 percent of lead to the environment. Area sources contribute the final 5 percent of lead emissions. Area source lead emissions result from prescribed burning, auto body refinishing and forest fires.

#### Trends

Point sources contribute 29 percent to the total state lead emissions. In Minnesota, estimated lead emissions from point sources have dropped significantly from nearly all sectors.



#### Lead Point Source Emission Trends by Sector in Minnesota, 1997-2001

#### References/Web Links

http://www.epa.gov/air/urbanair/lead/index.html http://www.pca.state.mn.us/air/lead.html#tips http://www.health.state.mn.us/divs/eh/lead/index.html

# **Carbon Dioxide**

Carbon dioxide is a gas that is primarily formed from the combustion of fossil fuels such as oil, gas, and coal. It is the major greenhouse gas that can contribute to warming of the earth's atmosphere. The earth's greenhouse effect is a natural phenomenon that helps regulate the temperature of our planet. Many greenhouse gases occur naturally, but fossil fuel burning and other human activities are adding gases to the natural mix at an accelerated rate.

#### **Emissions Data and Sources**

The estimate for statewide emissions of carbon dioxide in 2001 is 106 million short tons.

The pie chart below shows the breakdown of carbon dioxide emissions from fossil fuel burning by sector. The majority of the carbon dioxide emissions come from the electric utility (37%) and transportation (35%) sectors. The remaining 28 percent of the emissions come from fossil fuel combustion in the industrial, commercial, residential and agriculture sectors.

Sources of Carbon Dioxide Emissions from



#### Trends

Carbon dioxide emissions from fossil fuel burning in Minnesota increased slightly from 1997 to 1999 with an increase of 5.6 percent from 1999 to 2000. From 2000 to 2001, carbon dioxide emissions decreased 2.6 percent. The Taconite Harbor facility was taken off-line in 2001, which accounts for some of the reduction from 2000 to 2001 in the industrial category. Economic recession in 2001 also likely contributed to some of the decrease.



#### Carbon Dioxide Emission Trends from Fossil Fuel Burning in Minnesota, 1997-2001

# Mercury

Mercury contamination of fish is a well-documented problem in Minnesota. The Minnesota Department of Health advises people to restrict their consumption of sport fish due to mercury on virtually every lake tested. Nearly all — probably about 98% — of the mercury in Minnesota lakes and rivers comes from the atmosphere. Consequently, the data presented here only include releases to the atmosphere.

#### **Emissions Data and Sources**

Mercury emitted to the atmosphere due to human activities is divided by the MPCA into three categories: (1) Emissions incidental to energy production, (2) emissions due to purposeful use, and (3) emissions due to material processing. Although emissions from fossil fuel combustion and the processing of metal ores are both the result of the incidental release of trace contaminants of natural geological materials, we have placed them in separate categories (energy production and material processing, respectively).



Because mercury vapor can be transported long distances by the atmosphere, most of Minnesota's emissions are deposited in other states and countries, and Minnesota receives their emissions. MPCA staff estimates that only about 10% of mercury deposition in rural Minnesota is the result of emissions originating within the state.

MPCA staff estimates that the remaining 90% of the deposition is due to three roughly equal sources: 30% from human-generated sources in the rest of North America, 30% from human sources in the rest of the world, and 30% naturally cycling mercury.

#### Trends

MPCA staff estimates that total mercury emissions in Minnesota declined significantly from 1990 to 2000. In 1990, emissions are estimated to have been about 11,300 pounds. By 2000, mostly due to discontinued use of mercury in products and mandated controls on incineration of solid waste, emissions were about 3,600 pounds, a 68% reduction from 1990 levels.



#### Trends in Minnesota Mercury Emissions from Human Activities

Sediment core studies from lakes in Minnesota and elsewhere show slight declines in atmospheric deposition relative to a peak in the 1970s and 1980s. There is some evidence that concentrations of mercury in fish have also declined, but not to the point of eliminating concerns about fish consumption. But, it is encouraging that efforts to reduce the use and release of mercury appear to have resulted in measurable environmental improvement.

#### **References/Web Links**

For more information on mercury, see the following web sites:

http://www.pca.state.mn.us/air/mercury.html

http://www.epa.gov/mercury/
# **Air Toxics**

Through modeling and MPCA air toxics monitoring, several chemicals besides criteria pollutants have been identified at concentrations of potential concern in Minnesota air. These chemicals include compounds such as benzene, and formaldehyde. Chemicals of potential concern in Minnesota are identified in the MPCA's 2003 Legislative Report—Air Quality in Minnesota: Into the Future, <u>http://www.pca.state.mn.us/hot/legislature/reports/index.html</u>, the MPCA's preliminary report on Air Toxics Monitoring in the Twin Cities Metropolitan Area, <u>http://www.pca.state.mn.us/hot/legislature/reports/2003/lr-airtoxmonitoring-1sy03.pdf</u>, and in the EPA's National Air Toxics Assessment (NATA), http://www.epa.gov/ttn/atw/nata/.

EPA refers to chemicals that cause serious health and environmental hazards as hazardous air pollutants or air toxics. EPA defines air toxics as pollutants that cause or may cause cancer or other serious health effects, such as reproductive effects or birth defects, or adverse environmental and ecological effects.

The Minnesota Air Toxics Emission Inventory estimates emissions of air toxics. Air toxic emission inventories are generally compiled every three years. The most recent inventory for Minnesota is from 1999. The inventory includes three principal source categories: point, area, and mobile sources.

- **1. Point Sources**: Typically large, stationary sources with relatively high emissions, such as electric power plants and refineries.
- 2. Area Sources: Typically stationary sources, but generally smaller sources of emissions than point sources. Examples include dry cleaners, gasoline service stations and residential wood combustion. Area sources may also include a diffuse stationary source, such as wildfires or agricultural tilling. These sources do not individually produce sufficient emissions to qualify as point sources. For example, a single gasoline station typically will not qualify as a point source, but collectively the emissions from many gas stations may be significant.
- **3. Mobile Sources**: Mobile sources are broken up into two categories; on-road vehicles and nonroad sources. On-road vehicles include vehicles operated on highways, streets and roads. Nonroad sources include lawn and garden equipment, construction equipment, aircraft and locomotives.

MPCA staff compiled the emissions estimates for the point and area sources in the 1999 inventory. The results for mobile sources were obtained from EPA's 1999 National Emission Inventory Version 3 for Hazardous Air Pollutants.

Table 3 provides a summary of air toxics emissions from principal source categories taken from the 1999 Minnesota Air Toxics Emission Inventory. The table gives total statewide emissions of each chemical, along with the percent from point, area, highway, and off-highway sources. The inventory includes 156 chemicals: 17 polycyclic organic matters (POMs), 126 non-metal compounds (excluding POMs), and 13 metal compounds.

Pollutant	Total	Point	Area	<b>On-road</b>	Non-road
	(short	(%)	(%)	Vehicles	Sources
	tons)			(%)	(%)
Polycyclic Organic Matter (POMs)					
Acenaphthene	41	90%	6%	1%	2%
Acenaphthylene	59		93%	4%	3%
Anthracene	8.9	2%	88%	6%	4%
Benz[a]Anthracene	11	1%	96%	2%	1%
Benzo[a]Pyrene	2.4		92%	4%	4%
Benzo[b]Fluoranthene	1.7		90%	6%	4%
Benzo[g,h,i,]Perylene	5.7		91%	3%	6%
Benzo[k]Fluoranthene	2.8		94%	4%	2%
Chrysene	8.4		98%	1%	1%
Dibenzo[a,h]Anthracene	0.003	11%	5%	1%	84%
Fluoranthene	13	2%	86%	5%	8%
Fluorene	9.0	1%	70%	11%	18%
Indeno[1,2,3-c,d]Pyrene	3.0		95%	2%	3%
Naphthalene	468	12%	70%	14%	4%
Phenanthrene	30	1%	83%	5%	10%
Pyrene	16	1%	87%	5%	7%
Other POM not included above	171	8%	92%		
POM Total	850	13%	75%	9%	4%
Metal Compounds					
Antimony Compounds	1.4	85%	15%		
Arsenic Compounds	9.2	92%		4%	3%
Beryllium Compounds	0.21	85%	8%		7%
Cadmium Compounds	10	10%	89%		
Chromium Compounds	15	94%	5%	1%	
Chromium (VI)	0.28	55%	4%	36%	4%
Cobalt Compounds	2.7	91%	9%		
Copper Compounds	16	95%	5%		
Lead Compounds	55	72%	7%		22%
Manganese Compounds	107	97%	3%		
Mercury Compounds	2.6	68%	5%	18%	9%
Nickel Compounds	30	79%	17%	1%	3%
Selenium Compounds	2.0	95%	4%		
Metal Compound Total	250	85%	9%	1%	5%

### Table 3: 1999 Minnesota Air Toxics Emissions Inventory Statewide Summary

Pollutant	Total (short tons)	Point (%)	Area (%)	On-road Vehicles (%)	Non-road Sources (%)
Non-Metal Compounds (Excluding POMs)					
1,1,2,2-Tetrachloroethane	0.6	6%	94%		
1,1,2-Trichloroethane	0.05	100%			
1,2,4-Trichlorobenzene	3.7	100%			
1,2,4-Trimethylbenzene	78	88%	12%		
1,3,5-Trimethylbenzene	0.16	100%			
1,3-Butadiene	946		35%	41%	23%
1,3-Dichloropropene	382		100%		
1,4-Dichlorobenzene	186		100%		
2,2,4-Trimethylpentane	8315		2%	39%	59%
2,3,7,8-Tetrachlorodibenzo-p-Dioxin	0.000005	27%	73%		
2,3,7,8-Tetrachlorodibenzofuran	0.0002	6%	94%		
2,4-D (2,4-Dichlorophenoxyacetic Acid)(Including Salts	84		100%		
2,4-Dinitrophenol	0.07	100%			
2,4-Dinitrotoluene	0.003	100%			
2,4-Toluene Diisocyanate	2.5	99%	1%		
2-Chloroacetophenone	0.07	100%			
2-Nitropropane	0.005	,.	100%		
4,4'-Methylenedianiline	0.08	100%	,.		
4,4'-Methylenediphenyl Diisocyanate (MDI)	32	99%	1%		
4-Nitrophenol	0.21	100%	.,,		
Acetaldehyde	2308	3%	30%	41%	25%
Acetamide	0.0003	0,0	100%	,0	
Acetone	828	19%	81%		
Acetonitrile	6.1	100%			
Acetophenone	0.8	22%	78%		
Acrolein	508	2%	70%	14%	14%
Acrylamide	0.12	100%			
Acrylic Acid	6.9	100%			
Acrylonitrile	2.7	38%	62%		
Aldehydes	445	6%	94%		
Allyl Chloride	0.004	100%			
Aniline	0.0006	100%			
Atrazine	90		100%		
Benzaldehyde	0.7	100%			
Benzene	7035	1%	27%	46%	26%
Benzyl Chloride	6.0	100%			
Biphenyl	1.1	64%	36%		
Bis(2-Ethylhexyl)Phthalate (Dehp)	4.9	100%			
Bromoform	0.36	100%			
Butyraldehyde	0.08	100%			
Carbon Disulfide	1.4	84%	16%		
Carbon Tetrachloride	0.8	47%	53%		

 Table 3: 1999 Minnesota Air Toxics Emissions Inventory Statewide Summary

Pollutant	Total (short	Point (%)	Area (%)	On-road Vehicles	Non-road Sources
	(short tons)	(%)	(%)	(%)	(%)
C. 1 10 10 1	,	000/	4.0/	(70)	(,,,)
Carbonyl Sulfide	106	99%	1%		
Catechol	0.32	100%	070/		
Chlorine	261	3%	97%		
Chloroacetic Acid	0.000	100%	1000/		
Chlorobenzene	172	0.00/	100%		
Chloroform	27	80%	20%		
Chloroprene	0.0005	100%			
Cresol/Cresylic Acid (Mixed Isomers)	26	100%			
Crotonaldehyde	0.06	100%			
Cumene	23	72%	28%		
Cyanide Compounds	96	26%	74%		
Di-N-Octylphthalate	0.5	100%			
Dibenzofuran	0.02	10%	90%		
Dibutyl Phthalate	1.3	94%	7%		
Dichlorobenzenes	0.03	100%			
Diethanolamine	0.09	82%	18%		
Diethyl Sulfate	0.003	100%			
Dimethyl Phthalate	1.8	99%	1%		
Dimethyl Sulfate	0.45	100%			
Ethyl Acrylate	2.3	100%			
Ethyl Chloride	27	22%	78%		
Ethylbenzene	2750	5%	2%	50%	44%
Ethylene Dibromide (Dibromoethane)	0.28	99%	1%		
Ethylene Dichloride (1,2-Dichloroethane)	1.3	60%	40%		
Ethylene Glycol	101	23%	77%		
Ethylene Oxide	57	10%	90%		
Ethylidene Dichloride (1,1-Dichloroethane)	0.49	2%	98%		
Formaldehyde	5916	7%	43%	25%	25%
Glycol Ethers	1616	30%	70%		
Hexamethylene Diisocyanate	1.8	100%			
Hexane	4964	24%	34%	24%	17%
Hydrazine	0.0005	100%			
Hydrochloric Acid (Hydrogen Chloride [Gas Only])	12938	100%			
Hydrogen Fluoride (Hydrofluoric Acid)	1365	100%			
Hydroquinone	3.3	36%	64%		
Isophorone	13	42%	58%		
Lindane, (All Isomers)	0.002	100%	0		
M-Dichlorobenzene	0.7	7%	93%		
Maleic Anhydride	0.32	100%	5070		
Methanol	2513	31%	69%		
Methyl Bromide (Bromomethane)	537	1%	99%		
Methyl Chloride (Chloromethane)	173	29%	71%		
Methyl Chloroform (1,1,1-Trichloroethane)	866	23/0	100%		
Methyl Ethyl Ketone (2-Butanone)	2367	25%	75%		
Methyl Ethyl Ketone (2-Butanone) Methyl Iodide (Iodomethane)	0.003	100%	13%		

### Table 3: 1999 Minnesota Air Toxics Emissions Inventory Statewide Summary

Pollutant	Total (short tons)	Point (%)	Area (%)	On-road Vehicles (%)	Non-road Sources (%)
Methyl Isobutyl Ketone (Hexone)	1074	16%	84%		
Methyl Methacrylate	41	100%			
Methyl Tert-Butyl Ether	8.6	26%	1%	73%	
Methylene Chloride (Dichloromethane)	379	24%	76%		
Methylhydrazine	1.6	100%			
N,N-Dimethylformamide	29	18%	82%		
Nitrobenzene	0.24	100%			
O-Dichlorobenzene	202		100%		
Pentachlorophenol	0.000005	100%			
Phenol	108	100%			
Phosphine	0.43	51%	49%		
Phosphorus Compounds	38	55%	45%		
Phthalic Anhydride	0.38	100%			
Polychlorinated Biphenyls (Aroclors)	0.0006	91%	9%		
Polychlorinated Dibenzo-P-Dioxins And Furans, Total	0.00001	100%			
Polychlorinated Dibenzodioxins, Total	0.009	8%	92%		
Propionaldehyde	218	2%		37%	61%
Propylene Dichloride (1,2-Dichloropropane)	0.10	3%	97%		
Propylene Oxide	0.32	100%			
Quinoline	0.0001	100%			
Quinone (p-Benzoquinone)	0.9	100%			
Styrene	1418	73%		20%	8%
Tetrachloroethylene (Perchloroethylene)	202	19%	81%		
Toluene	27872	4%	19%	33%	44%
Trichloroethylene	213	93%	7%		
Trichlorofluoromethane (CFC-11, R-11)	20	1%	99%		
Trichlorotrifluoromethane (CFC-113, R-113)	277		100%		
Triethylamine	2.3	13%	87%		
Trifluralin	42		100%		
Trimethylbenzene	44	18%	82%		
Vinyl Acetate	21	70%	30%		
Vinyl Chloride	6.7	6%	94%		
Vinylidene Chloride (1,1-Dichloroethylene)	1.2	9%	91%		
Xylenes (Mixed Isomers)	14797	7%	24%	35%	34%
m-Xylene	1.7	9%	91%		
o-Xylene	104	4%	96%		
p-Dioxane	6.2	99%	1%		
p-Phenylenediamine	0.05	100%			
p-Xylene	0.07	100%			
Non-Metal Compound Total	105336	21%	26%	25%	27%
Grand Total	106436	22%	26%	25%	27%

 Table 3: 1999 Minnesota Air Toxics Emissions Inventory Statewide Summary

The following pie chart summarizes air toxics pollutant emissions in Minnesota from 1999. Each principal source category is responsible for approximately a quarter of total emissions with slightly more from non-road mobile sources (26.9%) and slightly less from point sources (21.5%).



# Contribution of Principal Source Categories to 1999 Air Toxics Emissions in Minnesota

Total air toxics emissions in 1999: 212,872,544 pounds

A more detailed breakdown of emissions for each principal source category is shown in the following three pie charts. For point sources, there are nine categories that collectively account for about 72% of the total point source emissions. The largest source category is Electric Utilities, which accounts for 47.8% of point source emissions.



Contribution of Major Categories to 1999 Point Source Air Toxic Emissions in Minnesota

Total air toxics point source emissions: 45,774,769 pounds

For area sources, the major contributors of emissions are Industrial Surface Coating and Commercial/Consumer Solvent Products. About half of the area source emissions are attributed to these two source categories.



#### Contribution of Major Categories to 1999 Area Source Air Toxics Emissions in Minnesota

For mobile sources, the largest emission contributor is Highway Vehicles – Gasoline, which accounted for 47% of total mobile source emissions in 1999. The second largest contributor of mobile source emissions is Non-road Vehicles – Gasoline, which is primarily made up of recreational vehicles. Snowmobiles contribute a significant fraction (70%) of emissions from recreational vehicles.



Contribution of Major Categories to 1999 Mobile Source Air Toxics Emissions in Minnesota

Total emissions from mobile sources of air toxics in 1999: 111,106,673 pounds

Total emissions of area sources of air toxics in 1999: 55,991,116 pounds

For more information on air toxics, the Minnesota Air Toxics Emission Inventory and the Great Lakes Air Emissions Inventory, see the following web sites:

http://www.pca.state.mn.us/air/toxics/toxicsinventory.html

http://www.epa.gov/ttn/atw/index.html

http://www.glc.org/air/

# Chapter 2: Water Pollutant Discharges Overview

Minnesota's rivers, streams and lakes provide great natural beauty, and supply the water necessary for recreation, industry, agriculture and aquatic life. The major goal of the MPCA's water-quality program is to protect and improve Minnesota's rivers, lakes, wetlands and ground water so that they support healthy aquatic communities and designated public uses such as fishing, swimming and drinking water. The key strategies for accomplishing this goal include regulating point-source discharges, controlling nonpoint sources of pollution, and assessing water quality to provide information and data to make sound environmental management decisions.

Point sources consist mainly of municipal and industrial wastewater discharges. Point sources are most significant during periods of low precipitation and stream flow. Nonpoint sources include runoff from agricultural fields, feedlots, urban areas, and on-site sewage treatment systems. Nonpoint sources are most significant during periods of high precipitation and stream flow.

Minnesota has been successful in controlling end-of-pipe discharges from wastewater treatment plants and industries to our state's waters. But at the same time, the challenges posed by nonpoint sources of pollution, for example, runoff from cities and agricultural areas, are increasing in proportion with changing land uses and expanding population and development.

The federal Clean Water Act requires states to adopt water quality standards to protect the nation's waters. These standards define how much of a pollutant can be in a surface or ground water supply while still allowing it to meet its designated uses, such as for drinking water, fishing, swimming, irrigation or industrial purposes.

For each pollutant that causes a water body to fail to meet state water quality standards, the federal Clean Water Act requires the MPCA to conduct a Total Maximum Daily Load (TMDL) study. A TMDL study identifies both point and nonpoint sources of each pollutant that fails to meet water quality standards. Rivers and streams may have several TMDLs, each one determining the limit for a different pollutant. Many of Minnesota's water resources cannot currently meet their designated uses because of pollution from a combination of point and nonpoint sources.

# **Major Water Discharge Parameters and Trends**

This section presents discharge information for the following water pollutants that are released by major facilities (point sources) into Minnesota's waters: total suspended solids (TSS); biochemical oxygen demand (BOD); total phosphorus (TP); nitrate (NO<sub>3</sub>); and ammonia (NH<sub>3</sub>). The MPCA continues to investigate ways to effectively measure and report water pollution from nonpoint sources. A summary table of the data from 1998-2002 (the most recent years for which data are available) and an analysis of trends for these pollutants are found on page 2 of this report.

### **Total Suspended Solids**

Total suspended solids is a measure of the material suspended in water or wastewater. Total suspended solids cause interference with light penetration, buildup of sediment and potential degradation of aquatic habitat. Suspended solids also carry nutrients that cause algal blooms that are harmful to fish and other aquatic organisms. Based on results of Discharge Monitoring Reports for 82 major treatment facilities, the estimated discharge of TSS to waters of the state for the year 2002 was 8,852,000 kilograms. This was an increase of 3.4% from the 8,552,000 kilograms reported in 2001. Much of this increase was likely due to high flows that persisted throughout the year over much of Minnesota due to much above average precipitation, coupled with the frequency of high-intensity precipitation events observed in widely scattered areas of the state. The state map below shows the 2002 TSS discharges to surface waters by major point sources of water pollutants, aggregated by county.

#### **Total Suspended Solids Discharges from Major Point Sources, 2002**



# **Biological Oxygen Demand and Carbonaceous Biological Oxygen Demand**

When organic wastes are introduced into water, they require oxygen to break down. High concentrations of organic materials characterize untreated domestic wastes and many industrial wastes. The amount of oxygen required for decomposition of organic wastes by microorganisms is known as biological oxygen demand (BOD). The carbonaceous biological oxygen demand (CBOD) is the amount of oxygen required for microorganisms to decompose waste carbonaceous materials. Both BOD and CBOD are indicators of the strength of waste effluent and the effectiveness of treatment. A high demand for oxygen (the higher the value for BOD or CBOD) causes reduction in the concentration of dissolved oxygen in the receiving waters. Depletion of oxygen deteriorates water quality and impacts aquatic life, including fish and other organisms. Since their effects on receiving waters are similar, discharge data for BOD and CBOD have been combined in this report.

Based on results of Discharge Monitoring Reports for 82 major treatment facilities, the estimated discharge of the combined total of BOD and CBOD to waters of the state for the year 2002 was 5,828,000 kilograms. The combined discharge of BOD and CBOD showed an increase of 15.6%, over the year 2001. As with TSS, discussed above, above average yearly precipitation totals and high runoff rates likely contributed to this increase. The state map below shows the 2002 BOD discharges to surface waters by major point sources of water pollutants, aggregated by county. Distribution of discharges for CBOD is similar.





### **Total Phosphorus**

Total phosphorus (TP) is the primary pollutant associated with the eutrophication of surface water from anthropogenic sources (sources that result from human activities). Excess phosphorus causes algae blooms and reduced water transparency, making water unsuitable for swimming and other activities. Phosphorus is released from both point and nonpoint sources of pollution. Minnesota has had point source effluent limitations for phosphorus since the early 1970s. According to Minn. Rule 7050.0211 subp. 1, "Where the discharge of effluent is directly to or affects a lake or reservoir, phosphorus removal to one milligram per liter shall be required. In addition, removal of nutrients from all wastes shall be provided to the fullest practicable extent whenever sources of nutrients are considered to be actually or potentially detrimental to the preservation or enhancement of designated waters."

Based on results of Discharge Monitoring Reports for 82 major treatment facilities, the estimated discharge of TP to waters of the state for the year 2002 was 1,289,000 kilograms, a decrease of 6.2% from 2001. Treatment advances combined with continued progress in removal of phosphorus from the waste stream likely contributed to the decline, despite increased flows and decreased residence times in some treatment systems. This is good news, as the headwaters state of Minnesota seeks to do its share to reduce its contribution from phosphorus to national problems, like the hypoxic zone in the Gulf of Mexico. The state map below shows the 2002 TP discharges to surface waters by major point sources of water pollutants, aggregated by county.



#### **Total Phosphorus Discharges from Major Point Sources, 2002**

### Nitrogen

Nitrogen, generally occurring as nitrate (NO<sub>3</sub>) or ammonia (NH<sub>3</sub>), is present in a wide variety of effluents including sewage (wastewater treatment plants and on-site sewage facilities), food processing wastes, mining effluents, landfill leachate, and agricultural and urban runoff. Nitrate and/or ammonia concentrations in most of these sources are monitored under permit requirements. Nitrogen as ammonia can be toxic to aquatic life and nitrogen in the form of nitrate can be a significant problem in ground water supplies. Nonpoint sources of nitrogen from agricultural and urban runoff are an important source of loading to waters of the state, although very little of this contribution is captured through Discharge Monitoring Reports required by permit.

Based on the results of Discharge Monitoring Reports for 82 major treatment facilities, the estimated discharges for the year 2002 were 1,127,000 kilograms of ammonia and 4,234,000 kilograms of nitrate, an increase of 9.2% for ammonia and a decrease of 0.1% for nitrate, respectively. For nitrate, the decrease continues a trend that began in 1998. After increasing somewhat from 1999-2000, ammonia discharges decreased significantly in 2001, before increasing again in 2002, but not to the levels seen prior to 2000. The state map below shows the 2002 ammonia discharges to surface waters by major point sources of water pollutants. Distribution of discharges for nitrate is similar.

#### Ammonia Discharges from Major Point Sources, 2002



# **Nonpoint Source Pollution**

As discussed above, Minnesota has made significant progress in cleaning up point sources of water pollution as measured by discharges of major pollutants in municipal and industrial wastewater. An indicator of this success is shown by the fact that the 82 major treatment facilities each discharging more than one million gallons per day of treated effluent have cut their total amount of pollutants discharged to waters of the state by over 3,000,000 kilograms since 1997, even accounting for the high flow conditions observed during the spring and summer of 2001 and throughout much of 2002. Since 2003 was a much drier year in most of the state, even approaching drought conditions in some of the state during the latter half of the year, it will be interesting to observe trends for discharge and flow in next year's (2005) Annual Pollution Report.

It is the nonpoint sources of pollution from rainfall or snow melt moving over or through the ground carrying natural and human-made pollutants into lakes, rivers, wetlands and ground water that now pose the greater challenge for cleanup. Both point and nonpoint sources of pollution must be controlled to reach the Clean Water Act goal of fishable, swimmable waters in the state. Too much phosphorus and nitrogen continue to reach our lakes, rivers and shallow ground water aquifers, carried in soil erosion and runoff from roads, yards, farms and septic systems.

Over the past few years, more regulatory controls for sources like feedlots, septic systems and stormwater have been implemented, but these sources of nonpoint source pollution can be diffuse and difficult to manage. Rural runoff is still largely unregulated. Much of the work to control nonpoint source pollution thus far has used financial incentives to encourage voluntary adoption of best management practices (BMPs). The Board of Water and Soil Resources (BWSR) has attempted to quantify the amount of nonpoint source pollutants like nitrogen, phosphorus and sediment avoided by use of BMPs over the past decade. See pages 13-15 of the 2003 "Watershed Achievements" report at <a href="http://www.pca.state.mn.us/publications/reports/wq-cwp8-03.pdf">http://www.pca.state.mn.us/publications/reports/wq-cwp8-03.pdf</a> for information on the pollution savings estimates for the last six years associated with two financial incentive programs administered by the MPCA, the Clean Water Partnership and Clean Water Act Section 319 programs.

Many of the stresses from nonpoint sources of pollution that affect Minnesota's surface and ground water resources are the result of choices that individuals make every day, such as lawn care, watercraft operation and waste disposal. The daily decisions that homemakers, developers, farmers and businesses make regarding land use are crucial to protecting water resources from the effects of nonpoint source pollution. Once a water resource declines in quality, recovery is costly and can take many years. Clearly, prevention is the key when it comes to nonpoint source pollution. What happens to Minnesota's water resources in the next 10 years will help determine the quality of those resources for the next 100 years.

The effects of solely nonpoint source pollution on a water resource are difficult and expensive to measure. The best long-term data about Minnesota streams comes from measuring six key pollutants at 80 stream locations over the past 40 years. These locations are chosen to not be unduly influenced by the effects of point source pollution, although the results certainly reflect the contribution of all discharges upstream of the monitoring point. The results agree well with those shown by point source discharges from Discharge Monitoring Reports in that significant reductions in ammonia and phosphorus have been observed. Nitrate, which is generally associated with nonpoint sources of pollution, increased over the same period, although as shown in Table 2, recent improvements have been made in removing nitrate from point source discharges. Ground water data collected by MPCA from 1992-1996 show that in aquifers that are sensitive to nitrate contamination, 60 percent of the wells monitored had nitrate levels above one part per million (ppm), suggesting some possible anthropomorphic impacts to the aquifer that the well taps. Of these, 18 percent contained nitrates above the drinking water standard of 10 ppm. Again, much

of this is likely due to the effects of land use practices at the surface and the effects of nonpoint source pollution.

For a further discussion of the effects of nonpoint source pollution on Minnesota's water resources see: http://www.pca.state.mn.us/about/pubs/mnereport/

# Pollutant Loading Case Study of the Crow River of the Upper Mississippi River Basin

A recent Clean Water Partnership study of the Crow River was completed by the C.R.O.W. (Crow River Organization of Water) Joint Powers Board in response to multiple water quality problems being experienced in this rapidly growing area of the state. This central Minnesota watershed covers an area of 1.76 million acres and is a significant tributary to the Mississippi River just above Anoka, Minnesota. An extensive network of 28 sampling stations along the North Fork, South Fork and Buffalo Creek tributaries was used to define water flows and quality in the Crow River Basin.



At the same time the stream sampling was being conducted, MPCA staff summarized point sources phosphorus loading occurring from municipal, industrial and commercial facilities to the Crow River for 2001 and 2002. The amount of P loading to the Crow River and its tributaries was tabulated from the Discharge Monitoring Reports (DMR) from the permitted facilities discharging effluent into the basin. For each permit, the DMR record was tabulated and summarized in electronic format by site and calendar year for reported effluent volumes and effluent P concentrations. Permits of facilities not discharging to

surface waters or with very limited discharges, such as noncontact cooling waters and gravel pit discharges, were not used in calculation of P mass loads. For estimating P loads resulting from adoption of 1.0 mg P/L effluent limits (for those sites without established P limits), reported effluent volumes were multiplied by 1.0 mg P in order to estimate wastewater P loads to the basin for these facilities. Stormwater (another type of point source) phosphorus loadings from municipal, industrial and commercial sources were not calculated.

A total of 57 permitted discharges to the Crow River system were assessed: 38 municipal and 19 industrial. The municipal wastewater facilities (WWTFs) with P limitations were tabulated and summarized into annual P loads as well as flow-weighted mean (FWM) P effluent concentrations. This analysis showed that all of the municipalities met their 1.0 mg P/L limits, or were scheduled to come into compliance as they met new requirements of their permits. For the study period, 2001-2002, those municipalities without P limits, averaged between 1.4 mg P/L and 7.2 mg P/L. Further analysis of the data showed that 17 municipal and industrial discharges exceeded 1,000 pounds of P per year to the Crow River system, while seven communities/industries had discharges over 5,000 pounds P per year.

Over the study period, total point source P loading to the basin was about 171,000 pounds of P/year (77,559 kg), corresponding to an average daily discharge on the order of 469 pounds of P/day. The study estimated that if all the WWWFs were to adopt a 1.0 mg P/L effluent limit then the combined municipal and industrial WWTF permitted discharge P loading to the Crow River system would correspond to an average daily discharge of about 148 pounds of P/day, or about a 68% reduction from 2001 and 2002 levels.

As the study years of 2001 and 2002 were very wet years (extensive flooding occurred in Wright County and the City of Buffalo), phosphorus loading from 2000, a dry year, was used to help place a better perspective to the range of flows and loadings that occur in the Crow River system. Total annual phosphorus loads at the U.S Geological Survey (USGS) Rockford site were calculated, using the Metropolitan Council monitoring data (102,214 kg P), then compared to the total annual point source loads resulting from treated effluent reaching the Crow River or its tributaries (based on 2001 and 2002 DMR data.). As shown in Table 4, the total P load in low flow years appears to be dominated by point sources, while in contrast total P loading in high flow years is dominated by nonpoint sources.

	CY2000 Dry Flows	Estimated Average Flows	Avg. of 2001/2002 Conditions
% Point Source P			
	76%	22%	15%
% Nonpoint Source P	14%	78%	85%

# Table 4: Point Source P Percent Contribution (Theoretical) of the Total P Load at Rockford USGS Site

Calendar year annual flows tabulated for the Crow River at the Rockford USGS site for 2000, 2001 and 2002 were approximately 4%, 12% and 20% of the flow totals of the Mississippi River at Anoka (Table 5). FLUX estimated loads for each site were calculated using the Metropolitan Council (Champion etal, 2002) data by calendar year for each site. Flux is a standard assessment technique to calculate loads, developed by the U.S. Army Corps of Engineers. The percentage of the Anoka Mississippi River annual total phosphorus loads estimated to be due to the Crow River vary from 17% in the dry 2000 to 46% during the wet 2002 conditions. In a similar, but more pronounced fashion, the total suspended solids contribution from the Crow River to the Mississippi River at Anoka varied from 16% to 59% of the annual loads.

	Crow River Percent of Mississippi Loads at Anoka				
Parameter	2000 Dry Year	2001 Wet Year	2002 Wet Year		
Flow	4%	12%	20%		
Total Phosphorus	17%	30%	46%		
Total Suspended Solids	16%	27%	59%		

# Table 5: Crow River Percent of Mississippi River Loads at Anoka (Calendar Year Basis)

# **Other Contaminants of Concern in Minnesota**

One of the greatest challenges of recent decades in protecting the environment is that the mix of chemicals used by society is continually changing. New compounds, or their by-products, eventually find their way into the waste stream, and can ultimately become part of what we inhale, eat, and drink. How do local and national agencies keep up with continuous change? This discussion explores other contaminants, unknown or practically unnoticed just a few years ago, that have emerged as concerns today and the research being undertaken and supported by the MPCA to understand the issues surrounding these contaminants.

Increasing knowledge of the environmental occurrence or toxicological behavior of these contaminants has resulted in concern for potential adverse environmental and human health effects. The lack of knowledge of the processes controlling contaminant transport and fate in the environment, and of the magnitude of exposure to ecological species and humans, has increased the need to study the presence of these contaminants in the environment. Public health experts have an incomplete understanding of toxicological effects of these contaminants, including the significance of long-term exposure.

### Polybrominated Diphenyl Ethers (PBDEs)

In recent years, unexpected and undesirable consequences from the widespread use of polybrominated diphenyl ethers (PBDEs) have been observed. PBDEs are used as additive flame retardants in plastics, textiles, coatings, and electrical components in products such as computers, TVs, electrical appliances, furniture, building materials, carpets, and automobiles. These chemicals have been found to persist in the environment and bioaccumulate in humans and wildlife. Concerns about PBDEs stem from their similarities in structure and properties to polychlorinated biphenyls (PCBs), chemicals with known bioaccumulative and toxic properties.

The toxicological profile of PBDEs suggests that exposure may interfere with development, behavior, and reproduction. Experimental animal studies have shown that prenatal exposure to PBDEs can affect neurodevelopment, resulting in decreased motor function. Skeletal abnormalities were also observed in rodents exposed prenatally to mixtures of PBDE varieties. Adult animals exposed to PBDEs have exhibited decreased reproductive success and impaired immune function. PBDEs can affect the normal functioning of endocrine or hormone systems and neurotransmitters in the central nervous system, both possible mechanisms of action behind the observed health effects in experimental animals. Thyroid disruption was one of the most common and sensitive endpoints observed in animal studies. Thyroid and neurological effects have also been observed in workers exposed to PBDEs and other brominated chemicals.

PBDEs have been detected globally from developed and remote environments. Monitoring studies have measured PBDEs in sediment, air, wildlife, fish, human blood, and human milk. A human-milk monitoring program in Sweden indicates that PBDE concentrations in breast milk are doubling every five years. Similar studies of breast milk conducted in other countries support the findings that human exposure to PBDEs is increasing. Monitoring and assessment of PBDEs in North America has only begun recently. In the Great Lakes, PBDE concentrations were measured in lake trout and salmon from Lakes Erie, Huron, Superior, and Ontario. When concentrations were compared on a fat basis, the fish from Lake Ontario had the highest concentrations of PBDEs, followed by Superior, Huron and Erie. The relatively high level of PBDEs in Lake Superior fish is surprising due to the more pristine character of this lake. In the state of Washington, the governor recently issued an executive order directing the state to develop a chemical action plan to reduce threats posed by PBDEs by December 2004, and to begin

implementing the plan by July 2005. In addition, the order requires the state to adopt a rule establishing criteria and procedures for selecting additional persistent bioaccumulative toxics for action plans in the future.

Recently, the MPCA conducted a study titled "Occurrence and Concentrations of Polybrominated Diphenyl Ethers (PBDEs) in Minnesota's Environment." The study focused on areas where PBDEs were most likely to be present with the assumption that if PBDEs are not found in these targeted areas, PBDEs are not likely to be a problem in more ambient locations in Minnesota. The targeted systems were landfill leachates, wastewater treatment plant (WWTP) sludges and effluents, as well as, fish and sediment collected from rivers below WWTP effluent discharges. Collecting fish and sediment samples from the major river basins in Minnesota (Mississippi, St. Louis, Red, Rainy, Minnesota and St. Croix) ensured geographical representation. PBDEs were detected in all sample categories at all sites.

The data from the investigation indicated that PBDEs are an environmental contaminant in Minnesota. The MPCA will begin creating a database of PBDE concentrations in Minnesota. Models designed to predict the transport and fate of PBDEs in aquatic ecosystems will use the data collected in the PBDE study. Measuring fish PBDE contamination helps to explain the movement and bioaccumulation of PBDEs in the aquatic food chain and predict potential exposure to humans from eating fish. The results of this study will help MPCA to better understand the environmental impacts of PBDEs as a contaminant in Minnesota; knowing the levels of background PBDE contamination will help establish benchmarks to guide future monitoring efforts and to track environmental trends.

#### Polybrominated Dioxins and Furans

The term PBDDs/PBDFs refers to a group of toxic chemicals, consisting of polybrominated dibenzo dioxins and polybrominated dibenzo furans. These compounds have similar chemical structures and mode-of-action biological characteristics to polychlorinated dibenzo dioxins and polychlorinated dibenzo furans. Chlorinated and brominated dioxins are by-products of a number of human activities. Major contributors of chlorinated dioxin to the environment include: municipal solid waste and medical incinerators, backyard trash burning, cement kilns, pulp and paper bleach plants, herbicide manufacture, copper smelters and iron sintering plants. Incineration of products containing brominated compounds and flame retardants (plastics and electrical appliances) causes emissions of brominated dioxins. Brominated and chlorinated dioxin may also have natural sources, but they are small compared to emissions arising from human activities.

Brominated and chlorinated dioxins are persistent, accumulate in biological tissues and enter the human body through consumption of fish, meat and dairy products. As a result, most people have detectable dioxin levels in their tissues that have been bioaccumulated over their lifetime. This "background exposure" may result in an increased risk of cancer and is close to levels that can cause adverse non-cancer effects in humans and animals (U.S. EPA, Persistent, Bioaccumulative, and Toxic Initiative, 2000). Dioxin is a public health and environmental concern because some dioxins have carcinogenic and toxic properties that can produce a broad spectrum of adverse effects such as reproductive and developmental abnormalities, suppression of the immune system, and cancer. EPA characterizes 2,3,7,8 TCDD as a "human carcinogen" and characterizes other dioxins as "likely human carcinogens" (U.S. EPA, Summary of Dioxin Reassessment Science, 2000).

Brominated and chlorinated dioxins are contaminants of concern in Lake Superior and it is important to assess their environmental prevalence in the Western Lake Superior watershed and St. Louis River Area of Concern. MPCA had the same fish and sediment composites collected from six major rivers in Minnesota for PBDE analyses in 2001 analyzed for brominated dioxins. There are also plans to have

wastewater treatment plant sludges, landfill leachates and landfill sludges, also sampled for the PBDE study, analyzed for these chemicals.

#### Pharmaceuticals and Household and Industrial Wastewater Products

A relatively new area of research is focusing on pharmaceuticals and industrial and household wastewater products, including personal care products, in the environment. Human and veterinary antibiotics and other prescription and non-prescription drugs, natural and synthetic hormones, detergents, disinfectants, plasticizers, fire retardants, insecticides, and antioxidants are all examples of pharmaceutical and wastewater contaminants. Sources of these contaminants include animal feedlots, wastewater treatment facilities, septic systems, and medical industry discharges.

A recent study by the Toxic Substances Hydrology Program of the USGS shows that a broad range of pharmaceuticals and household and industrial wastewater products, also called organic wastewater contaminants (OWCs), are found in mixtures at low concentrations downstream from areas of intense urbanization and animal production. Eighty percent of the streams sampled had one or more OWCs. The most abundant substances were insect repellents, non-prescription drugs, detergents, antibiotics, caffeine, and cotinine, a byproduct of tobacco. Difficulties measuring pharmaceuticals and personal care products occur, because many of the degradation products are unknown, drug compositions constantly change, and little data exists on environmental contamination. Implications of these substances being in the environment range from human and ecosystem health effects, possible cumulative and synergistic toxicity, and increased antibiotic resistance. The toxicity and environmental chemistry of most OWCs are not well known. Future research in this area should seek to improve analytical methods and determine concentrations in sediments and tissue.

During 2001, the MPCA began a cooperative study with USGS to assess the presence of several classes of pharmaceuticals, hormones, and industrial and household wastewater products in Minnesota waters. The objective was to determine whether selected Minnesota streams and ground-water resources contain measurable amounts of these biologically active chemicals. The study included water sampled from the main rivers of the state (Minnesota, Mississippi, Red, Rainy, St. Croix, and St. Louis) below WWTPs and at several smaller streams that have relatively high contributions from WWTP effluents (low dilution streams). The MPCA has also sampled ground water near septic systems, urban areas, and feedlots that may be contaminated by these chemicals. The study also assessed the presence of these chemicals in the waste stream by sampling wastewater treatment plant effluents and landfill leachates. USGS is in the process of analyzing samples and compiling results. USGS is also working with the Minnesota Department of Health (MDH) to evaluate the presence of these chemicals in ambient waters that serve as sources of drinking water in Minnesota.

#### Perfluorooctane Sulfonate (PFOS)

Another class of chemicals generating concern is fluorinated surfactants, particularly perfluorooctane sulfonate (PFOS). PFOS is used in the manufacture of numerous products and is thought to be a metabolite of several fluorinated surfactants. The uses of sulfonated surfactants are numerous and diverse: fabric and leather protectors, fire fighting foams, adhesives, pesticide formulations, and paper coatings. The 3M Company produced PFOS as a key ingredient in the fabric protector Scotchgard <sup>TM</sup>, and for paper coating. 3M eliminated their line of PFOS-related products in 2002.

Extremely resistant to environmental breakdown, PFOS is now a ubiquitous contaminant found in reptiles, amphibians, fish, and fish-eating mammals (including humans) and birds across north America. Traditional methods for analyzing persistent pollutants missed PFOS exposure for a long time, because unlike most persistent, bioaccumulative toxic chemicals, PFOS doesn't accumulate in fatty tissue.

Instead, the properties of PFOS result in protein binding and accumulation in blood and liver tissue. The estimated half-life of PFOS in humans is four years.

Future research is needed on PFOS to assess its presence and persistence in the environment, humans, and ecological species. The MPCA is working with the U.S. Environmental Protection Agency in Duluth to have carp collected below wastewater treatment plant discharges analyzed for PFOS. This data will provide preliminary information on PFOS contamination of natural resources in Minnesota.

.