WATER QUALITY MONITORING PROGRAM

MINNESOTA DEPARTMENT OF AGRICULTURE PESTICIDE MONITORING IN WATER RESOURCES:

2003 DATA REPORT

MONITORING AND ASSESSMENT UNIT
AGRICULTURAL CHEMICAL ENVIRONMENTAL SECTION
AGRONOMY & PLANT PROTECTION DIVISION

March 24, 2003
(revised March 25, see Errata)

Minnesota Department of Agriculture

RE: 2003 Data Report on Pesticide Monitoring in Water Resources

Dear Reader,

This report is a summary of surface and ground water monitoring data from the Monitoring and Assessment Unit of the Minnesota Department of Agriculture (MDA). Its primary purpose is to summarize data collected in 2001 and spring of 2002. It also provides general information regarding the MDA water monitoring program. The report uses the format for data analysis developed last year as an outcome of discussions with the Minnesota Pollution Control Agency (MPCA) and Minnesota Department of Health (MDH).

The MDA monitoring program is designed to provide scientifically defensible long-term trend data for pesticides in groundwater and surface water and is one of the few sources of this type of data in Minnesota. Monitoring activities are conducted by the MDA to address statutory mandates for ambient water resource condition monitoring under the Minnesota Groundwater Protection Act (Minn. Stat. Chapter 103H) and the Minnesota Pesticide Control Law (Minn. Stat. Chapter 18B). The immediate use of the data by the MDA is to evaluate the need for protective actions, including the development of pesticide best management practices (BMPs), to reduce the leaching or runoff of pesticides into ground or surface water. The data will also help evaluate the effectiveness of protective actions. In addition, we hope the high quality monitoring data collected by the MDA, from continuous surface water monitoring stations and a scientifically designed groundwater monitoring network, will provide considerable value to scientists, policy makers and other interested parties for a variety of purposes in the near and distant future.

This year finds the state of Minnesota facing one of the greatest budget deficits in its history. However, MDA Commissioner Gene Hugoson has maintained funding for the monitoring program despite significant cutbacks in funding.

There have been a number of developments in the monitoring program over the last year. The MDA Laboratory has completed method development and we are now analyzing groundwater samples for the degradation products of chloroacetamide pesticides including acetochlor, alachlor, dimethenamid and metolachlor. The Information Services Division has completed the development and testing of a new monitoring data management system which is now in use. Because of the loss of a staff person, and to support the new data management system, we have relocated one employee to the St. Paul office and have closed surface water monitoring stations at Bent and Chaska Creeks at the western edge of the Twin Cities metropolitan area. In addition, the Metropolitan Council and counties are facing their own budget cuts which may reduce or eliminate on-going cooperative monitoring efforts with the MDA.

The monitoring unit is finalizing plans for a cooperative effort with the Minnesota Department of Natural Resources (DNR) for sampling springs in southeast Minnesota. We also are continuing to move forward with evaluating methods and resource requirements for sampling groundwater statewide. The MDA submitted a proposal last year for statewide sampling of groundwater for pesticides, prepared in coordination with the MPCA, to the Legislative Commission on Minnesota Resources (LCMR). The proposal received a hearing by the Committee but was not funded. Last year the MDA conducted a statewide survey of pesticides in surface waters which is presented in this report.

I would like to thank the Monitoring and Assessment Unit (Bill VanRyswyk, Constance Holth, Marie Juenemann, Mark Zabel, Michele Puchalski, Paul Wotzka and unit supervisor John Hines) and, especially, Dr. Joseph Zachmann, for producing this report.

Respectfully,

Daniel Stoddard, Manager
Agricultural Chemical Environmental Section
Agronomy and Plant Protection Division
Minnesota Department of Agriculture

ERRATA – March 25, 2003

1. Page 26, Table 14: The column headings for Monthly Mean Concentration corrected to reflect the year 2002. All entries in the column titled Annual Average Flow-Weighted Mean corrected to read "not applicable."

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ACKNOWLEDGMENTS

Staff of the Monitoring and Assessment Unit thank the various people without whom MDA monitoring data could not have been collected, analyzed and summarized. Specific acknowledgements include: the many landowners, local units of government, counties and state agencies who serve as cooperators and help secure sampling locations, grant permission to access those locations, and provide valuable land management information, critical to the long-term goal of evaluating pesticide Best Management Practices; the local cooperators – County Soil and Water Conservation District Boards and member citizens – who provide political and administrative support and help secure local funding that allows local cooperation to develop; the legislative allocations that fund the program; cooperating state agencies that provide advice and assistance regarding technical aspects of the program; the MDA Laboratory Services Department staff who provide expert sample handling, analyses and methods development; and the Commissioner, who continues to support the program among many competing MDA priorities and interests.

ABBREVIATIONS

MDA	Minnesota Department of Agriculture
MDH	Minnesota Department of Health
MPCA	Minnesota Pollution Control Agency
USGS	United States Geological Survey
DNR	Department of Natural Resources
ppm	parts per million (equivalent to milligrams of chemical per liter of water sample)
ppb	parts per billion (equivalent to micrograms chemical per liter of water sample)
U.S. EPA	United States Environmental Protection Agency
HRL	Health Risk Limit
HBV	Health Based Value
MCL	Maximum Contaminant Level
MRL	Method Reporting Limit

DEFINITIONS

Chronic Standard, Criterion or Advisory Value	The highest water concentration of a chemical to which organisms can be exposed without causing chronic toxicity to organisms in question. Established for individual chemicals based on toxicity to aquatic life (the "toxicity-based") and based on toxicity to human life (the "human health-based"), when sufficient information exists to establish one or both of these numbers. The more stringent of the two numbers is used as the chronic standard, criterion or advisory value for purposes of implementation of Minnesota Rules Chapter 7050. The underlying exposure assumptions (e.g., timeframes for exposure comparisons) and applicability of any numbers are established by the MPCA and may vary depending on the state classification of the water body, the nature of the data comparisons being made, and the regulatory status of the number being used for comparison.
Final Acute Value (FAV)	An estimate of the concentration of a pollutant corresponding to the cumulative probability of 0.05 in the distribution of all the acute toxicity values for the genera or species from the acceptable acute toxicity tests conducted on a chemical. The FAV is the value found to be toxic in 5% of all studies conducted. Ninety five percent of all tests conducted found toxicity values to be higher than the FA V chosen. One-half the value of the FAV is the Maximum Standard (MS), and is the highest concentration of a toxicant in water to which aquatic organisms can be exposed for a brief time with zero to slight mortality. The MS is often used as a remedial action cleanup goal to protect surface waters in some ground water contamination situations.
Health Risk Limit (HRL)	The concentration of a substance or chemical (i.e., one that has been determined to be a potential private well drinking water contaminant) in drinking water that can produce a potential toxicological result due to systemic or carcinogenic effect in humans upon consumption. The underlying exposure assumptions (e.g., volume of water consumed and timeframes for exposure comparisons) and the general applicability of any HRL are established for Minnesota by the MDH and adopted by rule of the MDH Commissioner.
Health Based Value (HBV)	Identical to an HRL except that the value is issued on an interim basis for specific situations and until such time that the basis of its derivation and calculation are reviewed and subject to rule-making.
Maximum Contaminant Level (MCL)	A value set by the U.S. EPA as the maximum amount of a chemical allowed in a federally regulated public water supply, considering health, economic or other factors including technological factors such as treatment cost and feasibility.
Method Reporting Limit (MRL)	Represents the minimum concentration of an analyte that can be reliably quantitated and reported by the laboratory. Analytes may be positively identified via qualitative procedures and reported as "Present" below the MRL.

INTRODUCTION

This report is a summary of groundwater and surface water pesticide monitoring data and activities for the Monitoring and Assessment Unit of the Minnesota Department of Agriculture (MDA). Its primary purpose is to summarize analytical data collected by the MDA for calendar year 2001 and spring of 2002 for surface water, and calendar year 2002 for groundwater. Water quality data is provided for three separate monitoring or sampling efforts and are associated with specific reporting periods shown in Table 1:

Table 1 – List of MDA sampling and analysis efforts and associated reporting periods

Sampling and Analysis Effort	Reporting Period
Groundwater Monitoring Network	Calendar Years 2000 – 2002 (with emphasis on 2002)
Surface Water Monitoring Stations	Calendar Year 2001 and Partial Calendar Year 2002
Surface Water Statewide Sampling Survey	May – June, 2002

The scope of MDA groundwater resource monitoring activity has been guided primarily by the state Ground Water Protection Act,[1] and has emphasized areas of the state that are sensitive to human impact. MDA monitoring activity is also guided by the general requirements to determine pesticide impacts to surface water and groundwater outlined in the Pesticide Control Law.[2]

Groundwater monitoring data is focused in the central sand plains (Central Sands) area of the state. Similarly, surface water monitoring efforts are focused where agricultural chemicals have a relatively higher potential for resource impacts based on surface water-groundwater interactions. Therefore, monitoring stations have been established in the limestone bedrock (karst) regions in the southeastern corner of the state, in the Minnesota River basin, and in suburban-rural transitional watersheds. Other current monitoring efforts include analysis of samples collected from a set of tile drains on active farm fields in Nicollet County, two springs in southeast Minnesota, and analysis of pesticide concentrations in precipitation samples at a location in southeast Minnesota. Data for these efforts will be compiled separately and made available from the MDA on request.

This report contains water sampling results tables, summary tables, and graphical data displays. The contents of this report are used by MDA staff to fulfill statutory requirements for reporting on pesticide impacts to water resources and for developing a variety of associated response actions. The data is also used in the implementation of various MDA educational, voluntary and regulatory

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[1] Minn. Stat. Chapter 103H.
[2] Minn. Stat. Chapter 18B.

programs, and is made available to the MDA's multiple stakeholders for the purpose of characterizing pesticide impacts to state water resources.

Datasets used to produce this report, and historic groundwater and surface water data are available by contacting the MDA Monitoring and Assessment Unit and will be made available the MDA website at http://www.mda.state.mn.us/appd/ace/maace.htm

This report was produced by staff in the MDA Special Projects Unit and Monitoring and Assessment Unit. For questions or comments about the report's contents, contact Dan Stoddard, Manager, Agricultural Chemical Environmental Section. Inquiries can be made by phone at 651-297-8293 or by email at dan.stoddard@mda.state.mn.us

REPORTING METHODS AND ANALYTES

Reporting Methods

Methods employed by the MDA Monitoring and Assessment Unit for reporting results of chemical analyses received from the MDA Laboratory Services Division are designed to ensure that results of chemical analyses are reported in a manner conforming with program goals.

Environmental sample results reported from the MDA Laboratory Services Division as meeting qualitative requirements but not quantitated, i.e., “Present at less than the Method Reporting Limit (MRL),” are reported and entered into the database as “P” but, for statistical and general reporting purposes, will be assigned a numerical value of one-half the MRL. This is a reasonable approach to quantitating these “P” values because the analytes can be positively identified via qualitative procedures – indicating their actual presence, as opposed to being “non-detect.” Statistically, the actual value of these detections should be, on average, greater than one-half the MRL.

In cases where duplicate or replicate samples are collected with an environmental sample for purposes of quality control, the environmental sample is identified as the first sample collected sequentially. Only the environmental sample is reported in the dataset.

General analysis for reporting purposes is performed on environmental samples only. Analysis of quality control is reported separately as needed for data verification and qualification. Values reported to the database as non-detect are assigned a numerical value of zero for purposes of statistical analysis using non-parametric methods. If statistical analysis functions result in a value of zero, the result is reported as “non-detect.”

Metabolites or breakdown products (“degradates”) of a pesticide “parent” compound are summarized independently and, in some cases, in sum with the parent compound. Where degradates are identified in sum with the parent compound, the reference is to “parent plus parent degradates” (e.g., atrazine plus degradates).

Analytes

Water resource samples are analyzed for pesticides in the laboratory (where they are referred to as “analytes”). A pesticide may be included in a “target analyte” list for a given water resource sample based on the relative expectation of detecting the pesticide in the particular water sample. This expectation may depend on the mobility of the pesticide in soil or water, the general use of the pesticide in the watershed or on the landmass, or other programmatic reasons or concerns.

A target analyte list helps MDA Laboratory Services Division chemists focus limited resources on the calibration of machinery and sample preparation relative to the type of sample being analyzed. The target analyte list may not include many known pesticide products or degradates; however, laboratory chemists may detect additional pesticides that fall into the same chemical class, or analytical method as pesticides on the target analyte list. Therefore, “base-neutral” or “acid” pesticides that are not part of the target analyte list may be observed, quantified (if possible) and reported as non-target analyte detections, even though they may not be expected, or targeted for analysis.

In 2002, the MDA began analysis of groundwater monitoring samples for the primary (ESA) and secondary (OXA) degradates of acetochlor, alachlor, dimethenamid and metolachlor. This analysis began with the 2nd quarter of the calendar year.

Lists of target and non-target analytes specific to 2001 and 2002 monitoring efforts (the groundwater monitoring network, the surface water monitoring stations and the surface water statewide survey) are provided in their respective report sections.

For additional details regarding MDA sampling, analytical and reporting methods, contact the MDA Monitoring and Assessment Unit.

Trade Names for Pesticide Analytes

Pesticide analytes referenced in this report can be cross-referenced to sample trade names provided in Table 2.

Table 2 – Pesticides and their associated sample trade names for detected analytes and target analytes

Pesticide Analyte	Sample Trade Name(s)	Pesticide Type
Acetochlor and degradates	Surpass, Harness	Herbicide
Alachlor and degradates	Lasso	Herbicide
Atrazine and degradates	Atrazine, Aatrex	Herbicide
Bentazon	Basagran	Herbicide
Chlorothalonil	Bravo	Fungicide
Chlorpyrifos	Lorsban	Insecticide
Clomazone	Command	Herbicide
Clopyralid	Loncid	Herbicide
Cyanazine	Bladex	Herbicide
Diazinon	Diazinon	Insecticide
Dicamba	Banvel, Marksman	Herbicide
Dimethenamid and degradates	Frontier	Herbicide
Dichlorprop	Patron, Riverdale	Herbicide
Dimethoate	Cygon	Insecticide
EPTC	Eradicane	Herbicide
Fonofos	Dyfonate	Insecticide
Malathion	Malathion 50	Insecticide
Methyl Parathion	Penncap-M	Insecticide
MCPA	Weedone, Weedar	Herbicide
MCPP	Mecomec, Mecoprop	Herbicide
Metolachlor, s-metolachlor and degradates	Dual	Herbicide
Metribuzin and degradates	Lexone, Sencor	Herbicide
Pendimethalin	Prowl	Herbicide
Phorate	Thimet	Insecticide
Prometon	Pramitol, Gesafram	Herbicide
Propachlor	Ramrod	Herbicide
Terbufos	Counter	Insecticide
Trifluralin	Treflan	Herbicide
Triclopyr	Crossbow	Herbicide
2,4-D	Weedone, Weedar	Herbicide

GROUNDWATER MONITORING

Description of Groundwater Monitoring Network and Summary of Pesticide Detections

The area represented by the groundwater monitoring data in this report primarily includes the glacial outwash sand aquifers in the Central Sands of the state. Central Sands groundwater sampling locations (wells) are shown in Figure 1. Ten counties in the Central Sands monitoring network that currently have wells are Becker, Benton, Hubbard, Kandiyohi, Morrison, Otter Tail, Pope, Stearns, Todd and Wadena. Two additional counties – Sherburne and Wright – have agreements with the MDA to participate in the Central Sands network.

Table 3 lists target and non-target detected pesticide analytes and related analytical information for calendar year 2002. In 2002, the MDA began analysis of groundwater monitoring samples for the primary (ESA) and secondary (OXA) degradates of acetochlor, alachlor, dimethenamid and metolachlor. This analysis began with the 2nd quarter of the calendar year. Precipitation and precipitation departure from normal maps for 2001 and 2002 are provided for reference in Appendix A.

Figure 1 – MDA groundwater monitoring network locations for calendar year 2002

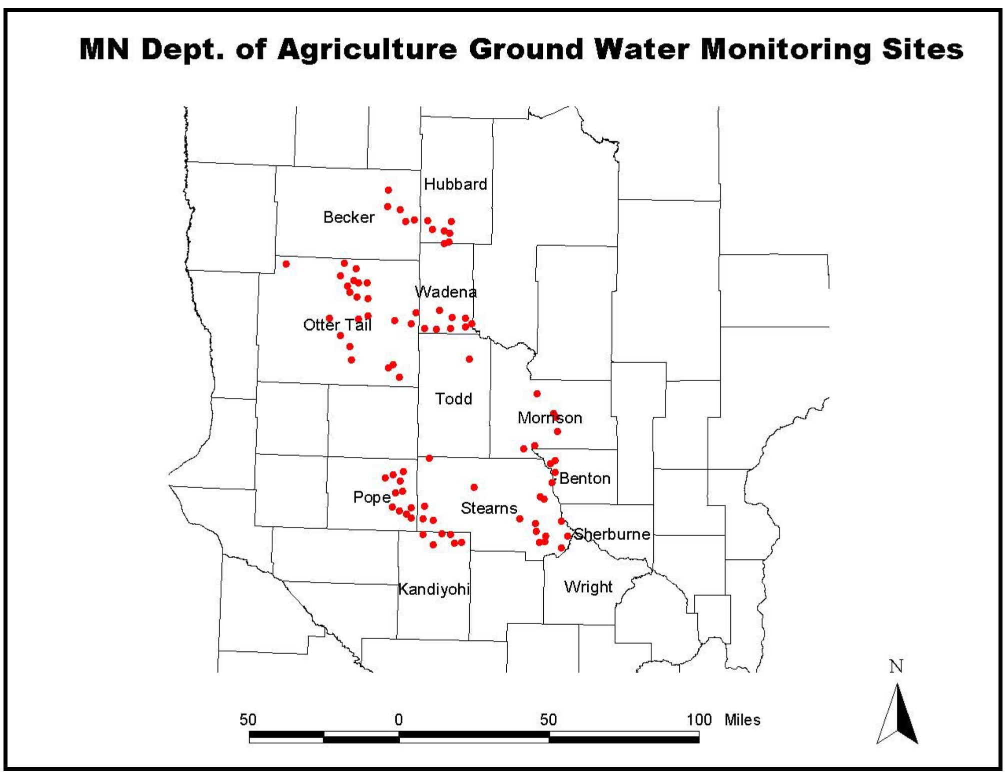

Table 3 – Summary of target and non-target detected pesticide analytes, associated methods and reporting limits for MDA groundwater monitoring network samples collected during calendar year 2002

Groundwater Monitoring Network Pesticide Analyte [a]	Detected in Groundwater	Analytical Method: B = Base Neutral D = Degradate	Method Reporting Limit (ug/L)
Acetochlor	X	B	0.05
Acetochlor ESA	X	D	0.07
Acetochlor OXA	X	D	0.07
Alachlor	X	B	0.05
Alachlor ESA	X	D	0.07
Alachlor OXA	X	D	0.07
Atrazine	X	B	0.05
Deethylatrazine	X	B	0.05
Deisopropylatrazine	X	B	0.20
Chlorothalonil (not a target analyte)		B	0.12
Clomazone[b]	X	B	in development
Cyanazine		B	0.20
Dimethenamid	X	B	0.05
Dimethenamid ESA	X	D	0.07
Dimethenamid OXA	X	D	0.07
Dimethoate (not a target analyte)	X	B	0.22
Metolachlor	X	B	0.07
Metolachlor ESA	X	D	0.07
Metolachlor OXA	X	D	0.07
Metribuzin	X	B	0.10
Metribuzin DADK	X	D	Estimated at 0.50
Metribuzin DK	X	D	Estimated at 0.50
Metribuzin DA	X	D	Estimated at 0.50
Prometon (not a target analyte)	X	B	in development

[a] In addition to the pesticide analytes detected in water resource samples collected during 2000 and 2001, the MDA Laboratory Services Division methods used in the routine analysis of monitoring program pesticide water samples may also detect and report the presence or possible presence of other pesticides in the analytical methods for base neutral and acid compounds. For a complete description of methods and associated detectable compounds, contact the MDA Monitoring and Assessment Unit.
[b] Clomazone detections are currently under investigation as part of a possible sample collection and equipment contamination problem and are not included in statistical analyses of detections in this report.

Results

Complete datasets used to construct groundwater results tables and figures in this report are available from the MDA Monitoring and Assessment Unit.

A summary of pesticide concentration data in the groundwater monitoring network since its inception in 2000 and through the third quarter of calendar year

2002 is provided in Tables 4 and 5. These tables also include information for pesticide degradates of acetochlor, alachlor, atrazine, dimethenamid, metolachlor and metribuzin. Not shown in these tables are the results for three pesticides not on the groundwater network target analyte list, and therefore not actually analyzed for in each collected sample (chlorothalonil was observed in 3 samples in 2000; dimethoate was observed in 1 sample in 2002; and prometon was observed in 1 sample in 2000 and 2001, and in 2 samples in 2002).

Groundwater sampling results have been summarized as plots of detections or as box plots for each quarter (2000 through 3rd-quarter 2002) for acetochlor, alachlor, atrazine, metolachlor and metribuzin (and their degradates). These plots are provided in Appendix D.

Although other pesticides were detected in the network, the frequency of their detection, the relatively low concentration of those detections and the distribution of the data within each quarter do not lend themselves to statistical analysis for percentage detection or box plot presentation; however, their detections are included in the total pesticide calculations used to develop Figure 5 in Appendix D.

Comparisons of pesticide concentrations in network samples to the Minnesota Department of Health (MDH) Health Risk Limits (HRLs) and Health Based Values (HBVs) for private well drinking water supplies are provided in Table 6 for samples collected since 2000. Also included is the comparison to U.S. Environmental Protection Agency (U.S. EPA) Maximum Contaminant Levels (MCLs) for public drinking water supplies (treated water). In making the comparisons, the network dataset for a pesticide or pesticide degradate (2000 through 3rd-quarter 2002) was compared to the available HRL and/or HBV.[3] When a pesticide parent compound has been assigned an HRL, and when no HRL or HBV exists for a degradate, the concentrations of the parent and degradate are added together, and it is assumed that a pesticide metabolite or degradation product has the same toxicological effect as its pesticide parent compound and that it is as potent as its pesticide parent compound.[4] If an HRL or HBV exists for a degradate, then concentrations of the degradate are compared separately to that value, and the degradate concentration is not added to that of the parent. For federally regulated public drinking water supplies, only the parent pesticide concentrations are compared to MCLs.

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[3] A pesticide can have both an HRL and an HBV, depending on the availability of toxicological data and associated toxic endpoints.

[4] MDH, February 15, 2002, "Memorandum: Evaluation of Human Health Risk From Mixtures of Pesticides and Their Metabolites or Degradation Products," from Larry Gust to Dan Stoddard.

Table 4 – Summary of pesticide and pesticide degradate concentrations in the MDA groundwater monitoring network, 2000 through 3rd-Quarter 2002

Pesticide	Detections			Concentration values of detections; all values in ug/L (nd = non detect)								
	2000 – 170 samples (4 quarters)	2001 – 188 samples (4 quarters)	2002 – 140 samples (3 quarters)[1]	Median (50th Percentile)			75th Percentile			Maximum		
				2000	2001	2002	2000	2001	2002	2000	2001	2002
Acetochlor	2	0	3	nd	nd	nd	nd	nd	nd	0.05	nd	0.025
Acetochlor ESA	degradate analysis not conducted		31	degradate analysis not conducted		nd	degradate analysis not conducted		0.14	degradate analysis not conducted		4.02
Acetochlor OXA			9			nd			nd			0.64
Acetochlor + degradates			33			nd			nd			4.66
Alachlor	1	2	2	nd	nd	nd	nd	nd	nd	0.72	0.21	0.54
Alachlor ESA	degradate analysis not conducted		46	degradate analysis not conducted		nd	degradate analysis not conducted		0.97	degradate analysis not conducted		14.4
Alachlor OXA			11			nd			nd			0.68
Alachlor + degradates			47			nd			0.25			14.4
Atrazine	74	89	54	nd	nd	nd	0.08	0.06	0.03	0.38	0.51	0.29
Deethylatrazine	111	127	83	0.08	0.09	0.05	0.17	0.18	0.15	1.11	1.28	0.67
Deisopropylatrazine	60	72	41	nd	nd	nd	0.10	0.10	0.10	3.40	1.91	1.55
Atrazine + Degradates	119	133	91	0.16	0.15	0.10	0.40	0.39	0.26	4.50	3.66	2.32
Dimethenamid	0	2	0	nd	nd	nd	nd	nd	nd	nd	0.18	nd
Dimethenamid ESA	degradate analysis not conducted		4	degradate analysis not conducted		nd	degradate analysis not conducted		nd	degradate analysis not conducted		1.68
Dimethenamid OXA			3			nd			nd			0.57
Dimethenamid + degradates			4			nd			nd			2.25
Metolachlor	47	31	49	nd	nd	nd	0.04	nd	0.04	31.20	31.50	1.12
Metolachlor ESA	degradate analysis not conducted		51	degradate analysis not conducted		0.07	degradate analysis not conducted		2.98	degradate analysis not conducted		17.7
Metolachlor OXA			35			nd			0.56			11.9
Metolachlor + degradates			68			nd			1.14			29.6
Metribuzin	24	12	11	nd	nd	nd	nd	nd	nd	2.34	0.62	1.33
Metribuzin DADK	38	47	39	nd	nd	nd	nd	0.05	0.83	38	4.88	7.98
Metribuzin DK	13	12	6	nd	nd	nd	nd	nd	nd	1.56	1.63	0.88
Metribuzin DA	14	7	11	nd	nd	nd	nd	nd	nd	1.18	0.59	0.82
Metribuzin + Degradates	45	48	39	nd	nd	nd	0.05	0.10	0.95	39.01	7.64	9.05

[1] Results for degradates of chloracetamide pesticides (acetochlor, alachlor, dimethenamid and metolachlor) are based on 95 samples collected during 2nd and 3rd quarter 2002.

Table 5 – Summary of pesticide and pesticide degradate detections in the MDA groundwater monitoring network, 2000 through 3rd-Quarter 2002

Pesticide	Percent Detections by Sample			Percent Detections by Site			Detections by County		
	2000 – 170 samples (4 quarters)	2001 – 188 samples (4 quarters)	2002 – 140 samples (3 quarters)[1]	2000 – 79 sites	2001 – 79 sites	2002 – 84 sites	2000 – 9 counties	2001 – 9 counties	2002 – 10 counties
Acetochlor	1%	0%	2%	3%	0%	4%	2 of 9	0 of 9	2
Acetochlor ESA	degradate analysis not conducted		33%	degradate analysis not conducted		34%	degradate analysis not conducted		6
Acetochlor OXA			9%			11%			4
Acetochlor + degradates			35%			35%			6
Alachlor	1%	1%	1%	1%	3%	1%	1 of 9	2 of 9	1 of 10
Alachlor ESA	degradate analysis not conducted		48%	degradate analysis not conducted		48%	degradate analysis not conducted		9 of 10
Alachlor OXA			12%			14%			7 of 10
Alachlor + degradates			49%			48%			9 of 10
Atrazine	44%	47%	39%	56%	62%	50%	8 of 9	8 of 9	10 of 10
Deethylatrazine	65%	68%	59%	76%	77%	69%	9 of 9	9 of 9	10 of 10
Deisopropylatrazine	35%	38%	29%	42%	44%	36%	5 of 9	5 of 9	7 of 10
Atrazine + Degradates	70%	71%	65%	80%	77%	74%	9 of 9	9 of 9	10 of 10
Dimethenamid	0%	1%	0%	0%	1%	0%	0 of 9	1 of 9	0 of 10
Dimethenamid ESA	degradate analysis not conducted		4%	degradate analysis not conducted		4%	degradate analysis not conducted		3 of 10
Dimethenamid OXA			3%			4%			3 of 10
Dimethenamid + degradates			4%			4%			3 of 10
Metolachlor	28%	16%	35%	41%	25%	43%	8 of 9	8 of 9	9 of 10
Metolachlor ESA	degradate analysis not conducted		54%	degradate analysis not conducted		49%	degradate analysis not conducted		10 of 10
Metolachlor OXA			37%			34%			9 of 10
Metolachlor + degradates			72%			69%			10 of 10
Metribuzin	14%	6%	8%	18%	10%	8%	5 of 9	4 of 9	5 of 10
Metribuzin DADK	22%	25%	28%	28%	34%	27%	7 of 9	7 of 9	8 of 10
Metribuzin DK	8%	6%	4%	11%	10%	5%	5 of 9	4 of 9	3 of 10
Metribuzin DA	8%	4%	8%	11%	6%	10%	5 of 9	3 of 9	4 of 10
Metribuzin + Degradates	26%	26%	28%	34%	34%	27%	8 of 9	7 of 9	8 of 10

[1] Results for degradates of chloracetamide pesticides (acetochlor, alachlor, dimethenamid and metolachlor) are based on 95 samples collected during 2nd and 3rd quarter 2002.

Table 6 – Comparison of pesticide and pesticide degradate concentrations to state and federal drinking water standards in the MDA groundwater monitoring network, 2000 through 3rd-Quarter 2002

Pesticide (number of samples collected for pesticide or degradate from 2000 through 3rd-quarter 2002)	**State Health Risk Limit (HRL)** for private well drinking water supplies and for public supplies when < MCL	**Number of HRL Exceedances**	**State Health Based Value (HBV)** an "interim" HRL; not promulgated in Minnesota Rules	**Number of HBV Exceedances**	**Federal Maximum Contaminant Level (MCL)** for federally-regulated public drinking water supplies	**Number of MCL Exceedances)**
Acetochlor (498)	no HRL	not applicable	10 ug/L	0	no MCL	not applicable
Acetochlor ESA (95)			use parent HBV	0		
Acetochlor OXA (95)			use parent HBV	0		
Acetochlor + degradates (95)			use parent HBV	0		
Alachlor (498)	4 ug/L	0	no HBV	not applicable	2 ug/L	0
Alachlor ESA (95)	no HRL (see HBV)	not applicable	100 ug/L	0	comparison of degradate concentrations to parent MCL not applicable	
Alachlor OXA (95)	use parent HRL	0	no HBV	not applicable		
Alachlor + OXA (95)	use parent HRL	0				
Atrazine (498)	20 ug/L	0	no HBV	not applicable	3 ug/L	0
Deethylatrazine (498)	use parent HRL	0			comparison of degradate concentrations to parent MCL not applicable	
Deisopropylatrazine (498)	use parent HRL	0				
Atrazine + Degradates (498)	use parent HRL	0				
Dimethenamid (498)	no HRL	not applicable	40 ug/L	0	no MCL	not applicable
Dimethenamid ESA (95)			use parent HRL	0		
Dimethenamid OXA (95)			use parent HRL	0		
Dimethenamid + degradates (95)			use parent HRL	0		
Metolachlor (498)	100 ug/L	0	no HBV	not applicable	no MCL	not applicable
Metolachlor ESA (95)	use parent HRL	0				
Metolachlor OXA (95)	use parent HRL	0				
Metolachlor + degradates (95)	use parent HRL	0				
Metribuzin (498)	200 ug/L	0	no HBV	not applicable	no MCL	not applicable
Metribuzin DADK (498)	use parent HRL	0				
Metribuzin DK (498)	use parent HRL	0				
Metribuzin DA (498)	use parent HRL	0				
Metribuzin + Degradates (498)	use parent HRL	0				

SURFACE WATER MONITORING

Description of Surface Water Monitoring Stations and Summary of Pesticide Detections

The MDA has developed a surface water monitoring system in which samples, collected from rivers and streams during storm events ("storm flow event samples") and during non-storm periods ("base flow samples") are used as a measure of pesticide impacts to water resources in select watersheds. Limited resources were used to focus surface water monitoring efforts in areas where agricultural chemicals have a relatively higher potential for resource impacts based on surface water-groundwater interactions.

Automated continuous storm event monitoring has been a strength of MDA's surface water monitoring program since its inception in 1990. The locations of automatic sampling equipment systems active during 2001 and 2002 are shown in Figures 2 and 3. A summary of MDA active surface water monitoring station names and characteristics is provided in Table 7. Although most storm events are monitored through automated equipment, grab samples are occasionally collected to characterize particular storm events at some monitoring stations.

Automated samplers are set to begin collecting samples after the streams or rivers respond to a rainfall-runoff event. This response by a stream or river is known as a storm hydrograph. Samples are collected throughout the storm hydrograph at predetermined intervals. These flow-weighted composite samples result in an estimate of the total load of pesticides in the water resource during the storm hydrograph and provide an event mean concentration. Grab samples (a single sample manually collected) are generally collected when the stream returns to base flow conditions, though they may also be collected during particular storm events.

Grab samples are also collected at least monthly during times of the year when streams do not respond to storm events. In some years during peak summer months, streams and rivers do not respond as significantly, or as often, to storm events because of high evapotranspiration or drought. Rivers and streams in Minnesota generally do not show a significant increase in water flow during the winter months of December, January and February.

For purposes of data summarization and reporting, MDA has developed protocols for integrating and assigning appropriate flow volumes for surface water composite and grab samples. The integration of chemical concentration with volume is necessary for the calculation of load and flow-weighted mean (or average) concentration.

The protocols also provide guidance on the calculation of four-day average concentrations and 30-day average concentrations of pesticides at each monitoring station. The MDA developed the protocols in consultation with MPCA staff and in consideration of MPCA guidance for assessing the quality of state waters.

Time Integration for Grab and Composite Samples: Because MDA surface water samples are collected utilizing different methods (grab and composite samples) and at varying time intervals as dictated by changing flow conditions, it is recognized that professional judgment plays a part in assigning volume to samples. MDA protocols provide guidance for interpreting the data and assigning the appropriate volume in a consistent fashion. Because MDA surface water samples are also utilized for comparison to water quality standards, criteria and advisory values, protocols have been developed for the calculation of four-day and 30-day average concentrations.

To the greatest degree possible, the following elements of MDA protocol are used to integrate time for surface water data analysis and reporting:

1. During all flow periods a base flow sample is assigned a time (flow period) equal to half that between it and the previous sample, plus half that between it and the next sample.

2. The assigned time for a base flow sample that is collected immediately before a storm flow event sample is extended to the beginning of the hydrograph event (marked by an increase in flow) or to the beginning of the storm flow event sample collection whichever is most appropriate.

3. The assigned time for a base flow sample collected between two storm flow event samples extends from the end of the storm flow sample collection time to the beginning of the next storm flow sample collection time. Therefore, the assigned time for the base flow sample should result in an appropriate representation of the flow period from which it was collected.

4. In some instances, storm flow event sample collection periods might be extended in order to better represent the event period, such as when a storm flow sample collection time ends half way down the descending leg of the hydrograph. In such cases, the time assigned to that storm flow sample might typically be extended to the end of that hydrograph. In rare instances where samples are not collected during a storm event hydrograph, concentrations are assigned from the nearest collection period, be it a base flow or storm flow sample, in order to adequately characterize that flow period.

Calculation of Flow-Weighted Mean Concentration: A properly collected equal flow increment storm flow event sample submitted to the laboratory will produce an analytical result that is essentially a flow-weighted mean concentration and is referred to as a sample event mean concentration. To calculate a flow-weighted mean concentration for a period of time that is longer than that represented by an individual storm event mean concentration (monthly or annual for instance) it is necessary to combine concentration and flow data from multiple samples. This is achieved by first calculating the individual mass of chemical that each sample period represents (sample concentration multiplied by flow period volume), then the masses for all of the respective sample periods are summed and divided by the total flow volume for the period of interest.

The equation used to calculate flow-weighted mean concentration for a compound is:

$$FWMC = \frac{(\Sigma\ C_i Q_i T_i)}{(\Sigma\ Q_i T_i)}$$

Where C_i is the concentration for the *i* th time period, Q_i is the flow during the time period, and T_i is the time characterized by that concentration.

Calculation of a Four-Day Average Concentration: For comparison with aquatic-toxicity standards developed using a four-day exposure assumption, it is sometimes necessary to calculate or estimate four-day average concentration values. This is accomplished by calculating a simple arithmetic mean utilizing the sample concentrations that occurred during the four-day period of interest. In some instances it is necessary to combine storm flow event sample concentrations with base flow sample concentrations to obtain a value. Under these circumstances the samples collected during the four-day period of interest are weighted equally in the calculation of the average. On larger river systems, storm flow samples will often last several days. As a result, four-day average concentrations can sometimes be equivalent to a single sample event mean concentration as defined above, provided the storm flow sample was collected over a period of four days or greater. Individual grab sample concentrations can also be utilized for comparison with standards or criteria provided no other samples were collected within the four-day period previous or subsequent to the collection of the sample.

Calculation of a 30-Day Average Concentration: For comparison with human health-based toxicity standards developed using a 30-day exposure assumption, it is sometimes necessary to calculate or estimate 30-day average concentration values. This is accomplished by calculating a simple arithmetic mean utilizing the sample concentrations that occurred during the 30-day period of interest (typically calculated on a calendar month basis). In some instances it is necessary to combine storm flow event sample concentrations with base flow sample concentrations to obtain a value. Under these circumstances the samples collected during the 30-day period (month) of interest are weighted equally in the calculation of the average.

The equation used to calculate both the four-day and 30-day average concentration for a compound is:

$$FDAC = \frac{1}{n} \sum_{i=1}^{n} x_i$$

Where n is the number of composite or grab samples collected during the four day period, and x_i is the concentration of the *i* th sample collected during the four-day period.

Monitoring data for sites monitored prior to this report can be found in previously published MDA Monitoring and Assessment Unit reports, and in the datasets used to prepare this report. Datasets and previously published reports are available from the MDA Monitoring and Assessment Unit.

Precipitation and precipitation departure from normal maps for 2001 and 2002 are provided for reference in Appendix A.

Table 8 lists target and non-target detected pesticide analytes and related analytical information for calendar year 2001 and partial calendar year 2002.

Figure 2 – Location of active MDA surface water monitoring stations for calendar year 2001 and 2002

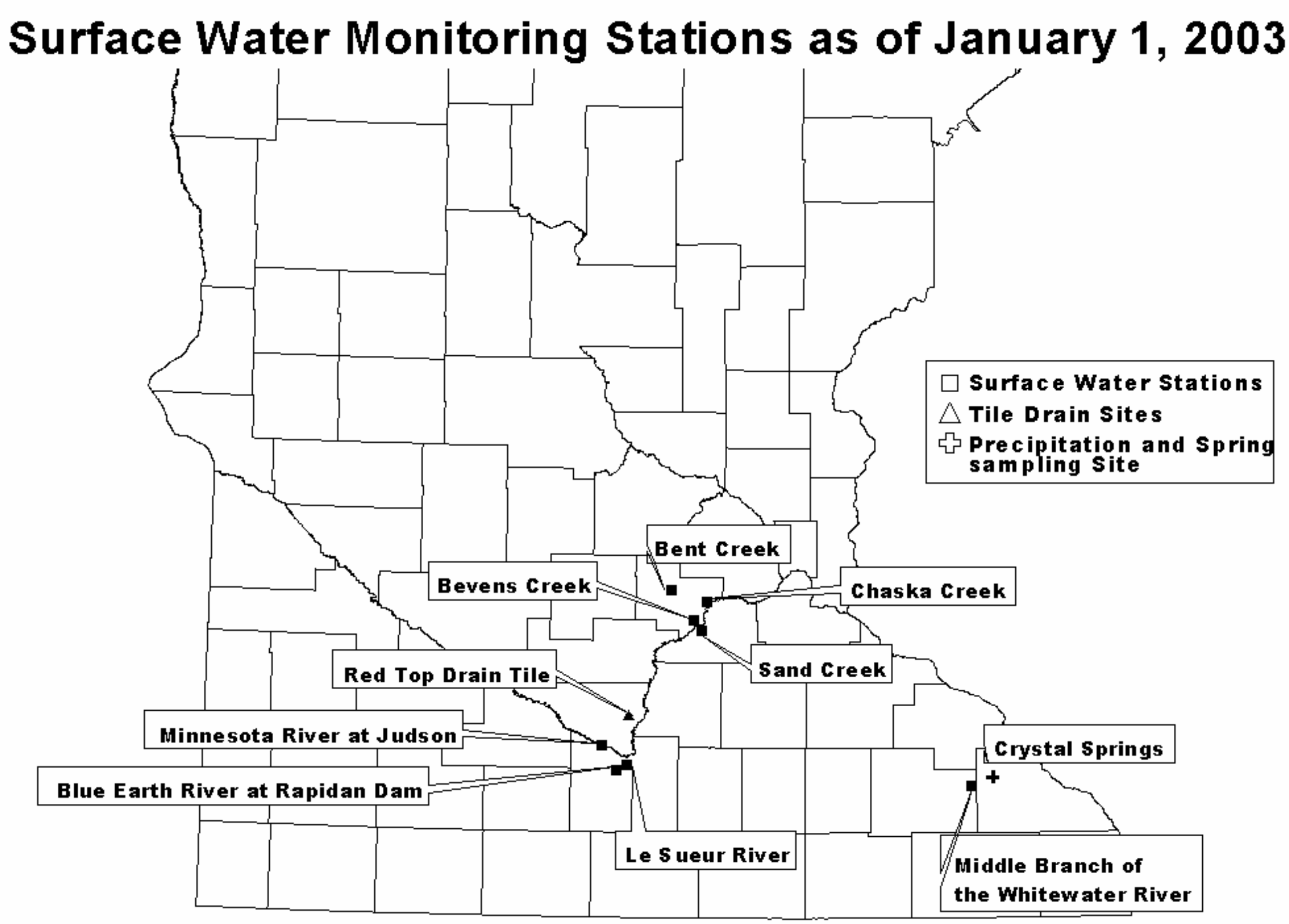


Figure 3 – Map of active MDA surface water monitoring stations and associated watersheds for calendar years 2001 and 2002

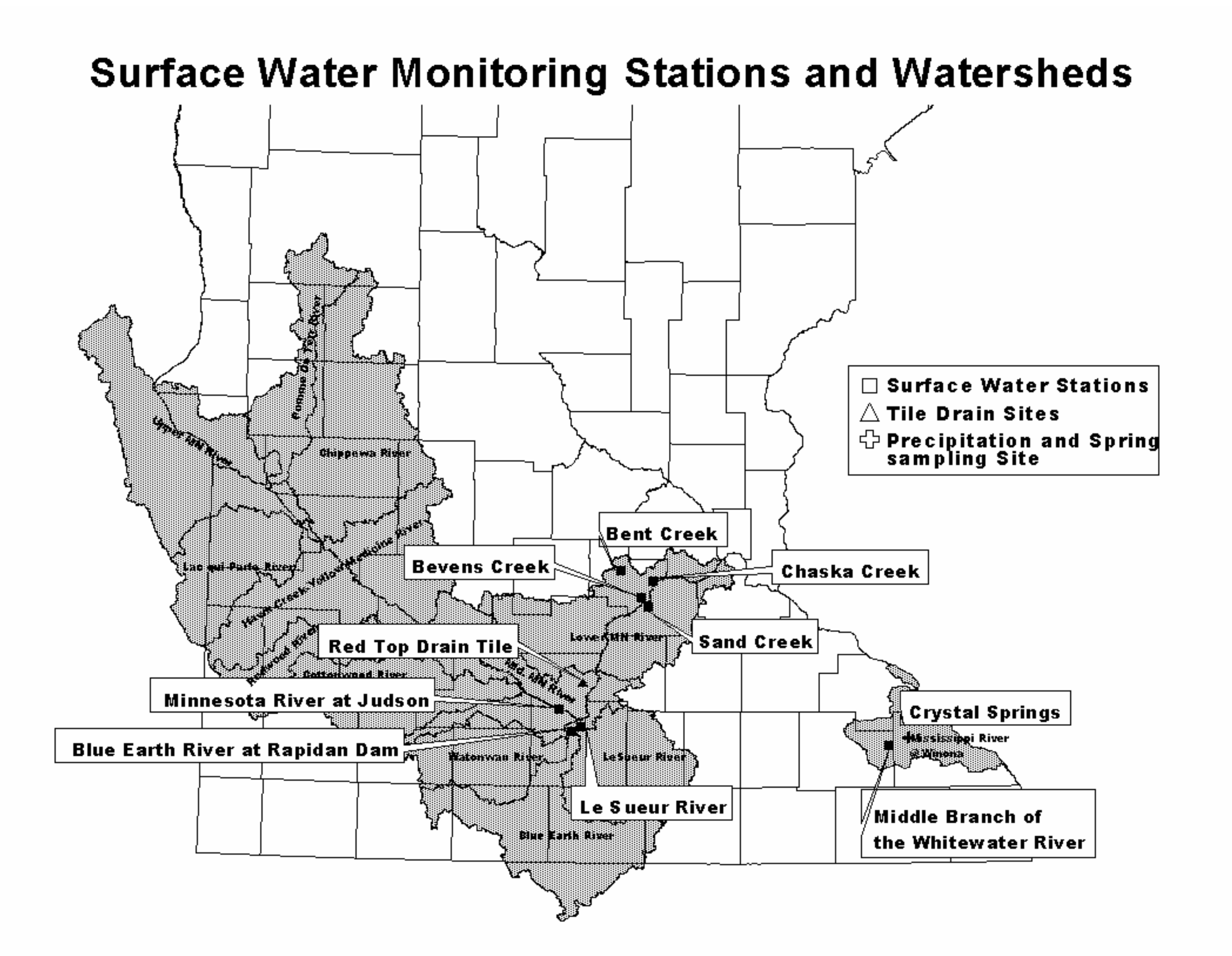


Table 7 – MDA surface water monitoring station names and characteristics for locations sampled in 2001 and 2002

Active Monitoring Stations	Location – Characteristics	State Water Classification	Associated Major River Basin	Approximate area (acres) of watershed effectively sampled by monitoring station	Sampling Period
Blue Earth River at Rapidan	Rural – agricultural; Minnesota River Basin	2B[a]	Minnesota	1,555,270	May 1999 – Present
Le Sueur River	Rural – agricultural; Minnesota River Basin	2B	Minnesota	710,400	May 1999 – Present
Minnesota River at Judson	Rural – agricultural; Minnesota River Basin	2B	Minnesota	7,168,000	May 1999 – Present
Whitewater, Middle Branch	Rural – agricultural; Southeast Minnesota	1B/2A/3B[b]	Lower Mississippi	16,096	March 1993 – Present
Bevens Creek	Rural – mixed agricultural & residential; Carver County	2B	Minnesota	83,776	April 1995 – Present
Sand Creek	Rural – mixed agricultural & residential; Scott County	2B	Minnesota	163,071	April 1995 – Present
Bent Creek	Metro-area suburban fringe; Carver County	2B	Minnesota	9,568	May 1998 – December 2002
Chaska Creek	Metro-area suburban fringe; Carver County	2B	Minnesota	9,000	August 1999 – December 2002

[a] For aquatic life (2B – sport and commercial; 2C – non-commercial; 2D – wetlands) & recreation 2B – all types; 2C,D – limited types). Not protected as a drinking water source.
[b] For aquatic life (cold) & all recreation. Protected as a drinking water source.

Table 8 – List of target and non-target detected pesticide analytes, detections, associated methods and reporting limits for MDA surface water monitoring station samples collected during calendar year 2001 and 2002

Surface Water Monitoring Station Pesticide Analyte [a]	Detected in at Least One Surface Water Monitoring Station Sample	Analytical Method: A = Acid B = Base Neutral	Method Reporting Limit (ug/L)
Acetochlor	X	B	0.05
Alachlor	X	B	0.05
Atrazine	X	B	0.05
Deethylatrazine	X	B	0.05
Deisopropylatrazine	X	B	0.20
Chlorothalonil		B	0.10
Chlorpyrifos		B	0.10
Clopyralid (not a target analyte)	X	A	0.20
Cyanazine	X	B	0.20
Diazinon	X	B	0.12
Dicamba	X	A	0.20
Dichlorprop		A	0.20
Dimethenamid	X	B	0.05
Dimethoate		B	0.22
EPTC		B	0.23
Fonofos		B	0.10
Malathion		B	0.09
Methyl Parathion		B	0.12
MCPA	X	A	0.20
MCPP	X	A	0.20
Metolachlor	X	B	0.07
Metribuzin	X	B	0.10
Pendimethalin	X	B	0.08
Phorate		B	0.12
Propachlor	X	B	0.10
Terbufos		B	0.19
Trifluralin		B	0.17
Triclopyr		A	0.20
2,4-D	X	A	0.20

[a] In addition to the pesticide analytes detected in water resource samples collected during 2000 and 2001, the MDA Laboratory Services Division methods used in the routine analysis of monitoring program pesticide water samples may also detect and report the presence or possible presence of other pesticides in the analytical methods for base neutral and acid compounds. For a complete description of methods and associated detectable compounds, contact the MDA Monitoring and Assessment Unit.

Results

Complete datasets used to construct surface water results tables and figures in this report are available from the MDA Monitoring and Assessment Unit.

A summary of surface water pesticide and pesticide degradate detections for calendar year 2001 and partial calendar year 2002 is provided in Tables 9 and 10, respectively.

Tables 11 and 12 show the highest four-day average concentration of select pesticides at each monitoring station in relation to the MPCA aquatic-toxicity chronic standard, criterion or advisory value for calendar year 2001 and partial calendar year 2002. If 10 % of the standard, criterion or advisory value for a given pesticide was exceeded when compared to the highest four-day average concentration, the pesticide was included in the table. MPCA standards, criteria and advisory values for toxicity to aquatic life are based on a four-day exposure assumption. A description of MPCA chronic standards, criteria and advisory values for surface waters of various classes can be found Appendix C in Table 19.

Tables 13 and 14 show the monthly mean concentrations and annual flow-weighted or arithmetic mean concentrations of select pesticides at the Whitewater River, Middle Branch monitoring station in relation to certain water quality or drinking water standards for calendar year 2001 and partial calendar year 2002. Surface water data collected from monitoring stations after July 2002 was not used in this report. The Whitewater River, Middle Branch is a Class 1B/2A/2C surface water protected as a source of drinking water, and Table 13 and 14 also show the 30-day (monthly) mean concentration of pesticides that exceed 10% of the MPCA human health-based chronic standard for drinking water and fish consumption, or the MDH drinking water HRLs or HBVs. A description of MDH HRLs and HBVs for drinking water can be found in Appendix B in Table 18.

Surface water sampling results are presented in Appendix E in graphical form for those monitoring stations where MPCA four-day toxicity-based or 30-day human health-based chronic standards, criteria or advisory values are exceeded by 10%. First, “flow hydrographs” of rivers or creeks are provided. The flow hydrographs present information on the volume of water passing a monitoring station from 2001 through July 2002. The hydrographs reflect periods of drought, stormwater inputs, and base flow conditions, during which groundwater is discharging to the river or stream. The volume of water passing by a station is used to help determine the rate of composite sampling during non-base flow water level events, and is also used to calculate the loading rate of pollutants from the river, stream or watershed to the next.

Following each hydrograph, chemistry graphs (“chemographs”) are provided to show the concentration of pesticides in storm flow event and base flow samples from 2001 through July 2002 for that monitoring station.

Comparisons made in Tables 11, 12, 13 & 14, and in Appendix E, are considered preliminary and were prepared in consultation with MPCA staff. These preliminary comparisons may be useful in assessing general surface water impacts but cannot be used to establish a violation of water quality standards, criteria or advisory values.

Before concluding that a water body is impaired for a given use, the MPCA may use numeric and narrative standards, and may employ professional judgments during data review. Generally, toxicity-based aquatic life standards must be exceeded twice in a three-year period using values averaged over a four-day period, and human health-based standards must be exceeded twice in a three-year period using values averaged over a 30-day period.

The MPCA, in its review of monitoring data, determines if a violation has occurred, or if a water body is impaired in accordance with the “Guidance Manual For Assessing the Quality Minnesota Surface Waters For the Determination of Impairment. 305(b) Report and 303(d) List, MPCA, January 2003.

See Appendix C for further information regarding applicable water quality criteria.

Table 9 – Summary of pesticide and pesticide degradate detections in MDA surface water monitoring station samples collected in calendar year 2001

Pesticide (Base-Neutrals)	Of 159 Storm Event Samples, Number Positive (and %) for Pesticide	Of 118 Base Flow Samples, Number Positive (and %) for Pesticide	Of 277 Total Samples, Number Positive (and %) for Pesticide	Detected In							
				Blue Earth R.	Le Sueur R.	Minn. R. at Judson	Whitewater R.	Bevens Creek	Sand Creek	Bent Creek	Chaska Creek
Acetochlor	104 (65%)	23 (20%)	127 (46%)	X	X	X	X	X	X	X	X
Alachlor	14 (9%)	0 (0%)	14 (5%)	X	X	X					
Atrazine	115 (72%)	67 (57%)	182 (66%)	X	X	X	X	X	X	X	X
Deethylatrazine	119 (75%)	69 (58%)	188 (68%)	X	X	X	X	X	X	X	X
Deisopropylatrazine	32 (20%)	21 (18%)	53 (19%)	X	X	X	X	X	X	X	X
Cyanazine	5 (3%)	2 (1%)	7 (3%)								X
Diazinon	2 (1%)	0 (0%)	2 (1%)							X	
Dimethenamid	60 (38%)	9 (8%)	69 (25%)	X	X	X	X		X		X
Metolachlor	113 (71%)	46 (39%)	159 (57%)	X	X	X	X	X	X		X
Metribuzin	3 (2%)	0 (0%)	3 (1%)	X							
Propachlor	1 (0.6%)	0 (0%)	1 (0.4%)	X							

Pesticide (Acids)	Of 81 Storm Event Samples, Number Positive (and %) for Pesticide	Of 75 Base Flow Samples, Number Positive (and %) for Pesticide	Of 156 Total Samples, Number Positive (and %) for Pesticide	Detected In							
				Blue Earth R.	Le Sueur R.	Minn. R. at Judson	Whitewater R.	Bevens Creek	Sand Creek	Bent Creek	Chaska Creek
Clopyralid	2 (2%)	0 (1%)	2 (1%)	X							X
Dicamba	29 (36%)	7 (9%)	36 (23%)	X	X	X	X			X	X
2,4-D	37 (46%)	16 (21%)	53 (34%)	X	X	X	X		X	X	X
MCPA	3 (4%)	2 (2%)	5 (3%)							X	
MCPP	15 (19%)	12 (12%)	27 (17%)							X	X

Table 10 – Summary of pesticide and pesticide degradate detections in MDA surface water samples collected in calendar year 2002 (through July)

Pesticide (Base-Neutrals)	Of 80 Storm Event Samples, Number Positive (and %) for Pesticide[a]	Of 47 Base Flow Samples, Number Positive (and %) for Pesticide[a]	Of 127 Total Samples, Number Positive (and %) for Pesticide[a]	Detected In							
				Blue Earth R.	Le Sueur R.	Minn. R. at Judson	Whitewater R.	Bevens Creek	Sand Creek	Bent Creek	Chaska Creek
Acetochlor	63 (79%)	17 (36%)	80 (63%)	X	X	X	X	X	X	X	X
Alachlor	11 (14%)	0 (0%)	11 (9%)		X	X			X		
Atrazine	68 (85%)	27 (57%)	95 (75%)	X	X	X	X	X	X	X	X
Deethylatrazine	62 (77%)	24 (51%)	86 (68%)	X	X	X	X	X	X	X	X
Deisopropylatrazine	26 (33%)	7 (15%)	33 (26%)	X	X	X	X	X	X		X
Cyanazine	3 (4%)	1 (2%)	4 (3%)			X		X			X
Dimethenamid	47 (59%)	8 (17%)	55 (43%)	X	X	X	X		X		X
Metolachlor	65 (81%)	20 (43%)	85 (67%)	X	X	X	X	X	X	X	X
Metribuzin	1 (1%)	0 (0%)	1 (1%)								X
Pendimethalin	3 (4%)	0 (0%)	3 (2%)							X	X

Pesticide (Acids)	Of 54 Storm Event Samples, Number Positive (and %) for Pesticide[a]	Of 35 Base Flow Samples, Number Positive (and %) for Pesticide[a]	Of 89 Total Samples, Number Positive (and %) for Pesticide[a]	Detected In							
				Blue Earth R.	Le Sueur R.	Minn. R. at Judson	Whitewater R.	Bevens Creek	Sand Creek	Bent Creek	Chaska Creek
Clopyralid	16 (30%)	3 (9%)	19 (21%)	X	X					X	X
Dicamba	48 (89%)	12 (34%)	60 (67%)	X	X	X	X	X	X	X	X
2,4-D	46 (85%)	10 (29%)	56 (63%)	X	X	X	X	X	X	X	X
MCPA	2 (4%)	0 (0%)	2 (2%)							X	X
MCPP	4 (7%)	3 (9%)	7 (8%)							X	X

[a] Because these results are based on a partial calendar year, caution should be used in comparing results to those of 2001.

Table 11 – Table of Surface Water *Toxicity-Based Aquatic Life* Comparisons (MPCA 4-day exposure standards, criteria, advisory values) for Calendar Year 2001

Table of CY2001 Surface Water *Toxicity-Based Aquatic Life* Comparisons (MPCA)
Show "Highest 4-day Average Concentration" for the given compounds during 2001.

Monitoring Station	MPCA 7050 Rule Water Class (see footnote)	Compound	Lowest Applicable Chronic Aquatic Life Standard, Criterion or Value (ug/L)	Modifying Information (see footnote)	Highest 4-Day Average Concentration (ug/L)	Percentage of Standard, Criterion or Value	Maximum Concentration Observed in 4-Day Event Shown (ug/L)	Number of Days that 10% of Standard, Criterion or Value is Exceeded	Number of Days that 50% of Standard, Criterion or Value is Exceeded	Number of Samples in Highest 4-Day Average
Bevens Creek	2B	Acetochlor	1.40	adv. value	2.08	149%	3.10	29	5	2
		Atrazine	10.00	standard	0.99	10%	1.33	2	0	2
Blue Earth @ Rapidan	2B	Acetochlor	1.40	adv. value	4.32	309%	6.50	62	23	2
		Atrazine	10.00	standard	1.77	18%	2.20	12	0	2
		Metolachlor	10.00	adv. value	2.38	24%	2.52	18	0	2
Chaska Creek	2B	Acetochlor	1.40	adv. value	0.23	16%	0.26	11	0	2
Le Sueur River	2B	Acetochlor	1.40	adv. value	6.75	482%	9.00	73	21	2
		Atrazine	10.00	standard	3.35	34%	3.70	12	0	2
		Metolachlor	10.00	adv. value	0.95	10%	1.05	6	0	2
Minnesota @ Judson	2B	Acetochlor	1.40	adv. value	0.37	26%	0.42	24	0	2
		Metolachlor	10.00	adv. value	2.56	26%	3.12	22	0	3
Sand Creek	2B	Acetochlor	1.40	adv. value	0.84	60%	1.44	26	2	2
Whitewater, Middle Branch	1B/2A/2C	Acetochlor	0.63	adv. value	2.95	468%	7.80	17	10	5
		Atrazine	10.00	standard	6.35	64%	17.40	9	7	5

Footnotes:
1. Waters not listed in MN Rules Chapter 7050 are classified as 2B, 3B, 4A, 4B, 5, and 6 waters; a classification of 2B in this table indicates an unlisted water body and comparisons are made for lowest applicable standard, criterion or advisory value. Waters with other specific classifications may be regulated according to specific Minnesota Pollution Control Agency (MPCA) guidance. Comparisons are preliminary and were made in consultation with the MPCA. Appearance of a water body in this table does not imply that a violation of water quality standards has occurred, and does not imply impairment for a given use.
2. "Advisory value" numbers have been provided by the MPCA, are not promulgated standards, and are based on toxicity to aquatic life only.
3. "Standard" numbers have been promulgated in MN Rule Chapter 7050.

Table 12 – Table of Surface Water *Toxicity-Based Aquatic Life* Comparisons (MPCA 4-day exposure standards, criteria, advisory values) for Partial Calendar Year 2002

Monitoring Station	MPCA 7050 Rule Water Class (see footnote)	Compound	Lowest Applicable Chronic Aquatic Life Standard, Criterion or Value (ug/L)	Modifying Information (see footnote)	Highest 4-Day Average Concentration (ug/L)	Percentage of Standard, Criterion or Value	Maximum Concentration Observed in 4-Day Event Shown (ug/L)	Number of Days that 10% of Standard, Criterion or Value is Exceeded	Number of Days that 50% of Standard, Criterion or Value is Exceeded	Number of Samples in Highest 4-Day Average
Bevens Creek	2B	Acetochlor	1.40	adv. value	1.69	121%	1.69	41	22	1
		Atrazine	10.00	standard	6.85	69%	9.10	28	9	2
Blue Earth @ Rapidan	2B	Acetochlor	1.40	adv. value	1.50	107%	1.50	63	17	1
		Atrazine	10.00	standard	2.82	28%	2.87	17	0	2
Chaska Creek	2B	Acetochlor	1.40	adv. value	0.17	12%	0.17	4.6	0	1
		Atrazine	10.00	standard	33.20	332%	33.2	4.6	5	1
Le Sueur River	2B	Acetochlor	1.40	adv. value	7.10	507%	7.10	47	16	1
		Atrazine	10.00	standard	2.97	30%	2.97	34	0	1
Minnesota @ Judson	2B	Acetochlor	1.40	adv. value	0.80	57%	1.09	41	3	2
		Atrazine	10.00	standard	2.24	22%	2.24	7	0	1
Sand Creek	2B	Acetochlor	1.40	adv. value	0.44	31%	0.72	17	3	2
		Atrazine	10.00	standard	7.05	71%	8.00	11	6	2
Whitewater, Middle Branch	1B/2A/3B	Acetochlor	0.63	adv. value	7.10	1127%	7.50	38	15	2
		Atrazine	10.00	standard	15.35	154%	29.40	29	2	2
		Metolachlor	10.00	adv. value	2.98	30%	3.84	19	0	2

Footnotes:

1. Waters not listed in MN Rules Chapter 7050 are classified as 2B, 3B, 4A, 4B, 5, and 6 waters; a classification of 2B in this table indicates an unlisted water body and comparisons are made for lowest applicable standard, criterion or advisory value. Waters with other specific classifications may be regulated according to specific Minnesota Pollution Control Agency (MPCA) guidance. Comparisons are preliminary and were made in consultation with the MPCA. Appearance of a water body in this table does not imply that a violation of water quality standards has occurred, and does not imply impairment for a given use.
2. "Advisory value" numbers have been provided by the MPCA, are not promulgated standards, and are based on toxicity to aquatic life only.
3. "Standard" numbers have been promulgated in MN Rule Chapter 7050.

Table 13 – Table of Surface Water *Human Health-Based Aquatic Life* (MPCA 30-day exposure standards) and *Health Risk Limit* or *Health Based Value* (MDH) Comparisons for Calendar Year 2001

Monitoring Station	MPCA 7050 Rule Water Class (see footnote)	Compound	Lowest Applicable Standard ug/L	Modifying Information (see footnote)	Monthly Mean Concentration												Annual Average Flow-Weighted Mean
					Jan-01	Feb-01	Mar-01	Apr-01	May-01	Jun-01	Jul-01	Aug-01	Sep-01	Oct-01	Nov-01	Dec-01	
Whitewater, Middle Branch	1B/2A/2C	**Acetochlor -arithmetic**	10.0	MDH HBV	0.00	0.00	0.00	0.00	0.11	1.87	0.00	0.00	0.00	0.00	0.00	0.00	**0.160**
		Atrazine -flow weighted	3.4	MPCA standard	0.16	0.17	0.19	0.11	0.15	3.21	0.19	0.09	0.14	0.15	0.14	0.06	**0.500**
		Atrazine -arithmetic	3.4	MPCA standard	0.16	0.18	0.18	0.10	0.16	4.43	0.19	0.13	0.14	0.15	0.14	0.06	**not applicable**
		Atrazine + degradates -arithmetic	20.0	MDH HRL	0.57	0.47	0.43	0.35	0.48	3.68	0.37	0.63	0.41	0.47	0.38	0.18	**0.800**

Footnotes:
1. Waters with specific classifications may be regulated according to specific Minnesota Pollution Control Agency (MPCA) guidance. Comparisons are preliminary and were made in consultation with the MPCA. Appearance of a water body in this table does not imply that a violation of water quality standards has occurred, and does not imply impairment for a given use.
2. "MDH HBV" numbers have been provided by MDH, are not promulgated standards, and are designed to evaluate drinking water risks.
3. "MPCA Standard" numbers are promulgated standards that apply to 30-day human exposure.
4. "MDH HRL" numbers are promulgated standards and are designed to evaluate drinking water risks.

Table 14 – Table of Surface Water *Human Health-Based Aquatic Life* (MPCA 30-day exposure standards) and *Health Risk Limit* or *Health Based Value* (MDH) Comparisons for Partial Calendar Year 2002

Monitoring Station	MPCA 7050 Rule Water Class (see footnote)	Compound	Lowest Applicable Standard ug/L	Modifying Information (see footnote)	Monthly Mean Concentration (see footnote)												Annual Average Flow-Weighted Mean
					Jan-02	Feb-02	Mar-02	Apr-02	May-02	Jun-02	Jul-02	Aug-02	Sep-02	Oct-02	Nov-02	Dec-02	
Whitewater, Middle Branch	1B/2A/2C	**Acetochlor -arithmetic**	10.0	MDH HBV	0.00	0.00	0.00	0.00	4.74	1.61	0.00	U	U	U	U	U	**not applicable**
		Atrazine -flow weighted	3.4	MPCA standard	U	U	U	U	U	U	U	U	U	U	U	U	**not applicable**
		Atrazine -arithmetic	3.4	MPCA standard	0.00	0.00	0.05	0.14	1.61	8.01	0.15	U	U	U	U	U	**not applicable**
		Atrazine + degradates -arithmetic	20.0	MDH HRL	0.00	0.11	0.10	0.40	2.98	8.67	0.42	U	U	U	U	U	**not applicable**

Footnotes:
1. Waters with specific classifications may be regulated according to specific Minnesota Pollution Control Agency (MPCA) guidance. Comparisons are preliminary and were made in consultation with the MPCA. Appearance of a water body in this table does not imply that a violation of water quality standards has occurred, and does not imply impairment for a given use.
2. "MDH HBV" numbers have been provided by MDH, are not promulgated standards, and are designed to evaluate drinking water risks.
3. "MPCA Standard" numbers are promulgated standards that apply to 30-day human exposure.
4. "MDH HRL" numbers are promulgated standards and are designed to evaluate drinking water risks.
5. U = Data unavailable for report.

SURFACE WATER STATEWIDE SURVEY

Description of Surface Water Statewide Survey and Summary of Pesticide Detections

In May and June of 2002 the Monitoring and Assessment Program conducted a survey to evaluate pesticide detection patterns in watersheds beyond the existing monitoring system watershed boundaries. The scope of the statewide survey was similar to one conducted by MDA in the early 1990s with the cooperation of the MPCA. The original survey – conducted from 1991 through 1993 – consisted of grab samples collected from 50 long-term surface water sampling sites located in major river basins from agricultural regions of the state. The statewide survey conducted in May and June of 2002 re-sampled many of the locations sampled in the original survey but differed in that it targeted anticipated peak pesticide detection periods (storm events and associated flow) during the month of May and June. The original survey consisted of random monthly samples. The goal of this effort was to evaluate the presence of commonly used pesticides in the rivers and streams of the agricultural areas of the state. The data collected from this effort might be used to support decisions made regarding the extrapolation of pesticide water quality data from MDA's intensively monitored watersheds to other areas of the state, and it might also be beneficial in determining that pesticide best management practices (BMPs), once developed, are applicable to specific geographic areas.

The specific objectives of the Statewide Survey were to:

1) Collect pesticide data from watersheds that currently are not represented in the existing MDA monitoring network;
2) Determine whether pesticide occurrence, detection and general magnitude patterns identified from existing site data is similar in other watersheds during peak detection periods;
3) Identify other potential pesticide detection patterns that may need further evaluation and;
4) Sample watersheds that were part of the previous MDA statewide survey for a general indication of long-term trends.

Samples were collected from May 28 to June 24, 2002, at the 25 locations shown on Figure 4 and listed in Table 15. Due to restrictions in laboratory and personal resources, only limited pesticide sampling was possible. The sampling effort targeted anticipated storm flow events during the months of May and June, 2002. Analysis was generally limited to the base neutral pesticide list used for MDA surface water monitoring station network samples, although analysis was also completed for a few acid herbicide samples. Additionally, some non-target analytes were reported by the laboratory as "present" if they were encountered in the routine processing of samples using particular laboratory methods. All analysis was conducted by the MDA laboratory in St. Paul.

Table 16 lists target and non-target detected pesticide analytes and related analytical information for the May – June, 2002 survey.

Figure 4 – Map of MDA surface water statewide survey sampling sites, and associated rivers and watersheds, May – June, 2002

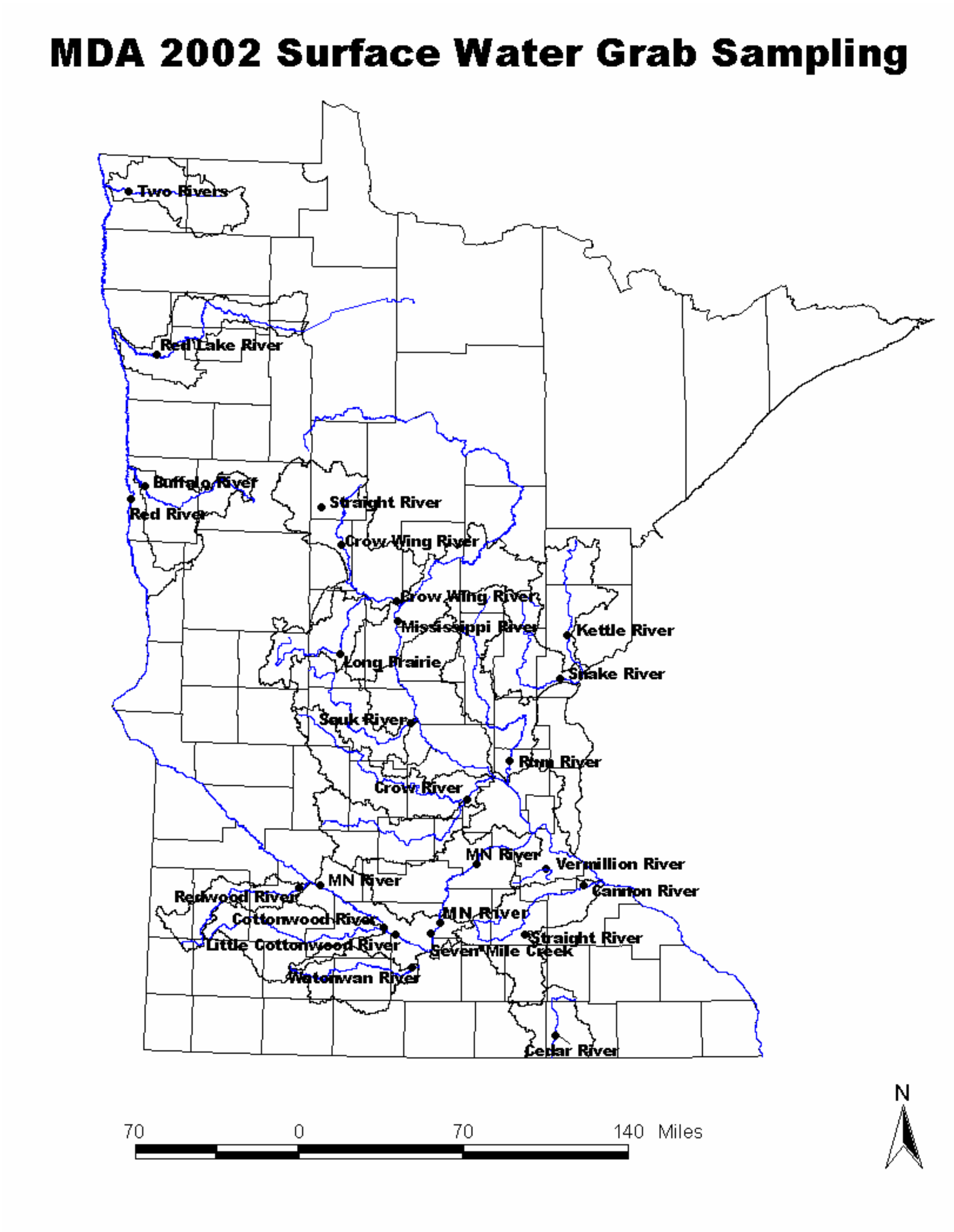


Table 15 – List of locations sampled in MDA surface water statewide survey, May-June 2002

Surface Water Statewide Survey Sampling Site – Water Body	Associated Major River Basin	Sampling Point (see footnotes)	County
Buffalo River - Dilworth	Red	Bridge on Co Rd 11	Clay
Cannon River - Red Wing	Mississippi	Bridge on Co Hwy 7 W of Red Wing	Goodhue
Cedar River - Austin	Cedar	Bridge on CSAH 28 (29th Ave NW)	Mower
Cottonwood River	Minnesota	Bridge on Hwy 15 S of New Ulm	Brown
Crow River	Mississippi	Bridge on Hwy 55 near/in Rockford	Wright
Crow Wing River - Nimrod	Mississippi	Bridge on Co Hwy 12 in Nimrod	Wadena
Crow Wing River - Pillager	Mississippi	Bridge (main) on Co Rd. 1 in Pillager	Cass
Kettle River	St. Croix	Hwy 123 in Sandstone	Pine
Little Cottonwood River	Minnesota	Bridge on State Hwy 68	Blue Earth
Long Prairie	Mississippi	MNDOT bridge on Hwy 71 in Long Prairie	Todd
Minnesota River - Jordan	Minnesota	Bridge on Co Hwy 45 (Quaker Ave) N of Jordan	Scott
Minnesota River - Morton	Minnesota	Bridge on Hwy 71 in Morton	Renville
Minnesota River - St. Peter	Minnesota	Bridge on Hwy 99 in St. Peter	Le Sueur
Mississippi River - Little Falls	Mississippi	Bridge on Hwy 10 in Little Falls 7 miles S of Camp Ripley	Morrison
Red River	Red	Bridge on Hwy 10 in Moorehead	Clay
Redwood River - Redwood Falls	Minnesota	Bridge on Co Hwy 7	Redwood
Rum River	Mississippi	Bridge on Hwy 7, 3 miles S of Oak Grove	Anoka
Sauk River	Mississippi	Bridge on Hwy 15 in St. Cloud	Stearns
Seven Mile Creek # 3	Minnesota	Bridge on Hwy 169 S of St. Peter	Nicollet
Snake River	Mississippi	Bridge on main road in Pine City	Pine
Straight River - Faribault	Mississippi	227th St E (Twp Rd 45) SE of Faribault	Rice
Straight River - Park Rapids	Mississippi	MNDOT bridge on Hwy 71 S of Park Rapids	Hubbard
Two Rivers - Hallock	Red	Bridge on Hwy 175 Hallock	Kittson
Vermillion River - Farmington	Mississippi	Bridge on Co Rd 79 (Blaine Ave E) E of Farmington	Dakota
Watonwan River - Garden City	Minnesota	Bridge on Co Hwy 13	Blue Earth

Footnotes:
1. CSAH = County State Aid Highway
2. Co = County; Twp = Township
3. Hwy = Highway; Rd = Road; Ave = Avenue; St = Street
4. MNDOT = Minnesota Department of Transportation

Table 16 – List of target pesticide analytes, detections, associated methods and reporting limits for MDA surface water statewide survey samples, May – June, 2002

Surface Water Statewide Survey Target Pesticide Analyte	Detected in at Least One Surface Water Statewide Survey Sample	Analytical Method: A = Acid B = Base Neutral	Method Reporting Limit (ug/L)
Acetochlor	X	B	0.05
Alachlor	X	B	0.05
Atrazine	X	B	0.05
Deethylatrazine	X	B	0.05
Deisopropylatrazine	X	B	0.20
Bentazon (not a target analyte)	X	A	0.20
Chlorothalonil		B	0.12
Chlorpyrifos		B	0.10
Clopyralid (not a target analyte)	X	A	0.20
Cyanazine	X	B	0.20
Diazinon	X	B	0.12
Dicamba	X	A	0.20
Dichlorprop		A	0.20
Dimethenamid	X	B	0.05
Dimethoate		B	0.22
EPTC		B	0.23
Fonofos		B	0.10
Malathion		B	0.09
Methyl Parathion		B	0.12
Metolachlor	X	B	0.07
Metribuzin	X	B	0.10
Metribuzin DADK (not a target analyte)	X	B	Estimated at 0.50
MCPA		A	0.20
MCPP		A	0.20
Pendimethalin	X	B	0.08
Propachlor (not a target analyte)	X	B	0.10
Phorate		B	0.12
Terbufos		B	0.19
Triclopyr		A	0.20
Trifluralin	X	B	0.17
2,4-D	X	A	0.20

Results

Complete datasets used to construct surface water statewide survey results tables and figures in this report are available from the MDA Monitoring and Assessment Unit.

As discussed above, anticipated storm flow events in the rivers were targeted for sampling. Most samples were collected using a weighted sampler lowered from a bridge deck. However, the unpredictable nature of collecting samples during storm events from different locations around the state proved difficult. Many of the samples were collected during storm flow periods but some were not. For practical purposes, storm flow was distinguished from base flow periods by a doubling of flow over the lowest flow during the month of June.

A summary of the May – June, 2002 surface water statewide survey pesticide detections and concentrations relative to MPCA chronic standards, criteria and advisory values for surface waters of various classes is provided in Table 17.

Comparisons made in Table 17, and in Appendix E, are considered preliminary. These preliminary comparisons may be useful in assessing general surface water impacts but cannot be used to establish a violation of water quality standards, criteria or advisory values.

Before concluding that a water body is impaired for a given use, the MPCA may use numeric and narrative standards, and may employ professional judgments during data review. Generally, toxicity-based aquatic life standards must be exceeded twice in a three-year period using values averaged over a four-day period.

The MPCA, in its review of monitoring data, determines if a violation has occurred, or if a water body is impaired in accordance with the “Guidance Manual For Assessing the Quality Minnesota Surface Waters For the Determination of Impairment. 305(b) Report and 303(d) List, MPCA, January 2003.

See Appendix C for further information regarding applicable water quality criteria.

Table 17 – Summary of pesticide and pesticide degradate detections in MDA surface water statewide survey samples collected in calendar year 2002

Pesticide (Base-Neutrals)	Of 26 Grab Samples, Number Positive (and %) for Pesticide	Maximum Value Detected	Median Value of Samples	Comparison to Standards: Based on Maximum Value (not a 4-day average)[a]	
				# Samples > MPCA Class 2B Standard, Criterion or Advisory Value	# Samples > 10% of MPCA Class 2B Standard, Criterion or Advisory Value
Acetochlor	22 (85%)	4.20	0.18	2	16
Alachlor	3 (12%)	0.09	non detect	0	0
Atrazine	26 (100%)	5.80	0.67	0	9
Deethylatrazine	23 (88%)	0.37	0.14	not applicable	not applicable
Deisopropylatrazine	10 (38%)	0.25	non detect	not applicable	not applicable
Cyanazine	1 (4%)	1.47	non detect	0	1
Diazinon	1 (4%)	0.06	non detect	not applicable	not applicable
Dimethenamid	15 (58%)	0.60	0.05	not applicable	not applicable
Metolachlor	18 (69%)	2.10	0.10	0	2
Metribuzin	5 (19%)	0.55	non detect	not applicable	not applicable
Metribuzin DADK	1 (4%)	0.67	non detect	not applicable	not applicable
Pendimethalin	2 (8%)	0.14	non detect	not applicable	not applicable
Propachlor	1 (4%)	0.50	non detect	not applicable	not applicable
Trifluralin	1 (4%)	0.09	non detect	not applicable	not applicable

Pesticide (Acids)	Of 5 Grab Samples, Number Positive (and %) for Pesticide	Maximum Value Detected	Median Value of Samples	Comparison to Standards: Based on Maximum Value (not a 4-day average)[a]	
				# Samples > MPCA Class 2B Standard, Criterion or Advisory Value	# Samples > 10% of MPCA Class 2B Standard, Criterion or Advisory Value
Clopyralid	4 (80%)	0.29	non detect	not applicable	not applicable
2,4-D	4 (80%)	0.64	0.36	0	0
Bentazon	1 (20%)	< 0.20	non detect	not applicable	not applicable
Dicamba	5 (100%)	1.17	0.29	0	0

[a] Appearance of a water body in this table does not imply that a violation of water quality standards has occurred, and does not imply impairment for a given use.

A table of individual sample results for each site is provided in Appendix F. Also provided in Appendix F are hydrographs for each river corresponding to the period of time associated with sample collection, along with a plot of the sampling date and associated pesticide detections. Hydrographs were developed from available USGS provisional daily average flow hydrographs for the sampling period.

In general, samples collected during storm flow events had a greater frequency and magnitude of detection of pesticides than those collected during base flow periods, illustrating an important difference associated with assessing pesticide impacts to water bodies using storm event versus base flow sampling results.

Because of the variability in sample collection times with respect to a given storm event hydrograph, it is difficult to draw many conclusions from the analysis. By comparing results from samples collected only during storm flow events with samples collected from more intensively monitored sites – such as the MDA Le Sueur River monitoring station near Mankato – it appears that the magnitude of detection is generally similar and that the number of detected compounds is also quite similar. A possible exception includes the detection of metribuzin in some of the samples.

Some general conclusions might be drawn from the survey:

- The magnitude of detected pesticide concentrations in grab samples collected during anticipated storm flow events is generally similar to or less than the magnitude of pesticide concentrations detected at more intensively monitored sites; and

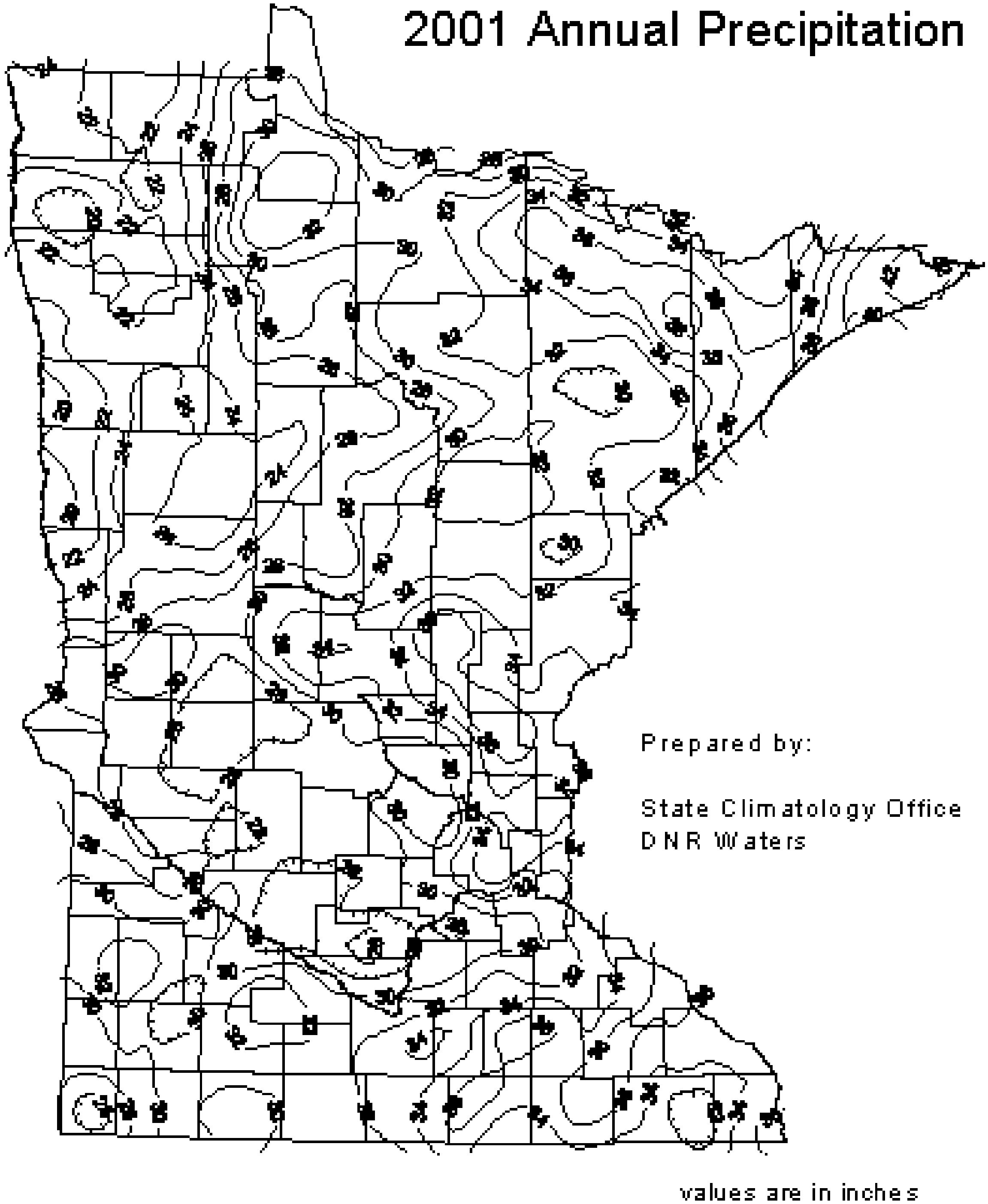
- The base neutral compounds detected most frequently are the same compounds detected at more intensively monitored sites.

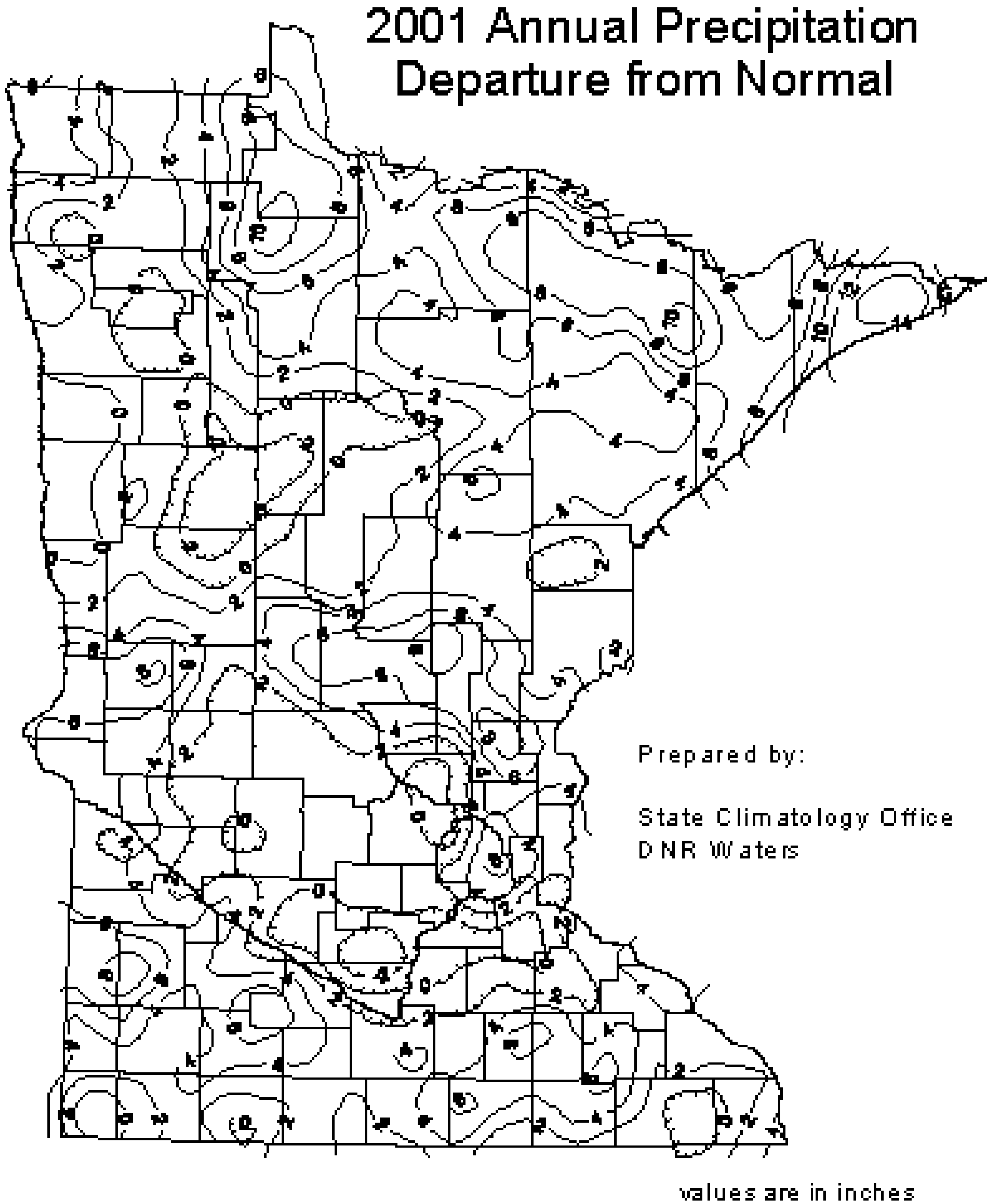
Metribuzin was detected in five samples, though it is not frequently detected in any of the MDA sites that are more intensively monitored.

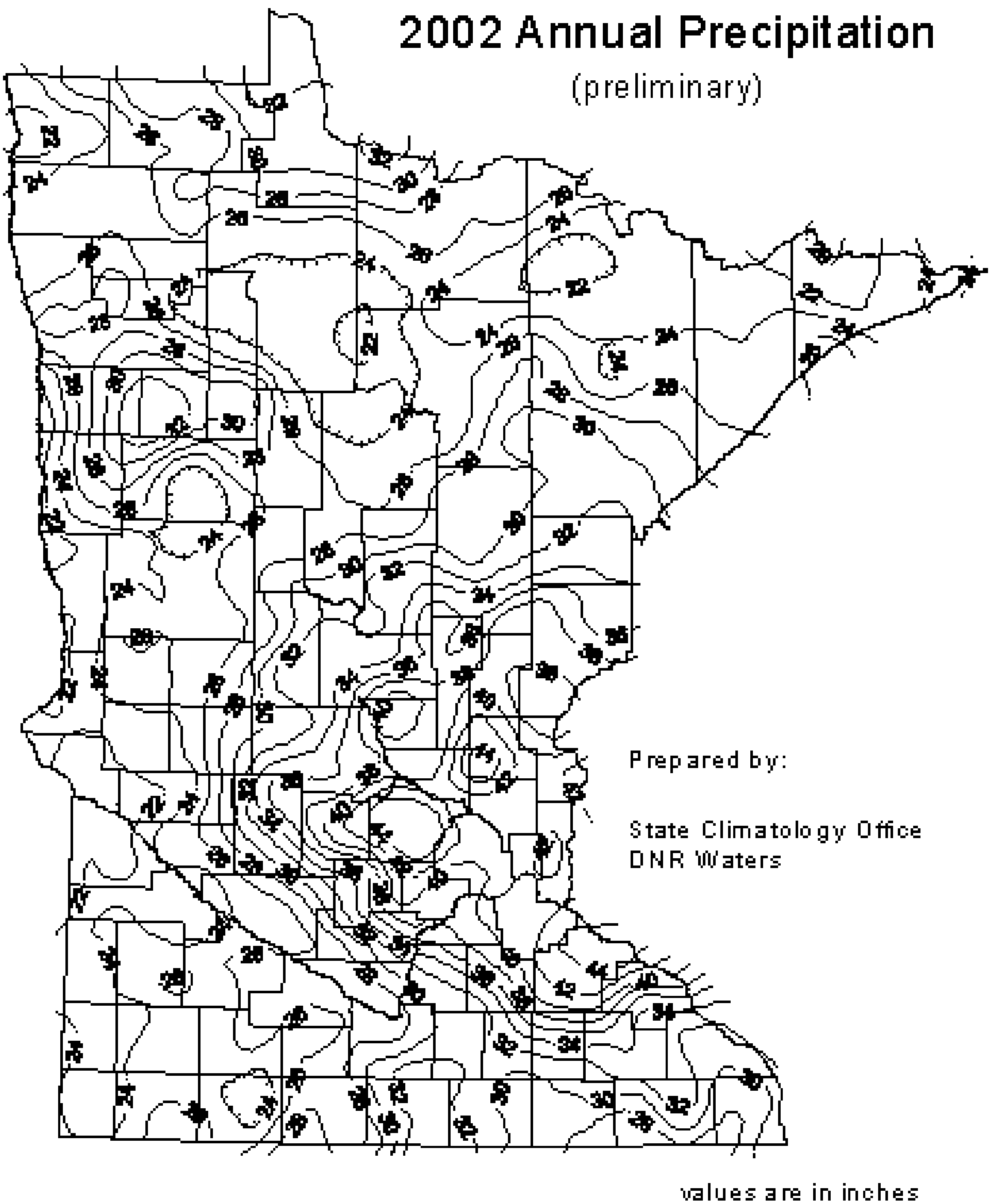
APPENDICES
MDA
PESTICIDE MONITORING
IN
WATER RESOURCES:

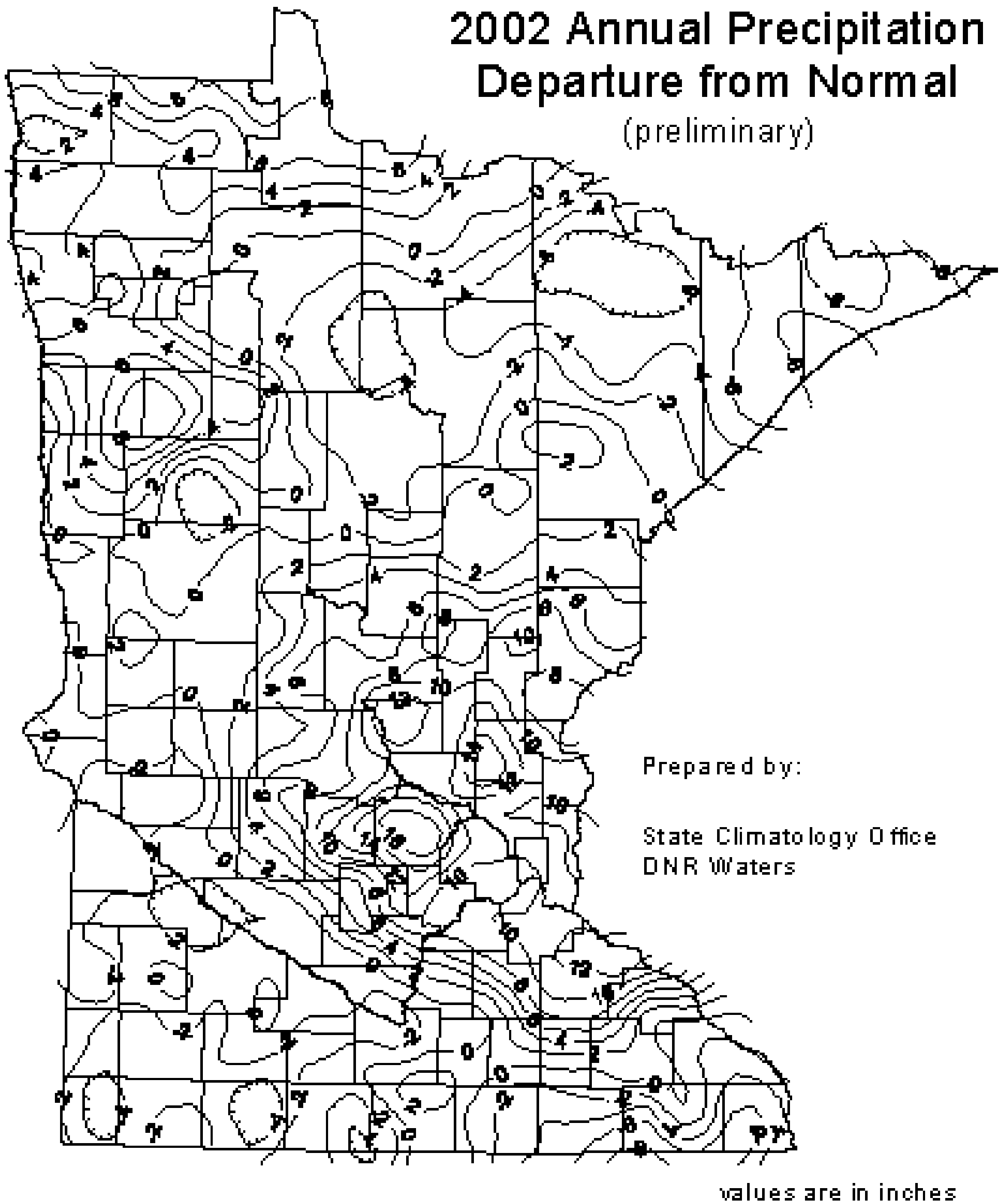
PRELIMINARY 2003 DATA REPORT

APPENDIX A – Precipitation and Precipitation Departure from Normal Maps for 2001 and 2002
(Maps provided by the Minnesota Department of Natural Resources)




2001 Annual Precipitation
Departure from Normal
Prepared by:
State Climatology Office
DNR Waters
values are in inches


2002 Annual Precipitation
(preliminary)
Prepared by:
State Climatology Office
DNR Waters
values are in inches


2002 Annual Precipitation
Departure from Normal
(preliminary)
Prepared by:
State Climatology Office
DNR Waters
values are in inches

APPENDIX B – MDH Health Risk Limits and Health Based Values for Select Pesticides in Groundwater Used as a Source of Drinking Water

For purposes of the Ground Water Protection Act, a pollutant is defined as a "chemical or substance for which a health risk limit has been adopted." Minn. Stat. 103H.005 subd. 11.

The Minnesota Department of Health (MDH) develops, through a rule-making process, Health Risk Limits (HRLs) for pollutants detected in groundwater, and are used to evaluate contaminated wells and provide advice to consumers and well owners about he suitability of their water supply for consumption and other uses. If a pollutant is detected between rule-making events and it does not have an HRL, the MDH will issue, with sufficient toxicological data, an interim Health Based Value (HBV) unless the MDH Commissioner determines the need for emergency HRL development. The U.S. EPA has established a set of Maximum Contaminant Levels (MCLs) used to protect federally-regulated public drinking water sources (usually treated, or "finished" water).

When the MDA detects pollutants in water resource samples for which an HRL has not been developed, a request is made to the MDH for HRL or HBV development.

A summary of human health-based drinking water standards, values or limits and the toxicological endpoints used by state and federal agencies in risk evaluation for select registered and commonly used pesticides is provided in Table 18 on the next page.

Table 18 – Summary of drinking water standards, values or limits associated with detected analytes and target analytes (numbers provided by Minnesota Department of Health)

Analyte	MDH Standards & Values			Federal (U.S. EPA) MCL[c] / MCLG[d] (ug/L)
	HRL[a] (ug/L)	HBV[b] (ug/L)	Toxicological Endpoint	
Acetochlor		10	hematological, liver	
Alachlor	4		cancer	2 / 0
Alachlor ESA		100	hematology, clin. chem.	
Atrazine	20		cardiovascular system	3 / 3
Bentazon		200	hematological	
Chlorothalonil	30	100	30=cancer/100=kidney	
Chlorpyrifos		20	acetylcholinesterase inhibition	
Cyanazine		0.4	cancer	
Dicamba	200		developmental effects	
Dimethenamid		40	liver effects	
Dimethoate		1	brain ChE inhibition	
2,4-D	70		hematologic system, kidney, liver	70 / 70
EPTC	200		cardiovascular system, nervous system	
Fonofos		10	acetocholinesterase inhibition	
Malathion		100	decreased acetocholinesterase activity	
MCPA	3		kidney, liver	
MCPP		7	kidney	
Methyl Parathion		2	RBC, plasma ChE inhibition, reduced hemoglobin, brain	
Metolachlor	100		developmental effects	
Metribuzin	200		kidney, liver	
Pendimethalin		90	liver	
Phorate		1	nervous system	
Prometon	100		---	
Propachlor	90		---	
Terbufos		0.2	nervous system	
Triclopyr		300	kidney	
Trifluralin		5	hematological, liver	

[a] Health Risk Limit (promulgated in Minnesota Rules) for private well drinking water supplies. HRLs are used to evaluate contaminated wells and provide advice to consumers and well owners about the suitability of their water supply for consumption and other sues. In instances where no federal drinking water standard exists for the contaminant in public water supplies, HRLs are used as criteria to evaluate options for reducing the community's exposure to the contaminant.

[b] Health Based Value (an "interim" HRL; not promulgated in Minnesota Rules).

[c] Maximum Contaminant Level – For federally-regulated public drinking water supplies, the highest level of a contaminant that is allowed in drinking water. MCLs are set as close to MCLGs as feasible using the best available treatment technology.

[d] Maximum Contaminant Level Goal – For federally-regulated public drinking water supplies, the maximum level of a contaminant in drinking water below which there is no known or expected risk to health. MCLGs allow for a margin of safety and are non-enforceable public health goals.

APPENDIX C – MPCA Chronic Standards, Criteria or Advisory Values for Select Pesticides in Surface Water of Various Classes

The Minnesota Pollution Control Agency develops, through a rule-making process, toxicity-based (for aquatic life) or human health-based chronic standards for pollutants detected in surface water. The toxicity-based standard (protective for aquatic life exposure) is based on an exposure duration of four days. The human health-based standard (protective for drinking water plus fish consumption) is based on an exposure duration of 30 days. If a pollutant is detected between rule-making events and it does not have an chronic standard, the MPCA will issue, with sufficient toxicological data, an unenforceable interim chronic criterion. In the absence of complete toxicological data, an unenforceable advisory value will be developed. The MPCA should be contacted for specific information related to the development of these values. When the MDA detects pollutants in water resource samples for which a chronic standard has not been developed, a request is made to the MPCA for standards development. A summary of applicable toxicity-based and human health-based chronic standards, criteria or advisory values used by the MPCA in risk evaluation for pesticides detected in surface water is provided in Table 19.

Table 19 – Summary of standards, criteria or advisory values associated with detected analytes and target analytes (numbers provided by Minnesota Pollution Control Agency)

Analyte	Surface Water Values (ug/L) (h) = human health-based value[a] (t) = toxicity-based value[b]				Standard[g]	Criterion[h]	Advisory Value[i]
	Class 2A[c]	Class 2Bd[d]	Class 2B,C,D[e]	FAV[f]			
Acetochlor	0.63 (t)	1.4 (t)	1.4 (t)	35 (t)			✓
Alachlor	3.8 (h); 59 (t)	4.2 (h); 59 (t)	59 (t)	1600 (t)	✓		
Atrazine	3.4 (h); 10 (t)	3.4 (h); 10 (t)	10 (t)	645 (t)	✓		
Chlorpyrifos	0.041 (t)	0.041 (t)	0.041 (t)	0.17 (t)	✓		
Cyanazine	4.5 (t)	4.5 (t)	4.5 (t)	250 (t)		✓	
Dicamba	85 (t)	85 (t)	85 (t)	4667 (t)			✓
2,4-D	97 (t)	97 (t)	97 (t)	2095 (t)			✓
MCPA	18 (t)	18 (t)	18 (t)	1000 (t)			✓
Metolachlor	10 (t)	10 (t)	10 (t)	not available			✓

[a] Value is human health-based and is protective for an exposure duration of 30 days.
[b] Value is toxicity-based for aquatic organisms and is protective for an exposure duration of 4 days.
[c] For aquatic life (cold) & all recreation. Protected as drinking water sources.
[d] For aquatic life (cool/warm) & all recreation. Protected as drinking water sources.
[e] For aquatic life (2B – sport and commercial; 2C – non-commercial; 2D – wetlands) & recreation (2B – all types; 2C,D – limited types). Not protected as drinking water sources.
[f] Final Acute Value for or Aquatic Life & Recreation, values are the same for all classes of surface waters. One-half the FAV is the Maximum Standard. See Definitions, page xi.
[g] Standard appears in Minn. Rule Chap. 7050.
[h] Criterion provided by MPCA; process for determining standard complete, but not yet promulgated.
[i] Value provided by MPCA; based on incomplete information, to be used as guideline.

APPENDIX D – Groundwater Detection Plots and Box Plots

A FEW WORDS ABOUT THE "BOX PLOT"

The box plot, or box and whisker plot, is a concise means of presenting information about a sampled population. The bounds and brackets of the box plot's parameters can be set to describe significant characteristics within the population and the plot also provides a graphic depiction of the distribution of the population. A fairly standard approach in plotting a "box plot" is to depict a portion of the population around the central tendency value (the mean or median) by the use of a box and adding whiskers above and below the box to depict important information outside the box itself. In all of the box plots presented here:

- the bottom whisker begins with the value for the 10th percentile of the population,
- the bottom of the box begins with the 25th percentile of the population,
- the median is described by a point (the 50th percentile of the population),
- the top of the box ends with the 75th percentile of the population, and the top of the whisker ends with the 90th percentile of the population,
- outliers (points outside the 10th and 90th percentile) are plotted as points,
- the median and maximum values are labeled directly.

Since groundwater samples for pesticide compounds contain data where the pesticide was "not detected", populations are "truncated" at the non-detection level. The box plots depicting this situation are truncated to match the information provided in the data. A label noting the percentage of the population data that was reported as "non-detect" is provided. An example is shown below:

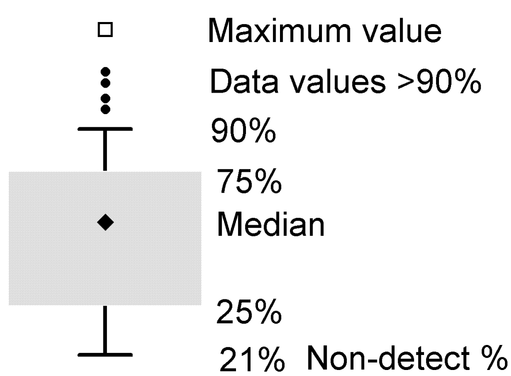


Figure 5 – Box Plot summary of pesticide and pesticide degradate concentrations in the Central Sands groundwater monitoring network

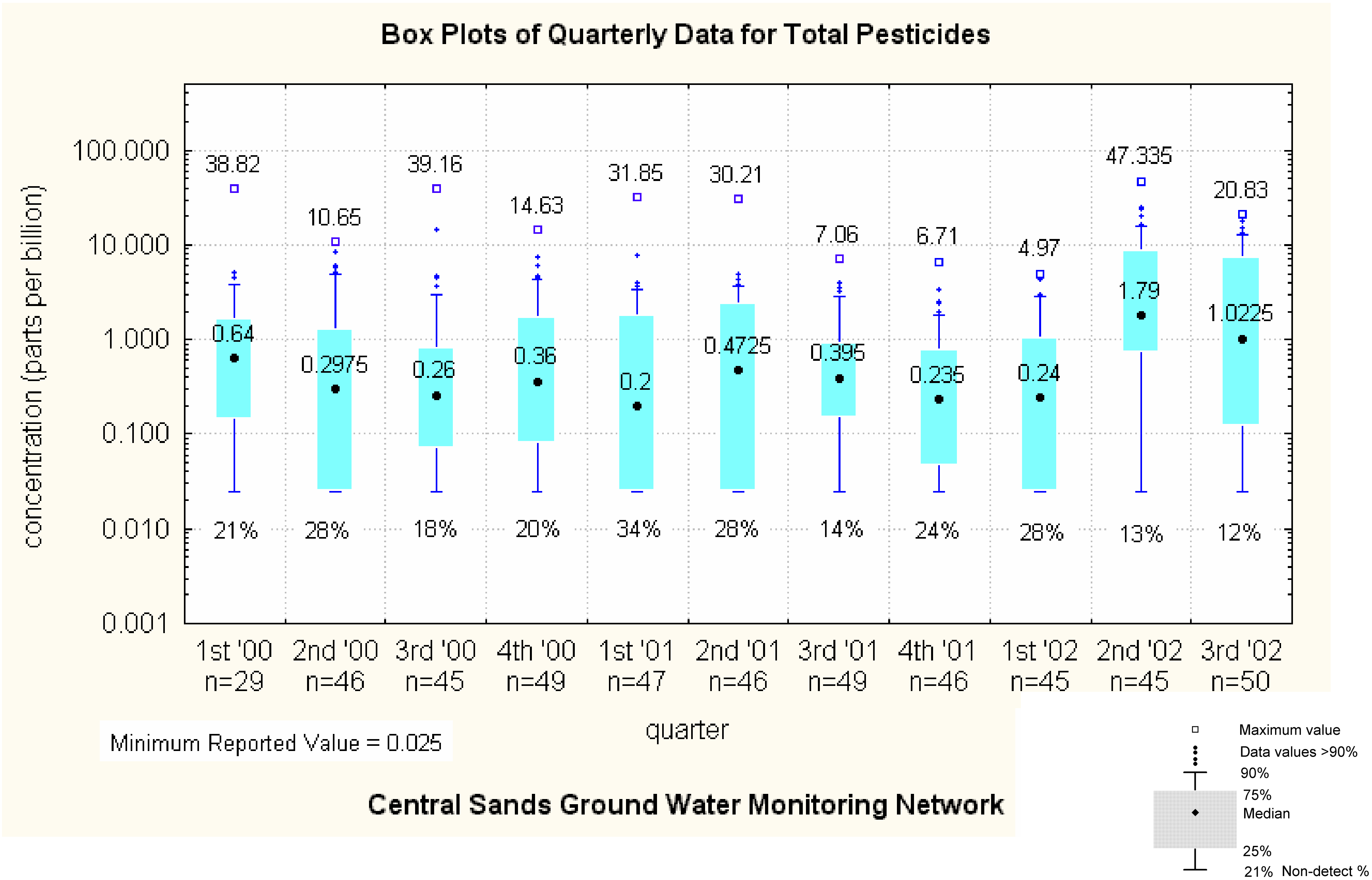


Figure 6 – Box Plots of acetochlor ESA detections and concentrations in Central Sands groundwater by quarter

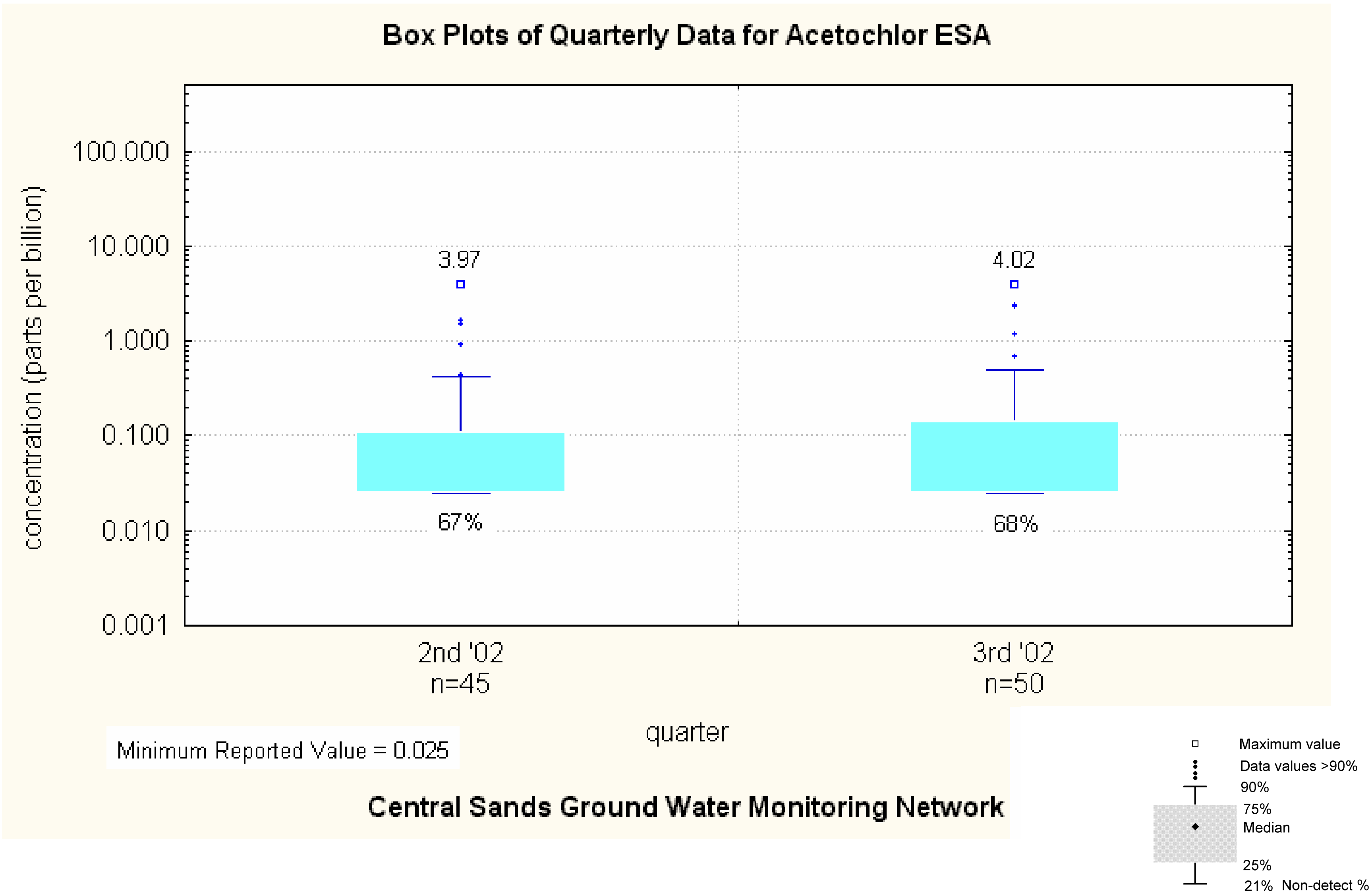


Figure 7 – Box Plots of acetochlor OXA detections and concentrations in Central Sands groundwater by quarter

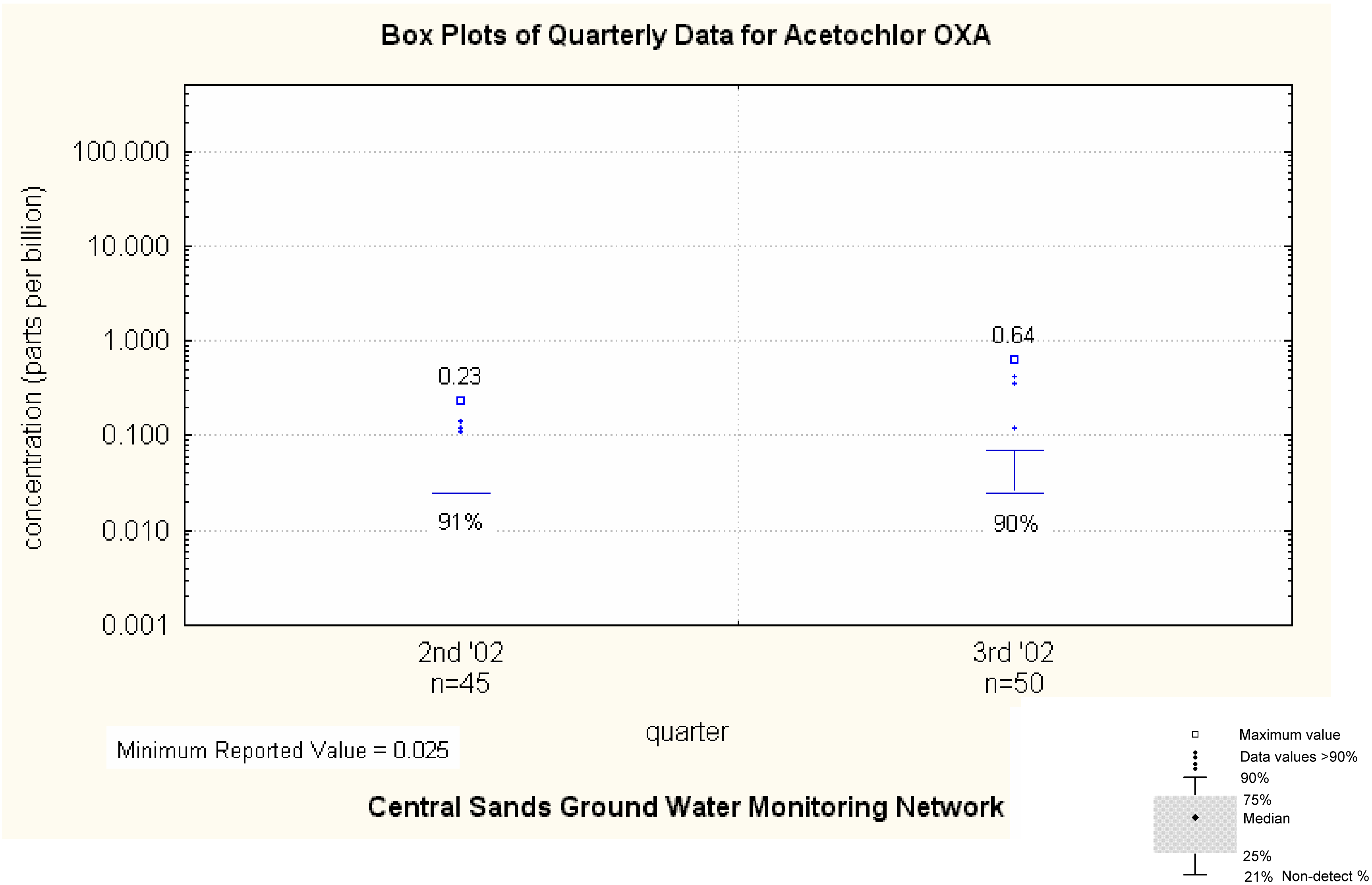


Figure 8 – Box Plots of acetochlor plus acetochlor degradates detections and concentrations in Central Sands groundwater by quarter

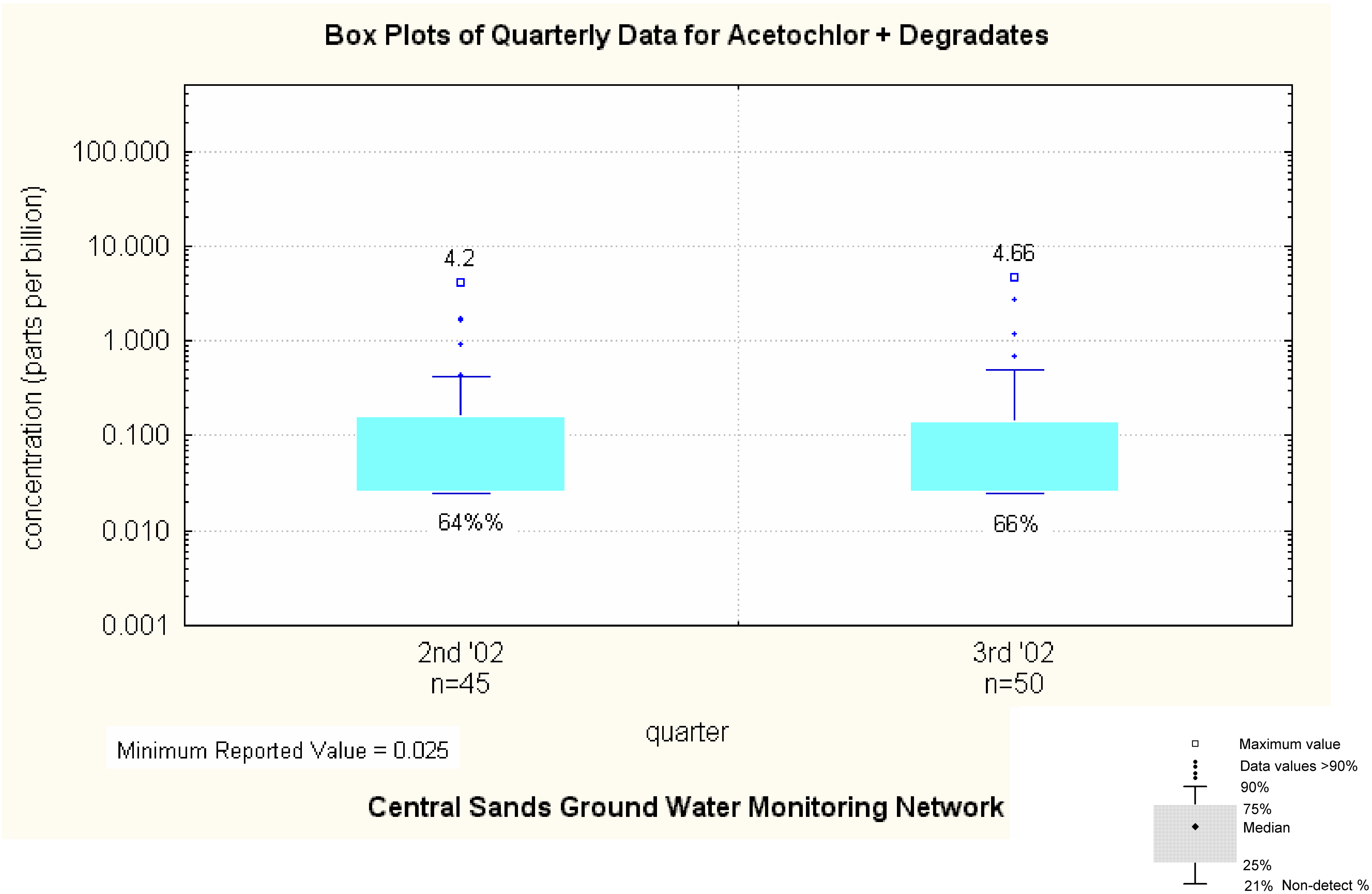


Figure 9 – Box Plots of alachlor plus alachlor degradates detections and concentrations in Central Sands groundwater by quarter

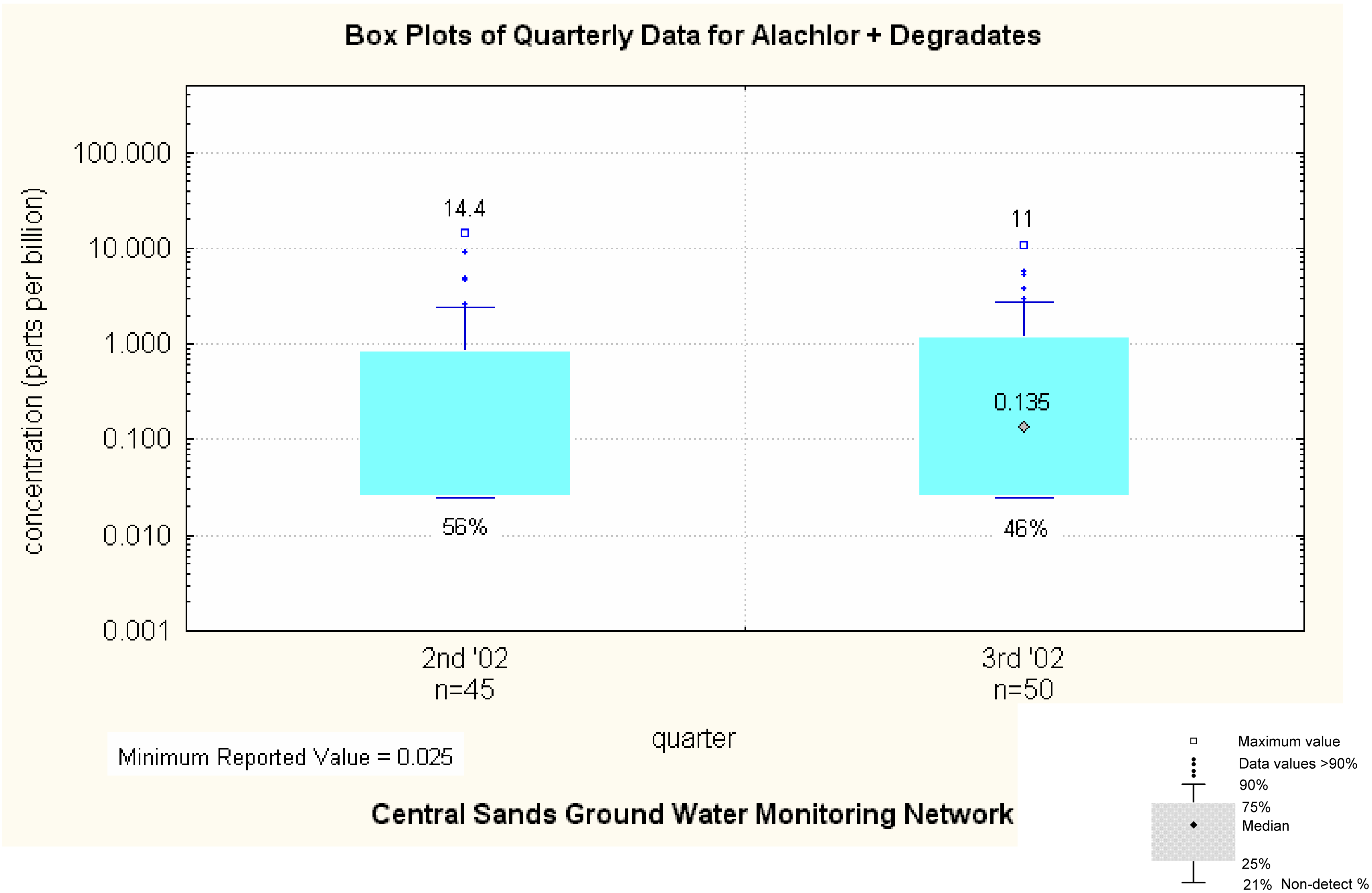


Figure 10 – Box Plots of alachlor ESA detections and concentrations in Central Sands groundwater by quarter

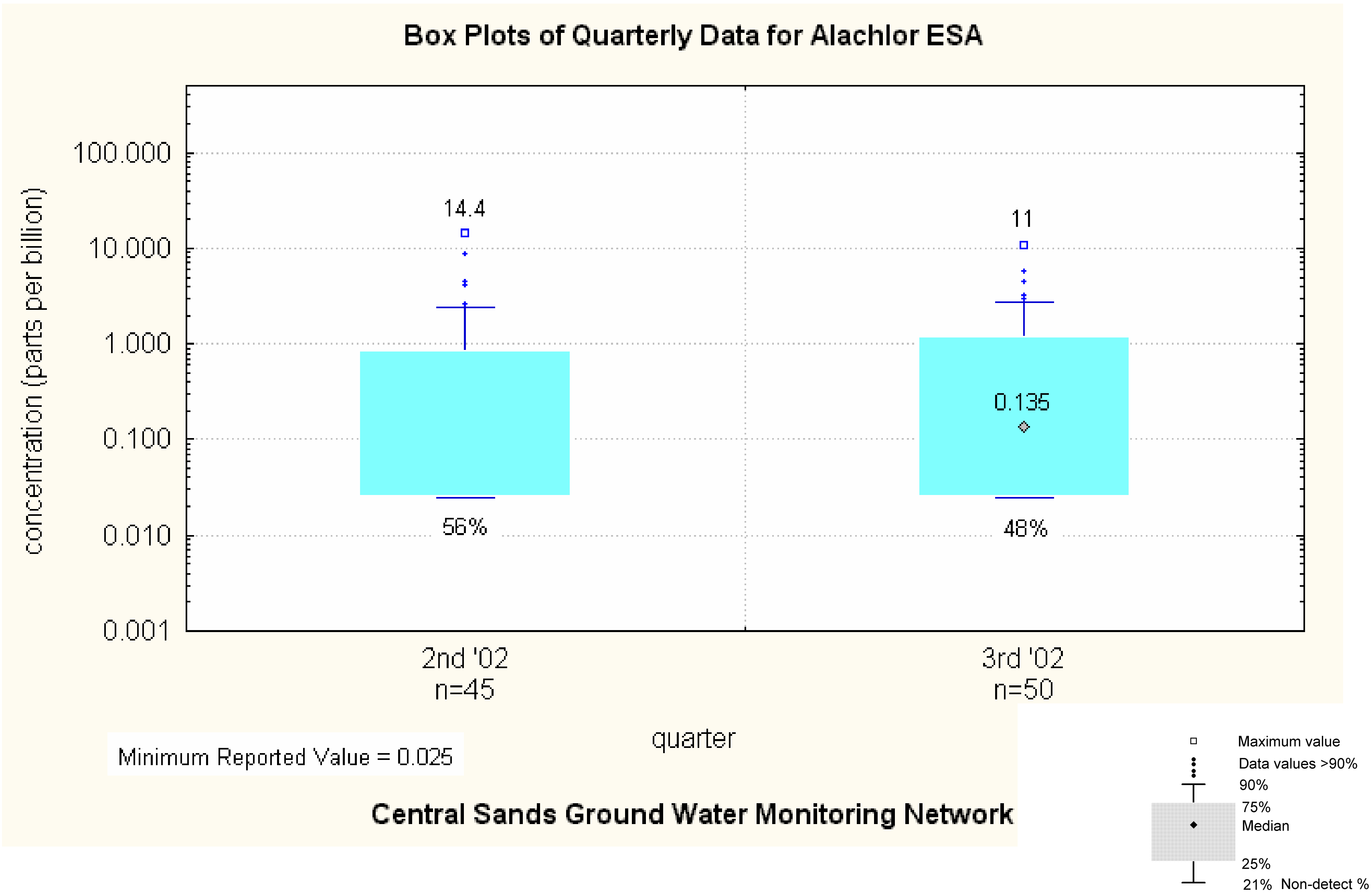


Figure 11 – Box Plots of alachlor OXA detections and concentrations in Central Sands groundwater by quarter

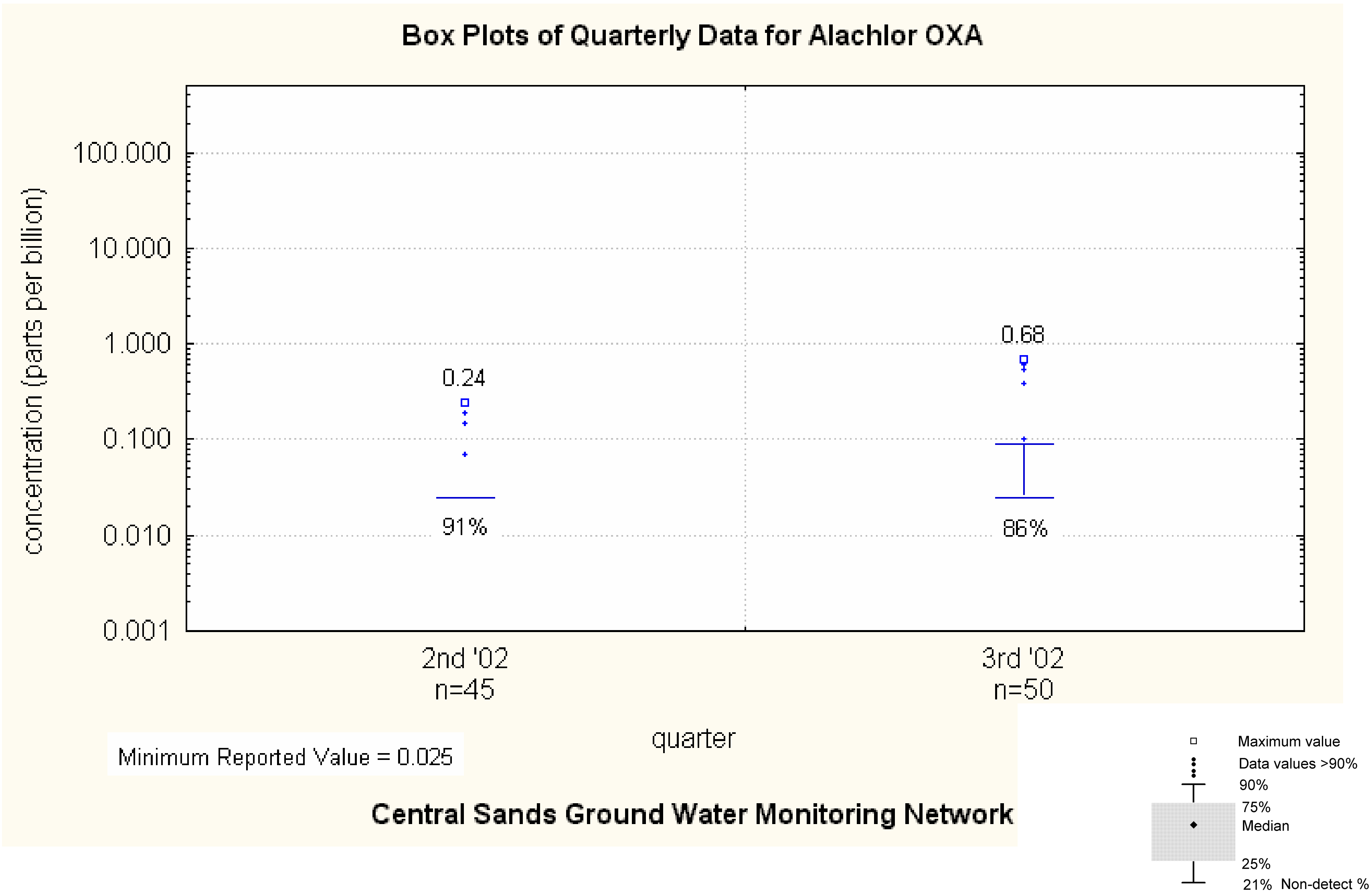


Figure 12 – Percentage detections of atrazine in Central Sands groundwater by quarter

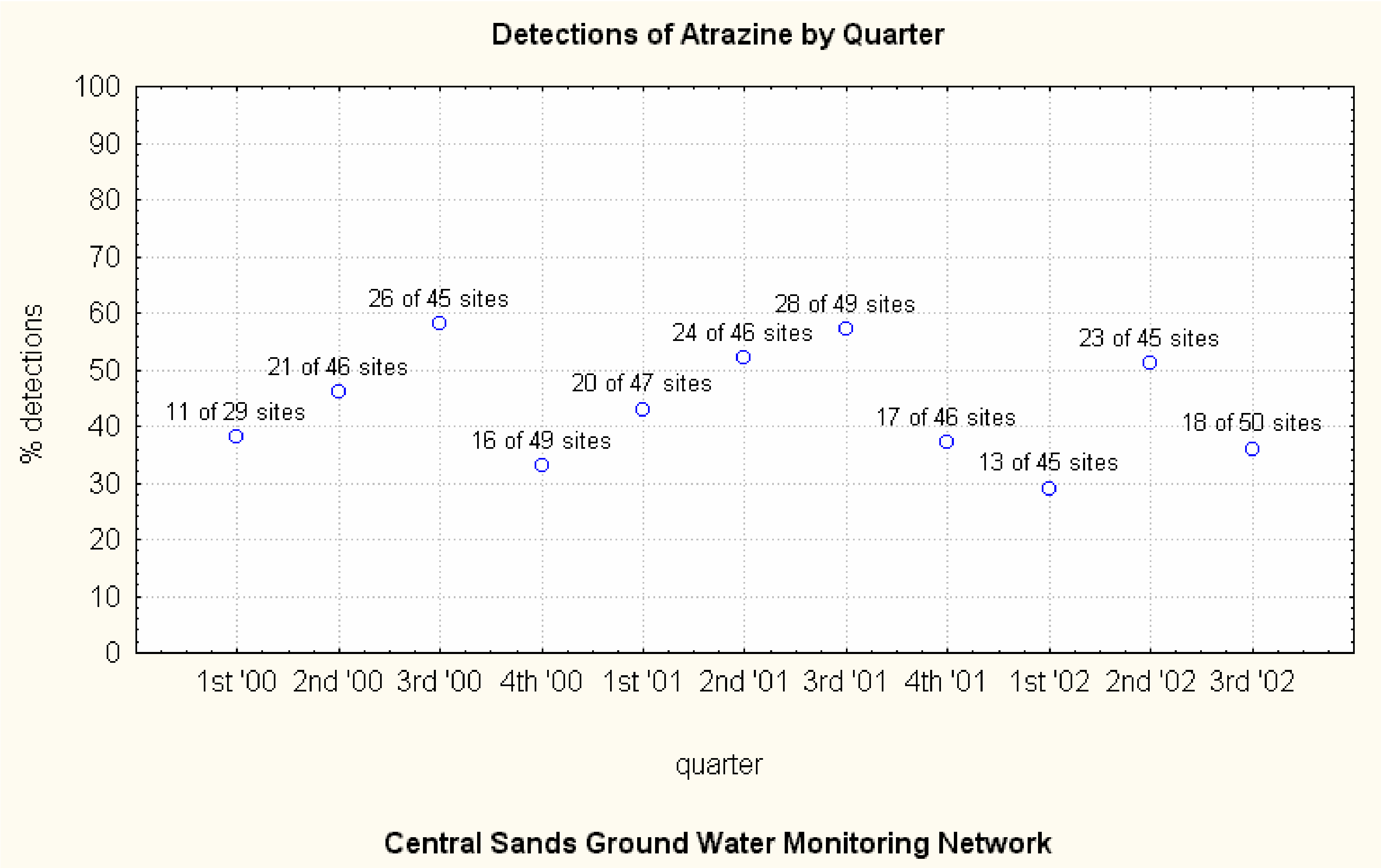


Figure 13 – Percentage detections of deethylatrazine in Central Sands groundwater by quarter

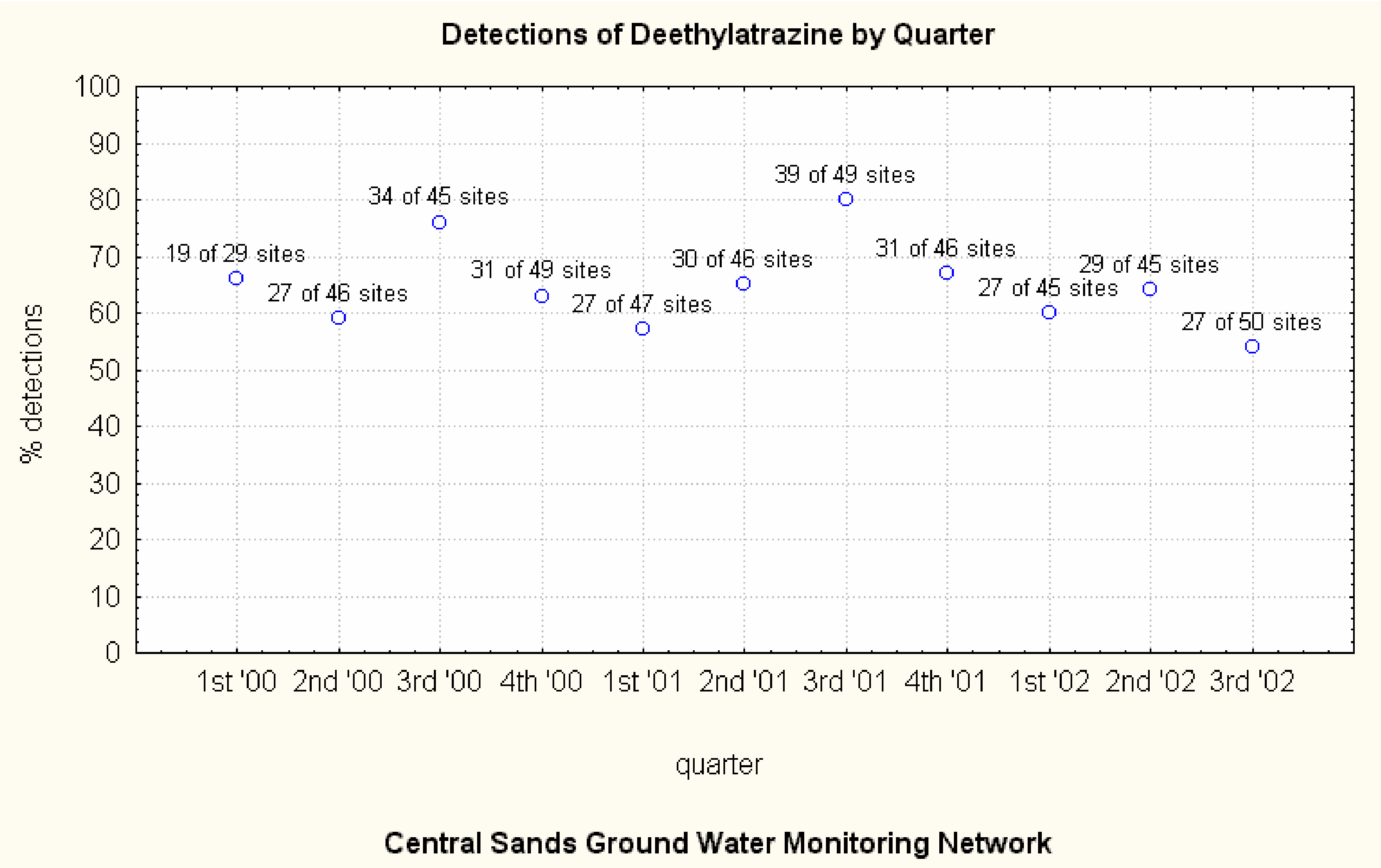


Figure 14 – Percentage detections of disopropylatrazine in Central Sands groundwater by quarter

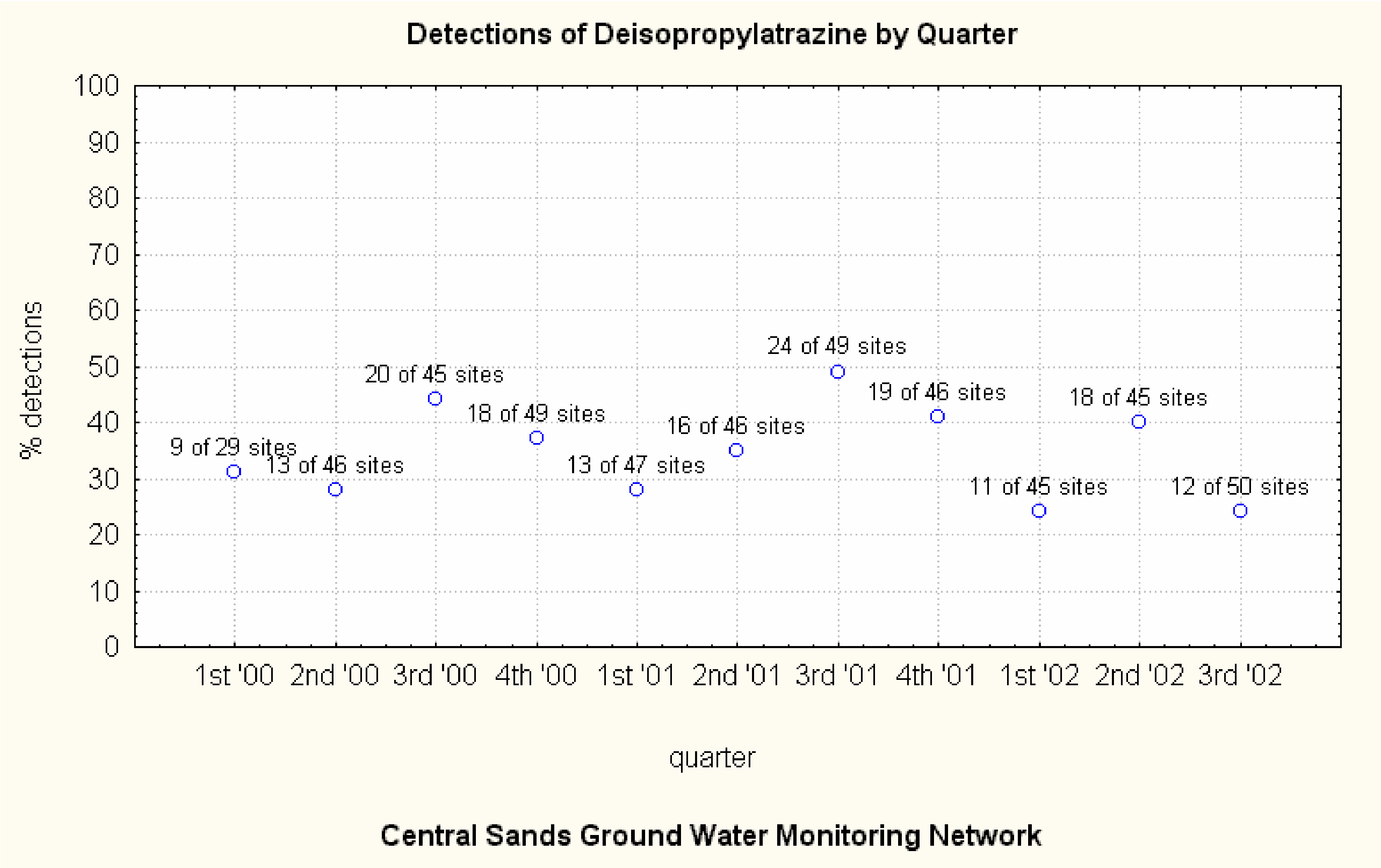


Figure 15– Percentage detections of atrazine plus atrazine degradates in Central Sands groundwater by quarter

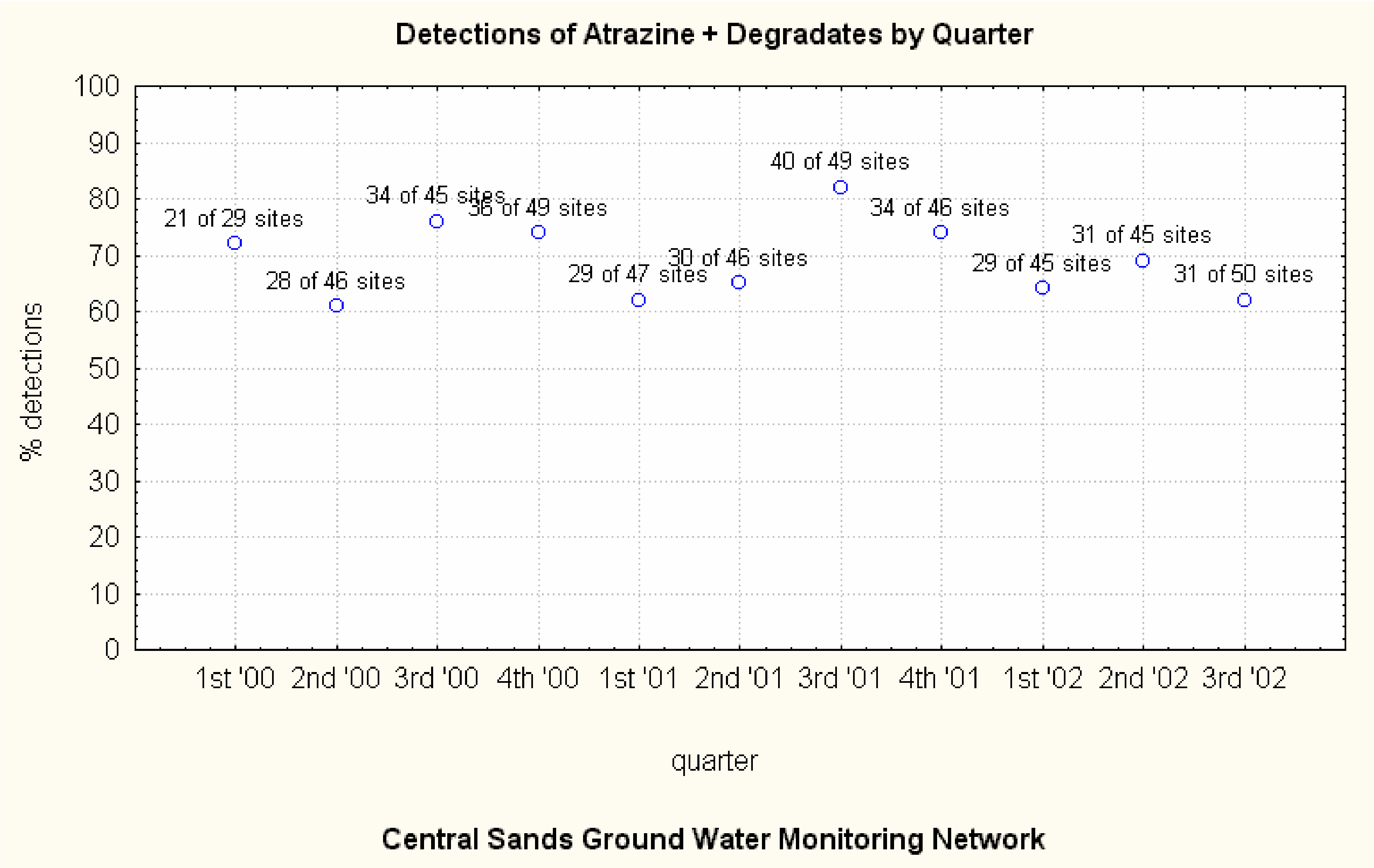


Figure 16 – Box Plots of atrazine detections and concentrations in Central Sands groundwater by quarter

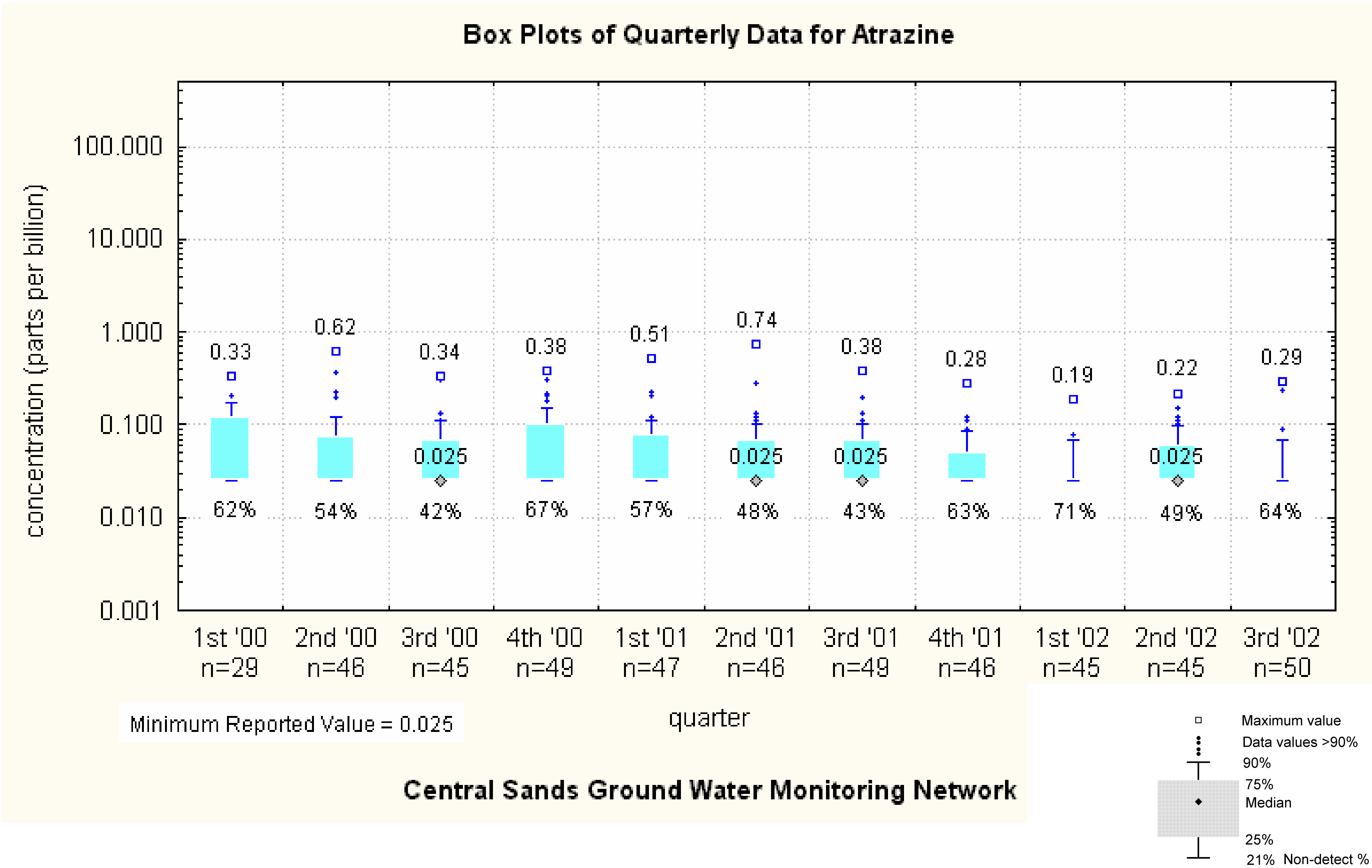


Figure 17 – Box Plots of deethylatrazine detections and concentrations in Central Sands groundwater by quarter

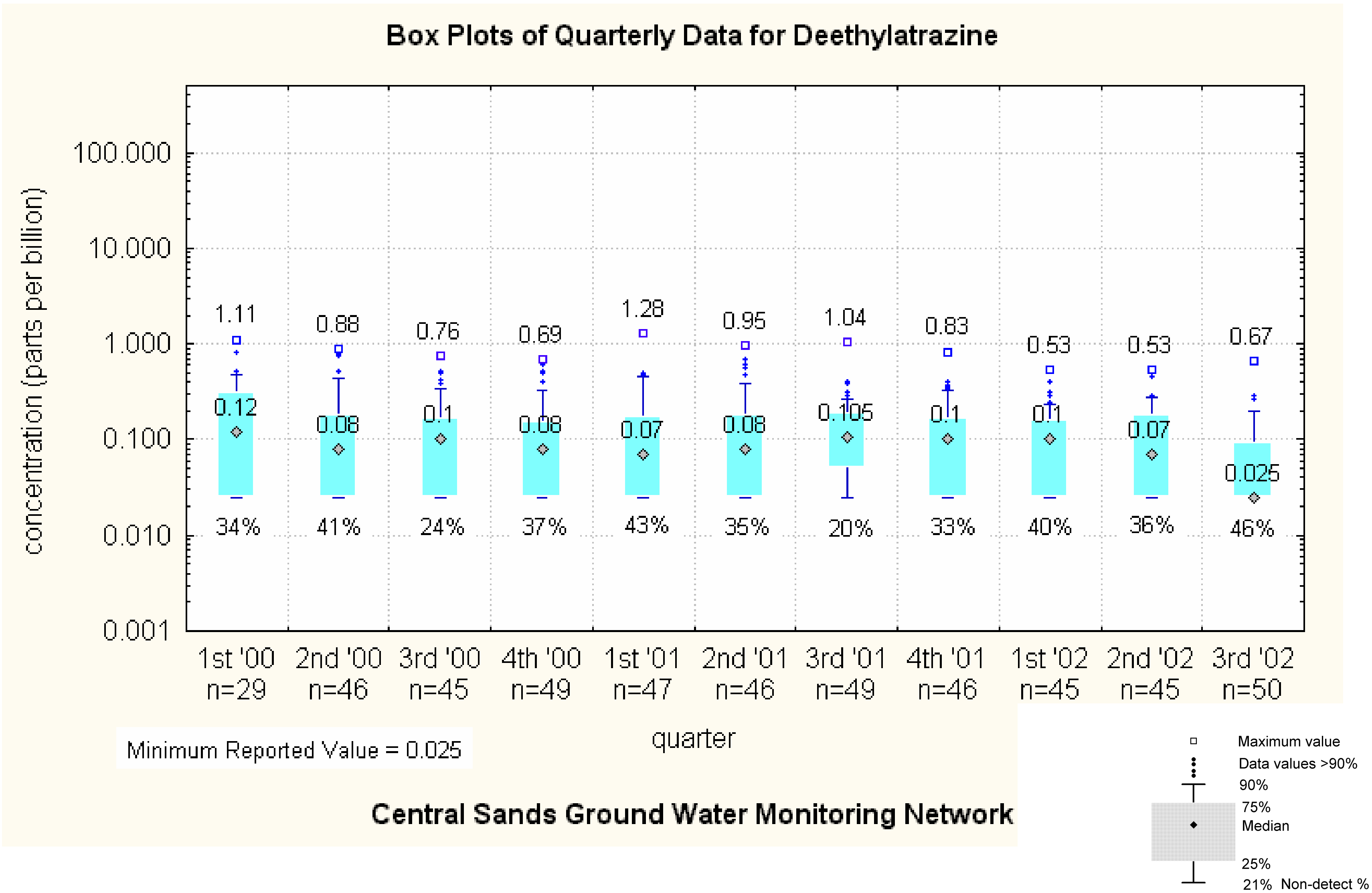


Figure 18 – Box Plots of deisopropylatrazine detections and concentrations in Central Sands groundwater by quarter

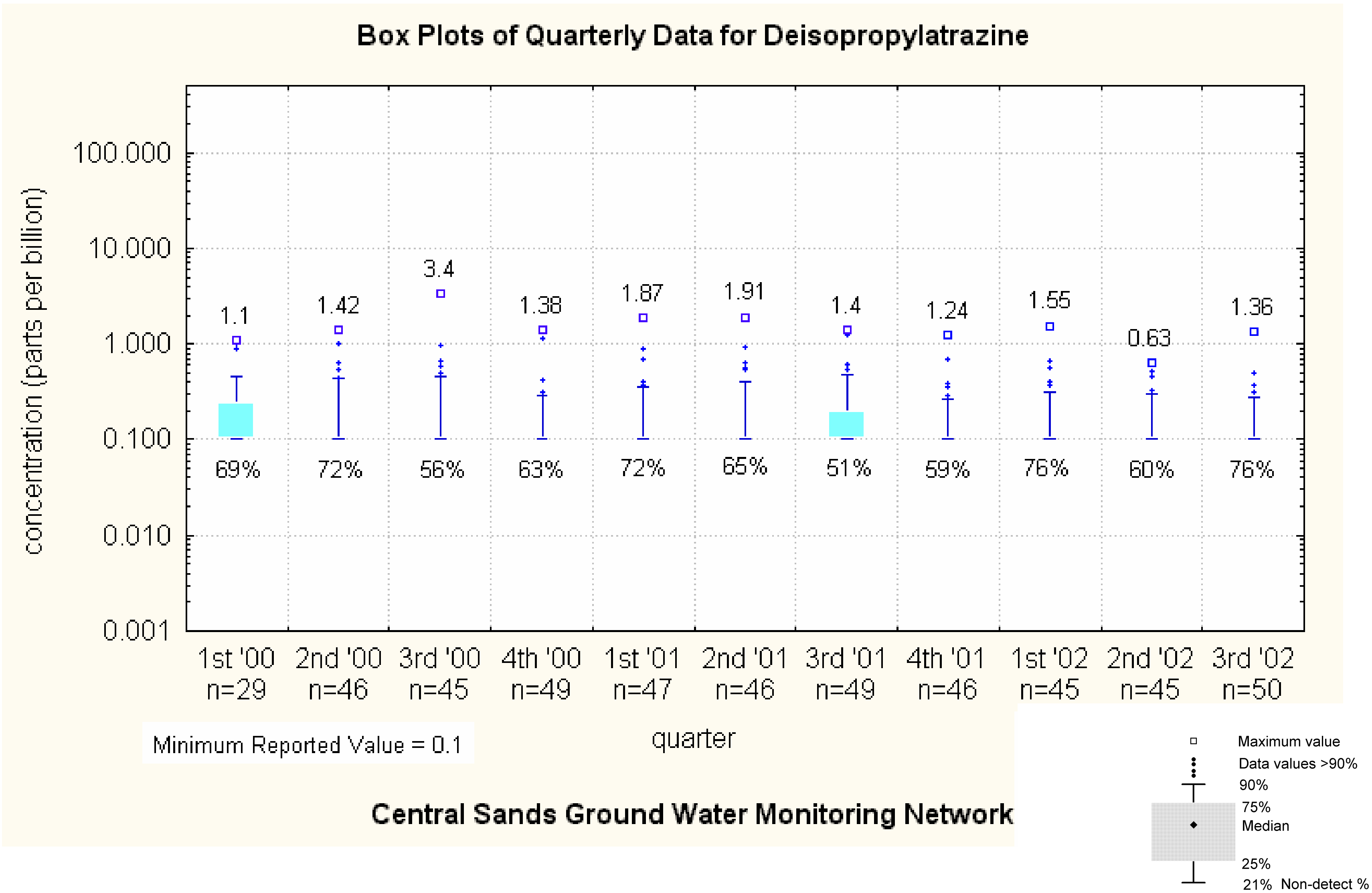


Figure 19 – Box Plots of atrazine plus atrazine degradate detections and concentrations in Central Sands groundwater by quarter

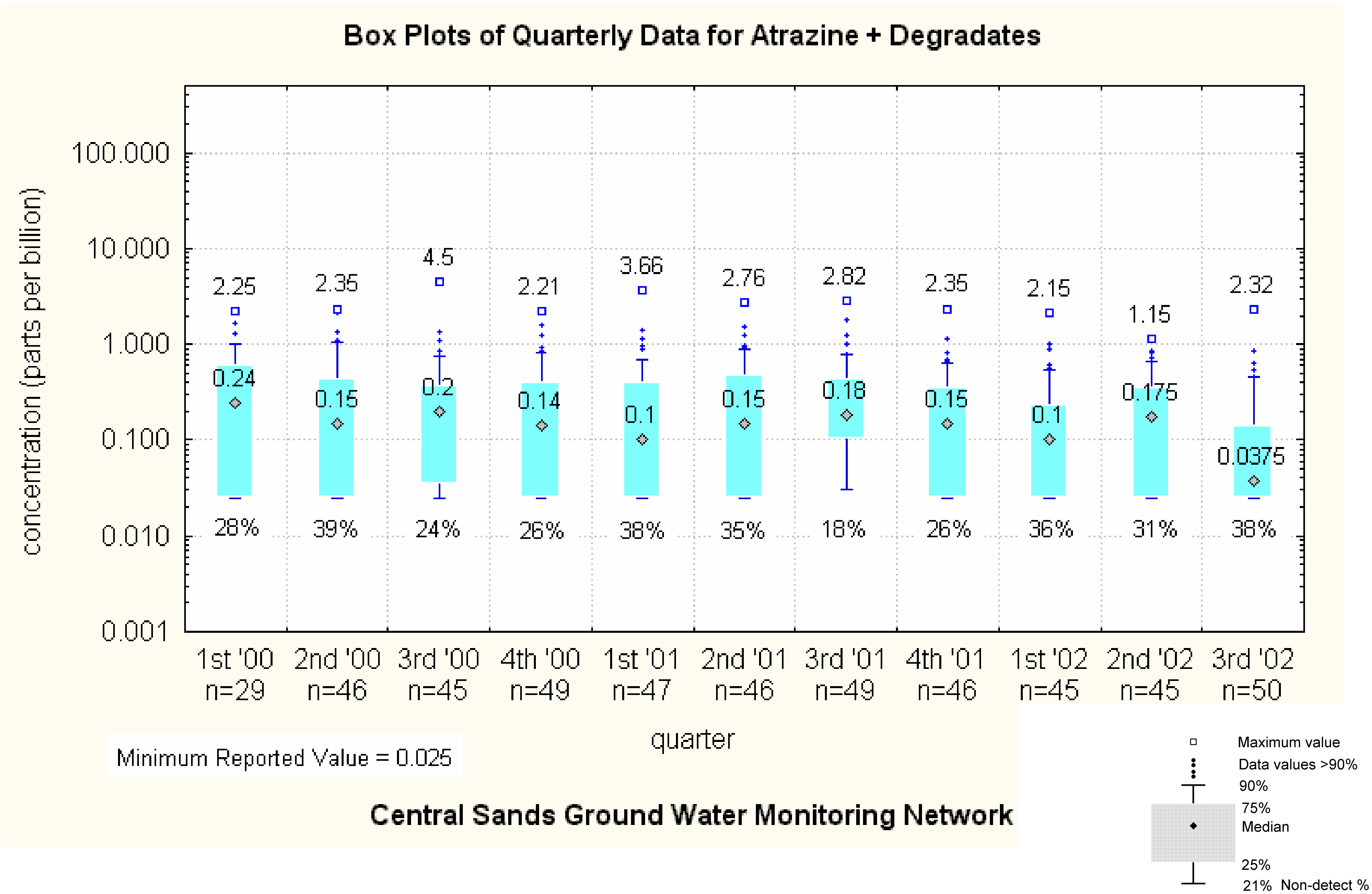


Figure 20 – Percentage detections of metolachlor in Central Sands groundwater by quarter

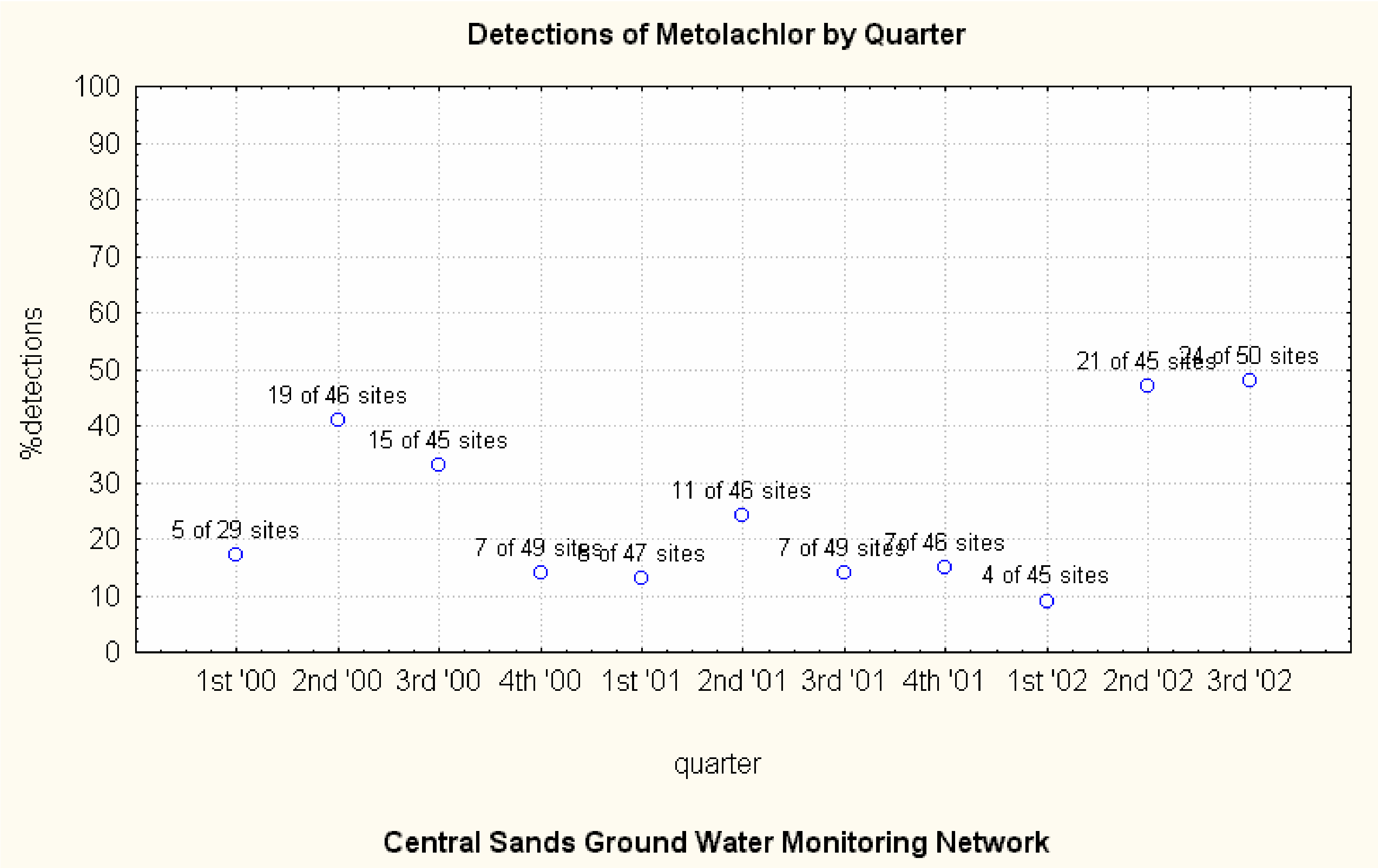


Figure 21 – Box Plots of metolachlor detections and concentrations in Central Sands groundwater by quarter

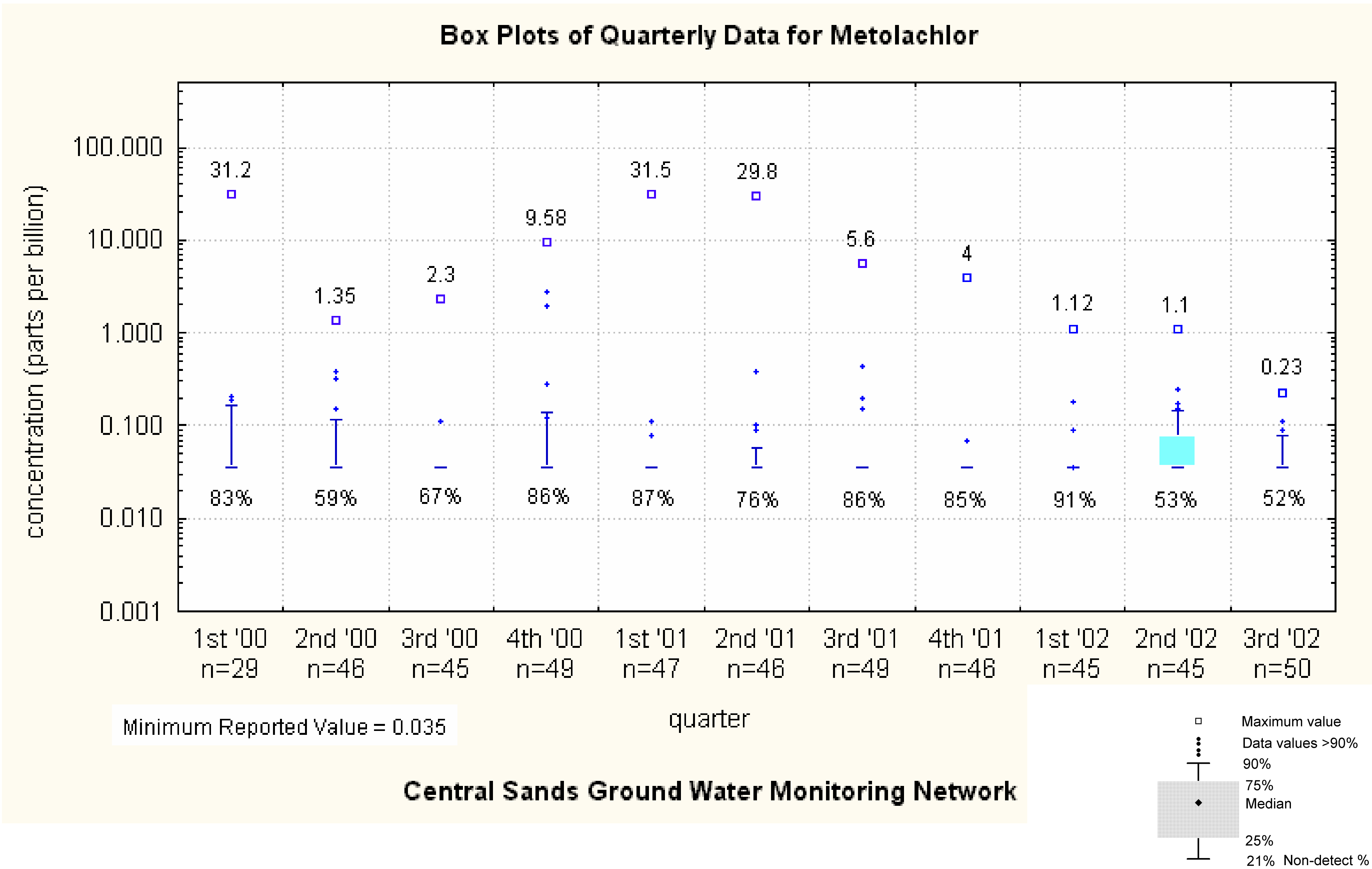


Figure 22 – Box Plots of metolachlor ESA detections and concentrations in Central Sands groundwater by quarter

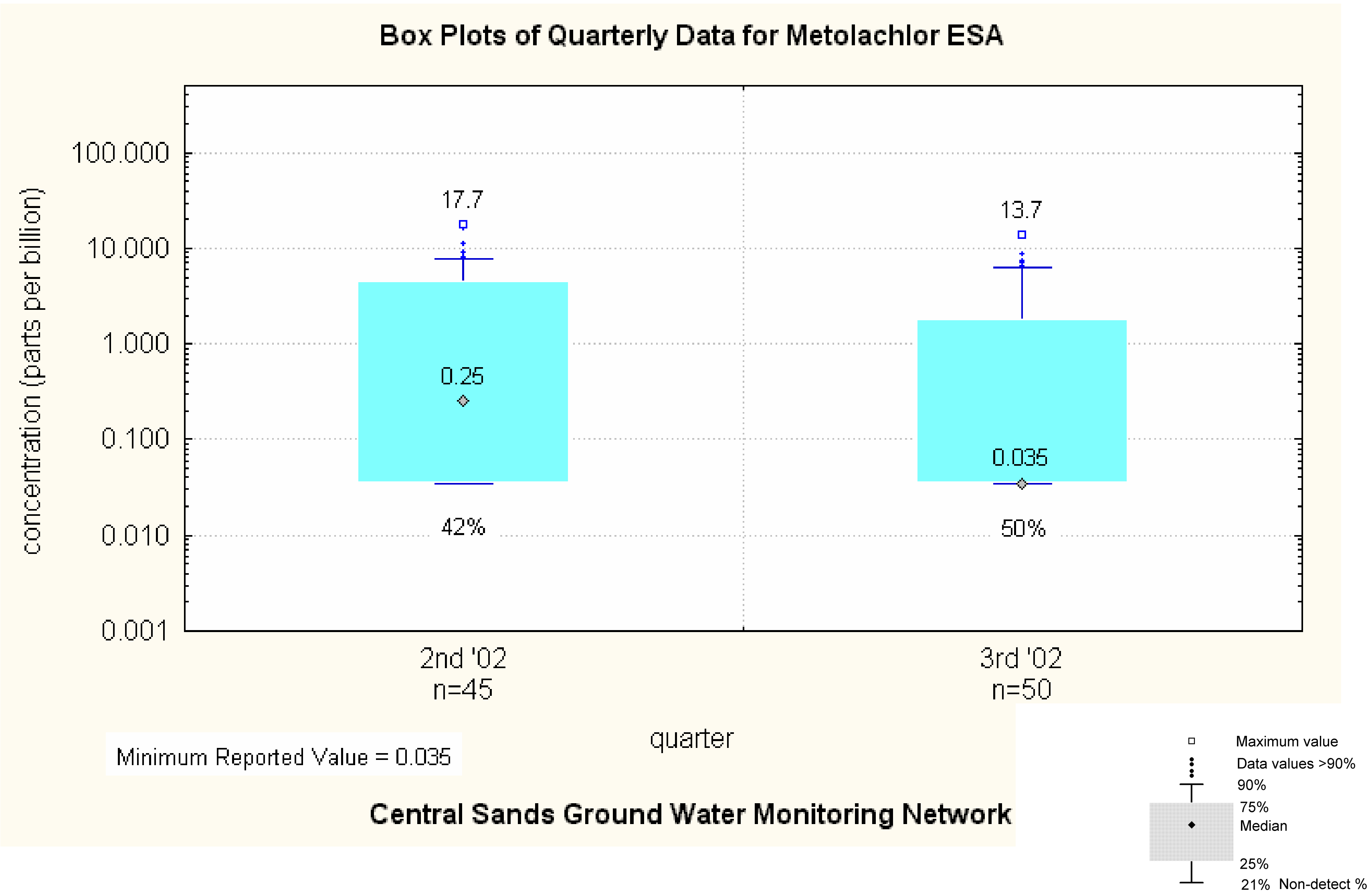


Figure 23 – Box Plots of metolachlor OXA detections and concentrations in Central Sands groundwater by quarter

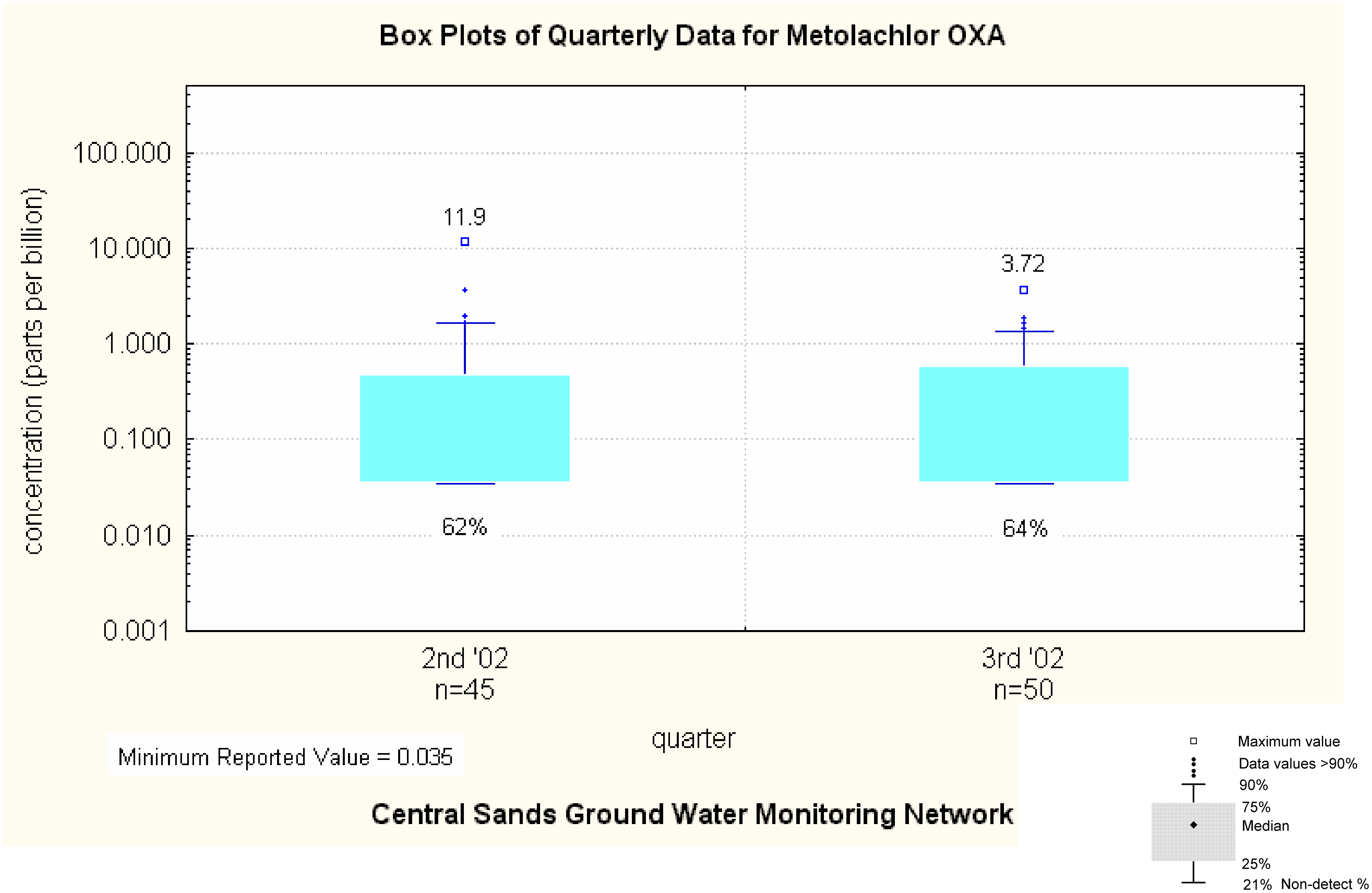


Figure 24 – Box Plots of metolachlor plus metolachlor degradate detections and concentrations in Central Sands groundwater by quarter

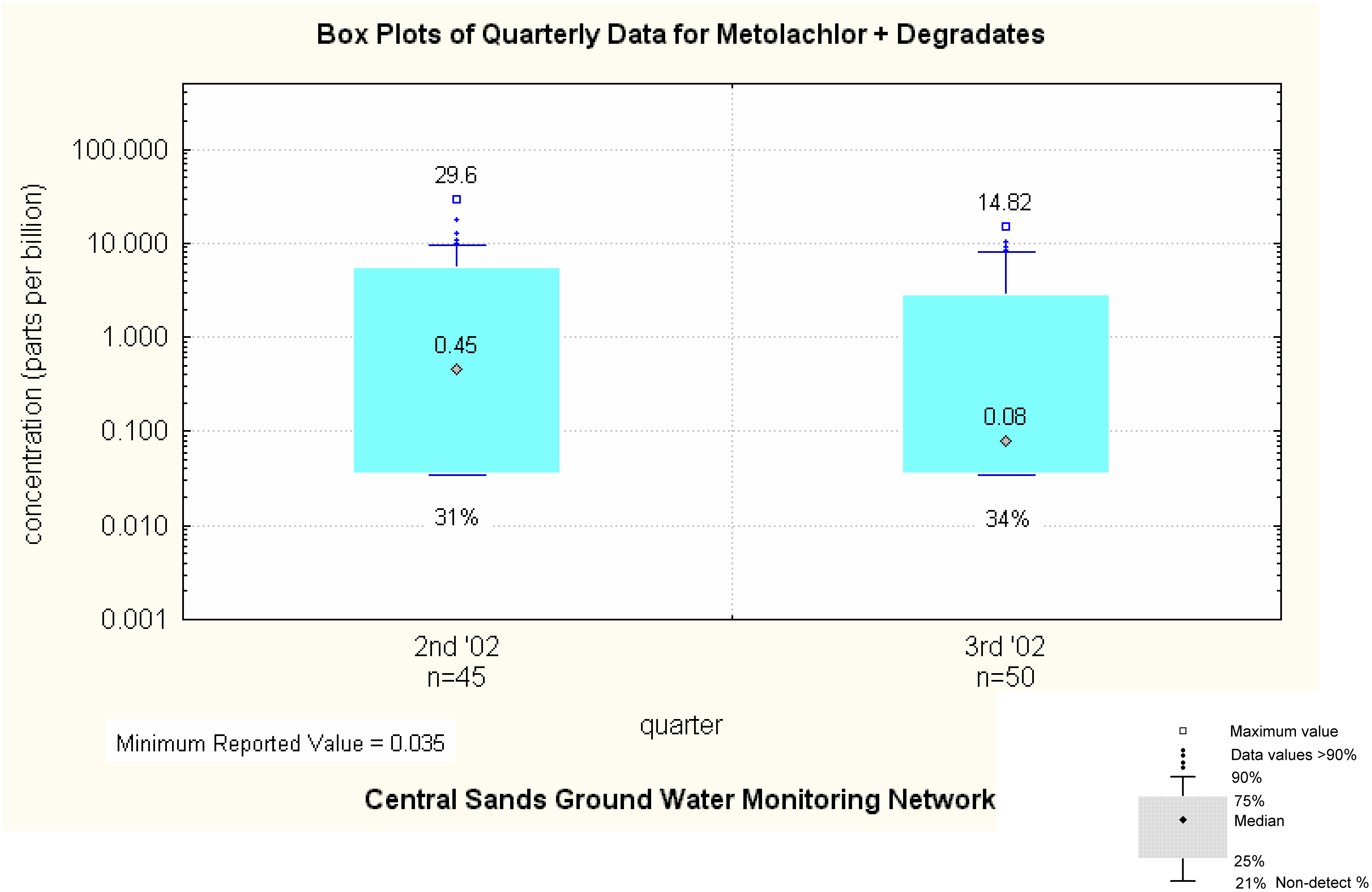


Figure 25 – Percentage detections of metribuzin in Central Sands groundwater by quarter

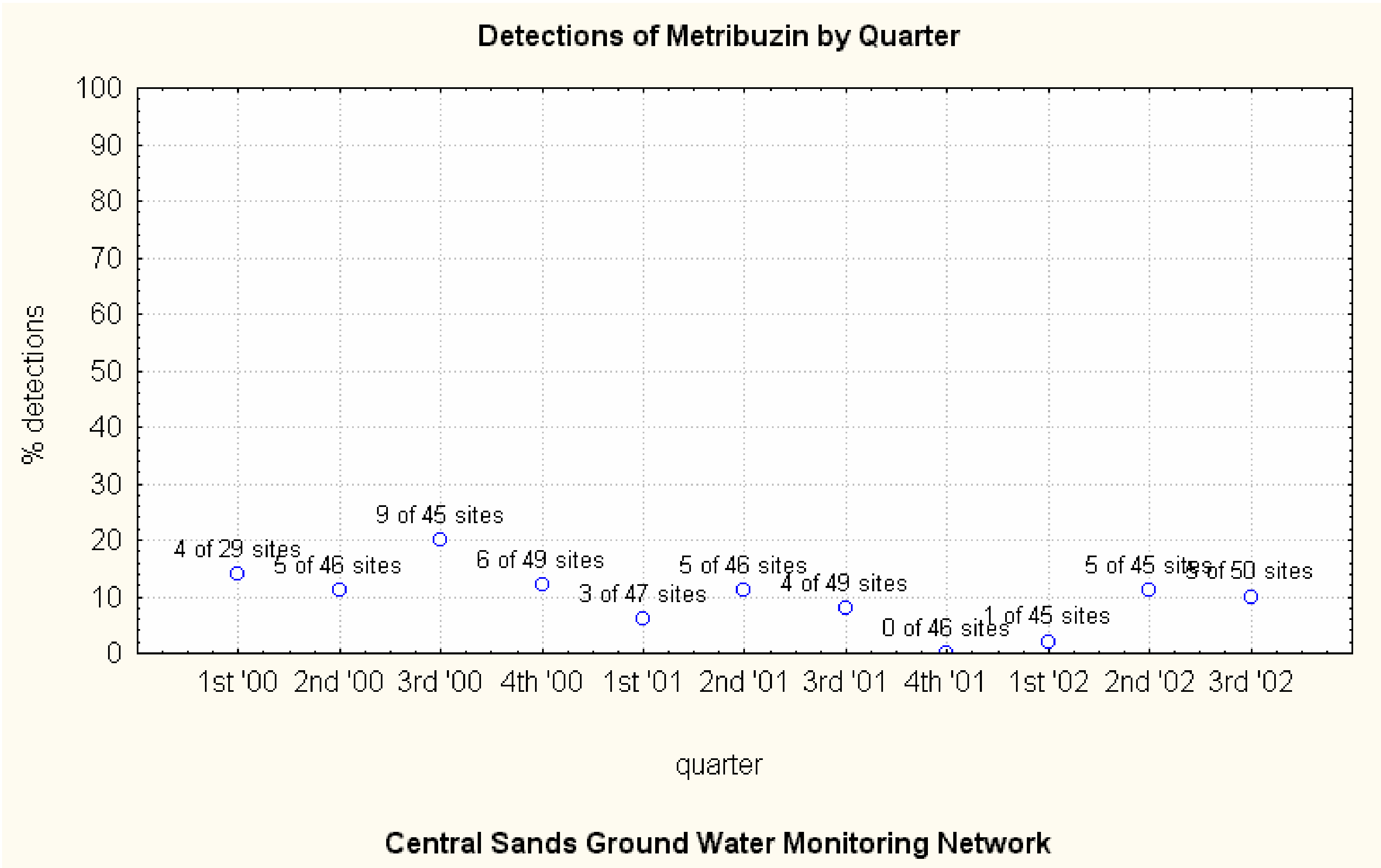


Figure 26 – Percentage detections of metribuzin dadk in Central Sands groundwater by quarter

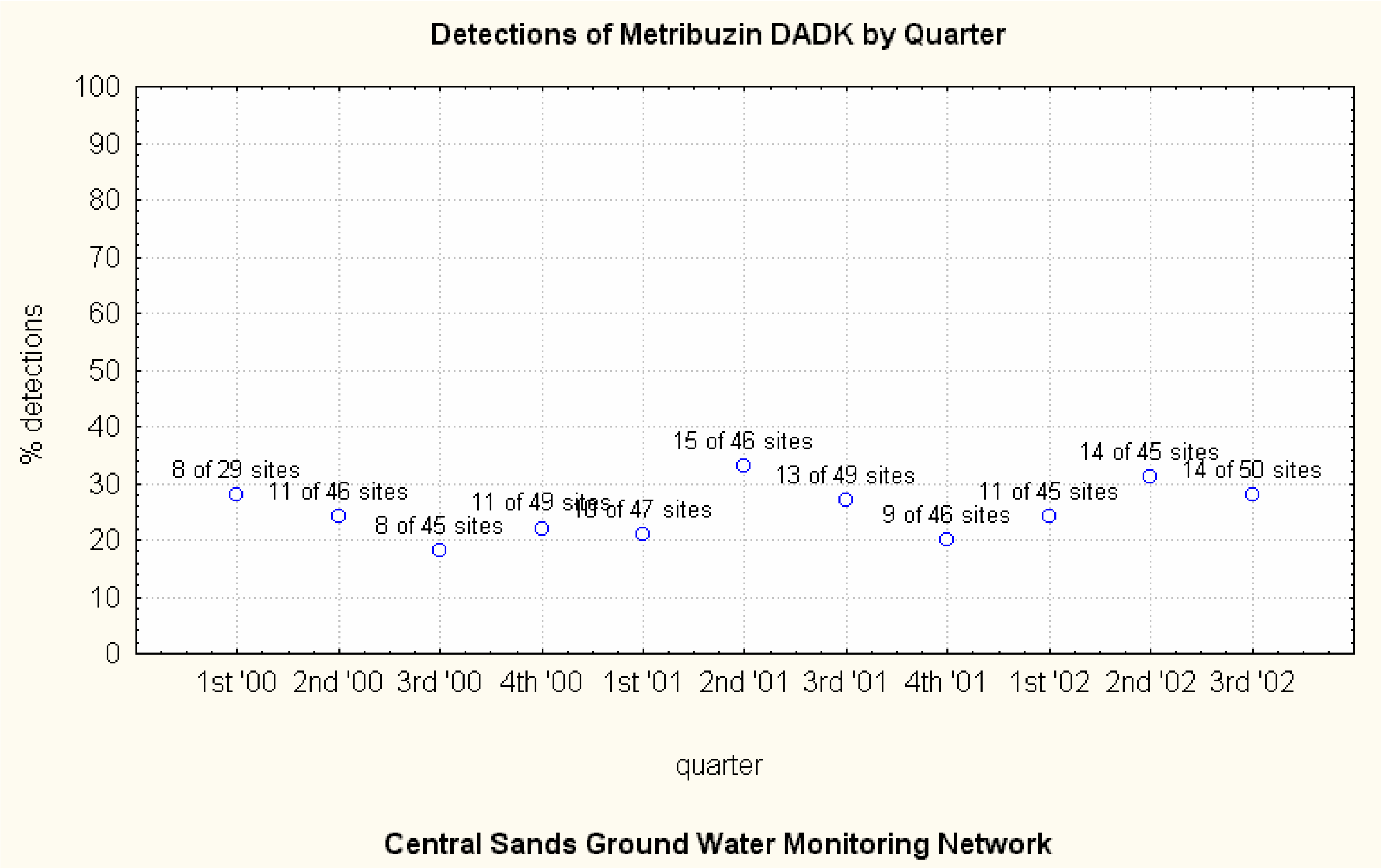


Figure 27 – Percentage detections of metribuzin dk in Central Sands groundwater by quarter

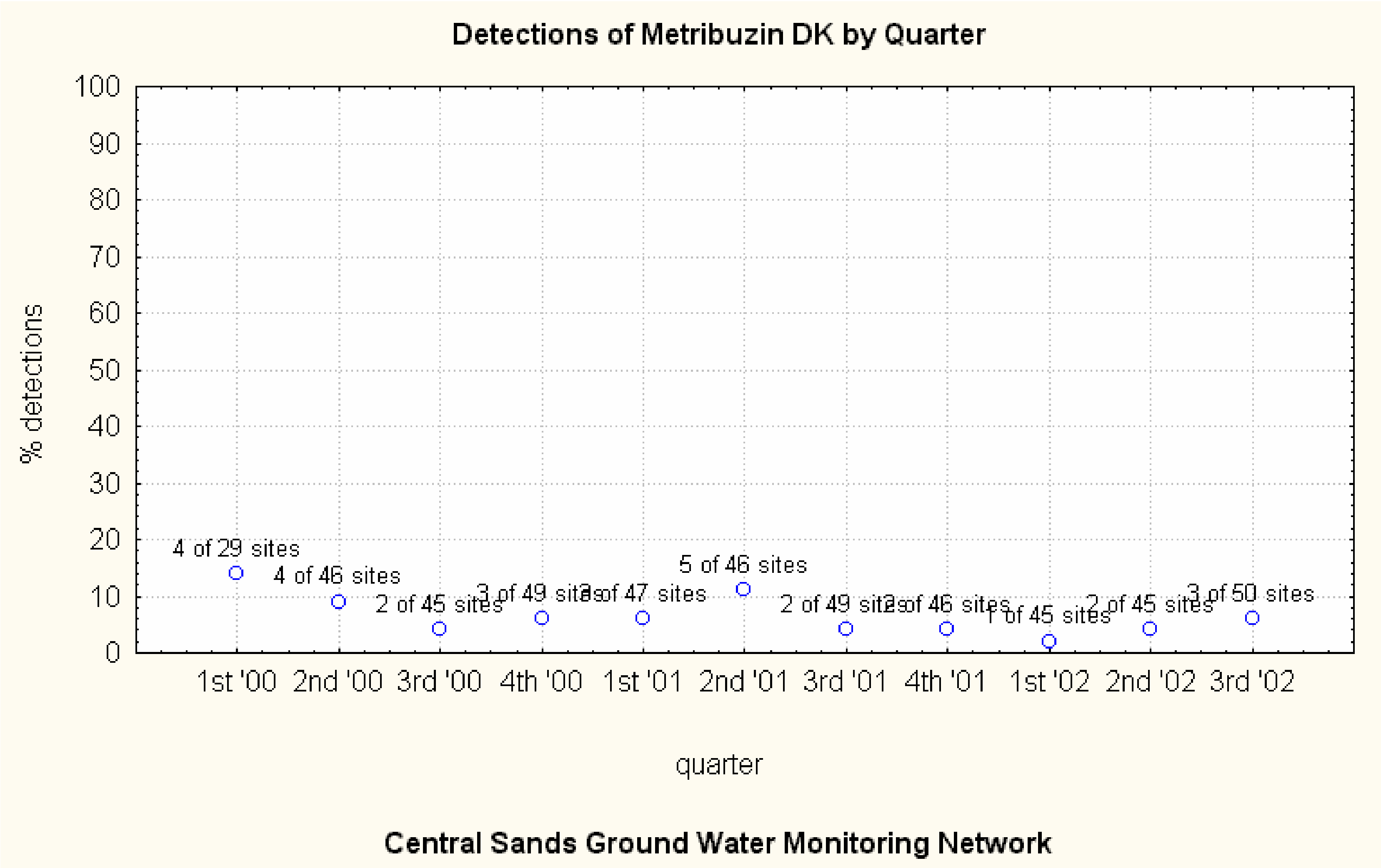


Figure 28 – Percentage detections of metribuzin da in Central Sands groundwater by quarter

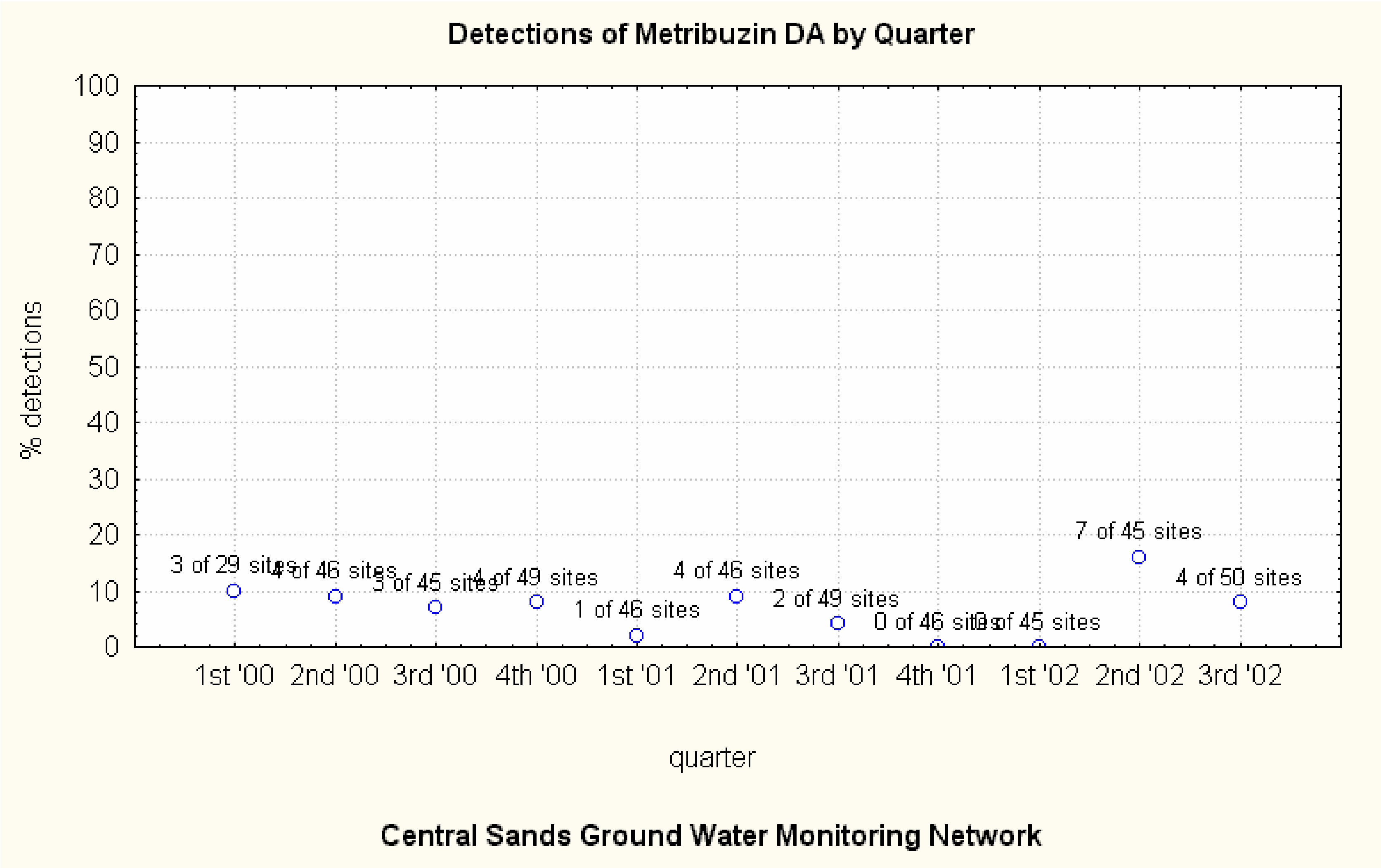


Figure 29 – Percentage detections of metribuzin plus metribuzin degradates in Central Sands groundwater by quarter

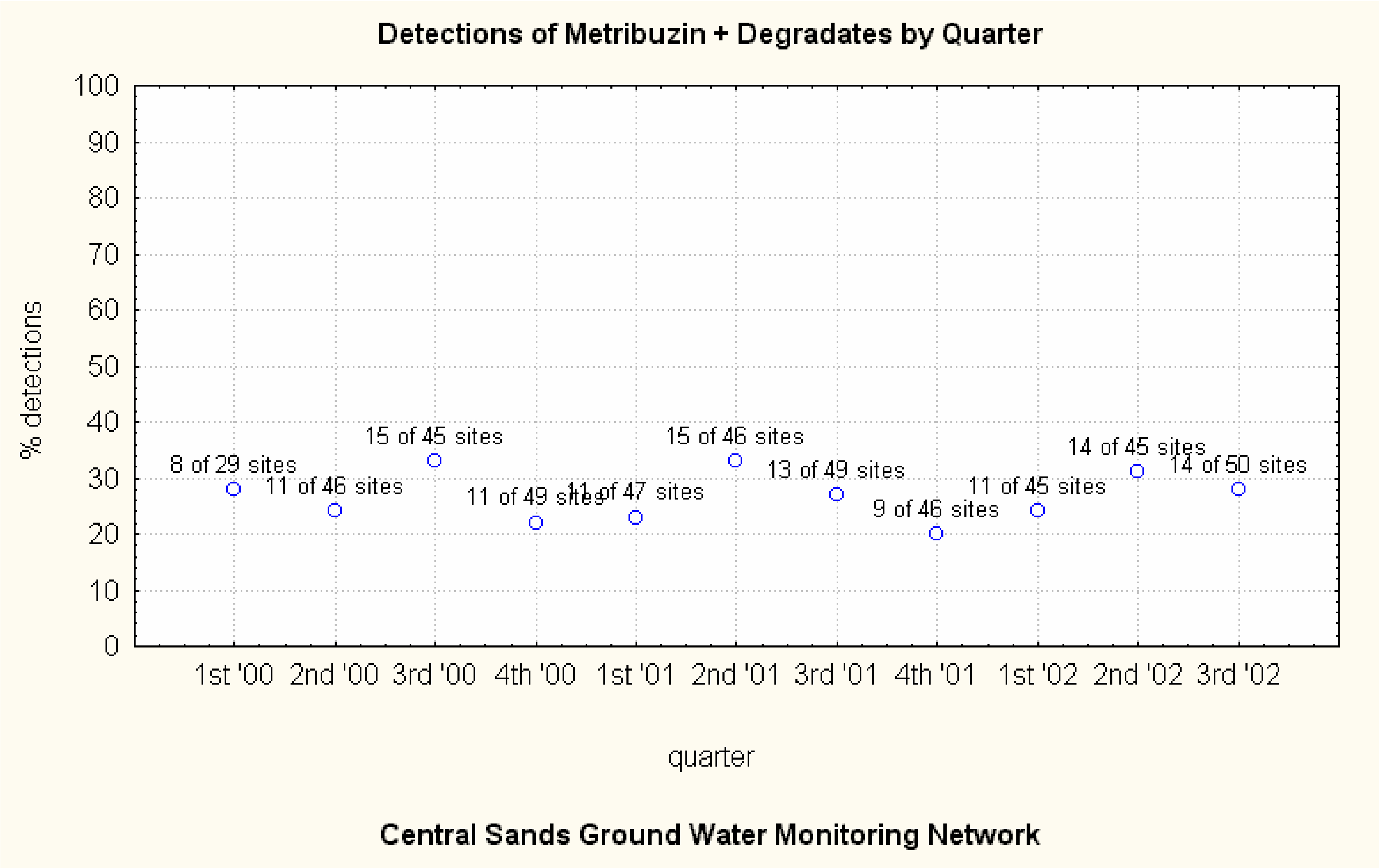


Figure 30 – Box Plots of metribuzin detections and concentrations in Central Sands groundwater by quarter

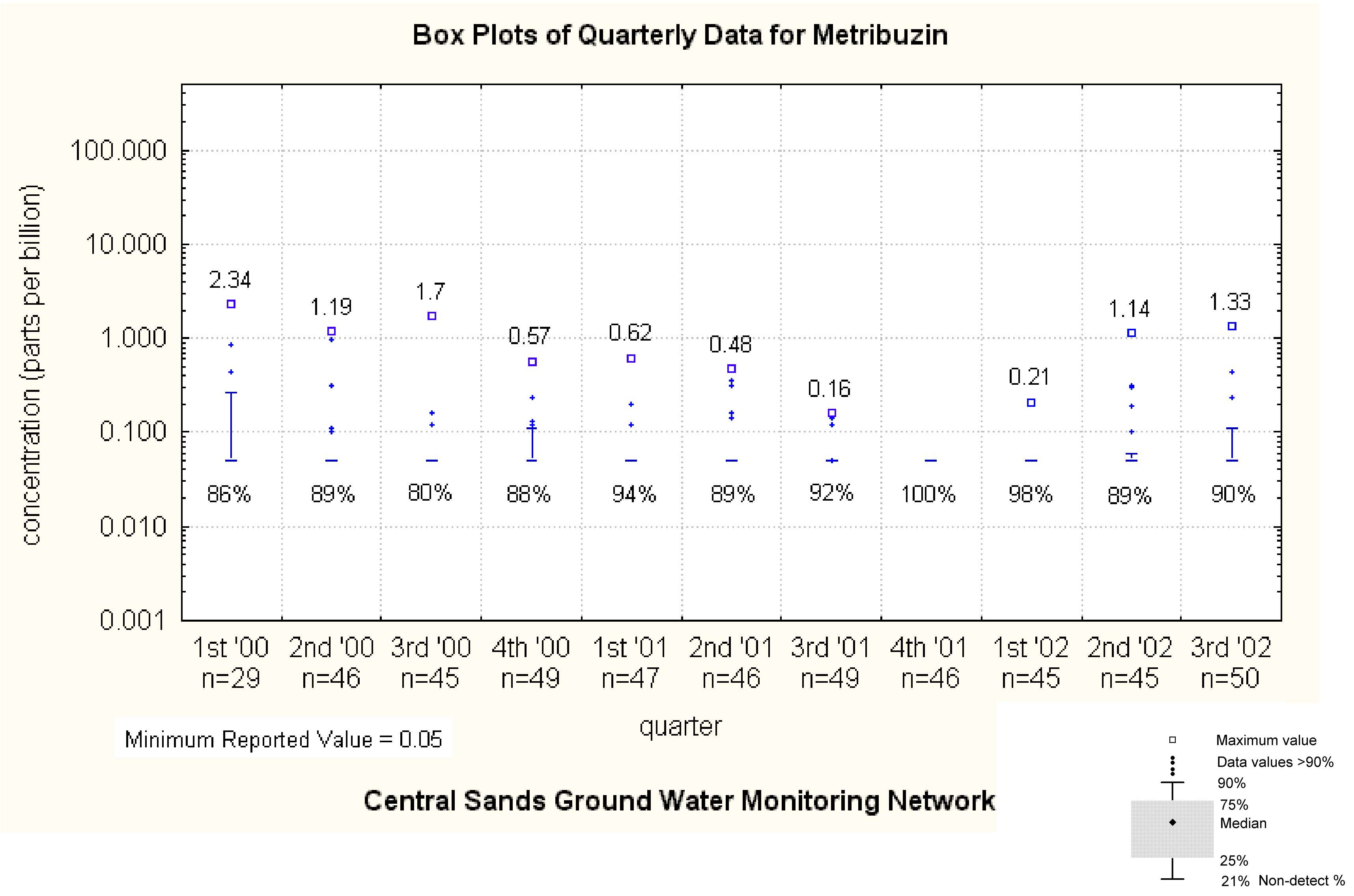


Figure 31 – Box Plots of metribuzin dadk detections and concentrations in Central Sands groundwater by quarter

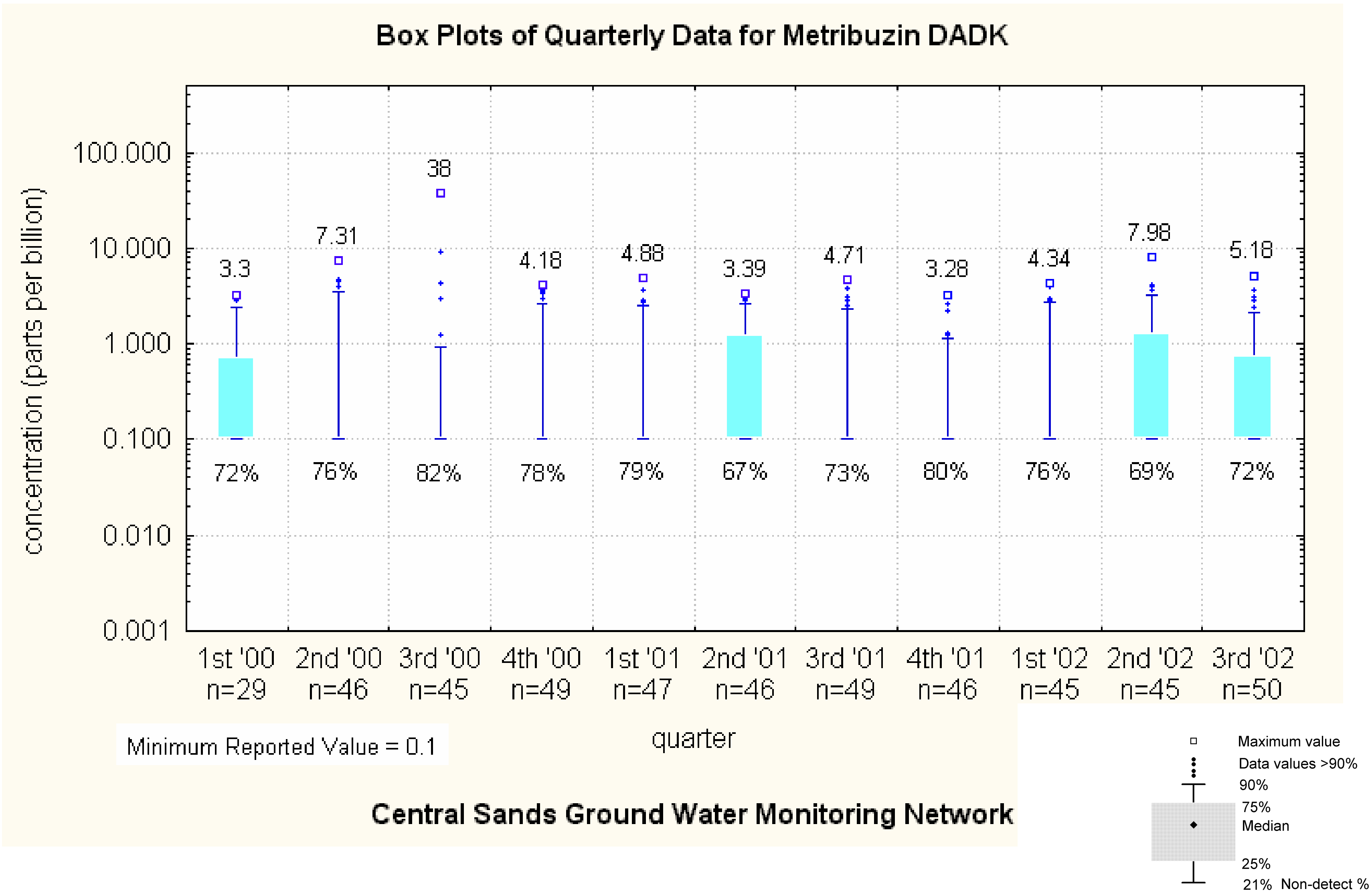


Figure 32 – Box Plots of metribuzin dk detections and concentrations in Central Sands groundwater by quarter

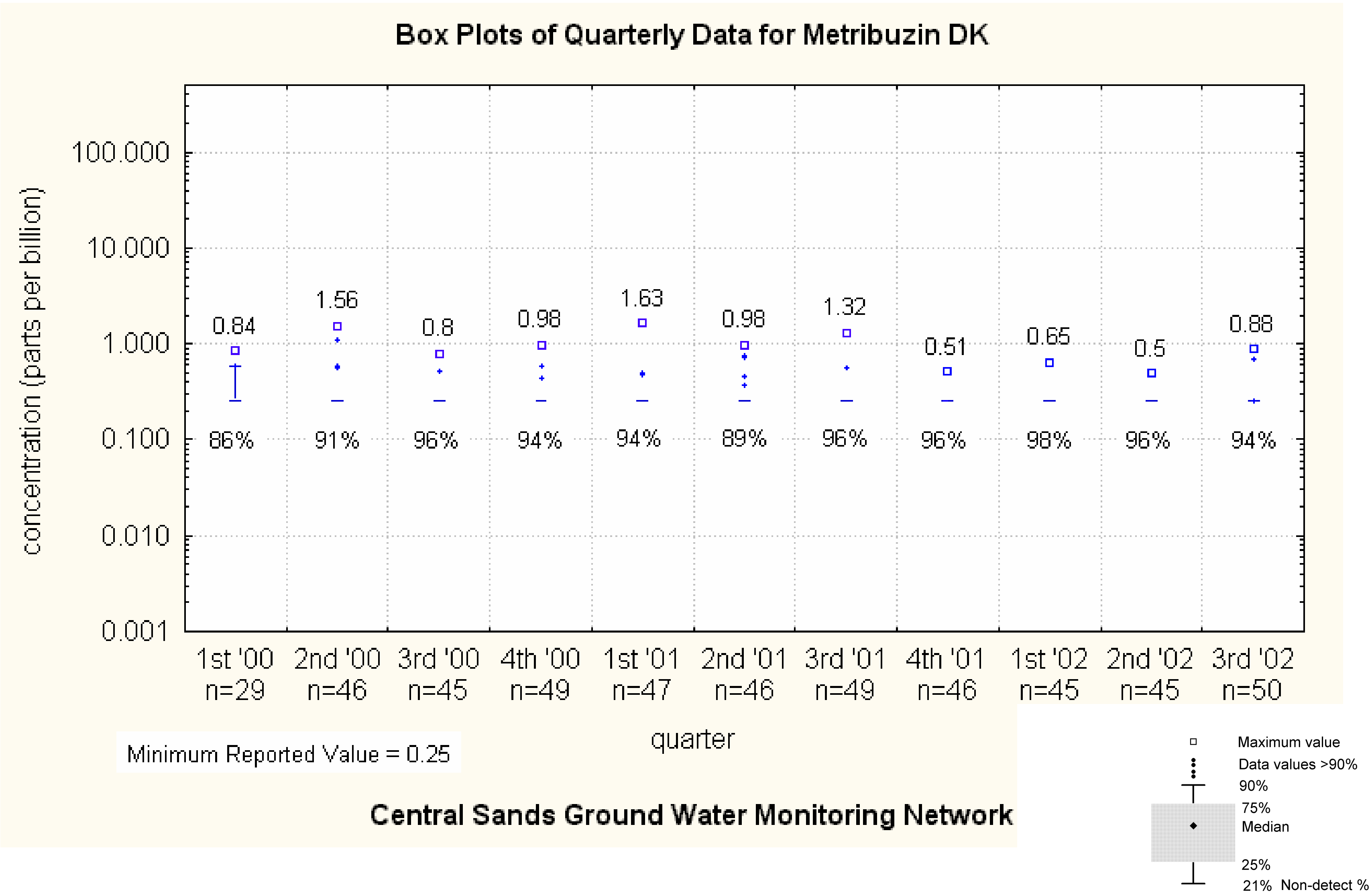


Figure 33 – Box Plots of metribuzin da detections and concentrations in Central Sands groundwater by quarter

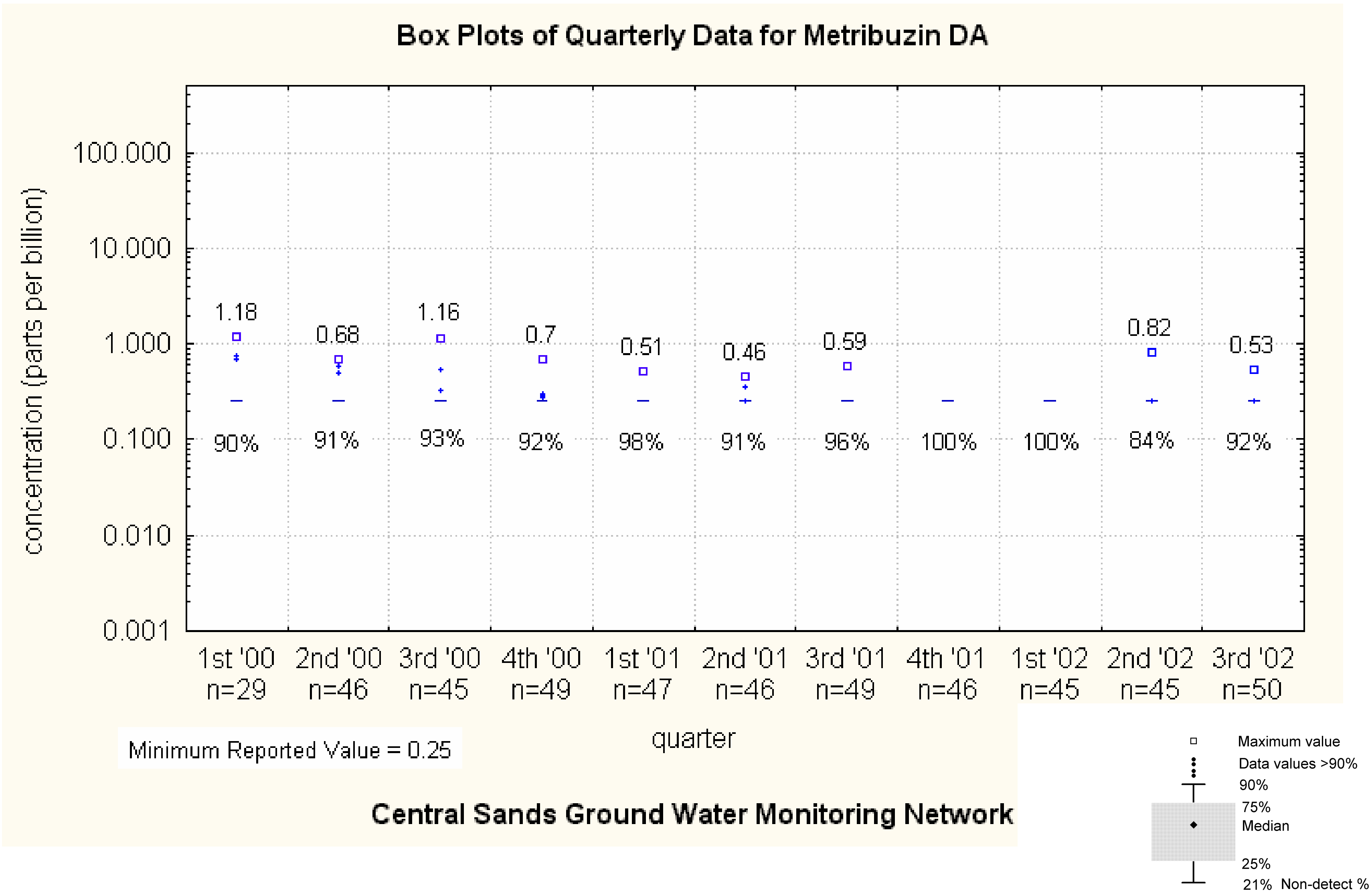
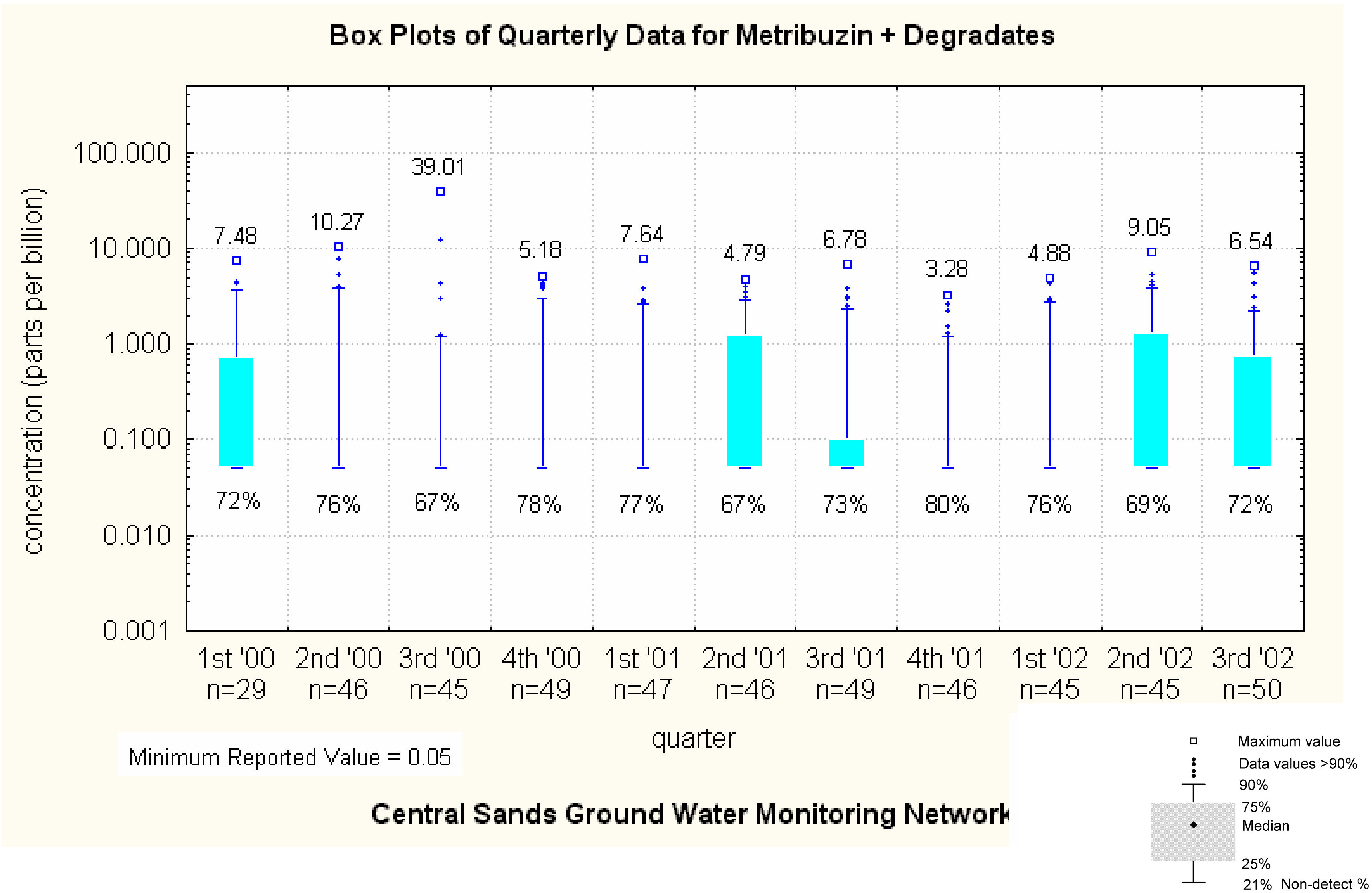


Figure 34 – Box Plots of metribuzin plus metribuzin degradate detections and concentrations in Central Sands groundwater by quarter



APPENDIX E – Surface Water Pesticide Detection Summaries, Hydrographs and Chemographs

Note:

Hydrographs and chemographs are provided only when concentrations of a pesticide exceed 10% of a Minnesota Pollution Control Agency water quality chronic standard, criterion or advisory value for a given calendar or partial calendar year. Graphs are provided only for the lowest applicable chronic standard, criterion or advisory value for a given water body classification. See Appendix C for further information regarding applicable water quality criteria.

Comparisons shown in graphs are preliminary and were made in consultation with the MPCA. Appearance of a water body in this appendix does not imply that a violation of water quality standards has occurred, and does not imply impairment for a given use.

Table 20 – Pesticide and pesticide degradate detections in storm and base flow events in MDA surface water monitoring stations, calendar year 2001

Calendar Year 2001		Storm Event Samples (concentrations in ug/L; nd = non detect)					Base Flow Samples (concentrations in ug/L; nd = non detect)				
Pesticide	Monitoring Station	No. of samples	% Detection	Max. Concentration	Date of Max.	Median Concentration	No. of samples	% Detection	Max. Concentration	Date of Max.	Median Concentration
Acetochlor	Blue Earth R.	22	100%	6.5	5/24	.29	12	25%	.07	7/11	nd
	Le Sueur R.	24	100%	9.0	5/24	.29	11	18%	.05	multiple	nd
	Minn. R. (Jud)	27	96%	.42	4/4	.09	10	0%	not applicable	not applicable	not applicable
	Whitewater R.	26	23%	7.8	6/12	nd	36	31%	1.98	6/19	nd
	Bevens Creek	11	82%	3.1	5/20	.07	6	0%	not applicable	not applicable	not applicable
	Sand Creek	9	56%	1.44	5/21	.025	8	25%	.23	5/25	nd
	Bent Creek	22	14%	.17	6/14	nd	17	12%	.025	multiple	nd
	Chaska Creek	18	50%	.26	5/22	.013	18	17%	.025	multiple	nd
Alachlor	Blue Earth R.	22	36%	.06	5/24	nd	12	0%	not applicable	not applicable	not applicable
	Le Sueur R.	24	21%	.13	5/24	nd	11	0%	not applicable	not applicable	not applicable
	Minn. R. (Jud)	27	4%	.025	6/20	nd	10	0%	not applicable	not applicable	not applicable
Atrazine	Blue Earth R.	22	86%	2.2	6/16	.09	12	42%	.33	7/11	nd
	Le Sueur R.	24	92%	3.8	6/16	.11	11	45%	.33	7/11	nd
	Minn. R. (Jud)	27	67%	.98	6/25	.06	10	50%	.15	8/22	.03
	Whitewater R.	26	100%	17.4	6/12	.105	36	94%	7.1	6/19	.14
	Bevens Creek	11	73%	1.33	6/13	.07	6	33%	.11	7/10	nd
	Sand Creek	9	56%	7	6/13	.07	8	63%	.27	6/18	.0375
	Bent Creek	22	36%	.36	6/14	nd	17	41%	.07	7/12	nd
	Chaska Creek	18	50%	.67	6/13	.01	18	22%	.28	6/19	nd
Deethylatrazine	Blue Earth R.	22	91%	.23	6/25	.075	12	42%	.1	7/11	nd
	Le Sueur R.	24	86%	.25	multiple	.08	11	36%	.10	7/11	nd
	Minn. R. (Jud)	27	74%	.14	6/25	.06	10	30%	.09	8/7	nd
	Whitewater R.	26	100%	.9	6/12	.18	36	97%	.66	8/17	.245
	Bevens Creek	11	91%	.13	6/13	.08	6	33%	.06	7/10	nd
	Sand Creek	9	89%	.11	6/13	.05	8	63%	.09	6/18	.025
	Bent Creek	22	5%	.025	5/20	nd	17	35%	.09	8/14	nd
	Chaska Creek	18	72%	.16	6/13	.065	18	50%	.09	6/19	.013
Deisopropyl-atrazine	Blue Earth R.	22	41%	.1	multiple	nd	12	0%	not applicable	not applicable	not applicable
	Le Sueur R.	24	21%	.1	multiple	nd	11	0%	not applicable	not applicable	not applicable
	Minn. R. (Jud)	27	19%	.1	multiple	nd	10	0%	not applicable	not applicable	not applicable
	Whitewater R.	26	27%	.29	6/12	nd	36	47%	.27	8/17	nd
	Bevens Creek	11	18%	.1	multiple	nd	6	0%	not applicable	not applicable	not applicable
	Sand Creek	9	11%	.1	5/21	nd	8	13%	.1	9/5	nd
	Bent Creek	22	5%	.025	5/20	nd	17	0%	not applicable	not applicable	not applicable
	Chaska Creek	18	11%	.1	multiple	nd	18	17%	.1	multiple	nd
Clopyralid	Blue Earth R.	11	9%	.20	6/13	nd	5	0%	not applicable	not applicable	nd
	Chaska Creek	16	6%	.32	6/13	nd	18	0%	not applicable	not applicable	not applicable

Calendar Year 2001		Storm Event Samples (concentrations in ug/L; nd = non detect)					Base Flow Samples (concentrations in ug/L; nd = non detect)				
Pesticide	**Monitoring Station**	**No. of samples**	**% Detection**	**Max. Concentration**	**Date of Max.**	**Median Concentration**	**No. of samples**	**% Detection**	**Max. Concentration**	**Date of Max.**	**Median Concentration**
Cyanazine	Chaska Creek	18	28%	2.1	4/22	nd	18	11%	.10	multiple	nd
Diazinon	Bent Creek	22	9%	.32	9/7	nd	17	0%	not applicable	not applicable	not applicable
Dicamba	Blue Earth R.	11	55%	1.07	6/16	.10	5	0%	not applicable	not applicable	not applicable
	Le Sueur R.	14	43%	1.27	6/15	nd	5	0%	not applicable	not applicable	not applicable
	Minn. R. (Jud)	10	50%	.61	6/25	.05	4	0%	not applicable	not applicable	not applicable
	Whitewater R.	4	75%	1.27	6/12	.325	20	5%	.10	6/19	nd
	Bent Creek	21	29%	.80	8/29	nd	16	31%	.10	multiple	nd
	Chaska Creek	16	19%	.10	multiple	nd	18	6%	.10	10/31	nd
Dimethenamid	Blue Earth R.	22	64%	.89	5/24	.055	12	17%	.06	7/11	nd
	Le Sueur R.	24	88%	2.1	5/23	.175	11	18%	.30	3/27	nd
	Minn. R. (Jud)	27	70%	.38	6/20	.03	10	0%	not applicable	not applicable	not applicable
	Whitewater R.	26	12%	.44	multiple	nd	36	8%	.25	6/15	nd
	Sand Creek	9	33%	.32	5/21	nd	8	13%	.1	5/25	nd
	Chaska Creek	18	0%	not applicable	not applicable	not applicable	18	6%	.025	6/19	nd
MCPA	Bent Creek	21	14%	.59	8/29	nd	16	13%	.38	8/30	nd
MCPP	Bent Creek	21	62%	3.55	8/29	.10	16	44%	.47	8/30	nd
	Chaska Creek	16	13%	.10	multiple	nd	18	17%	.78	10/23	nd
Metolachlor	Blue Earth R.	22	100%	2.52	4/1	.47	12	92%	2.0	3/27	.07
	Le Sueur R.	24	100%	1.44	5/23	.53	11	91%	.26	3/27	.035
	Minn. R. (Jud)	27	100%	3.36	4/11	.44	10	50%	1.44	3/27	.018
	Whitewater R.	26	88%	.69	6/14	.07	36	44%	.37	6/15	nd
	Bevens Creek	11	73%	.27	5/20	.035	6	17%	.035	11/15	nd
	Sand Creek	9	78%	.67	5/21	.035	8	38%	.15	5/25	nd
	Chaska Creek	18	11%	.035	multiple	nd	18	0%	not applicable	not applicable	not applicable
Metribuzin	Blue Earth R.	22	14%	.14	6/16	nd	12	0%	not applicable	not applicable	not applicable
2,4-D	Blue Earth R.	11	27%	.10	multiple	nd	5	0%	not applicable	not applicable	not applicable
	Le Sueur R.	14	43%	.97	6/15	nd	5	20%	.10	10/16	nd
	Minn. R. (Jud)	10	50%	.22	multiple	.05	4	0%	not applicable	not applicable	not applicable
	Whitewater R.	4	0%	not applicable	not applicable	not applicable	20	10%	.34	6/13	nd
	Sand Creek	5	0%	not applicable	not applicable	not applicable	7	14%	.1	6/18	nd
	Bent Creek	21	90%	4.65	8/29	.27	16	63%	1.7	6/19	.155
	Chaska Creek	16	25%	.26	multiple	nd	18	11%	.88	10/23	nd

Propachlor detected in one 2001 storm flow event in Blue Earth R. at 0.04 ug/L

Table 21 – Pesticide and pesticide degradate detections in storm and base flow events in MDA surface water monitoring stations, partial calendar year 2002

Partial Calendar Year 2002		Storm Event Samples (concentrations in ug/L; nd = non detect))					Base Flow Samples (concentrations in ug/L; nd = non detect)				
Pesticide	Monitoring Station	No. of samples	% Detection	Max. Concentration	Date of Max.	Median Concentration	No. of samples	% Detection	Max. Concentration	Date of Max.	Median Concentration
Acetochlor	Blue Earth R.	12	92%	1.5	6/3	.22	3	33%	.025	7/31	nd
	Le Sueur R.	12	100%	7.1	5/29	.35	5	40%	.06	7/16	.03
	Minn. R. (Jud)	15	80%	1.09	6/6	.11	5	0%	not applicable	not applicable	not applicable
	Whitewater R.	18	72%	9.6	6/13	.855	12	50%	7.5	5/30	.0125
	Bevens Creek	5	80%	1.69	5/8	.61	6	50%	.92	6/5	.01
	Sand Creek	7	86%	.72	6/3	.16	4	75%	.07	3/29	.038
	Bent Creek	4	25%	.11	5/9	nd	5	20%	.05	4/11	nd
	Chaska Creek	7	57%	.17	6/20	.08	7	14%	.07	6/5	nd
Alachlor	Le Sueur R.	12	50%	.13	6/12	.01	5	0%	not applicable	not applicable	not applicable
	Minn. R. (Jud)	15	20%	.05	6/6	nd	5	0%	not applicable	not applicable	not applicable
	Sand Creek	7	29%	.21	6/3	nd	4	0%	not applicable	not applicable	not applicable
Atrazine	Blue Earth R.	12	92%	2.87	6/12	.88	3	33%	.36	7/31	nd
	Le Sueur R.	12	75%	2.97	6/12	1.37	5	60%	.46	7/16	.03
	Minn. R. (Jud)	15	60%	2.24	6/23	.06	5	40%	.45	7/16	.375
	Whitewater R.	18	89%	29.4	6/21	4.25	12	83%	3.7	6/26	.145
	Bevens Creek	5	100%	9.1	6/20	1.11	6	67%	1.53	6/5	.09
	Sand Creek	7	100%	8.0	6/22	0.9	4	50%	.23	7/29	0.125
	Bent Creek	4	100%	0.2	6/21	.145	5	20%	.175	7/17	nd
	Chaska Creek	7	100%	33.2	6/20	.99	7	57%	.73	7/17	0.25
Deethylatrazine	Blue Earth R.	12	75%	.22	6/14	.14	3	33%	.14	7/31	nd
	Le Sueur R.	12	83%	.22	6/24	.13	5	40%	.11	7/16	nd
	Minn. R. (Jud)	15	60%	.26	6/24	.09	5	20%	.07	7/16	nd
	Whitewater R.	18	72%	.91	6/22	.435	12	92%	.77	6/22	.22
	Bevens Creek	5	80%	.35	6/20	.140	6	67%	.14	6/5	.025
	Sand Creek	7	100%	.03	6/22	.13	4	25%	.09	7/29	nd
	Bent Creek	4	75%	.12	6/21	.065	5	20%	.025	7/17	nd
	Chaska Creek	7	100%	.75	6/20	.11	7	43%	.1	7/17	nd
Deisopropyl-atrazine	Blue Earth R.	12	50%	.1	multiple	.05	3	0%	not applicable	not applicable	not applicable
	Le Sueur R.	12	25%	.1	multiple	Nd	5	0%	not applicable	not applicable	not applicable
	Minn. R. (Jud)	15	47%	.23	6/24	nd	5	0%	not applicable	not applicable	not applicable
	Whitewater R.	18	33%	.53	6/21	nd	12	58%	.48	6/26	.1
	Bevens Creek	5	20%	.1	6/22	nd	6	0%	not applicable	not applicable	not applicable
	Sand Creek	7	14%	.21	6/22	nd	4	0%	not applicable	not applicable	not applicable
	Chaska Creek	7	29%	.74	6/20	nd	7	0%	not applicable	not applicable	not applicable
Clopyralid	Bent Creek	4	25%	.20	6/21	nd	5	0%	not applicable	not applicable	not applicable
	Blue Earth	9	56%	.22	6/14	nd	1	0%	not applicable	not applicable	not applicable
	Chaska Creek	7	71%	1.31	6/25	.10	7	43%	.38	7/17	nd
	Le Sueur	9	56%	<.20	multiple	nd	2	0%	not applicable	not applicable	not applicable

Partial Calendar Year 2002		Storm Event Samples (concentrations in ug/L; nd = non detect)					Base Flow Samples (concentrations in ug/L; nd = non detect)				
Pesticide	**Monitoring Station**	**No. of samples**	**% Detection**	**Max. Concentration**	**Date of Max.**	**Median Concentration**	**No. of samples**	**% Detection**	**Max. Concentration**	**Date of Max.**	**Median Concentration**
Cyanazine	Minn. R. (Jud)	15	7%	.60	6/6	nd	5	0%	not applicable	not applicable	not applicable
	Bevens Creek	5	20%	.41	6/20	nd	6	17%	.38	6/5	nd
	Chaska Creek	7	14%	.27	6/25	nd	7	0%	not applicable	not applicable	not applicable
Dicamba	Blue Earth R.	9	78%	.52	6/12	.10	1	0%	not applicable	not applicable	not applicable
	Le Sueur R.	9	89%	1.35	5/29	.31	2	0%	not applicable	not applicable	not applicable
	Minn. R. (Jud)	7	100%	.70	6/3	.26	2	100%	.10	multiple	.10
	Whitewater R.	12	100%	.81	6/11	.265	8	63%	.72	6/26	.10
	Bevens Creek	3	67%	.26	6/20	.21	4	25%	.21	6/5	nd
	Sand Creek	3	100%	.26	6/3	.10	2	50%	.29	7/29	.145
	Bent Creek	4	75%	.25	6/21	.10	5	40%	.10	multiple	nd
	Chaska Creek	7	86%	.29	6/20	.10	7	14%	.10	6/5	nd
Dimethenamid	Blue Earth R.	12	83%	.25	6/3	.09	3	0%	not applicable	not applicable	not applicable
	Le Sueur R.	12	83%	1.8	5/29	.17	5	40%	.05	7/16	nd
	Minn. R. (Jud)	15	93%	.44	6/6	.08	5	40%	.025	Multiple	.053
	Whitewater R.	18	61%	1.48	6/26	.07	12	25%	2.52	6/26	nd
	Sand Creek	7	14%	.09	6/6	nd	4	0%	not applicable	not applicable	not applicable
	Chaska Creek	7	14%	.13	6/25	nd	7	14%	.05	6/5	nd
MCPA	Bent Creek	4	25%	.29	5/9	nd	5	0%	not applicable	not applicable	not applicable
	Chaska Creek	7	14%	.34	5/9	nd	7	0%	not applicable	not applicable	not applicable
MCPP	Bent Creek	4	75%	.31	5/9	.155	5	60%	.10	Multiple	.10
	Chaska Creek	7	14%	.10	5/9	nd	7	0%	not applicable	not applicable	not applicable
Metolachlor	Blue Earth R.	12	92%	.52	6/12	.14	3	66%	not applicable	not applicable	not applicable
	Le Sueur R.	12	100%	.65	5/29	.19	5	100%	.28	2/27	.04
	Minn. R. (Jud)	15	100%	.65	6/16	.17	5	0%	.42	6/3	.035
	Whitewater R.	18	72%	4.3	6/3	1.285	12	42%	3.84	6/26	nd
	Bevens Creek	5	80%	.47	6/20	.32	6	17%	.47	6/5	nd
	Sand Creek	7	100%	.5	6/3	.27	4	75%	.24	3/29	.035
	Bent Creek	4	0%	not applicable	not applicable	not applicable	5	20%	.014	5/21	nd
	Chaska Creek	7	43%	.16	6/25	nd	7	43%	.08	5/21	nd
Metribuzin	Chaska Creek	7	14%	.11	6/25	nd	7	0%	not applicable	not applicable	not applicable

Partial Calendar Year 2002		Storm Event Samples (concentrations in ug/L; nd = non detect)					Base Flow Samples (concentrations in ug/L; nd = non detect)				
Pesticide	**Monitoring Station**	**No. of samples**	**% Detection**	**Max. Concentration**	**Date of Max.**	**Median Concentration**	**No, of samples**	**% Detection**	**Max. Concentration**	**Date of Max.**	**Median Concentration**
Pendimethalin	Bent Creek	4	25%	.15	6/21	nd	5	0%	not applicable	not applicable	not applicable
	Chaska Creek	7	29%	.34	6/20	nd	7	0%	not applicable	not applicable	not applicable
2,4-D	Blue Earth R.	9	100%	.49	6/18	.165	1	0%	not applicable	not applicable	not applicable
	Le Sueur R.	9	100%	1.38	6/28	.24	2	50%	.22	7/16	.11
	Minn. R. (Jud)	7	100%	3.5	6/14	.27	2	50%	.10	6/31	.05
	Whitewater R.	12	58%	.93	6/26	.10	8	25%	.57	6/26	nd
	Bevens Creek	3	67%	1.09	6/22	.10	4	25%	.10	6/5	nd
	Sand Creek	3	100%	.35	7/29	.35	2	50%	.22	7/29	.11
	Bent Creek	4	75%	.74	6/25	.485	5	80%	.50	3/27	.32
	Chaska Creek	7	100%	.36	6/20	.20	7	0%	not applicable	not applicable	not applicable

Figure 35 – Average Daily Discharges for Bevens Creek, January 2001 through July 2002

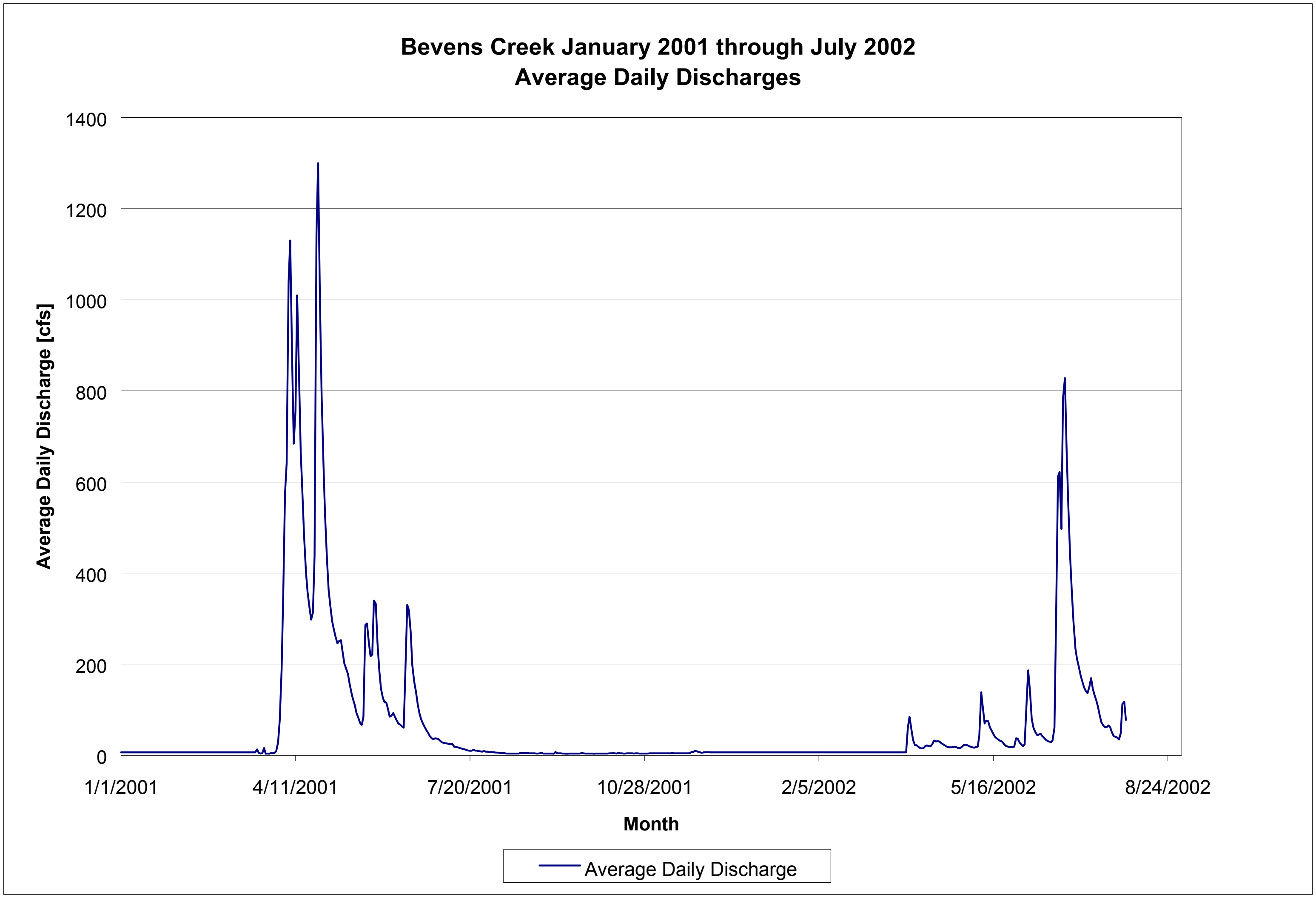


Figure 36 – Acetochlor concentrations for Bevens Creek, January 2001 through July 2002

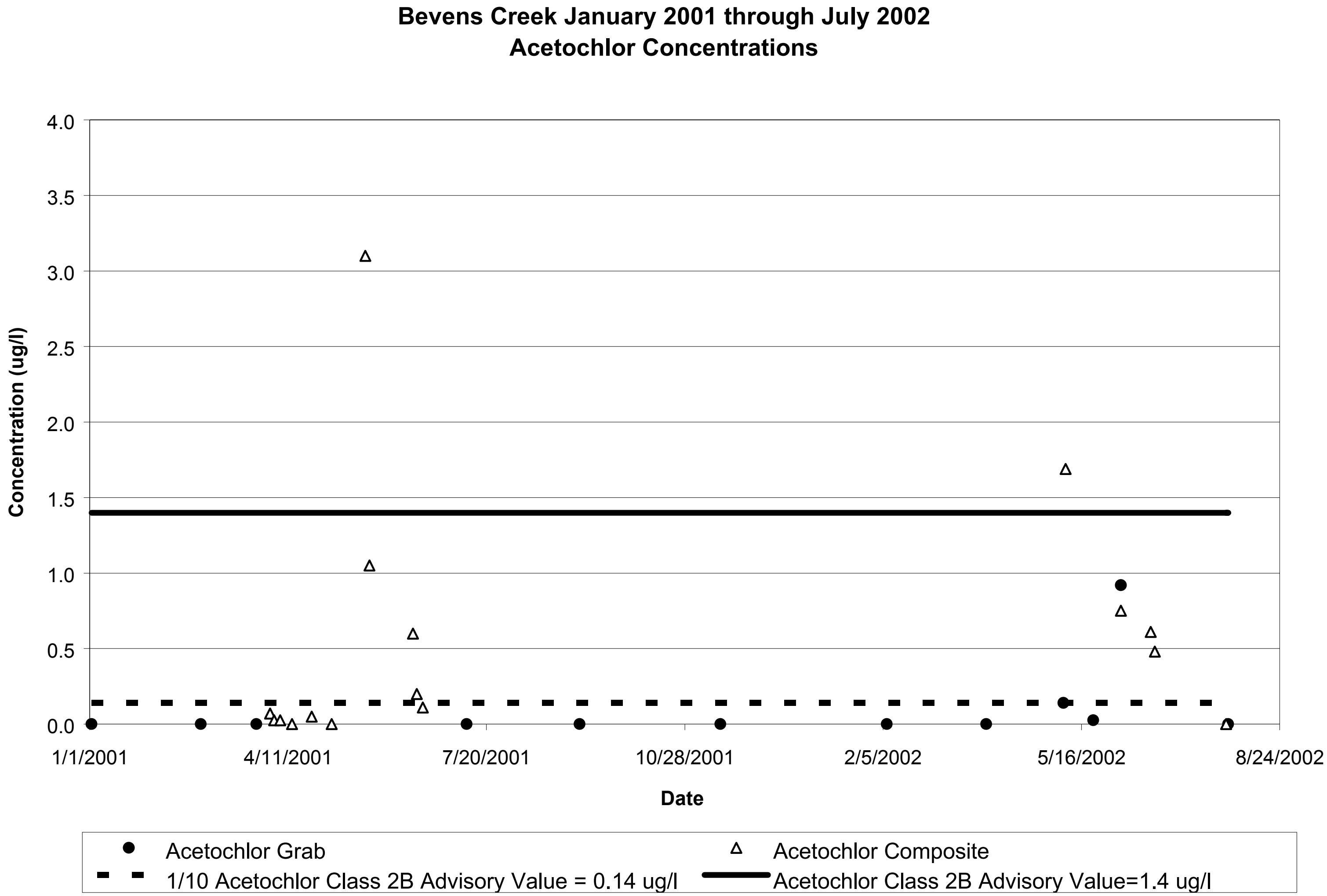


Figure 37 – Atrazine concentrations for Bevens Creek, January 2001 through July 2002

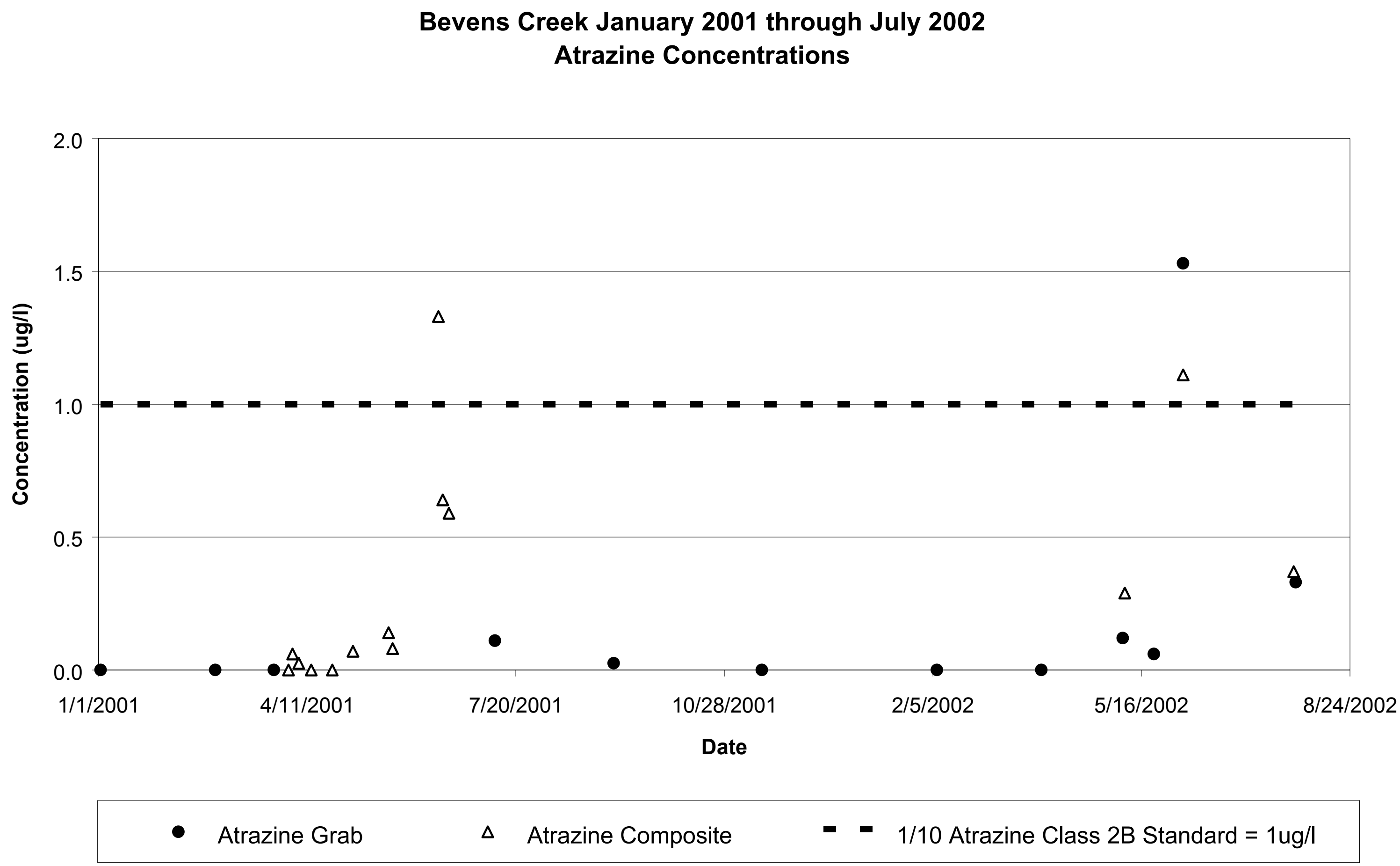


Figure 38 – Average Daily Discharges for Blue Earth River at Rapidan, January 2001 through July 2002

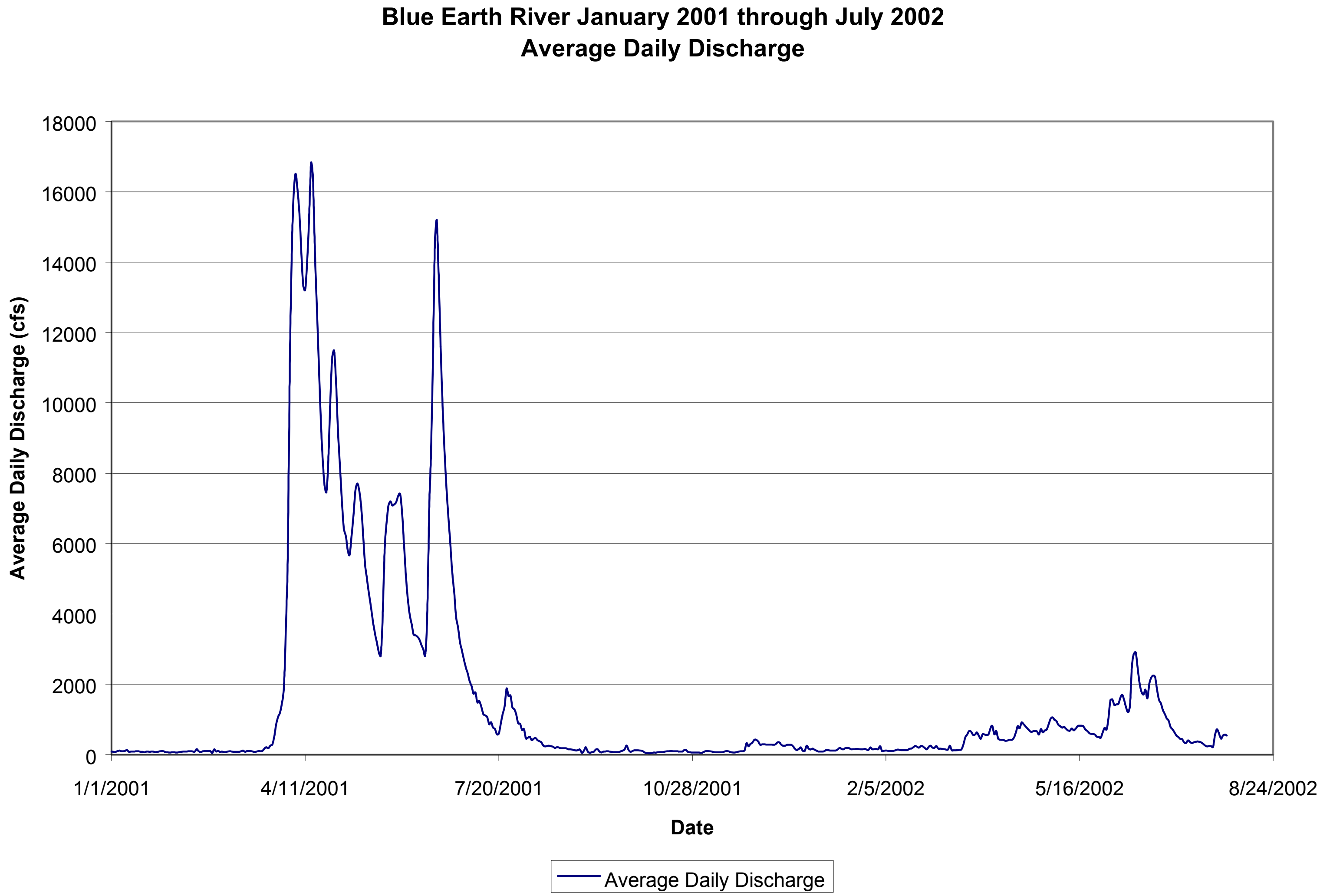


Figure 39 – Acetochlor concentrations for Blue Earth River at Rapidan, January 2001 through July 2002

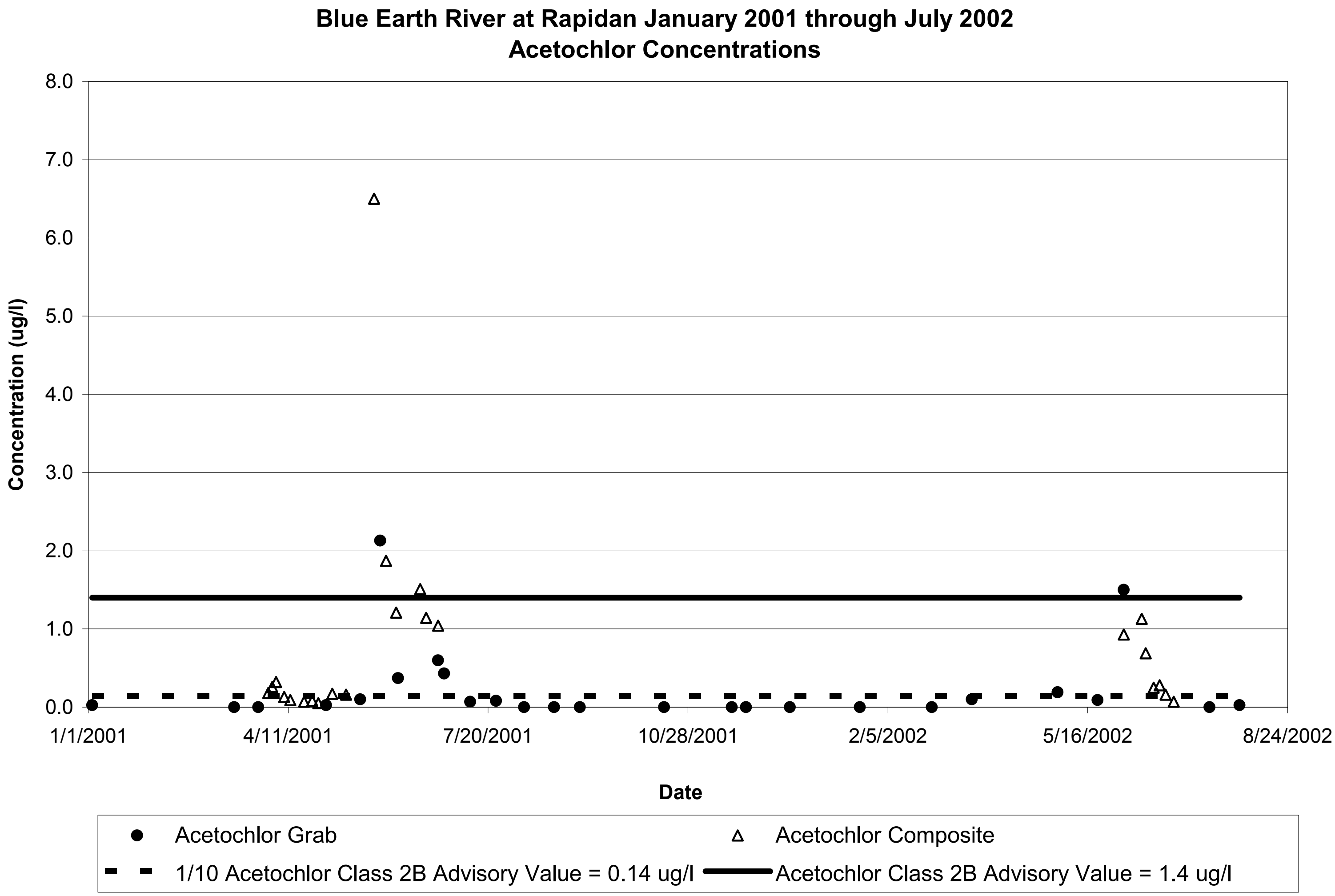


Figure 40 – Atrazine concentrations for Blue Earth River at Rapidan, January 2001 through July 2002

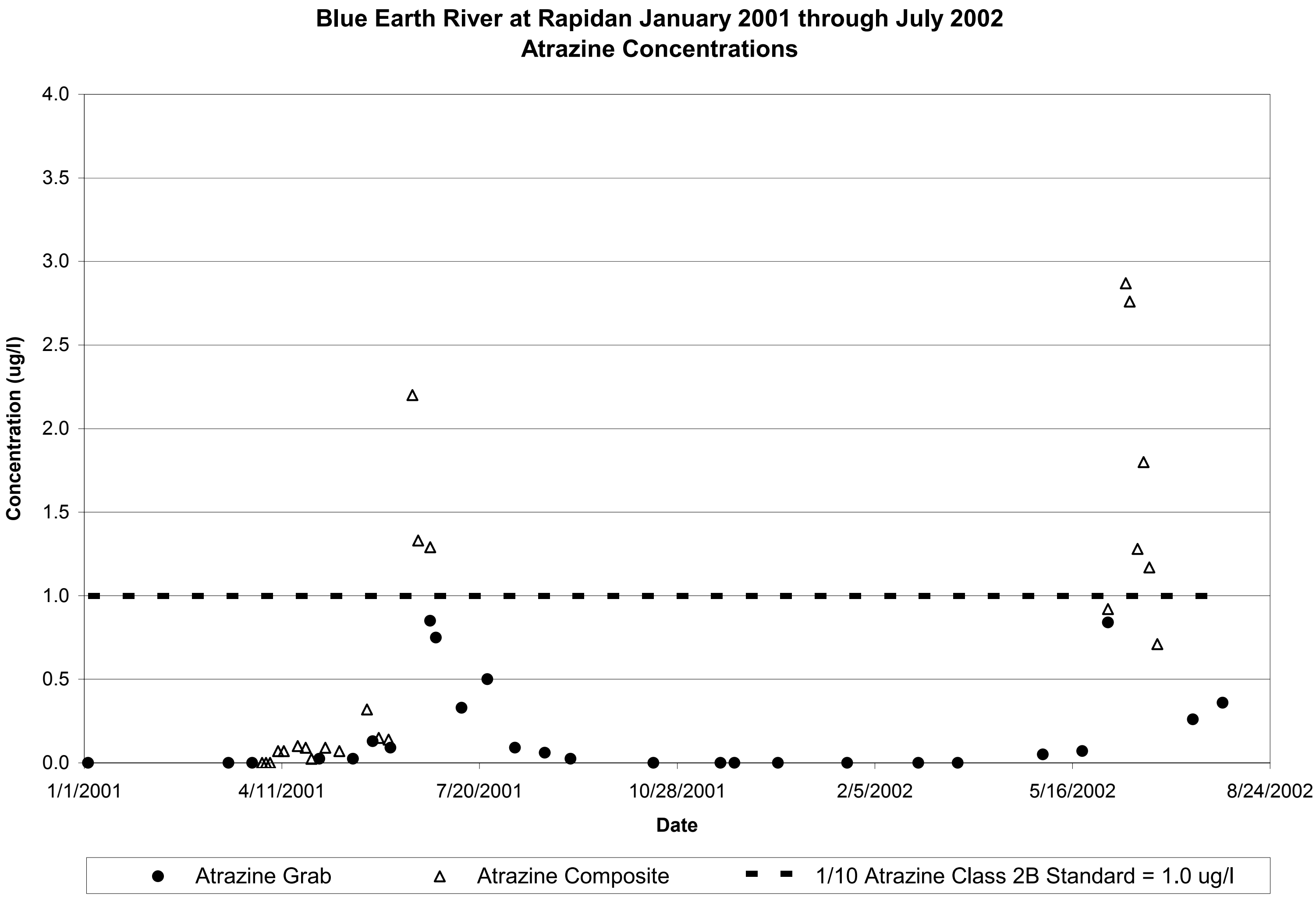


Figure 41 – Metolachlor concentrations for Blue Earth River at Rapidan, January 2001 through July 2002

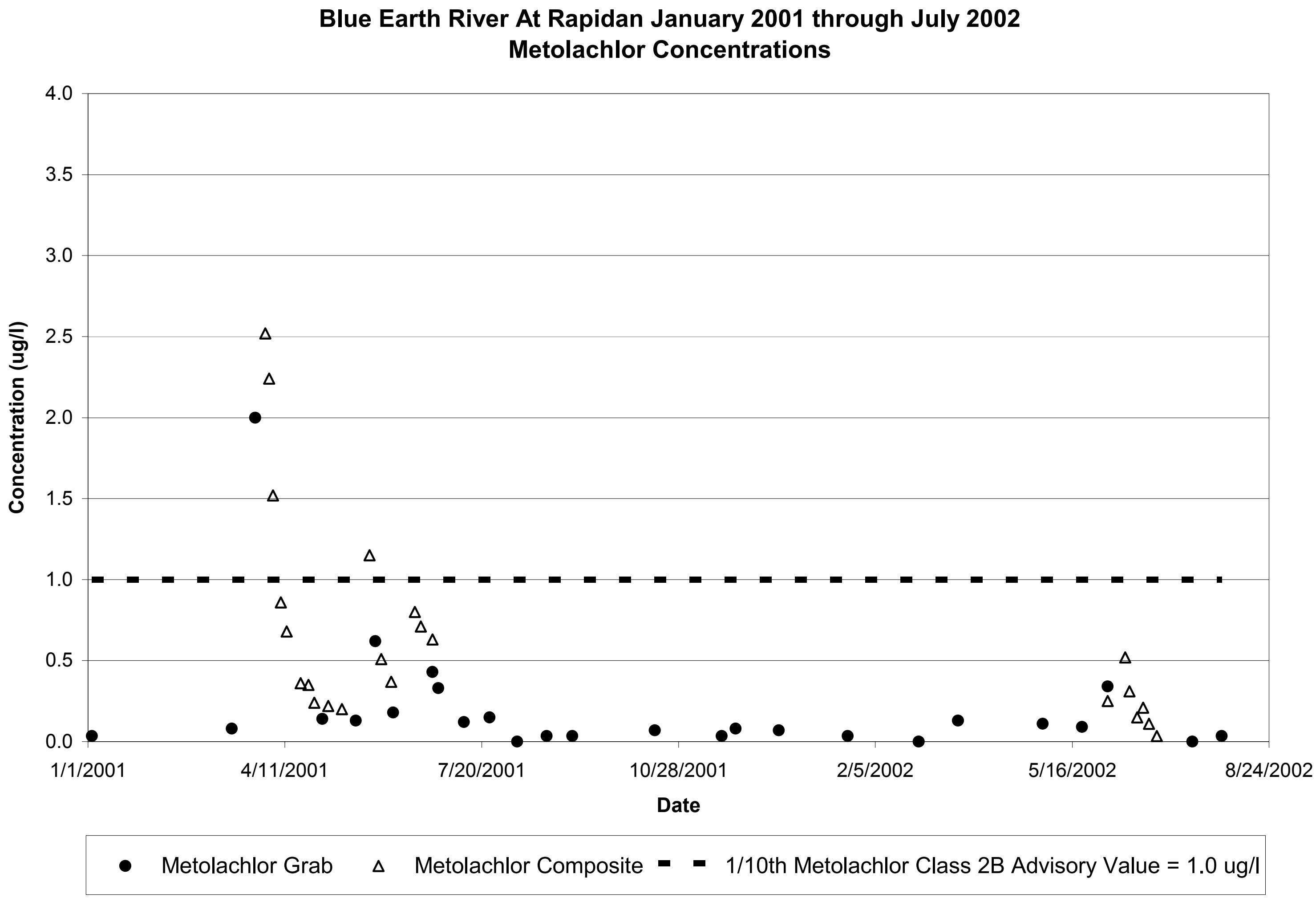


Figure 42 – Average Daily Discharges for Chaska Creek, January 2001 through July 2002

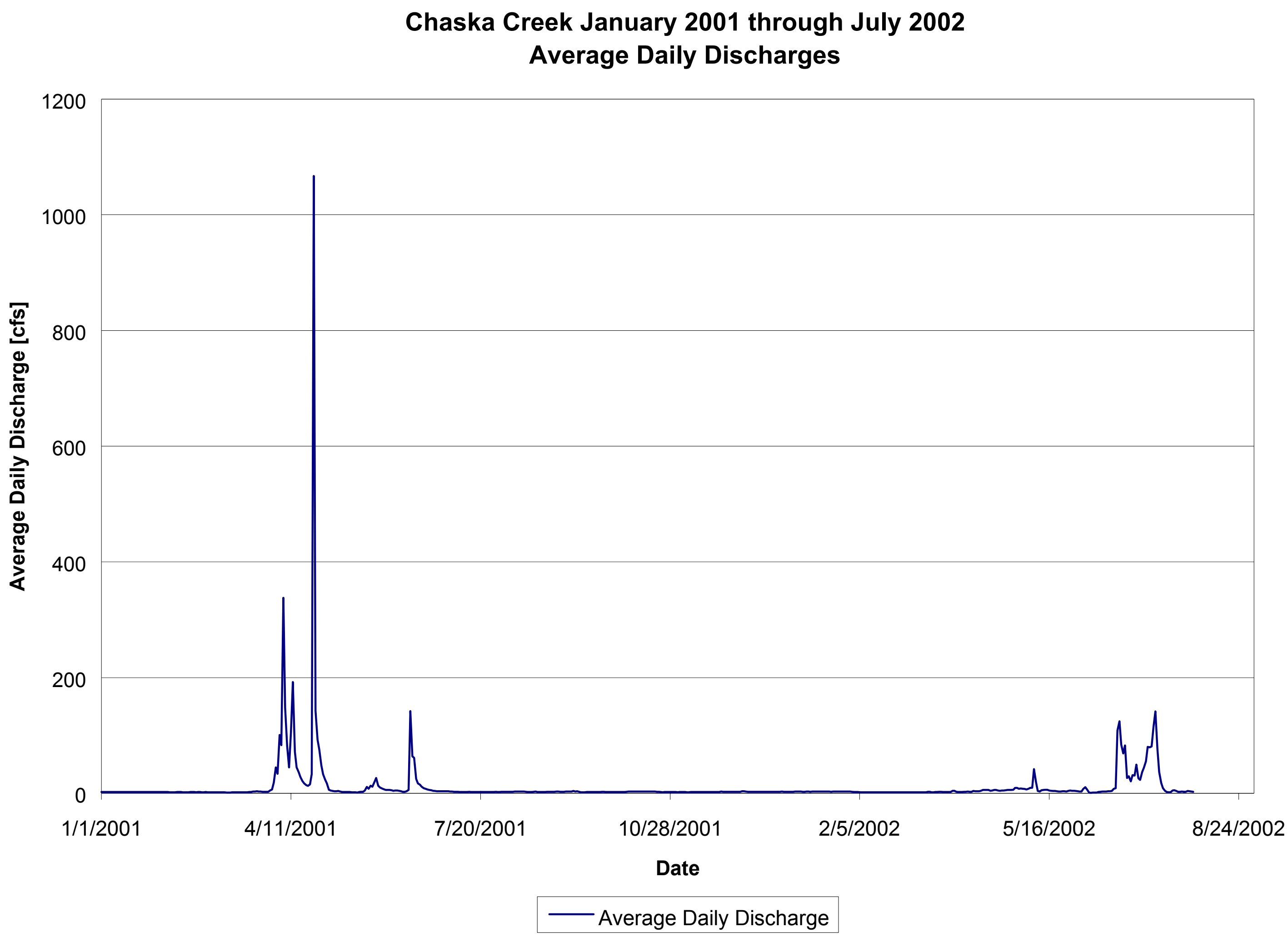


Figure 43 – Acetochlor concentrations for Chaska Creek, January 2001 through July 2002

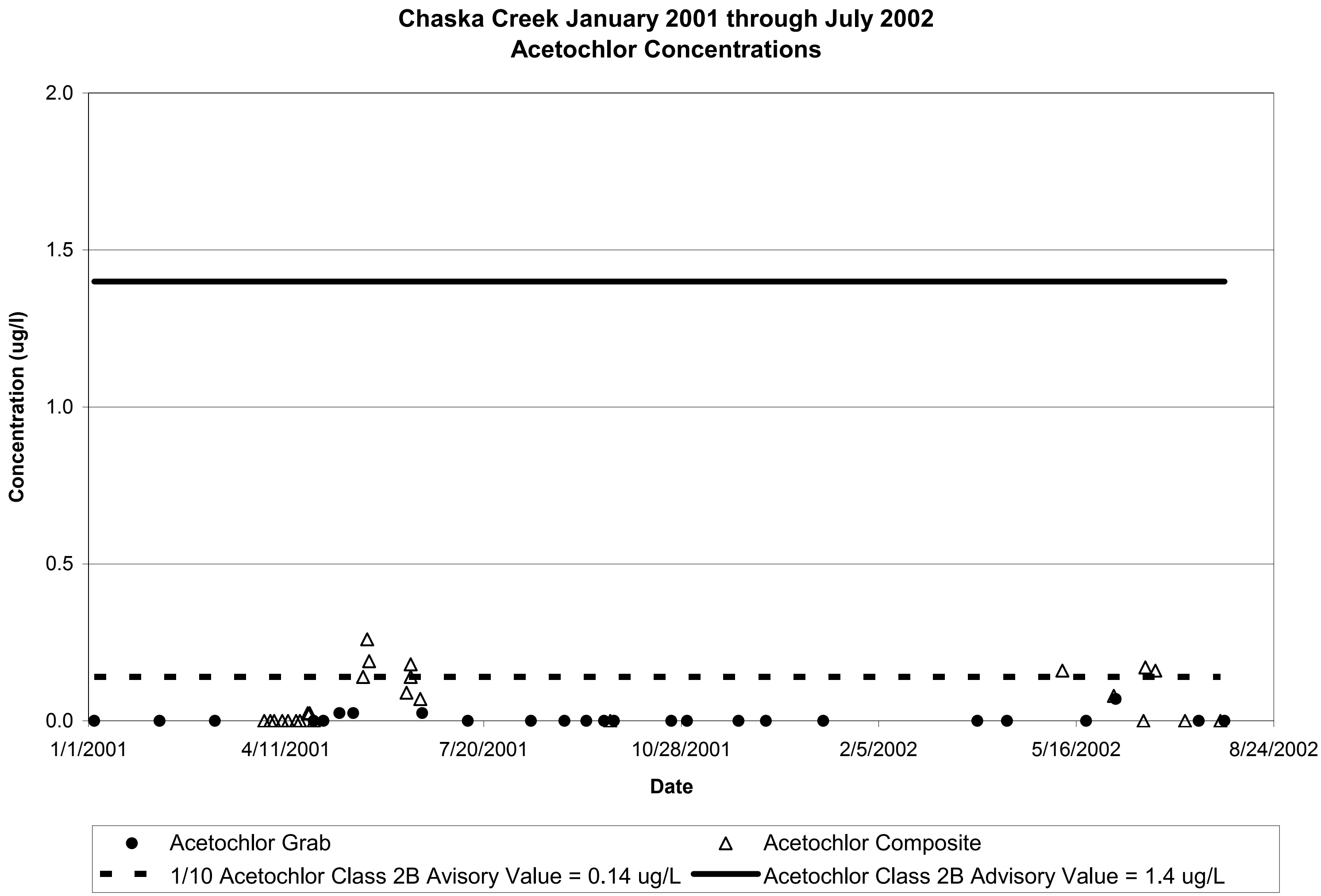


Figure 44 – Atrazine concentrations for Chaska Creek, January 2001 through July 2002

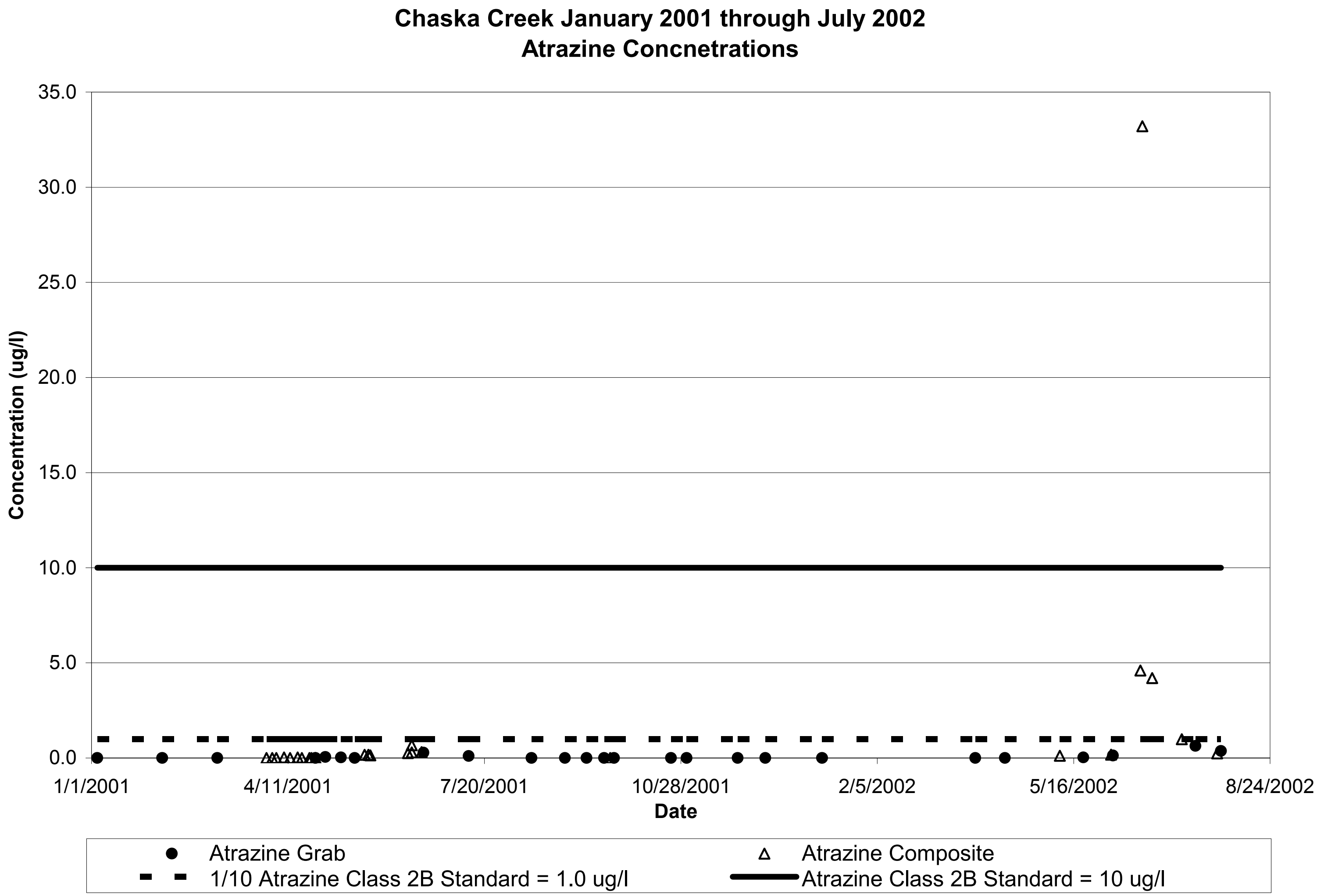


Figure 45 – Average Daily Discharges for Minnesota River at Judson, January 2001 through July 2002

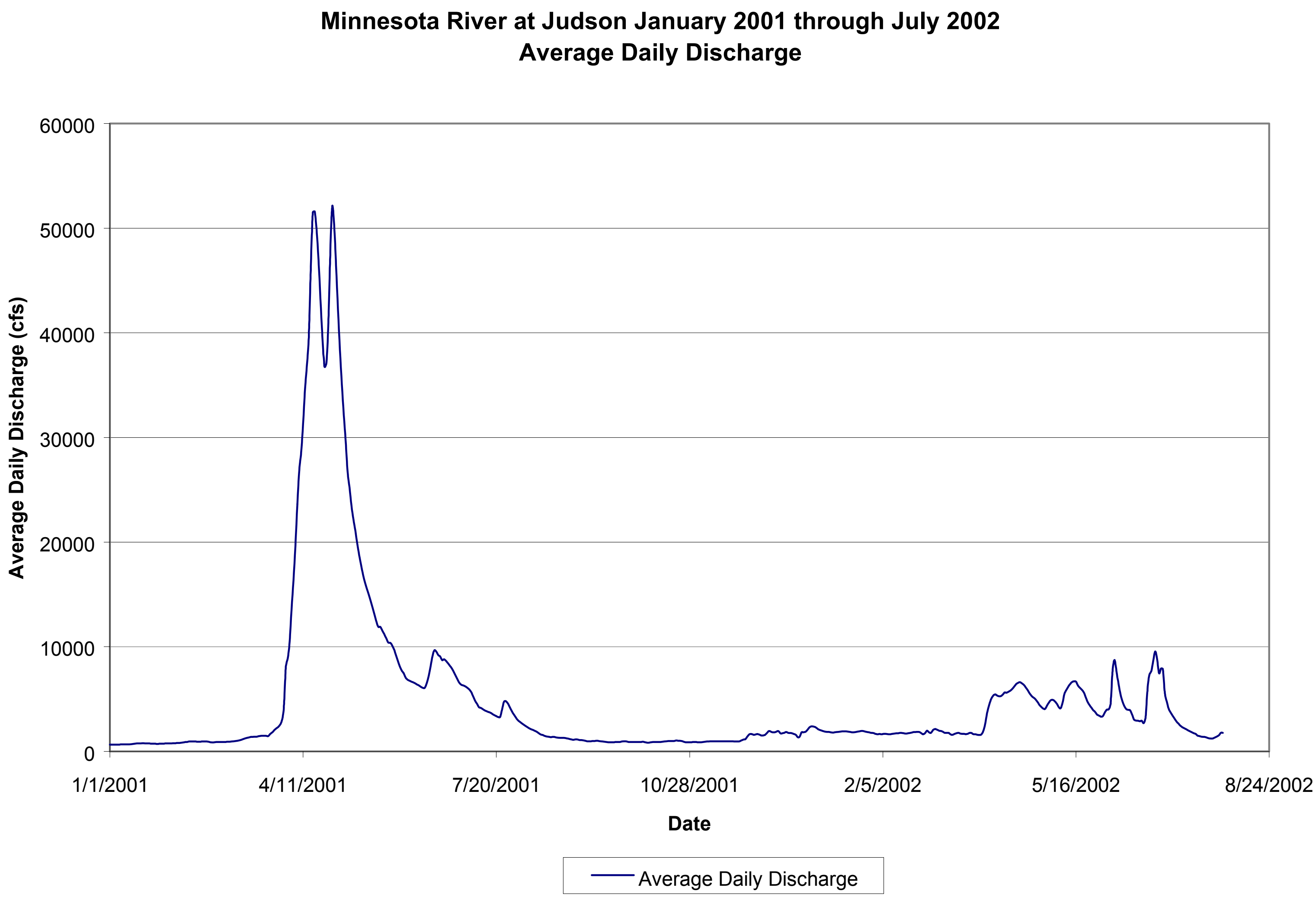


Figure 46 – Acetochlor concentrations for Minnesota River at Judson, January 2001 through July 2002

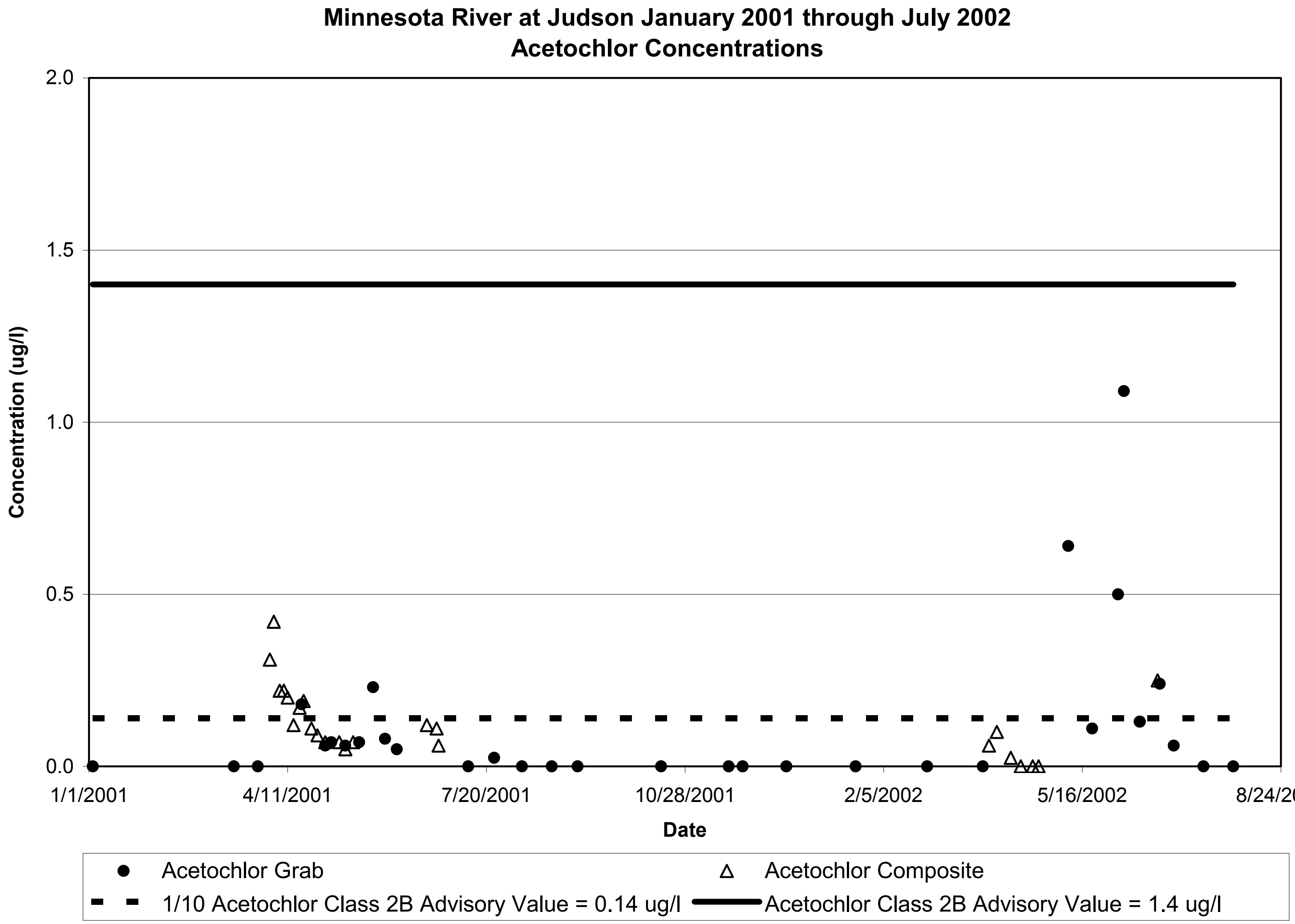


Figure 47 – Atrazine concentrations for Minnesota River at Judson, January 2001 through July 2002

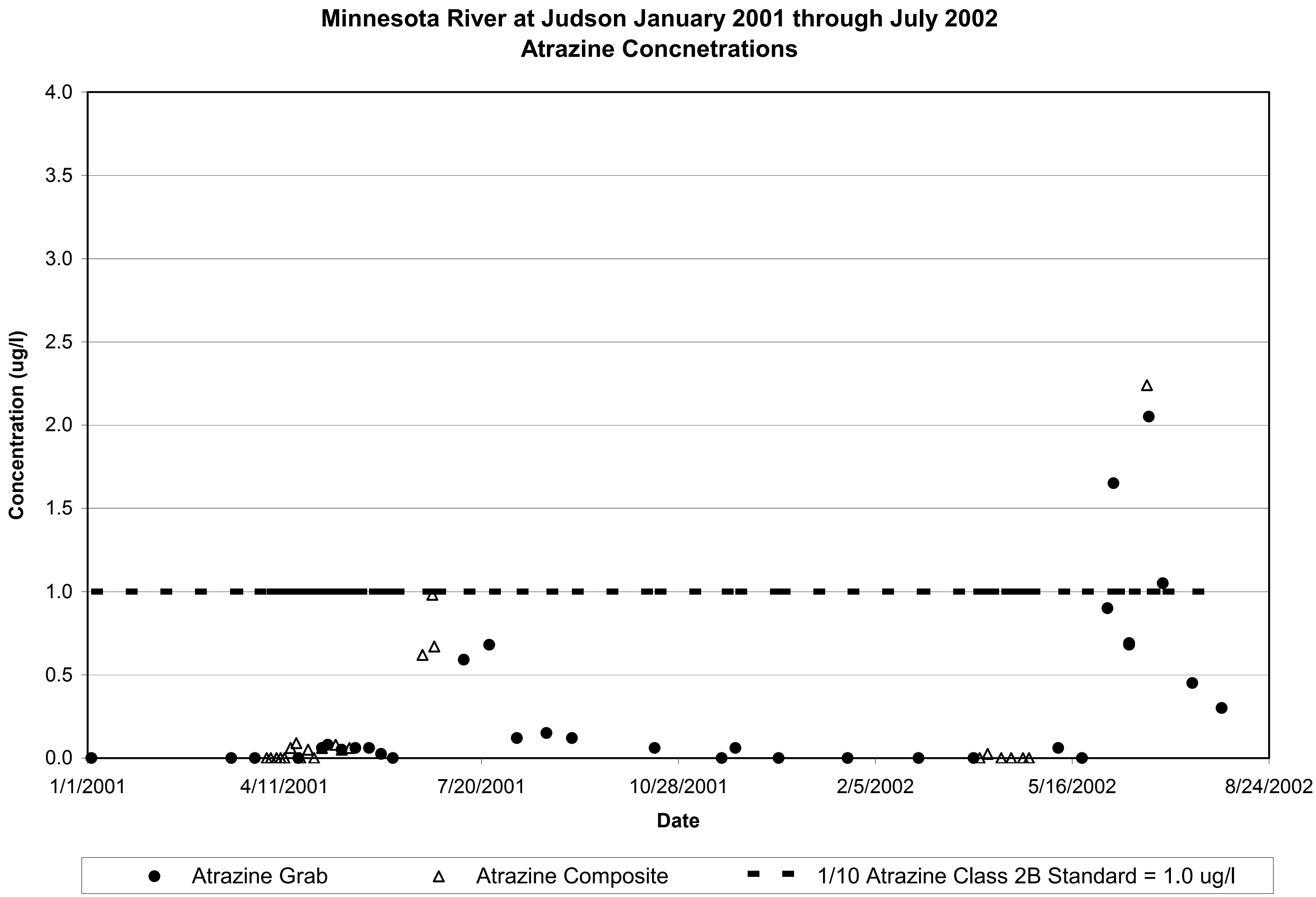


Figure 48 – Metolachlor concentrations for Minnesota River at Judson, January 2001 through July 2002

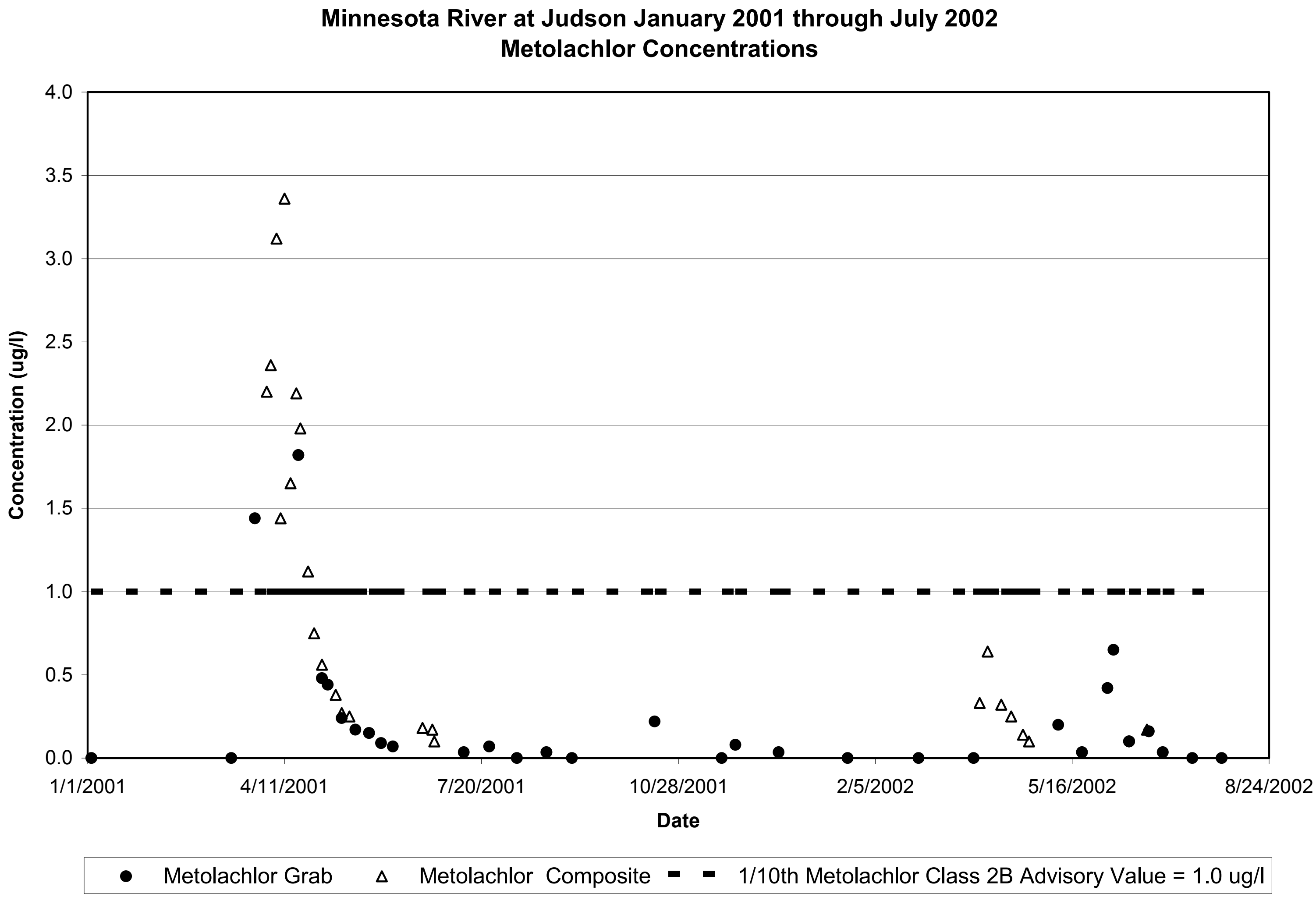


Figure 49 – Average Daily Discharges for Le Sueur, January 2001 through July 2002

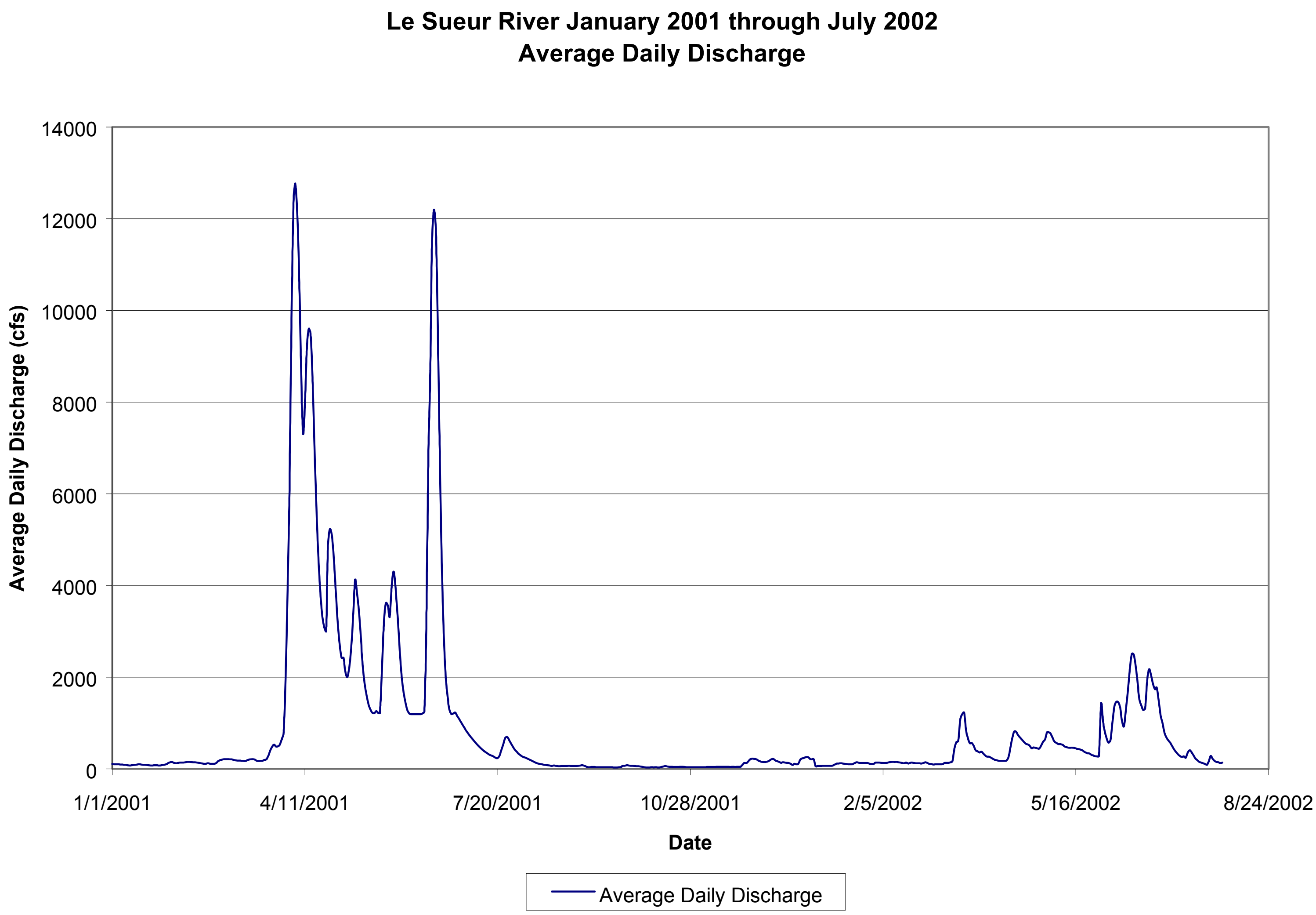


Figure 50 – Acetochlor concentrations for Le Sueur River, January 2001 through July 2002

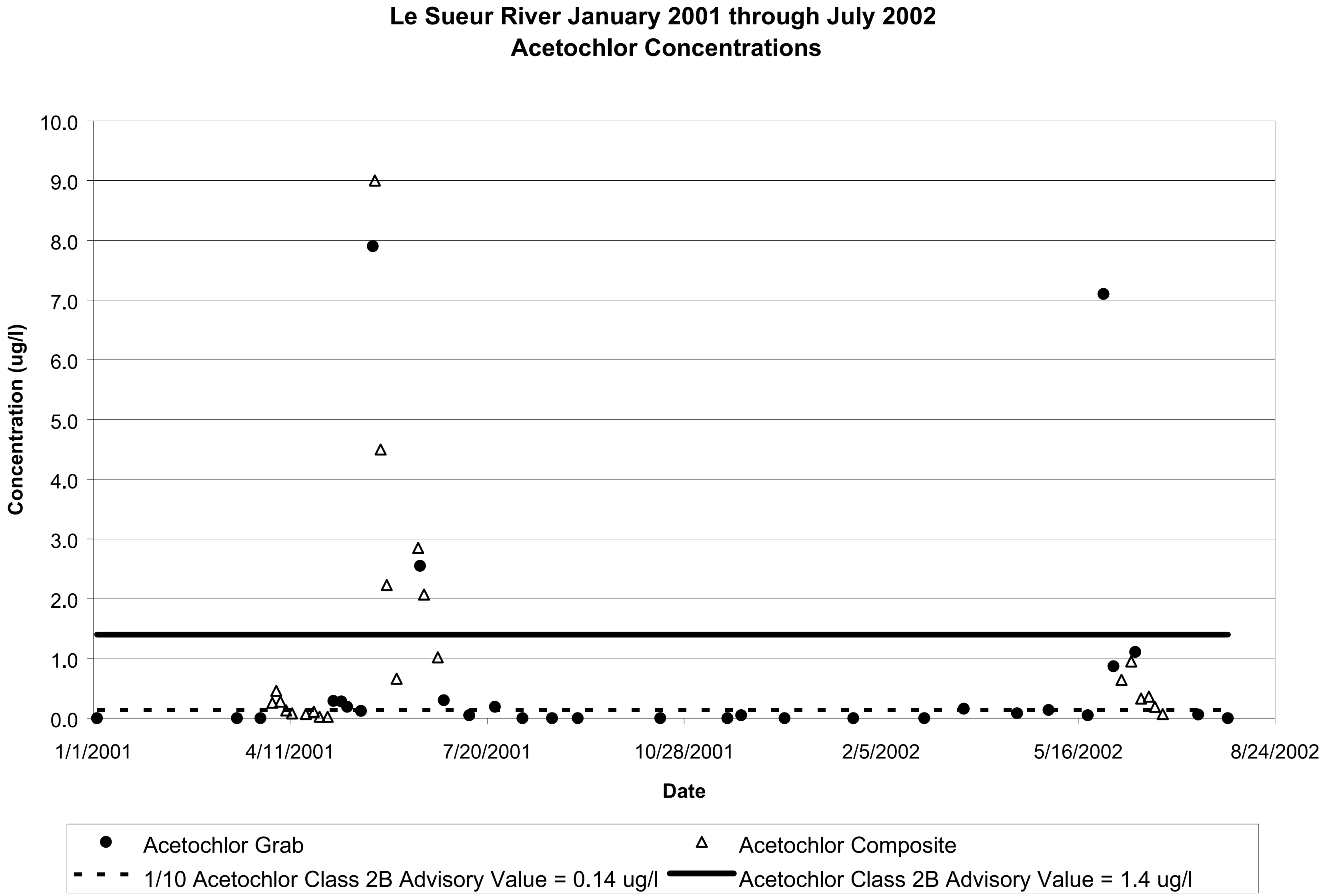


Figure 51 – Atrazine concentrations for Le Sueur River, January 2001 through July 2002

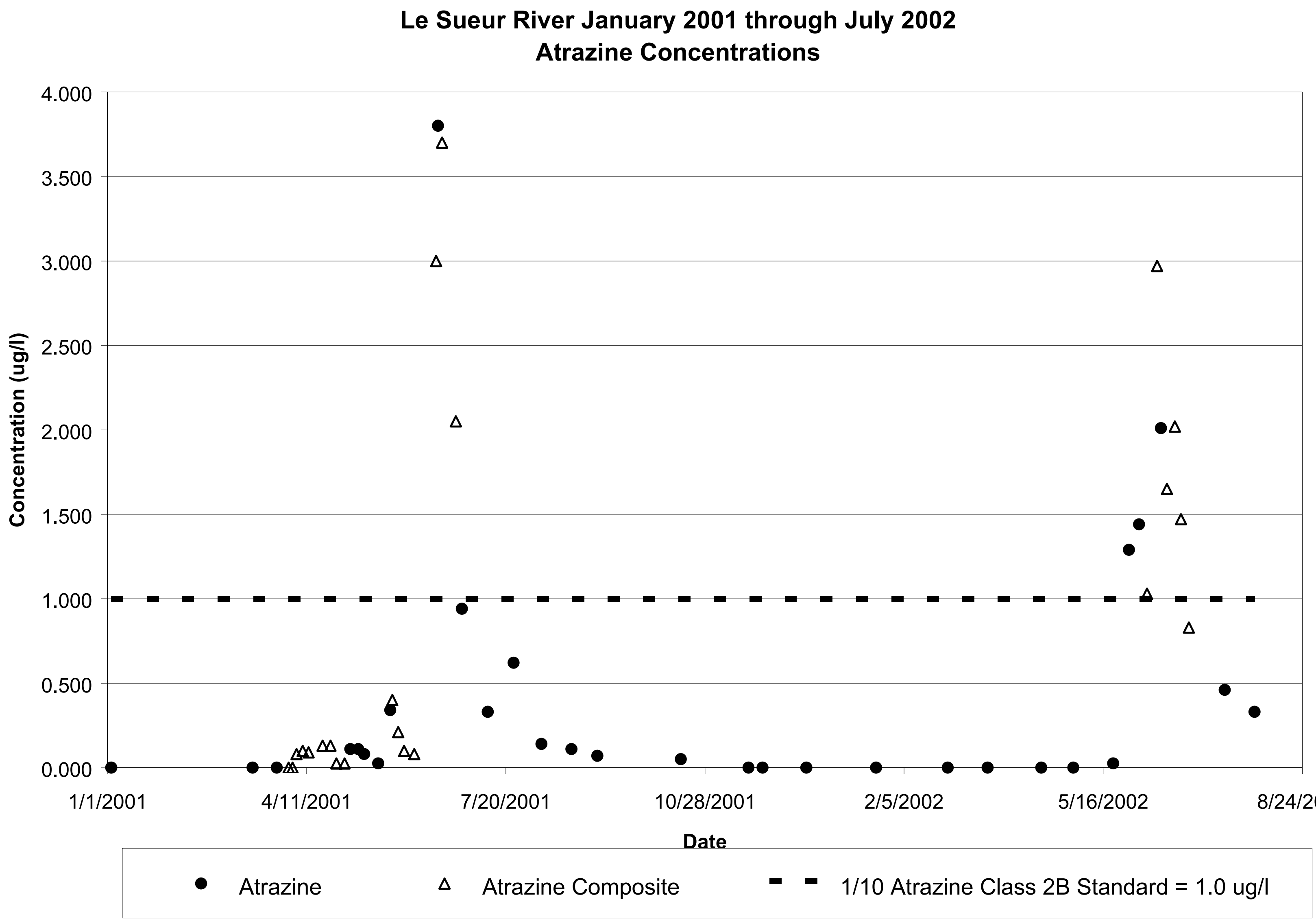


Figure 52 – Metolachlor concentrations for Le Sueur River, January 2001 through July 2002

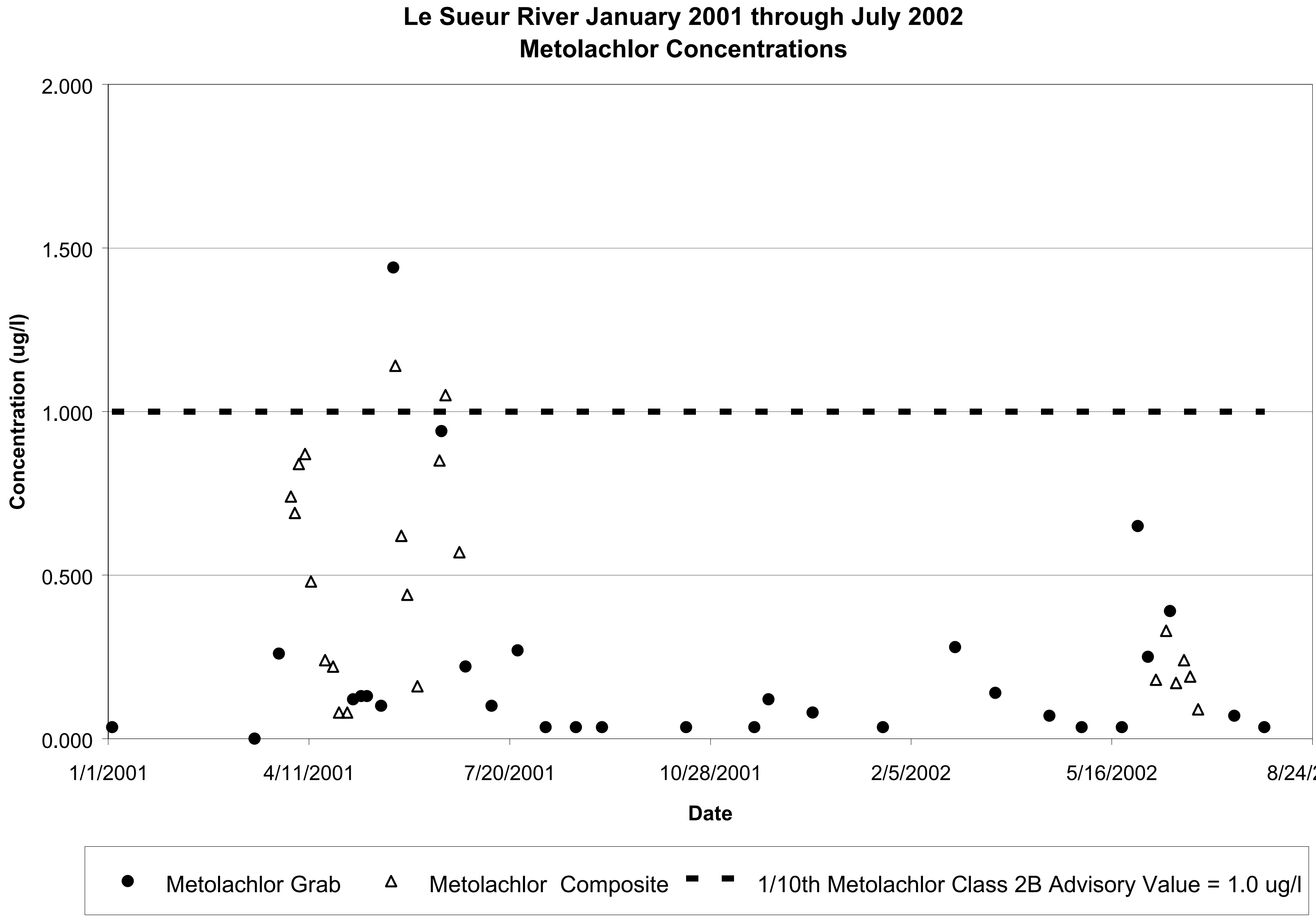


Figure 53 – Average Daily Discharges for Sand Creek, January 2001 through July 2002

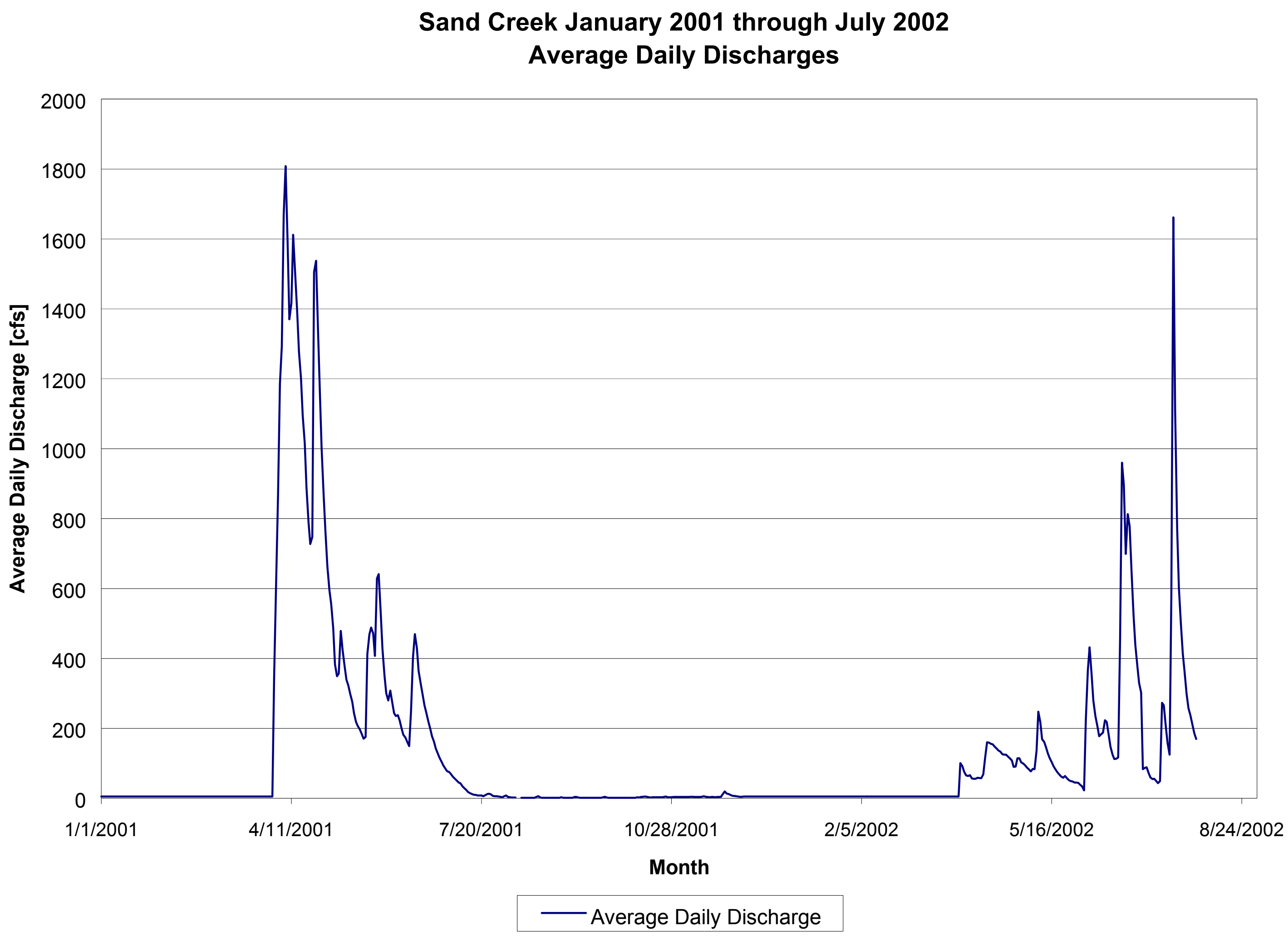


Figure 54 – Acetochlor concentrations for Sand Creek, January 2001 through July 2002

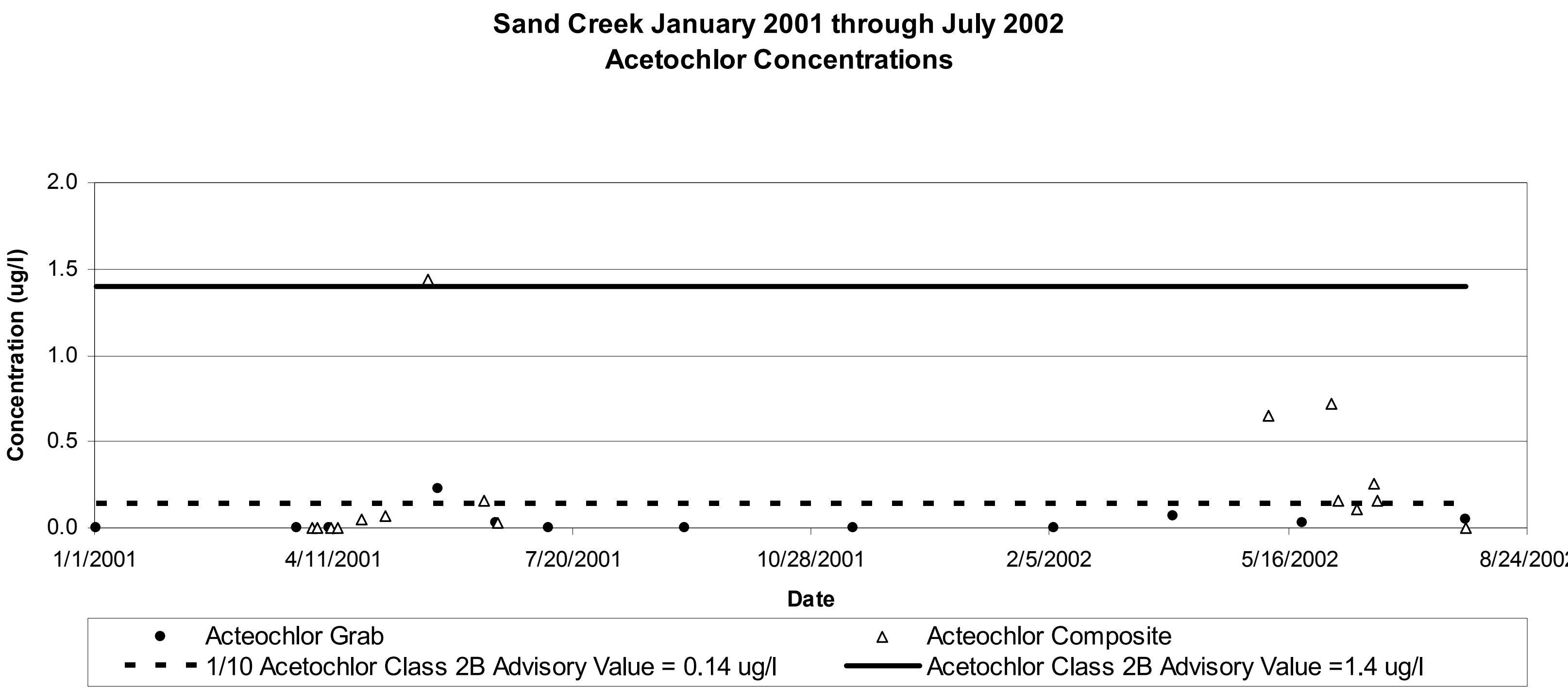


Figure 55 – Atrazine concentrations for Sand Creek, January 2001 through July 2002

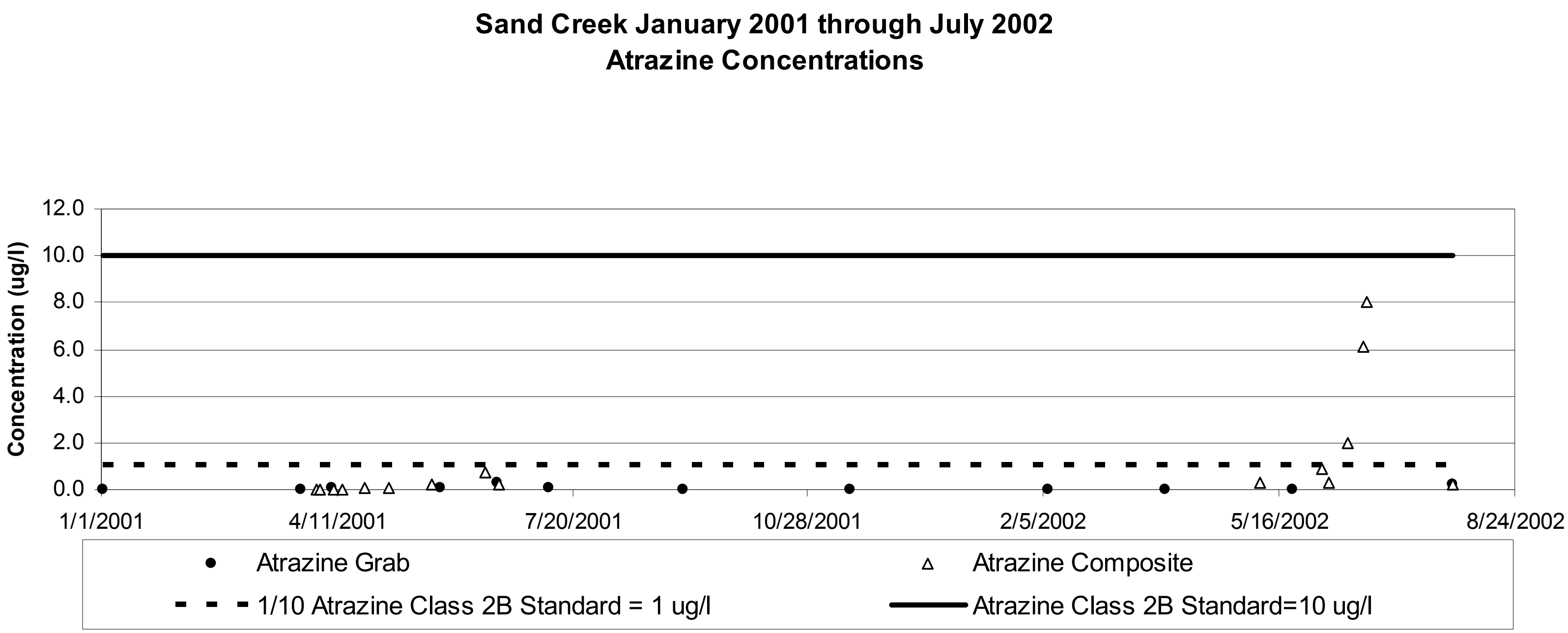


Figure 56 – Average Daily Discharges for Whitewater River-Middle Branch, January 2001 through July 2002

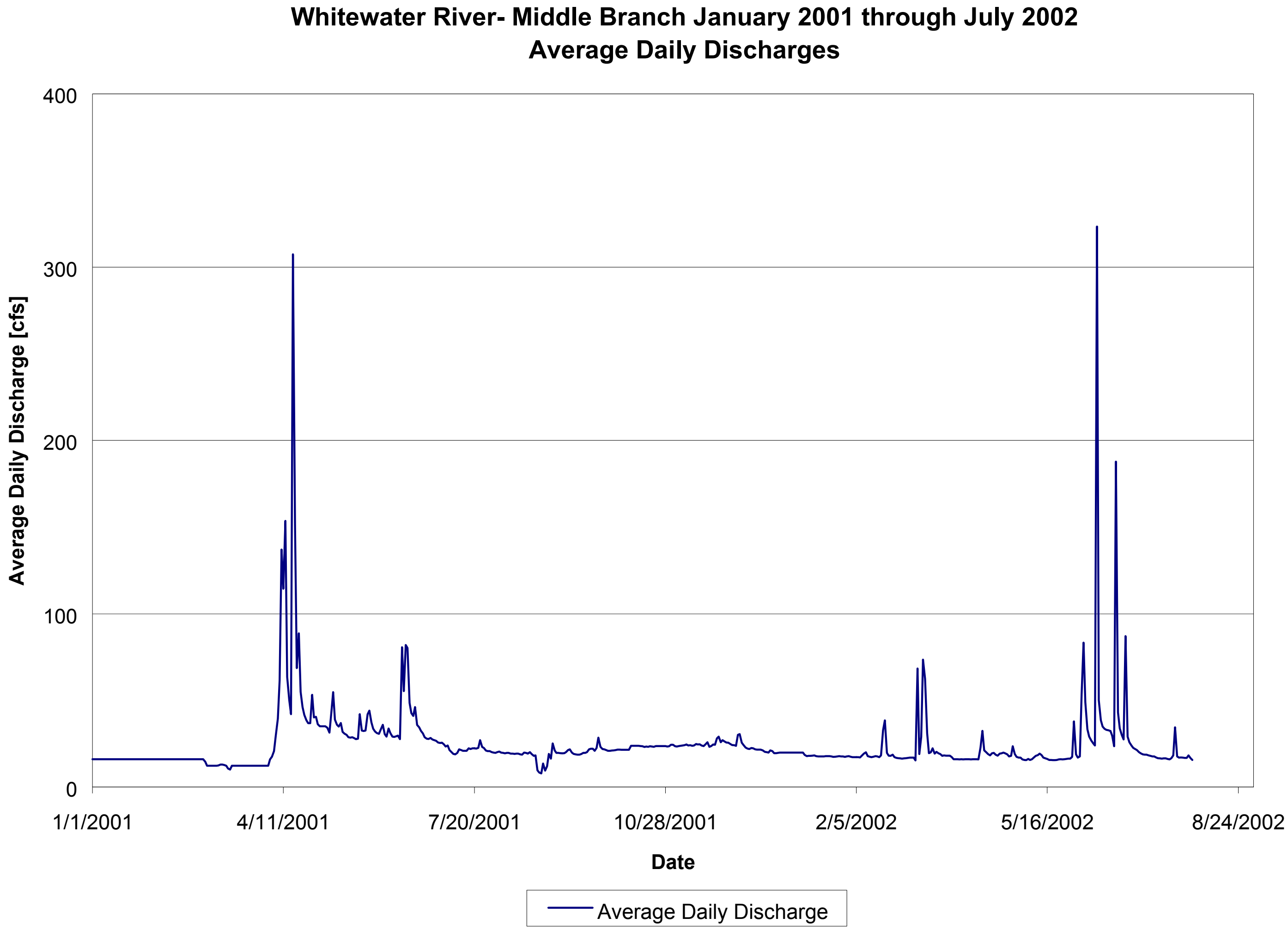


Figure 57 – Acetochlor concentrations for Whitewater River-Middle Branch, January 2001 through July 2002

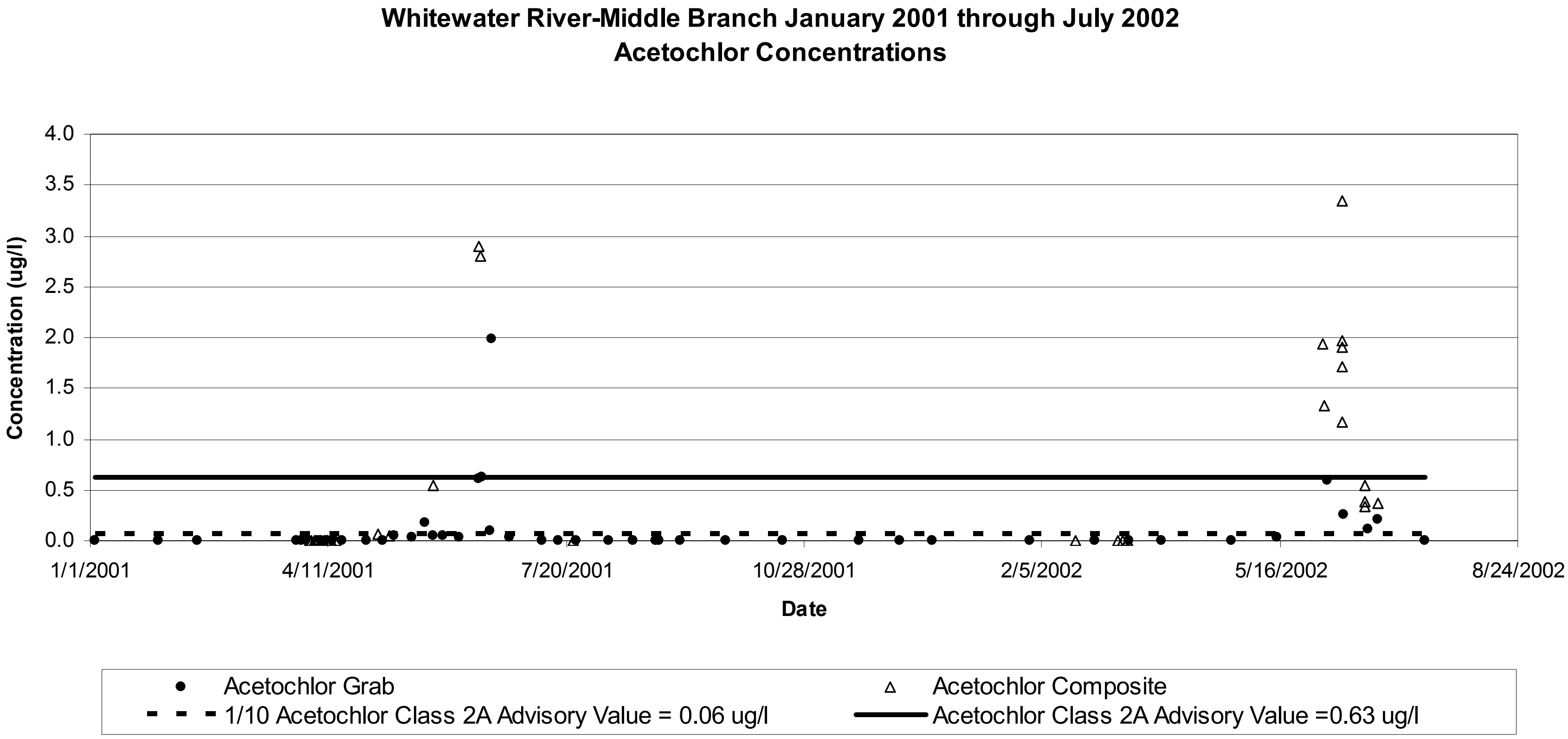


Figure 58 – Atrazine concentrations for Whitewater River-Middle Branch, January 2001 through July 2002 (comparison is for human health-based chronic standard only)

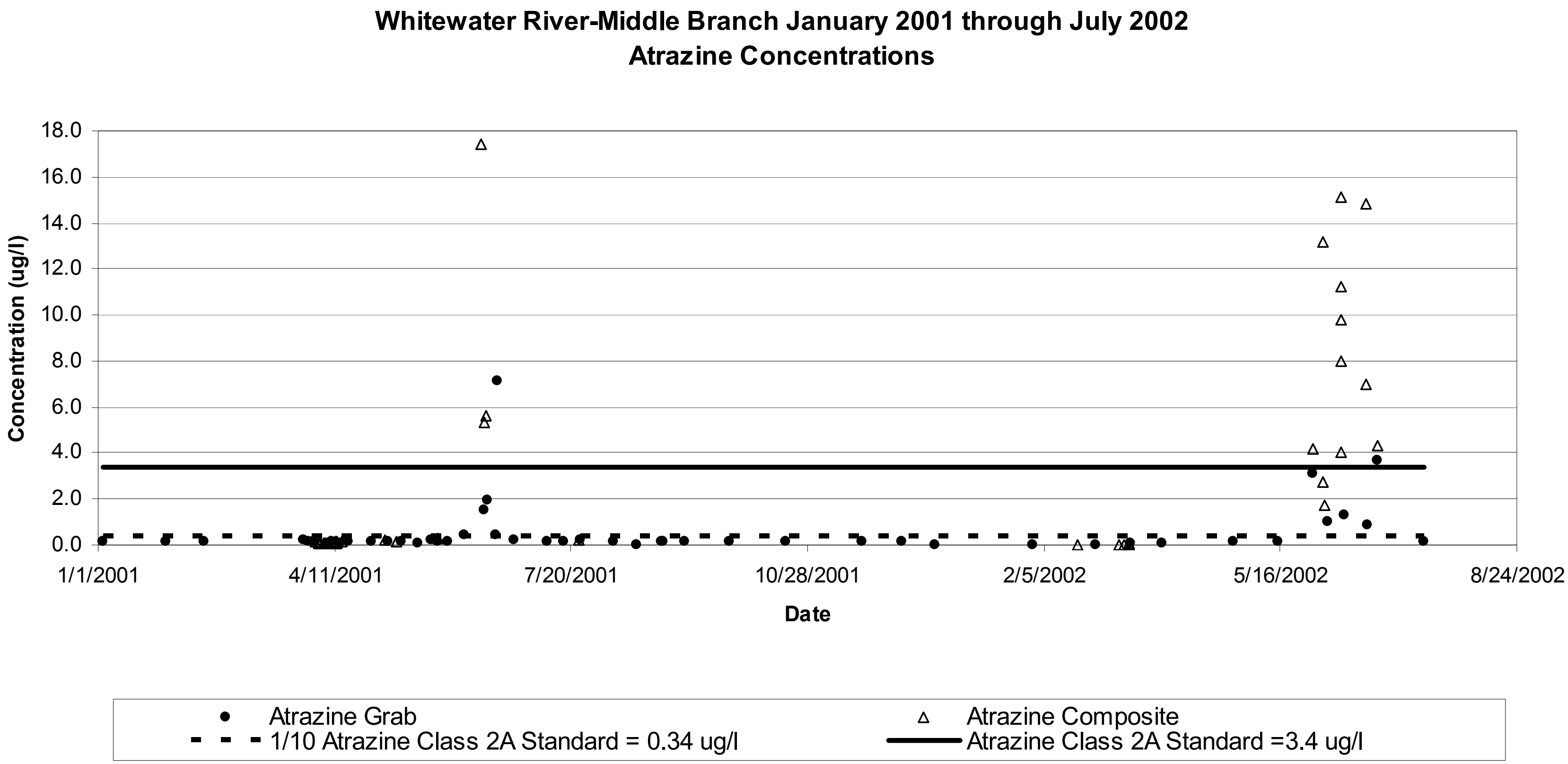
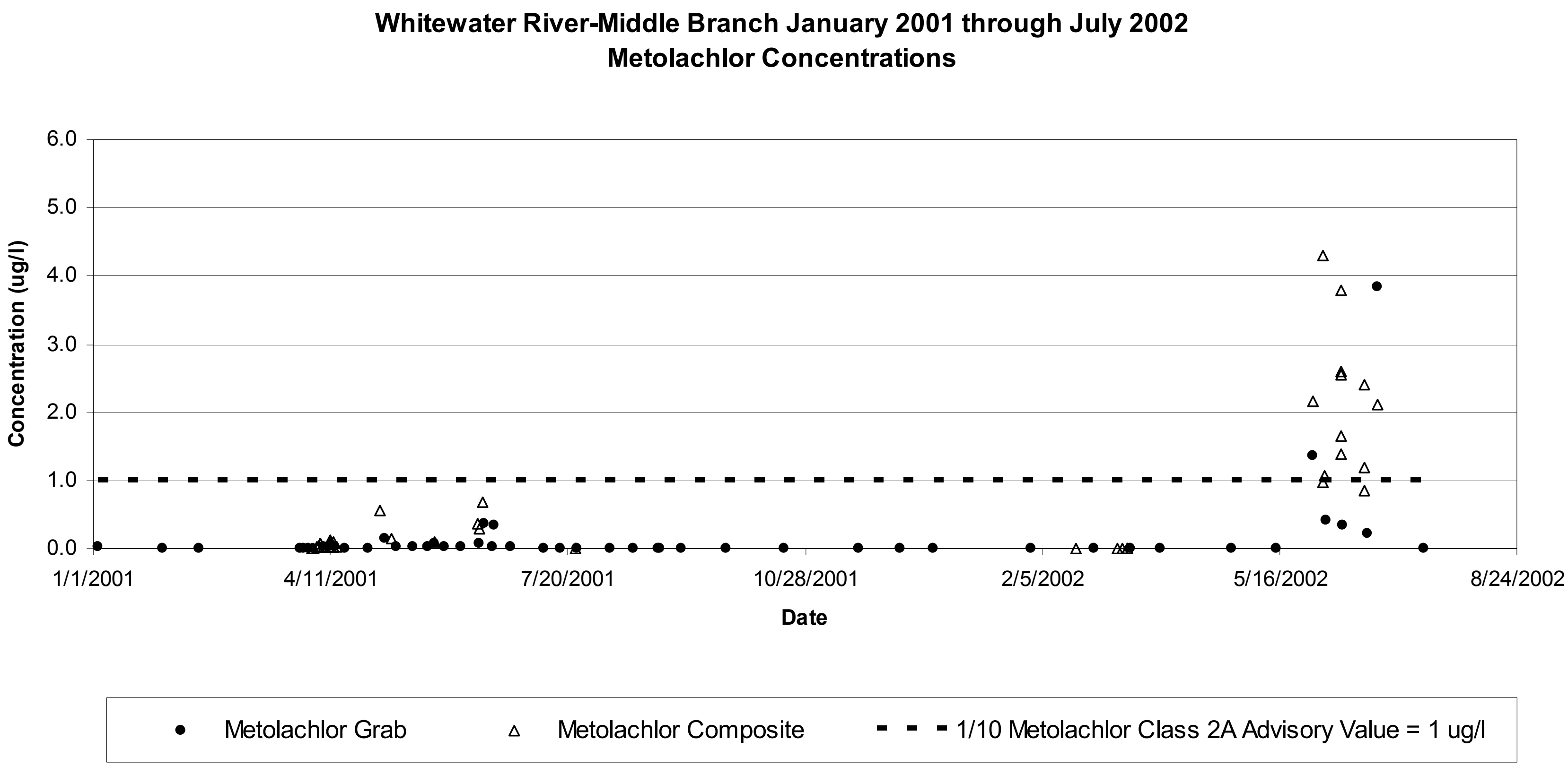


Figure 59 – Metolachlor concentrations for Whitewater River-Middle Branch, January 2001 through July 2002



APPENDIX F – Surface Water Statewide Survey Analytical Results and Hydrographs

Note:

Analytical results are provided in tabular form for all sample sites.

Hydrographs and associated analytical results are provided only for those sampling sites where a hydrograph was available for plotting, and where:

- **a grab sample collected had reportable results from the list of target analytes; and/or**
- **non-target detections were reported by the laboratory.**

A pesticide concentration value of "present" indicates a detection below the Method Reporting Limit. See the "Reporting Methods and Analyted" and "Surface Water Statewide Sampling Survey" sections of this report for more information on Method Reporting Limits.

Table 22 – Surface water statewide survey sampling sites and pesticide results, May – June, 2002

BASE NEUTRAL PESTICIDES		Pesticide and Concentration in ug/L (see footnote 1)																				
Site (see footnotes 3 - 4)	Sample Date	Acetochlor	Alachlor	Atrazine	Deethylatrazine	Disopropylatrazine	Chlorothalanil	Chlorpyrifos	Cyanazine	Diazinon	Dimethenamid	Dimethoate	EPTC	Fonofos	Malathion	Methyl Parathion	Metolachlor	Metribuzin	Pendamethalin	Phorate	Terbufos	Trifluralin
Buffalo River - Dilworth	06/12/2002	0.14	nd	0.67	0.15	nd	nd	nd	nd	nd	0.13	nd	nd	nd	nd	nd	0.32	0.10	0.14	nd	nd	nd
Cannon River - Red Wing	06/12/2002	0.54	nd	1.86	0.19	nd	nd	nd	nd	nd	0.24	nd	nd	nd	nd	nd	0.66	nd	nd	nd	nd	nd
Cedar River - Austin	06/05/2002	1.27	0.09	4.00	0.37	0.21	nd	nd	nd	nd	0.56	nd	nd	nd	nd	nd	1.77	nd	nd	nd	nd	nd
Cottonwood River	06/04/2002	1.66	0.06	1.87	0.19	0.20	nd	nd	1.47	nd	0.51	nd	nd	nd	nd	nd	0.55	0.21	nd	nd	nd	p
Crow River	06/14/2002	0.45	nd	0.82	nd	nd	nd	nd	nd	nd	0.24	nd	nd	nd	nd	nd	0.18	nd	nd	nd	nd	nd
Crow Wing River - Nimrod	06/19/2002	nd	nd	0.07	0.07	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Crow Wing River - Pillager	06/24/2002	0.15	nd	0.36	0.12	p	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.08	nd	nd	nd	nd	nd
Kettle River	06/20/2002	nd	nd	p	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Little Cottonwood River	06/22/2002	0.26	0.08	2.39	0.24	p	nd	nd	nd	nd	0.24	nd	nd	nd	nd	nd	0.80	0.12	0.14	nd	nd	nd
Long Prairie	06/24/2002	0.36	nd	0.92	0.27	0.20	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.11	nd	nd	nd	nd	nd
Minnesota River - Jordan	06/10/2002	0.33	nd	0.66	0.13	nd	nd	nd	nd	nd	0.24	nd	nd	nd	nd	nd	0.22	nd	nd	nd	nd	nd
Minnesota River - Morton	06/22/2002	0.24	nd	1.74	0.15	p	nd	nd	nd	nd	0.52	nd	nd	nd	nd	nd	0.09	nd	nd	nd	nd	nd
Minnesota River - St. Peter	06/10/2002	0.30	nd	0.75	0.15	0.20	nd	nd	nd	nd	0.21	nd	nd	nd	nd	nd	0.19	nd	nd	nd	nd	nd
Mississippi River - Little Falls	06/22/2002	nd	nd	0.11	0.05	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Red River	06/09/2002	0.07	nd	0.24	0.19	nd	nd	nd	nd	p	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Redwood River - Redwood Falls	06/22/2002	0.80	nd	5.80	0.32	0.25	nd	nd	nd	nd	0.22	nd	nd	nd	nd	nd	0.09	nd	nd	nd	nd	nd
Rum River	06/13/2002	p	nd	0.14	0.06	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Sauk River	06/22/2002	0.17	nd	0.21	0.08	nd	nd	nd	nd	nd	0.08	nd	nd	nd	nd	nd	0.08	nd	nd	nd	nd	nd
Seven Mile Creek# 3	06/03/2002	0.74	nd	4.30	0.24	p	nd	nd	nd	nd	0.60	nd	nd	nd	nd	nd	2.10	0.55	nd	nd	nd	nd
Seven Mile Creek# 3	06/24/2002	0.19	nd	2.12	0.29	p	nd	nd	nd	nd	0.16	nd	nd	nd	nd	nd	1.00	0.27	nd	nd	nd	nd
Snake River	06/20/2002	p	nd	0.06	0.06	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Straight River - Faribault	05/28/2002	0.17	nd	0.12	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.16	nd	nd	nd	nd	nd
Straight River - Park Rapids	06/11/2002	nd	nd	p	0.05	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Two Rivers - Hallock	06/12/2002	0.05	nd	0.07	0.05	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Vermillion River - Farmington	06/12/2002	0.07	nd	1.78	0.16	nd	nd	nd	nd	nd	p	nd	nd	nd	nd	nd	0.07	nd	nd	nd	nd	nd
Watonwan River - Garden City	05/28/2002	4.20	nd	0.14	0.08	nd	nd	nd	nd	nd	p	nd	nd	nd	nd	nd	0.60	nd	nd	nd	nd	nd
	Maximum	4.20	0.09	5.80	0.37	0.25	nd	nd	1.47	nd	0.60	nd	nd	nd	nd	nd	2.10	0.55	0.14	nd	nd	nd
	Median	0.18	nd	0.67	0.14	nd	nd	nd	nd	nd	0.05	nd	nd	nd	nd	nd	0.10	nd	nd	nd	nd	nd
MPCA 7050 Standard, Criterion or Adv. Value (see footnote 4)		1.40	59.00	10.00	NA	NA	NA	0.041	4.50	NA	NA	NA	NA	NA	NA	NA	10.00	NA	NA	NA	NA	NA

Footnotes:

1. nd = non-detect; p = present below method reporting limit
2. Cottonwood River: Propachlor present at 0.50 ppb on 06/04/2002
3. Straight River - Park Rapids: Metribuzin DADK present at 0.67ppb on 06/11/2002
4. Sample results are not time- or flow-weighted. No water quality violation or impairment is implied.

See Appendix C for applicability and enforceability of standards; NA = not applicable (i.e., no standard is available)

Table 20 (continued) – Surface water statewide survey sampling sites and pesticide results, May – June, 2002

ACID PESTICIDES		Pesticide and Concentration in ug/L (see footnote 1)					
Site (see footnotes 2 - 5)	**Sample Date**	**2,4-D**	**Dicamba**	**Dichlorprop**	**MCPA**	**MCPP**	**Triclopyr**
Little Cottonwood River	06/22/2002	0.64	p	nd	nd	nd	nd
Minnesota River - Morton	06/22/2002	p	0.74	nd	nd	nd	nd
Redwood River - Redwood Falls	06/22/2002	0.36	1.17	nd	nd	nd	nd
Seven Mile Creek# 3	06/03/2002	nd	0.29	nd	nd	nd	nd
Seven Mile Creek# 3	06/24/2002	0.36	p	nd	nd	nd	nd
Maximum		0.64	1.17	nd	nd	nd	nd
Median		0.36	0.29	nd	nd	nd	nd
MPCA 7050 Standard, Criterion or Adv. Value (see footnote 6)		97.00	85.00	NA	18.00	97.00	NA

Footnotes:

1. nd = non-detect; p = present below method reporting limit
2. Some acid herbicide samples exceeded laboratory analytical holding times
3. Seven Mile Creek# 3 (06/24/20020): Bentazon present below reporting limit
4. Little Cottonwood River, Minnesota River - Morton, Seven Mile Creek# 3 (06/24/20020): Clopyralid present below reporting limit
5. Redwood River - Redwood Falls: Clopyralid present at 0.29 ppb
6. Sample results are not time- or flow-weighted. No water quality violation or impairment is implied.

See Appendix C for applicability and enforceability of standards; NA = not applicable (i.e., no standard is available)

Figure 60 – Buffalo River Hydrograph and Analytical Results, June 12, 2002

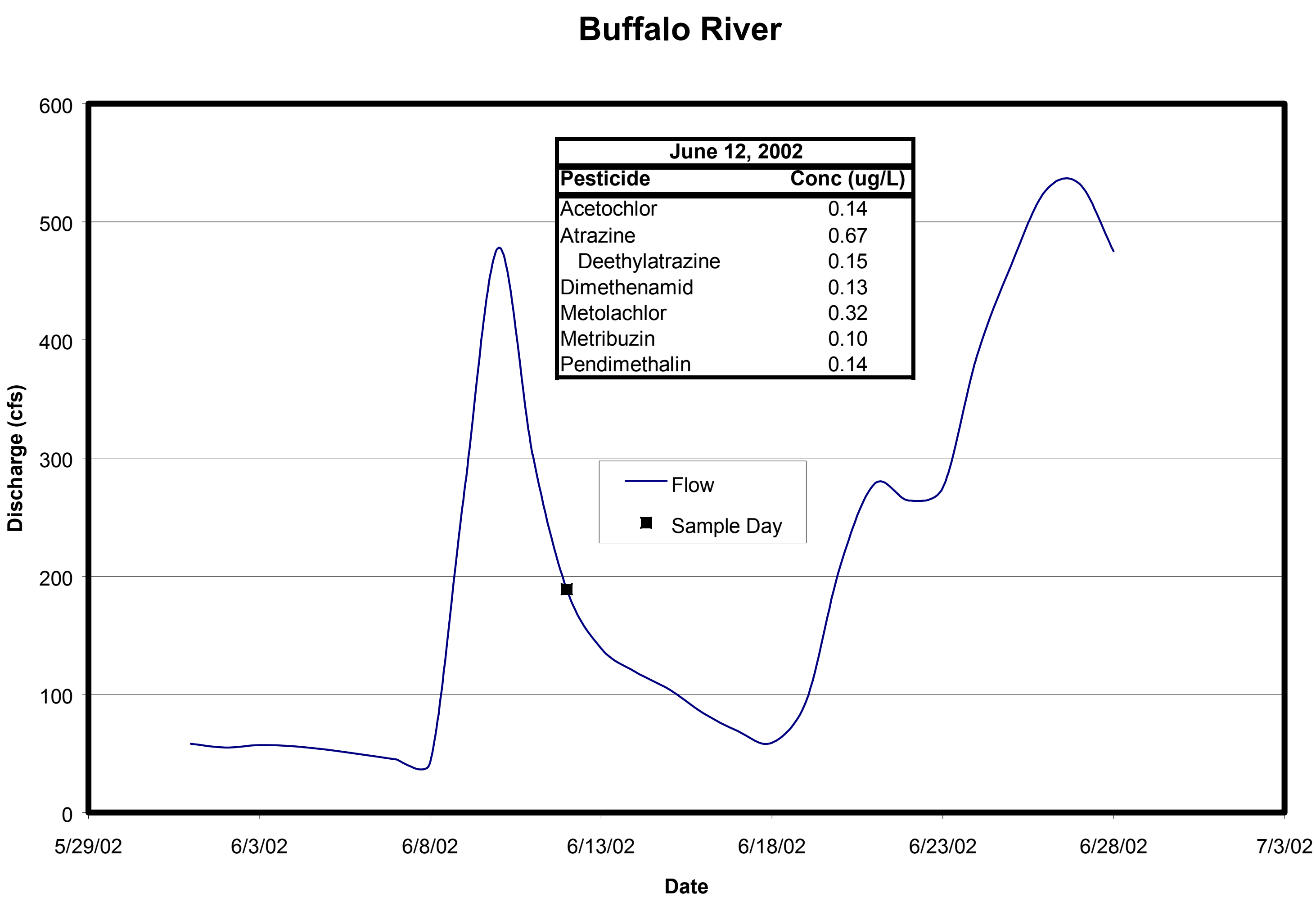


Figure 61 – Cannon River (at Welch) Hydrograph and Analytical Results, June 12, 2002

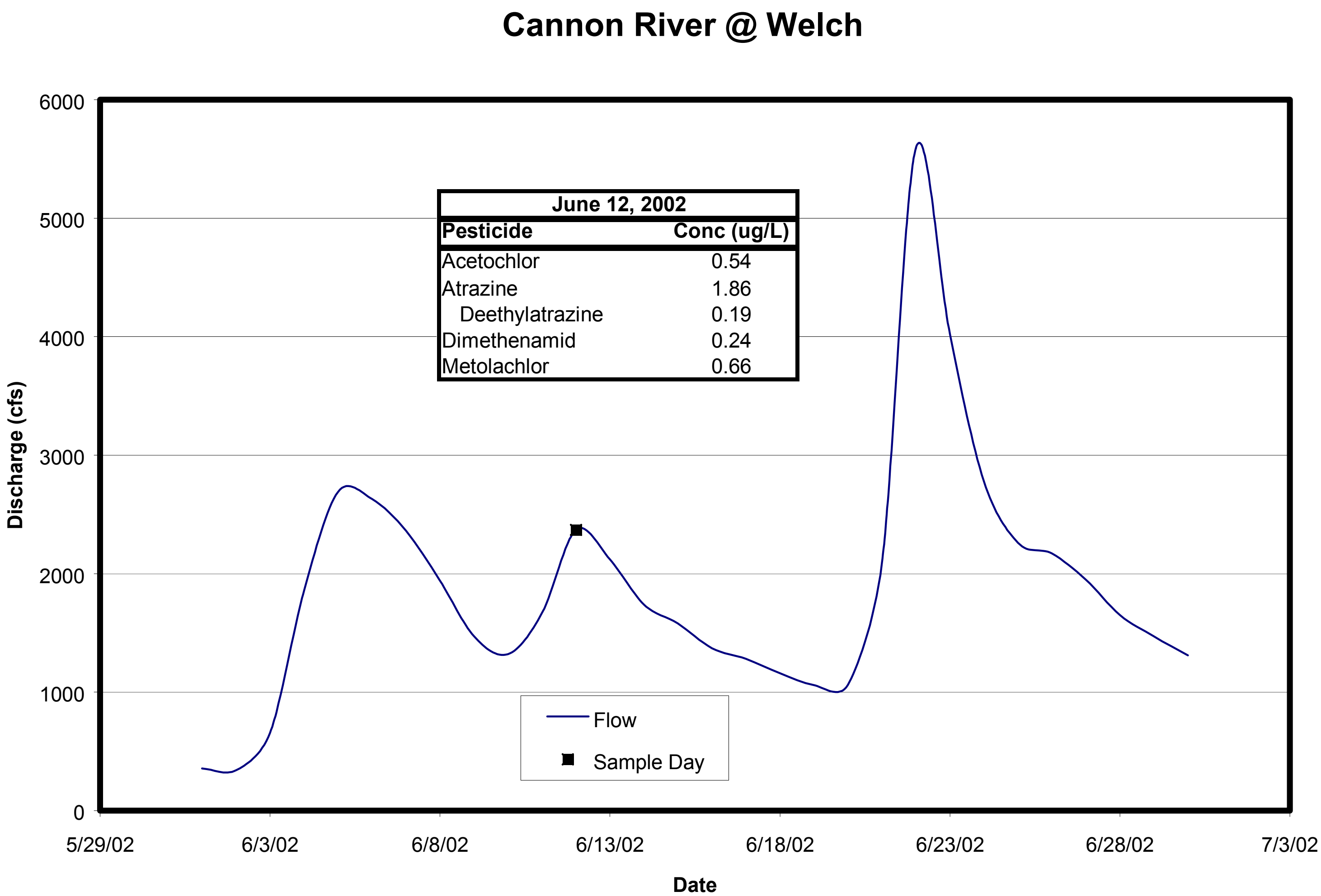


Figure 62 – Cedar River (at Austin) Hydrograph and Analytical Results, June 5, 2002

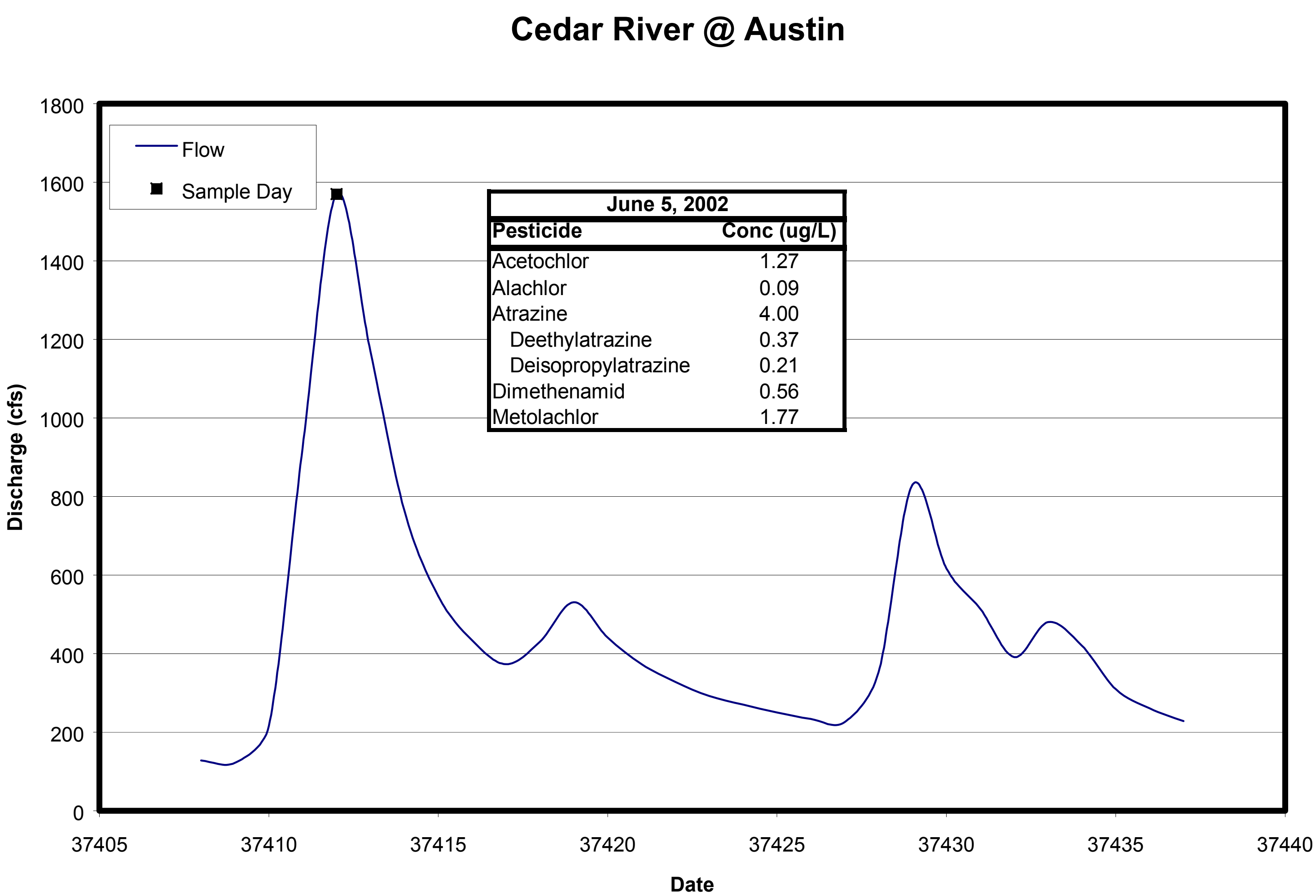
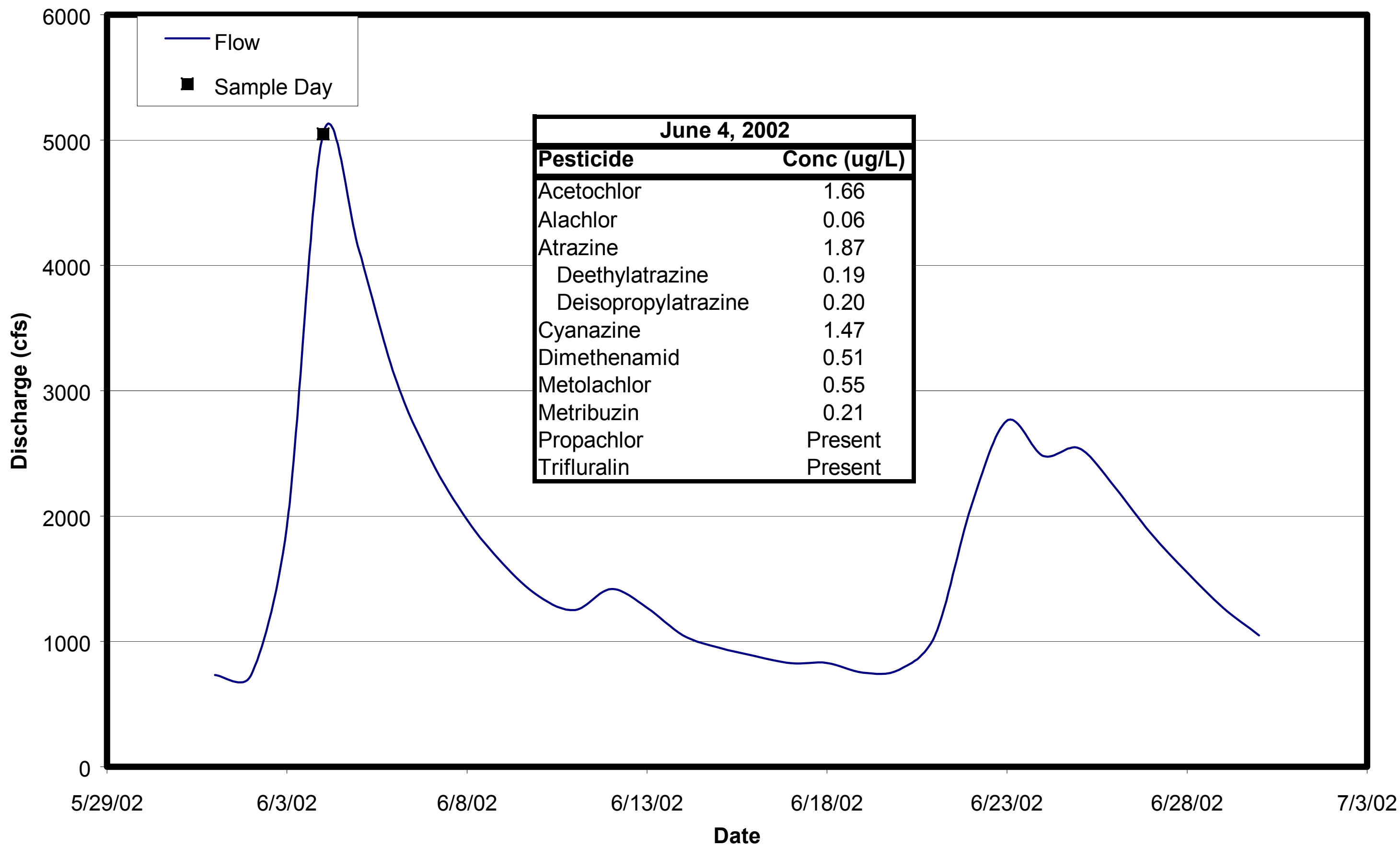


Figure 63 – Cottonwood River Hydrograph and Analytical Results, June 4, 2002

Cottonwood River



June 4, 2002	
Pesticide	**Conc (ug/L)**
Acetochlor	1.66
Alachlor	0.06
Atrazine	1.87
Deethylatrazine	0.19
Deisopropylatrazine	0.20
Cyanazine	1.47
Dimethenamid	0.51
Metolachlor	0.55
Metribuzin	0.21
Propachlor	Present
Trifluralin	Present

Figure 64 – Crow River (at Rockford) Hydrograph and Analytical Results, June 14, 2002

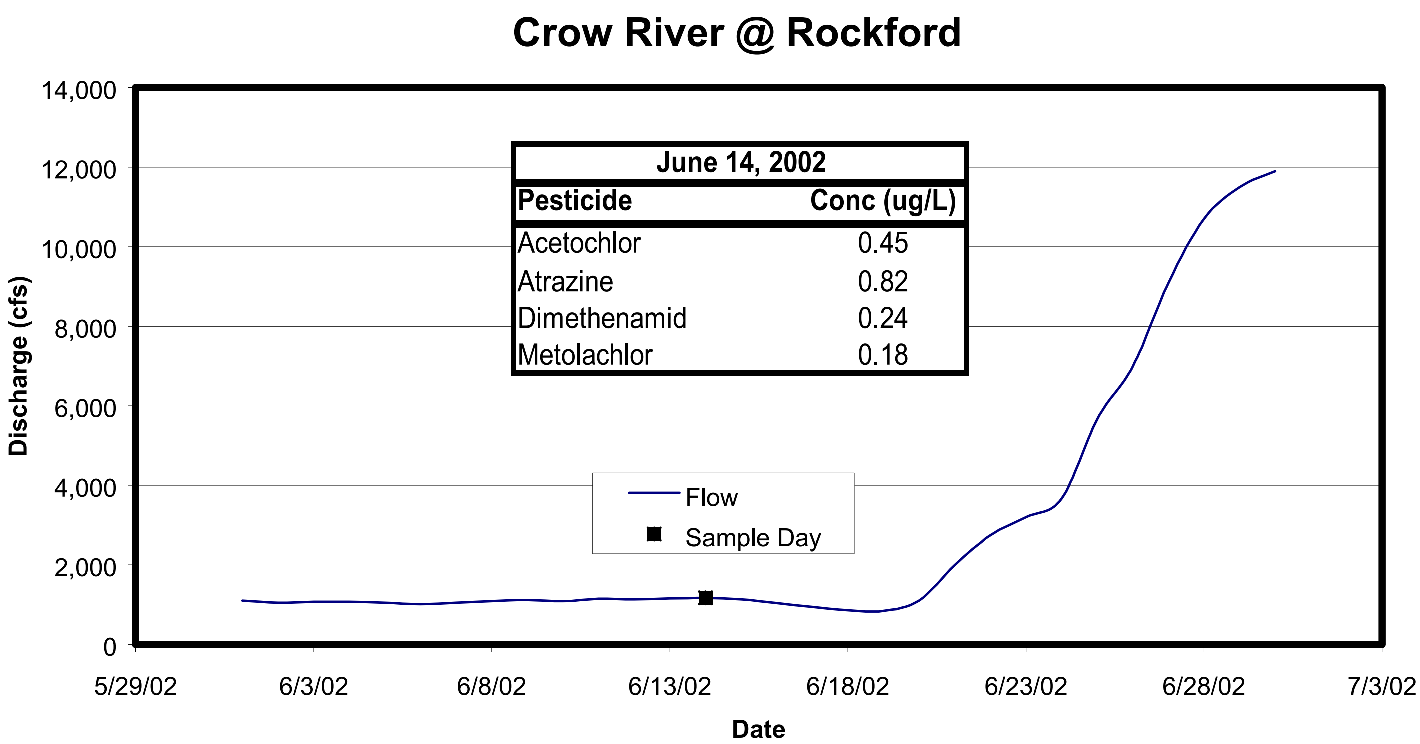


Figure 65 – Crow Wing River (near Nimrod) Hydrograph and Analytical Results, June 19, 2002

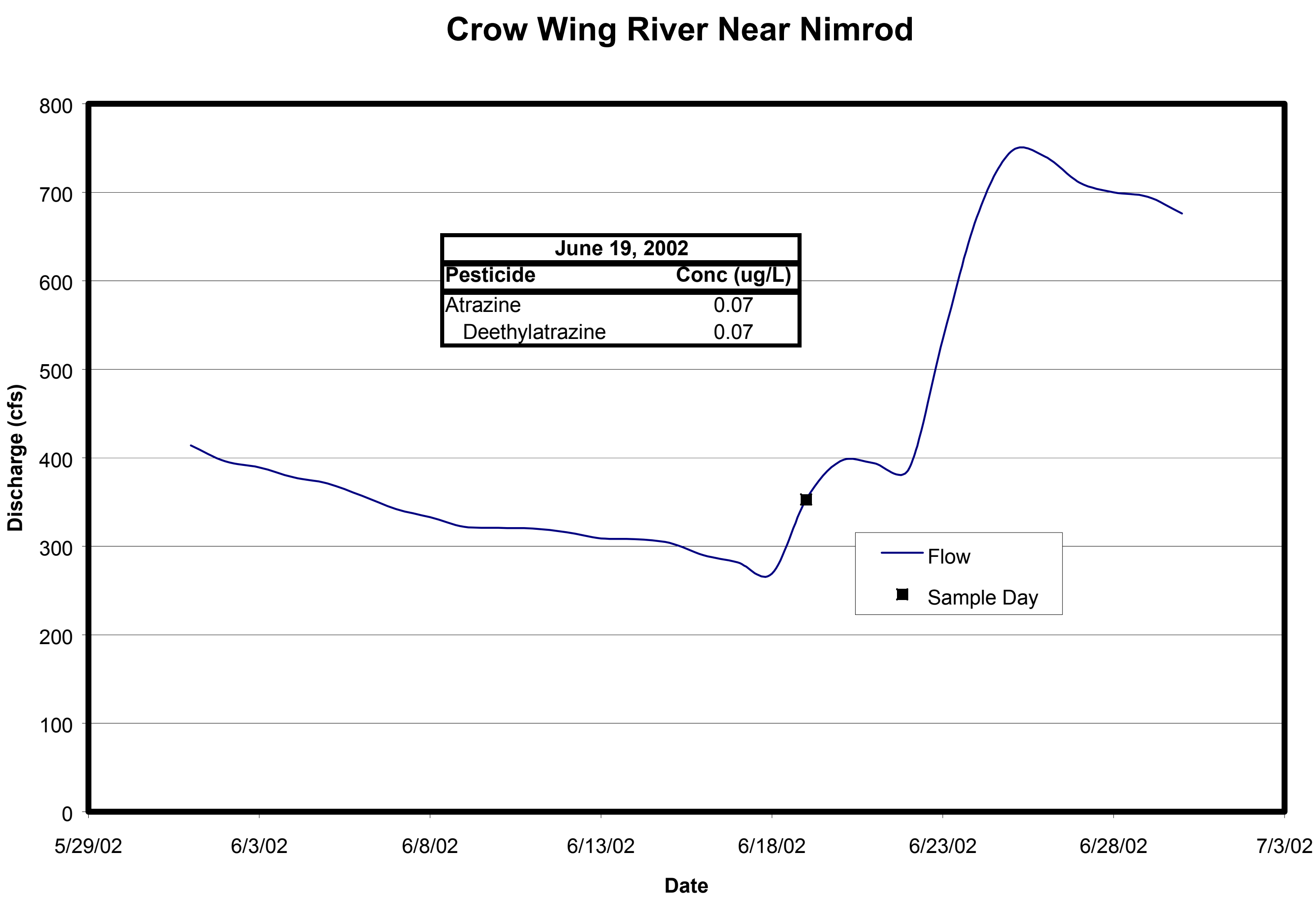
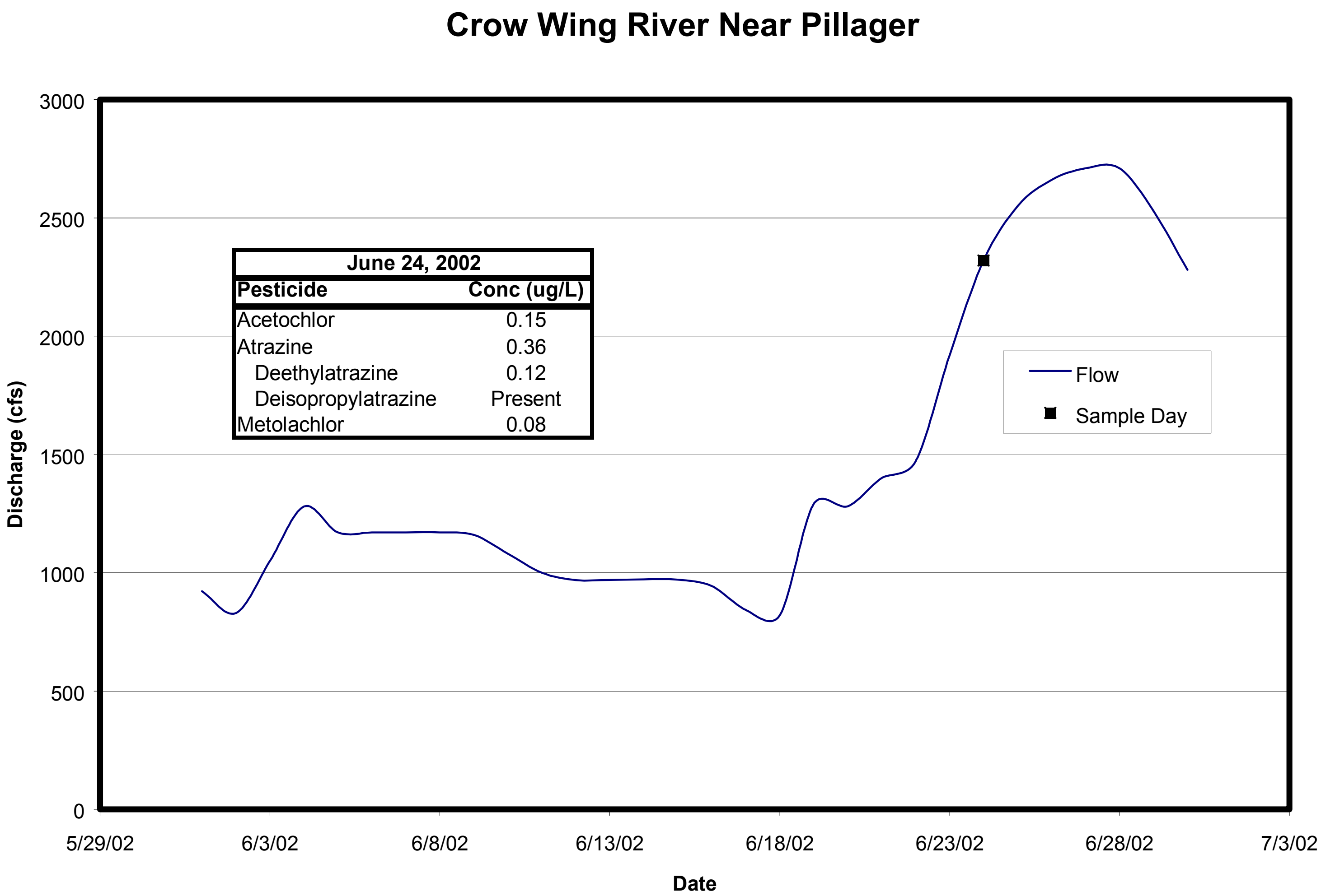
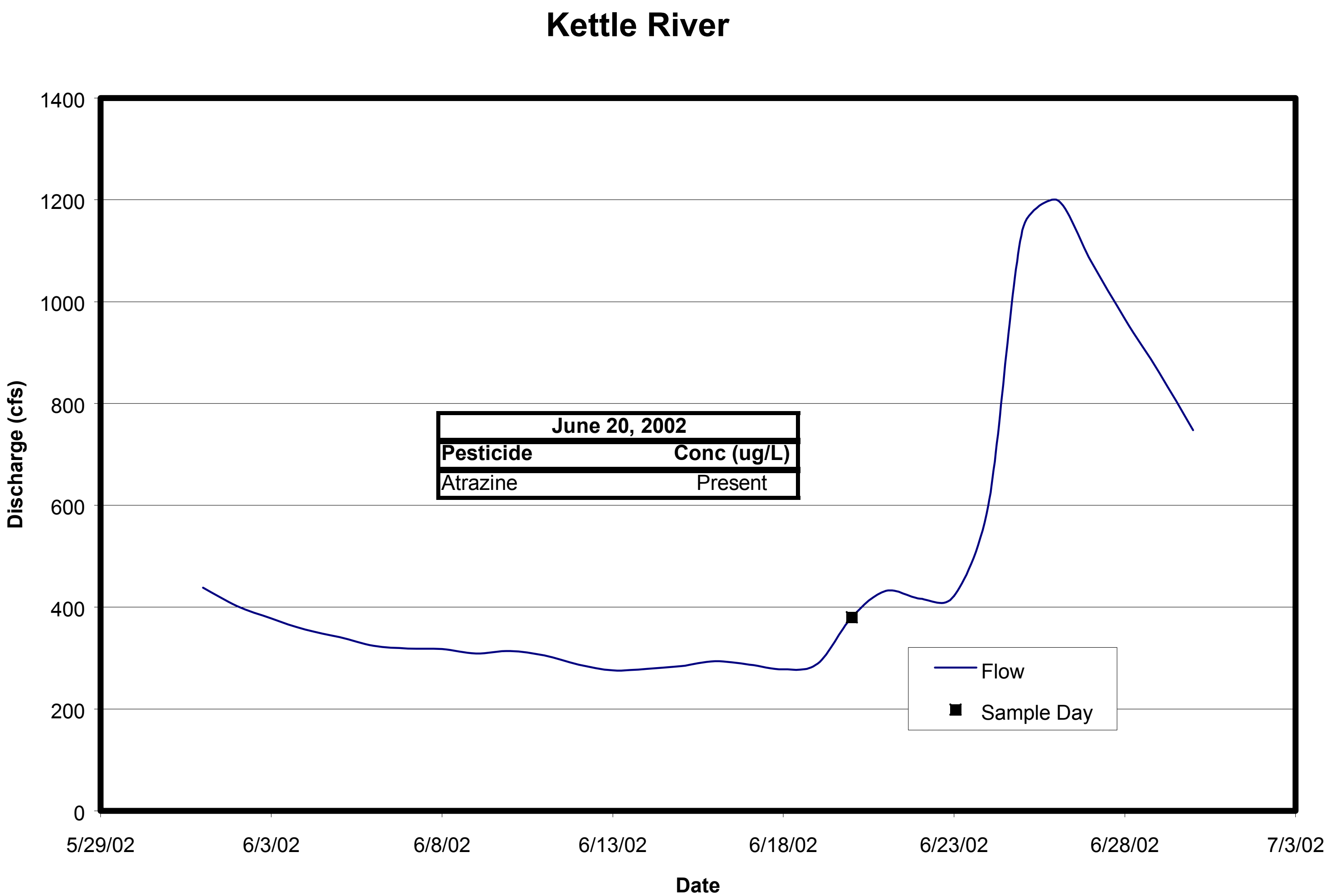


Figure 66 – Crow Wing River (near Pillager) Hydrograph and Analytical Results, June 24, 2002



June 24, 2002	
Pesticide	**Conc (ug/L)**
Acetochlor	0.15
Atrazine	0.36
Deethylatrazine	0.12
Deisopropylatrazine	Present
Metolachlor	0.08

Figure 67 – Kettle River Hydrograph and Analytical Results, June 20, 2002



June 20, 2002	
Pesticide	**Conc (ug/L)**
Atrazine	Present

Figure 68 – Little Cottonwood River Hydrograph and Analytical Results, June 22, 2002

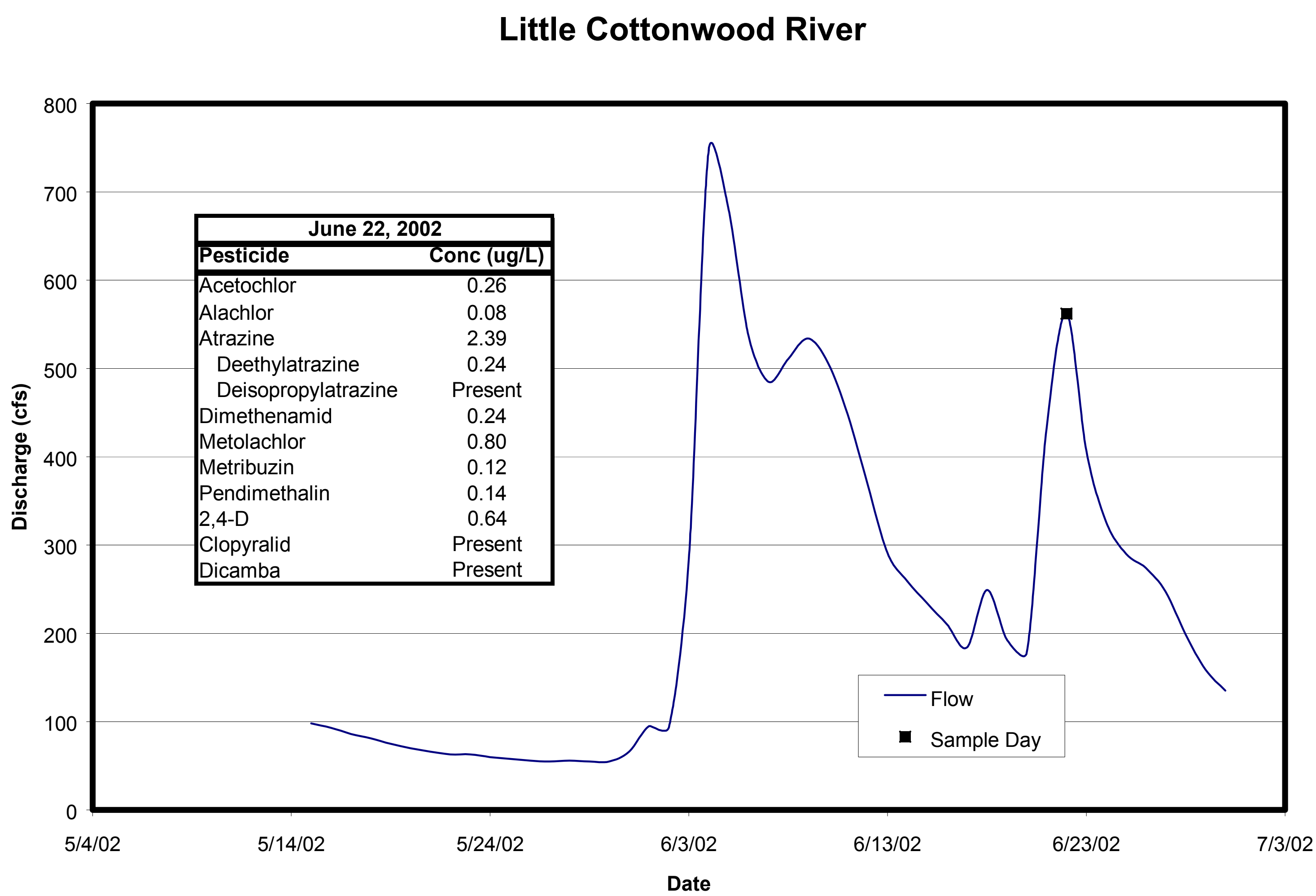
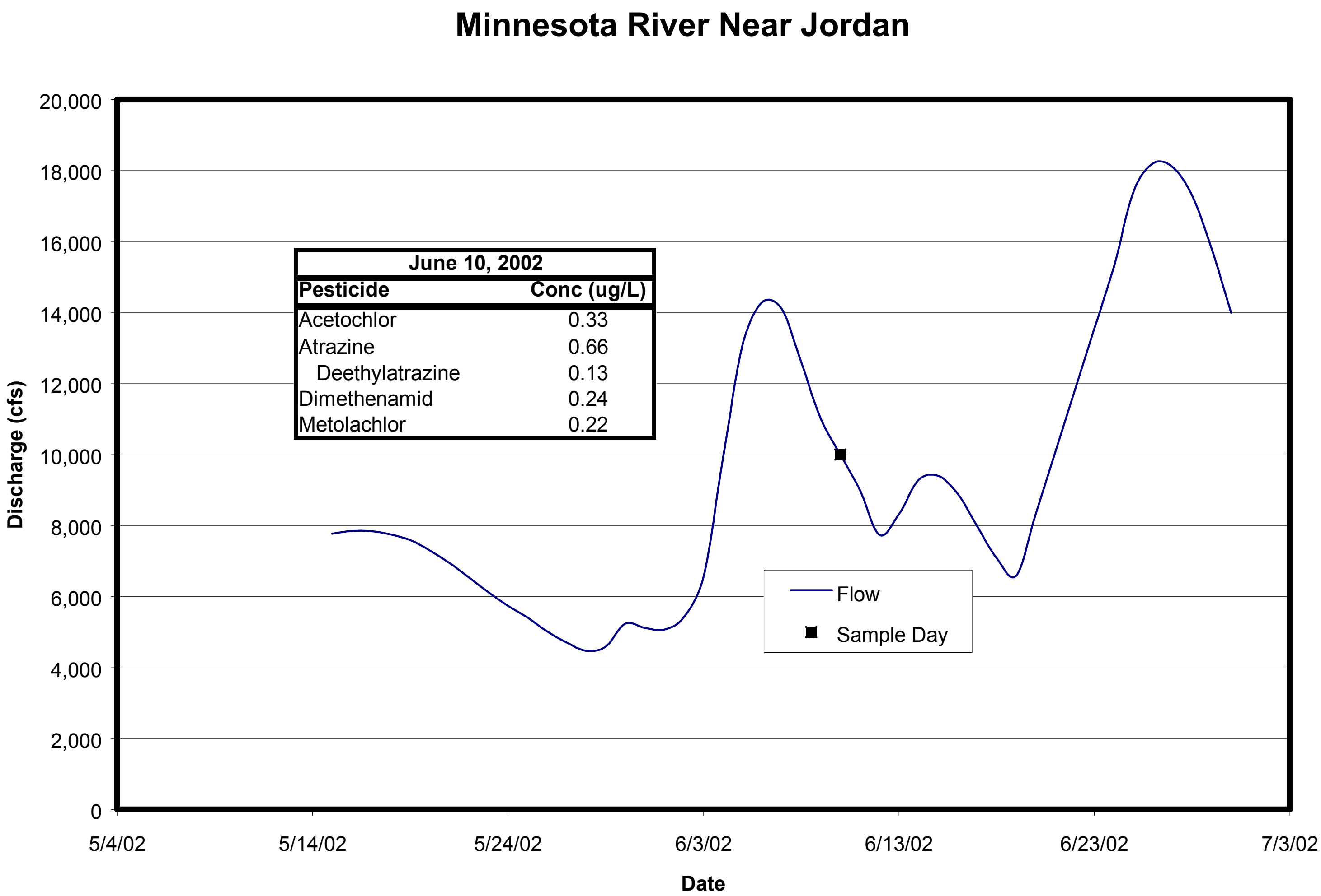
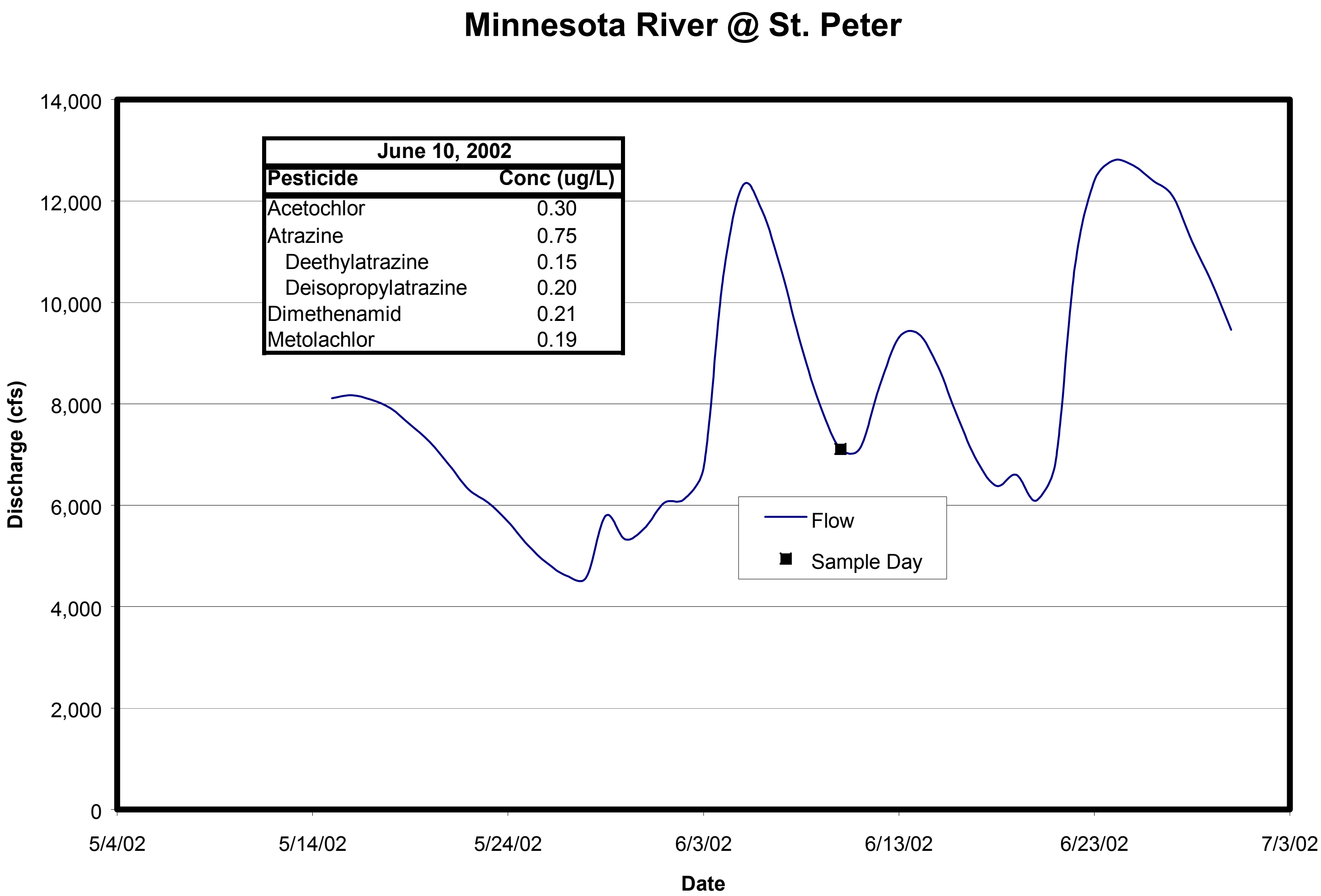


Figure 69 – Minnesota River (near Jordan) Hydrograph and Analytical Results, June 10, 2002



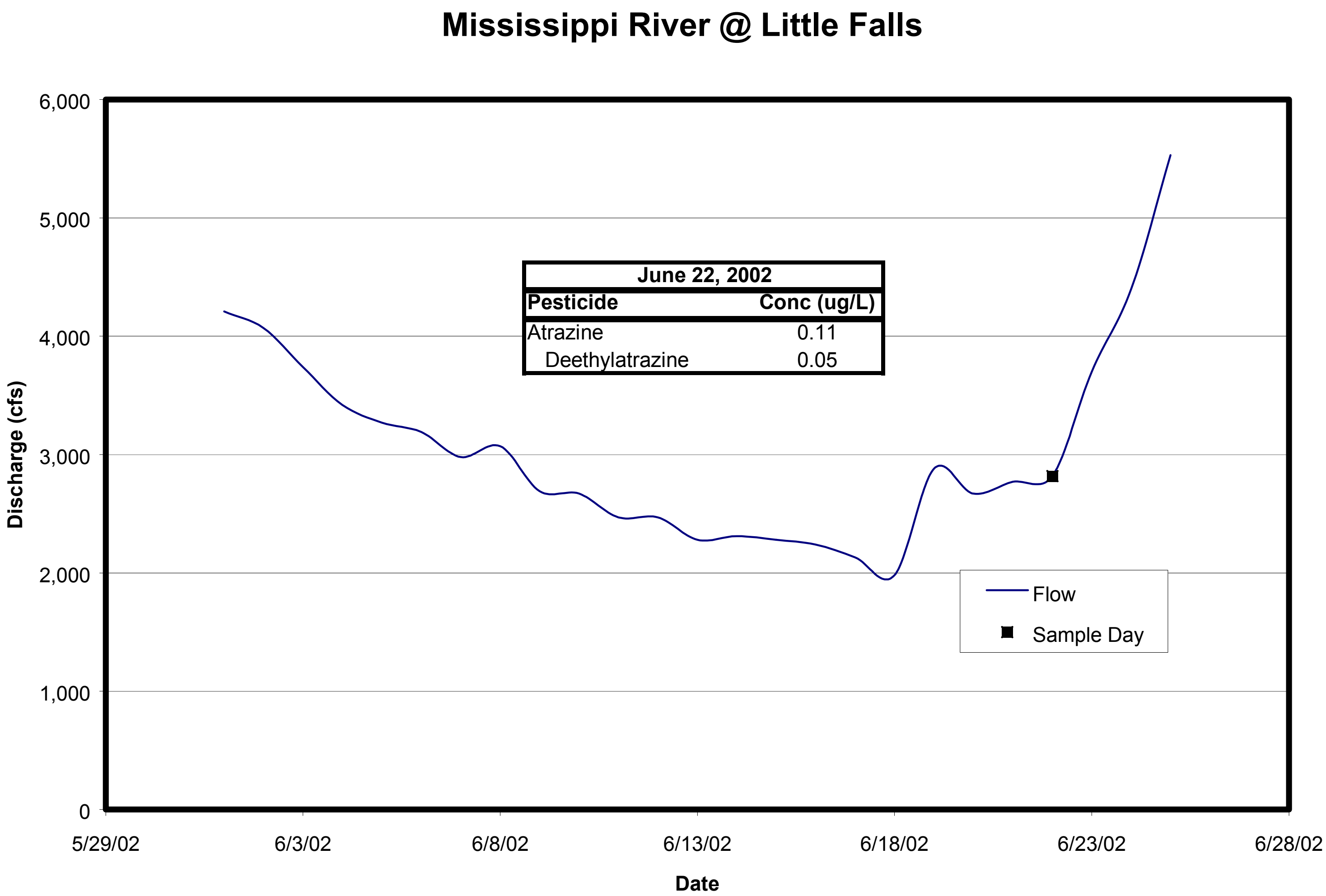
June 10, 2002	
Pesticide	**Conc (ug/L)**
Acetochlor	0.33
Atrazine	0.66
Deethylatrazine	0.13
Dimethenamid	0.24
Metolachlor	0.22

Figure 70 – Minnesota River (at St. Peter) Hydrograph and Analytical Results, June 10, 2002



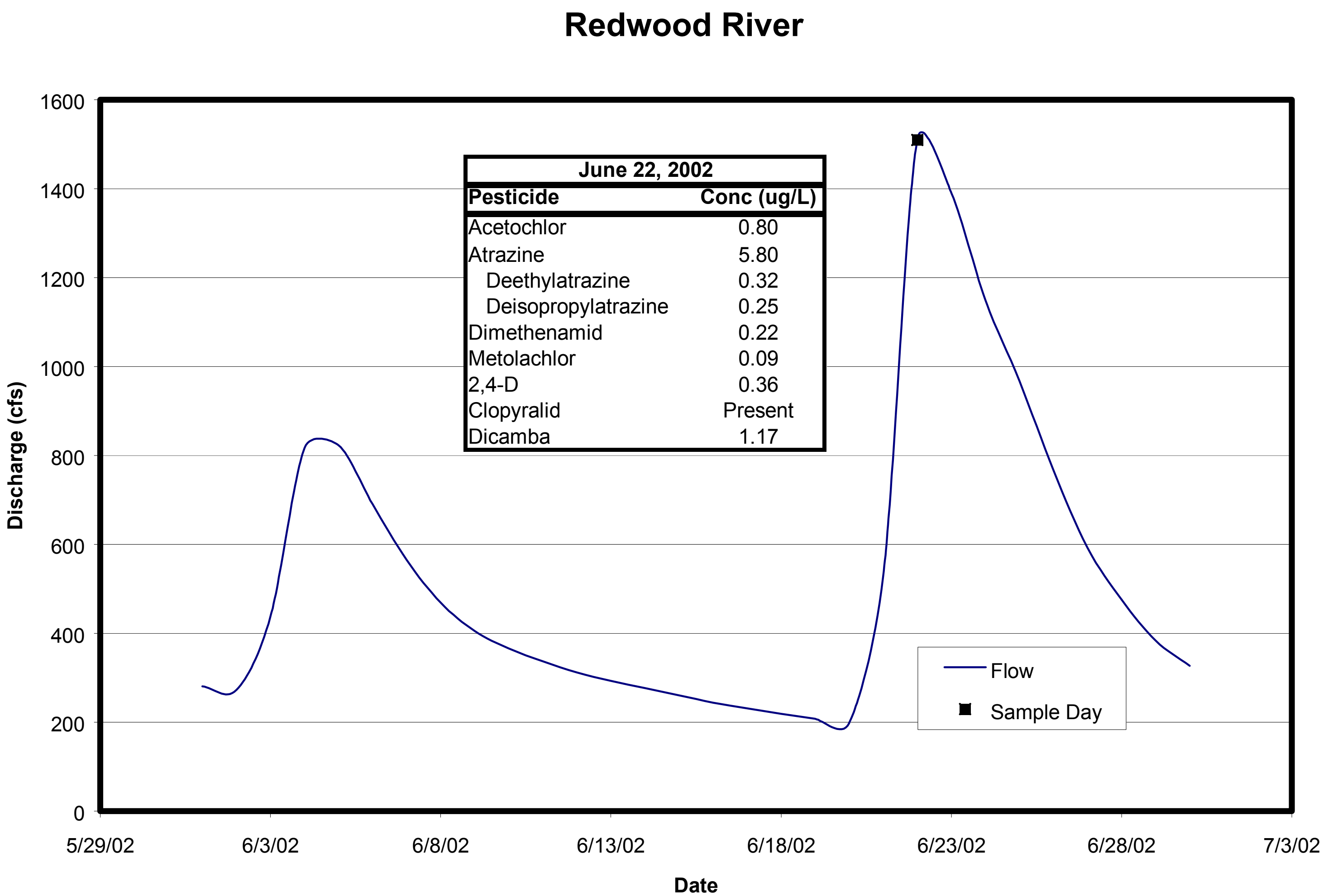
June 10, 2002	
Pesticide	**Conc (ug/L)**
Acetochlor	0.30
Atrazine	0.75
Deethylatrazine	0.15
Deisopropylatrazine	0.20
Dimethenamid	0.21
Metolachlor	0.19

Figure 71 – Mississippi River (at Little Falls) Hydrograph and Analytical Results, June 22, 2002



June 22, 2002	
Pesticide	**Conc (ug/L)**
Atrazine	0.11
Deethylatrazine	0.05

Figure 72 – Redwood River Hydrograph and Analytical Results, June 22, 2002



June 22, 2002	
Pesticide	**Conc (ug/L)**
Acetochlor	0.80
Atrazine	5.80
Deethylatrazine	0.32
Deisopropylatrazine	0.25
Dimethenamid	0.22
Metolachlor	0.09
2,4-D	0.36
Clopyralid	Present
Dicamba	1.17

Figure 73 – Rum River Hydrograph and Analytical Results, June 13, 2002

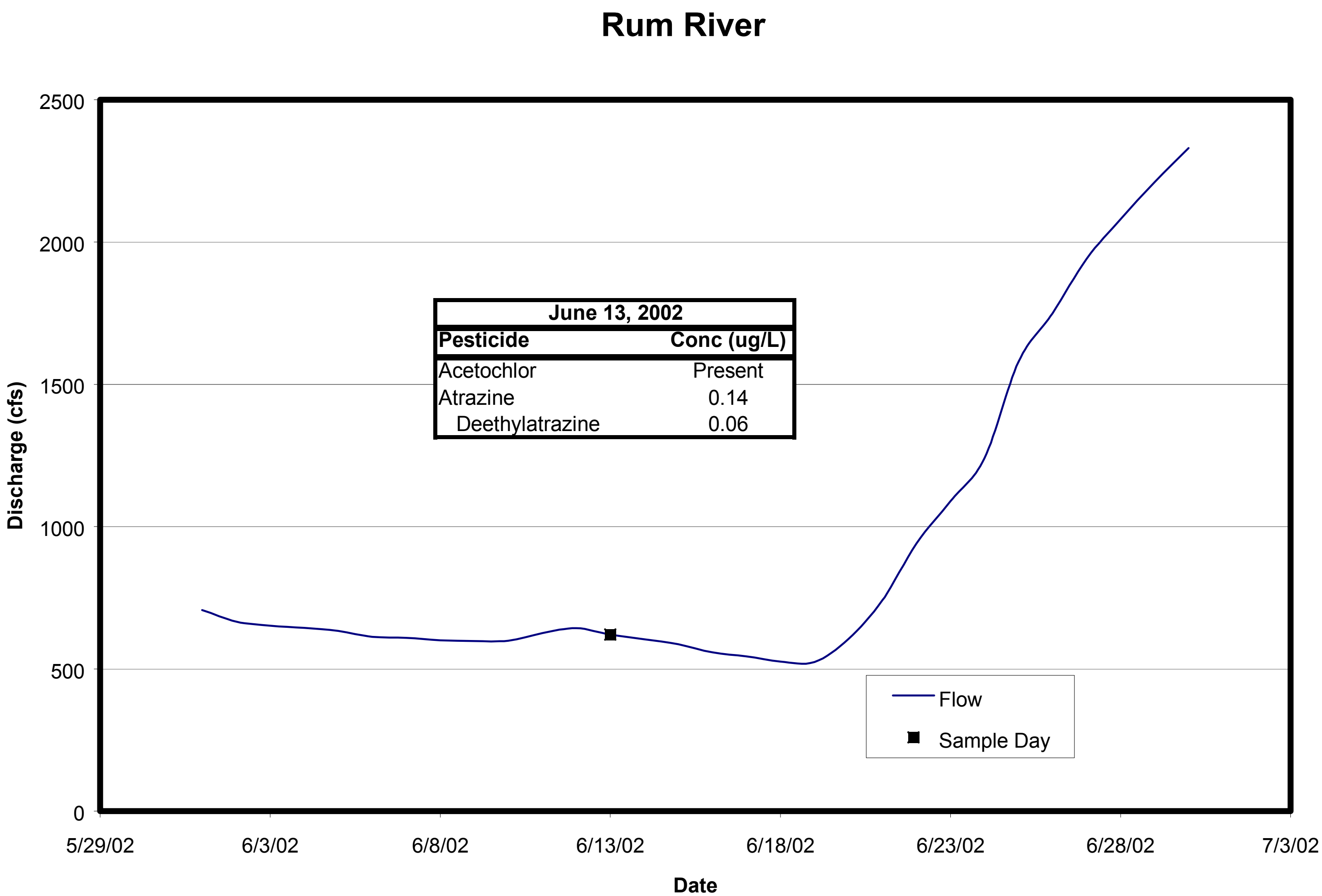
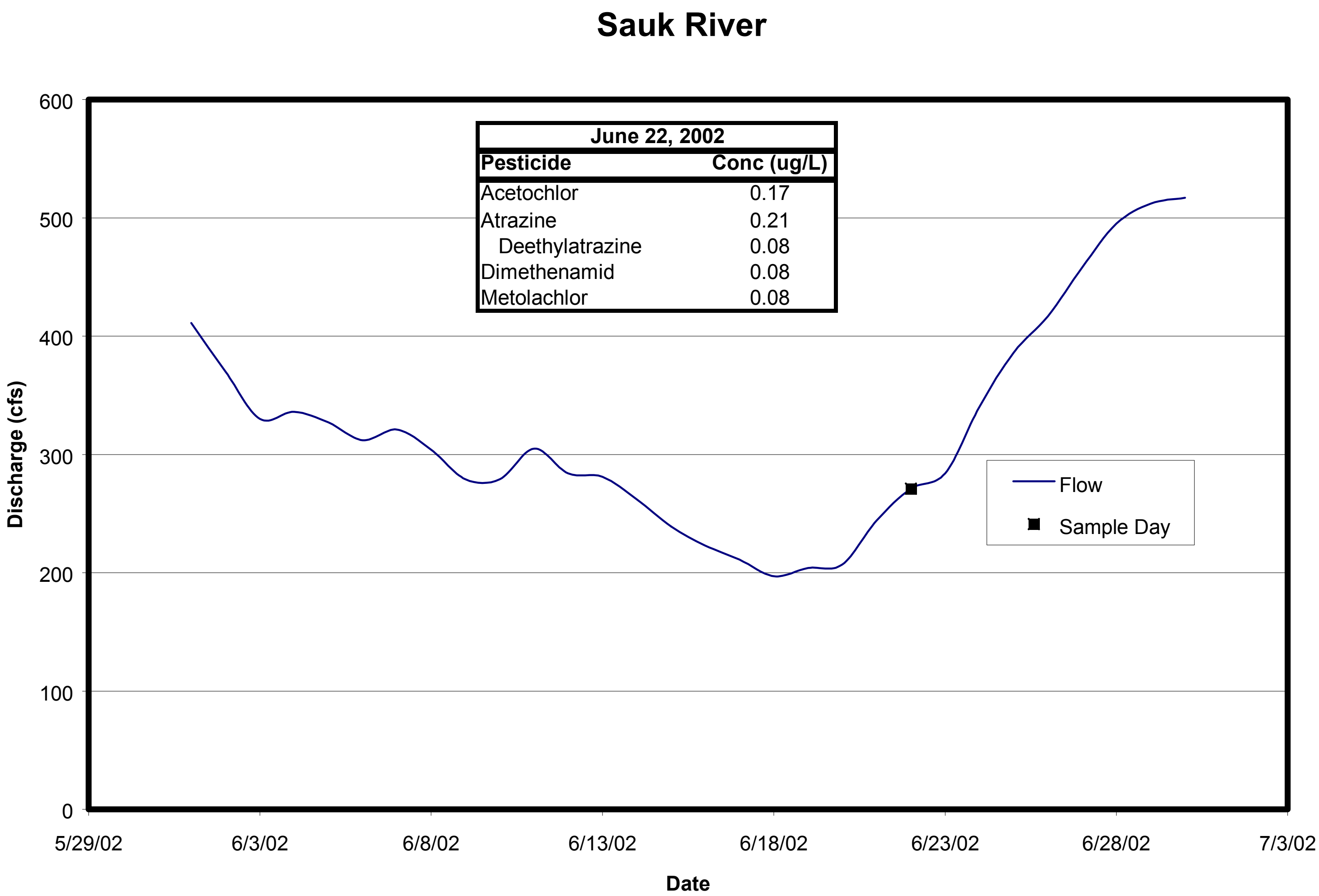


Figure 74 – Sauk River Hydrograph and Analytical Results, June 22, 2002



June 22, 2002	
Pesticide	**Conc (ug/L)**
Acetochlor	0.17
Atrazine	0.21
Deethylatrazine	0.08
Dimethenamid	0.08
Metolachlor	0.08

Figure 75 – Snake River Hydrograph and Analytical Results, June 20, 2002

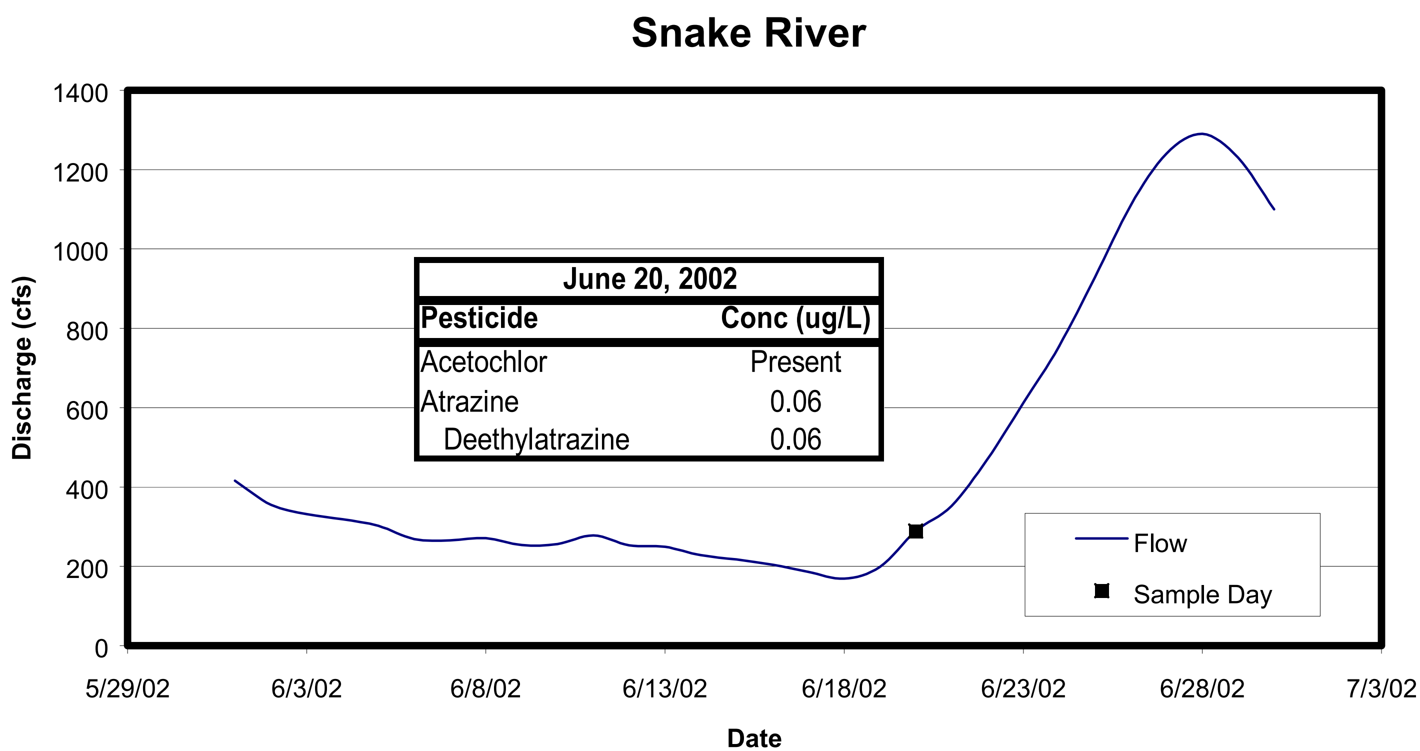
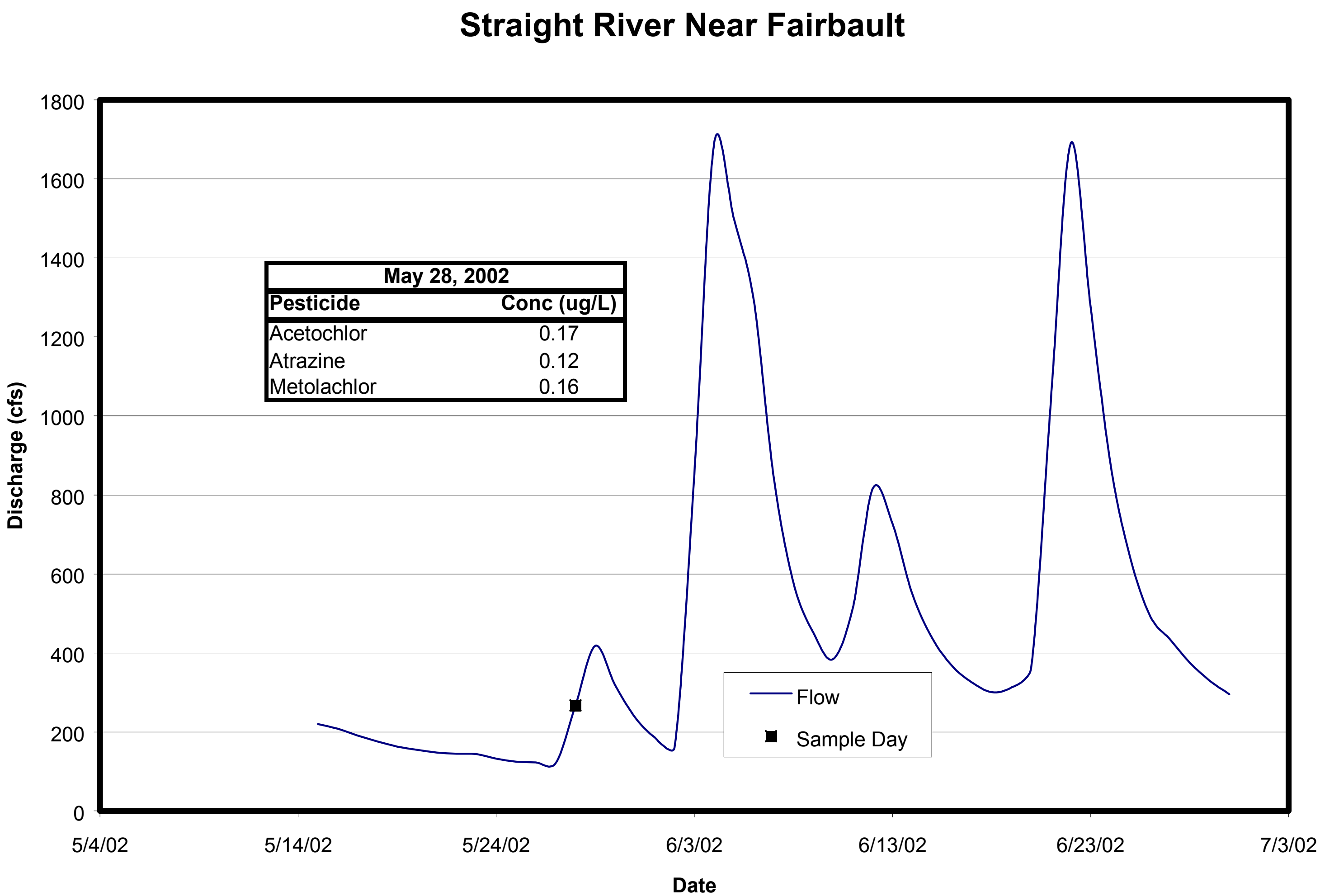


Figure 76 – Straight River (near Fairbault) Hydrograph and Analytical Results, May 28, 2002



May 28, 2002	
Pesticide	**Conc (ug/L)**
Acetochlor	0.17
Atrazine	0.12
Metolachlor	0.16

Figure 77 – Straight River (at Park Rapids) Hydrograph and Analytical Results, June 11, 2002

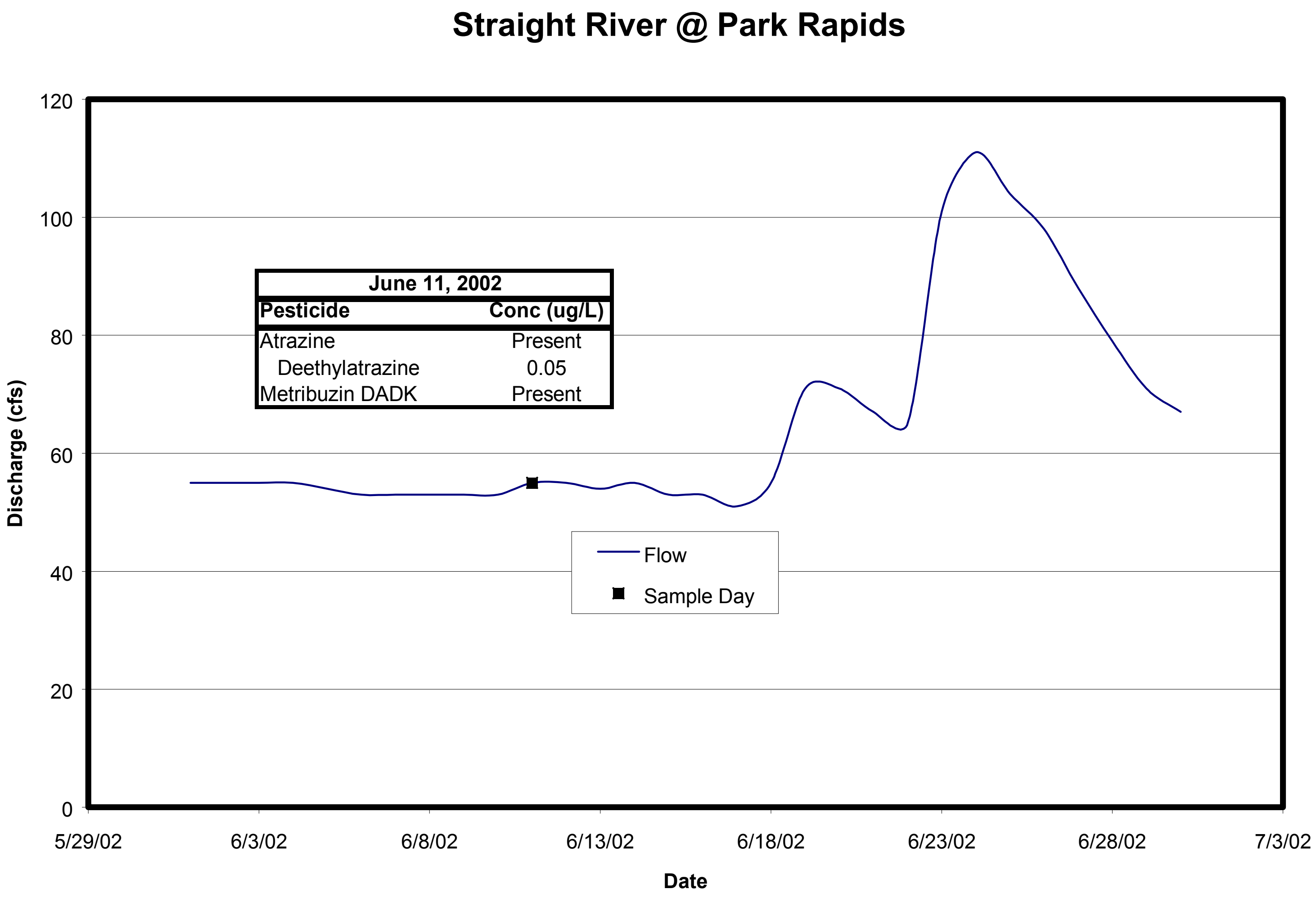


Figure 78 – Vermillion River Hydrograph and Analytical Results, June 12, 2002

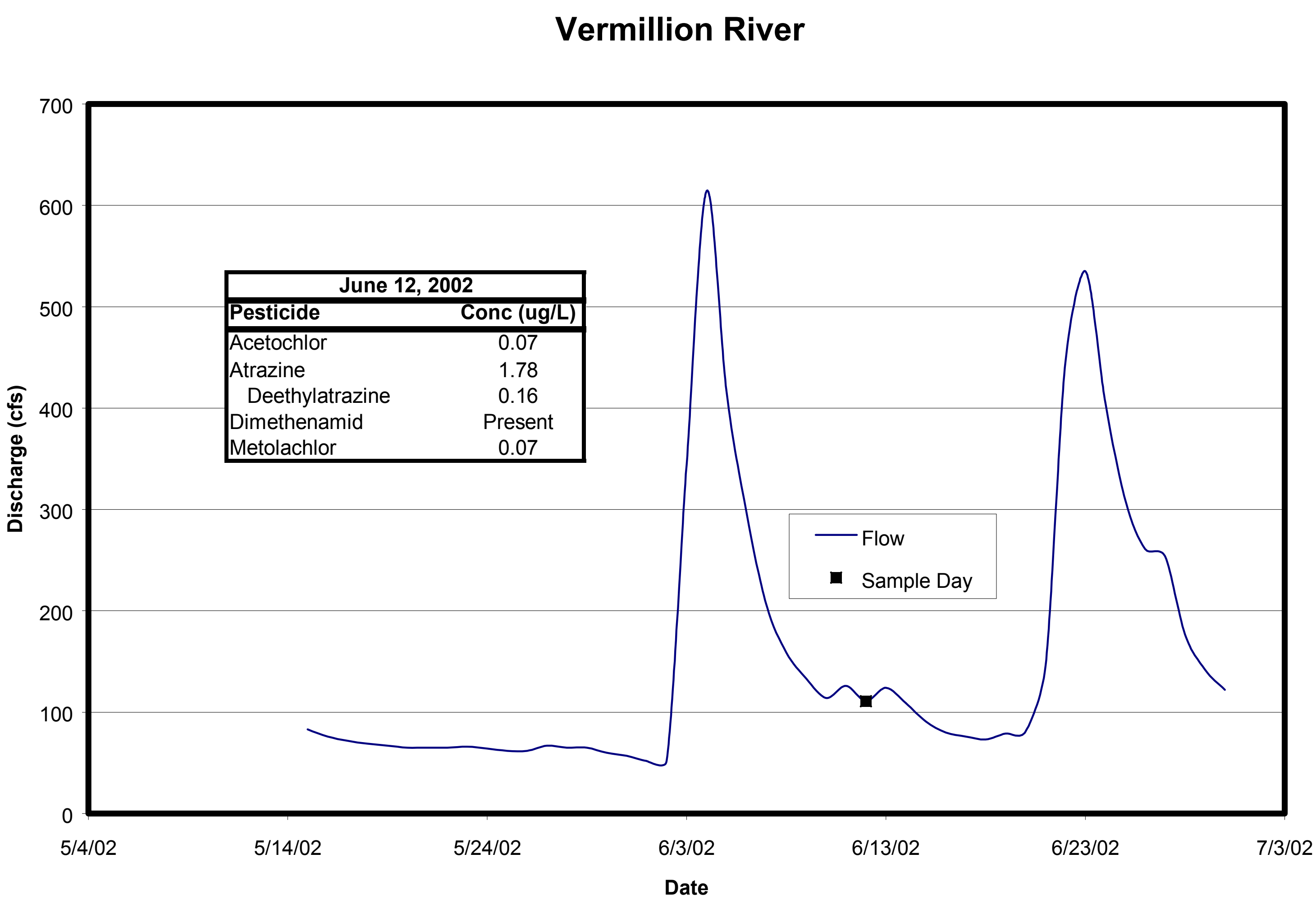


Figure 79 – Watonwan River Hydrograph and Analytical Results, May 28, 2002