Chemical Composition of Surficial Sediment in Geneva Lake, Wisconsin

Introduction

Intense recreational use of Geneva Lake and extensive residential and other development in its watershed (fig. 1) has created concern over a possible decline in water quality of the lake. Because of this concern, a collaborative effort between the U.S. Geological Survey (USGS), Wisconsin Department of Natural Resources (WDNR), and the Geneva Lake Environmental Agency was begun to document the present quality of the water and its sediments, to estimate the amount of nutrients (primarily phosphorus) coming into the lake, and to describe changes that have occurred in the lake over the past 200 years. In this fact sheet, we describe the quality of the surficial sediments of the lake.

Geneva Lake is about 12.2 km long, has a surface area of 2,117 ha, a mean depth of 19.1 m, and a maximum depth of 44 m. The lake was formed about 10,000 years ago during the late Wisconsin glaciation. The 52.6-km^2 watershed of the lake is comprised of various land uses: agriculture and grassland, 45 percent; forest and wetland, 37 percent; urban, 8 percent; and other uses, 10 percent (fig. 1). In recent years, the urban area of the watershed has been expanding into former agricultural and forested areas, especially near the communities of Lake Geneva, Williams Bay, and Fontana.

Geneva Lake is classified as mesotrophic; it is moderate in nutrient content and biological productivity, and has a tendency to become oxygen-depleted in deep-water zones. Surface total phosphorus concentrations range from less than 5 µg/L to 25 µg/L, surface chlorophyll *a* concentrations range from 2 to 7 µg/L, and Secchi depths range from 2 to 7 m (based on water-quality sampling during 1997–1999). Mean sedimentation rate for the past 150 years is 0.04 g/cm^2/yr—low compared to most other lakes in southern Wisconsin, but within a range commonly observed in lakes.

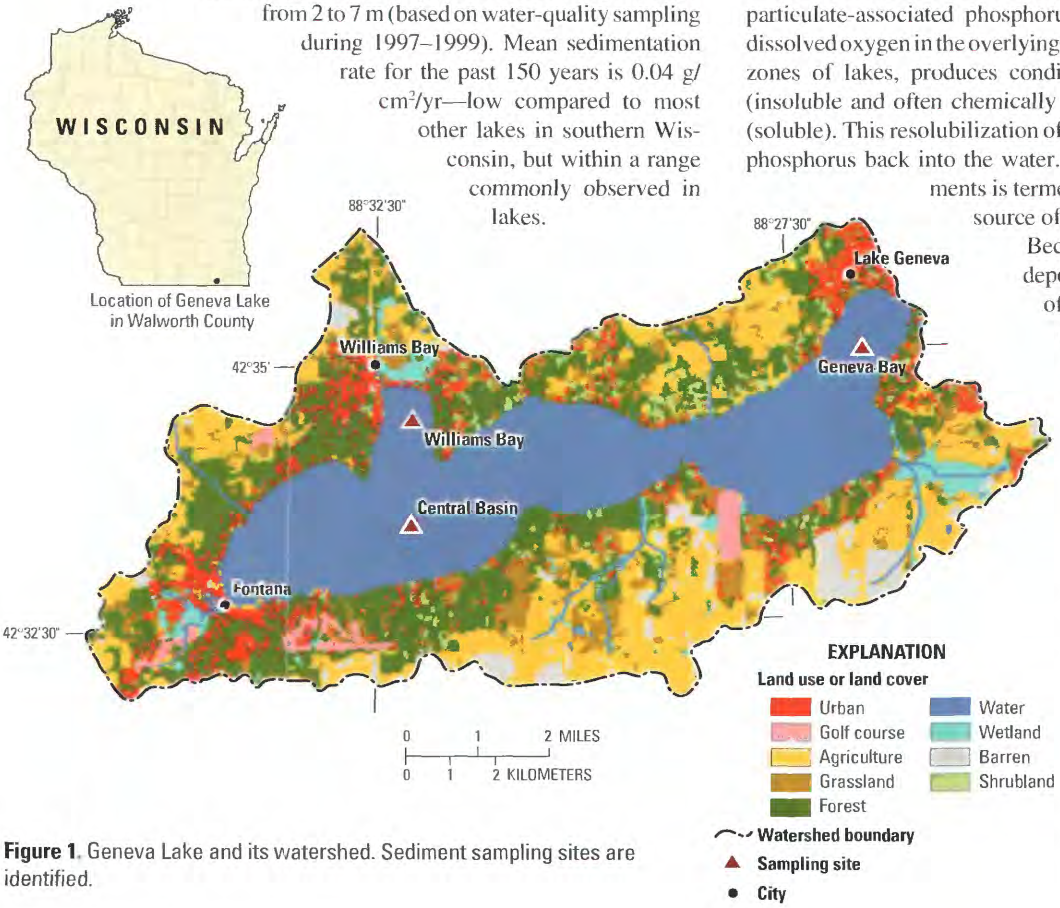

Figure 1. Geneva Lake and its watershed. Sediment sampling sites are identified.

Why examine the sediment chemistry of a lake?

The bottom sediments of a lake represent a natural record of its history because most substances entering the lake eventually find their way to the sediments. This is true not only for particles that sink directly to the bottom but also for substances dissolved in the water. With time, dissolved substances can be retained in the sediments by various processes, including adsorption to particles and chemical precipitation. Many synthetic organic chemicals, the so-called "hydrophobic compounds," are virtually insoluble and have especially strong tendencies to accumulate in the sediments.

Chemical compounds that reach the sediments do not necessarily remain there permanently. Sediments can function as a reservoir, or temporary resting place, for certain elements, which can be released back into the water column (resolubilized) with changing environmental conditions. For example, resolubilization can be triggered by changes in dissolved oxygen, pH, or temperature. Substances associated with the sediments can also be released by biological activity (such as burrowing of worms or aquatic insect larvae, algal productivity near the sediment surface, or microbial activity that causes biodegradation of certain complex compounds).

Phosphorus is a good example of an element that can move in both directions between water and sediments. A critical nutrient for algal growth, phosphorus exists in various chemical forms in both water and sediments, but it tends to move toward the sediments when it is incorporated into various kinds of particulate matter. However, most of this particulate-associated phosphorus is relatively unstable. Depletion of dissolved oxygen in the overlying water, which typically occurs in the deep zones of lakes, produces conditions that may reduce the ferric iron (insoluble and often chemically bonded to phosphorus) to ferrous iron (soluble). This resolubilization of iron compounds releases the associated phosphorus back into the water. Remobilization from the bottom sediments is termed "internal loading" and can be a major source of nutrients to the lake.

Because of the tendency for materials to be deposited in bottom sediments, a great deal of information about relatively recent chemical and particulate inputs and cycles in a lake can be extracted from examination of samples of the surface sediments. Also, because substances can be mobilized from the sediments to overlying water, sediment analysis can show what nutrients and contaminants may be readily available to the water through internal loading.

Collection and analysis of surficial-sediment samples

Surficial-sediment samples were collected from a depth of about 40 m in the Central Basin in October 1996 and about 20 m in Williams Bay and Geneva Bay in October

U.S. Department of the Interior
U.S. Geological Survey

USGS Fact Sheet FS-121-00
September 2000

1996 and in July 1997 (fig. 1). The two bay locations were chosen because they were thought to represent sites with most potential for contamination. The samples, which consisted of material from approximately the top 5-cm layer of sediments, were collected with a gravity corer (fig. 2) in 1996 and with an Ekman dredge (fig. 3) in 1997. The core samples from 1996 were cut into 1-cm-thick slices and sent to the Wisconsin State Laboratory of Hygiene for determination of sedimentation rates, water content, organic matter, and calcium carbonate ($CaCO_3$), as well as concentrations of aluminum (Al), arsenic (As), total nitrogen (TN), total phosphorus (TP), and zinc (Zn). In addition to these constituents, concentrations of calcium (Ca), copper (Cu), iron (Fe), manganese (Mn), and potassium (K) were determined in samples from the Central Basin. The concentrations from the top five discrete depths in the 1996 sample were averaged to obtain an average concentration in the surficial deposits. Analytical methods for these constituents followed approved protocols of the U.S. Environmental Protection Agency (1983). The samples from 1997 were chilled in ice and sent to the USGS National Water Quality Laboratory for determination of total organic carbon, polycyclic aromatic hydrocarbons (PAH's), chlorinated hydrocarbons (including DDT and its derivatives), polychlorinated biphenyls (PCB's), and some trace metals. Analytical methods for these constituents followed approved USGS protocols (Fishman and others, 1994).

Some of the priority pollutants identified by the U.S. Environmental Protection Agency were among the target elements and compounds of this study. These substances have been identified as suspected carcinogens or potentially toxic in other ways to wildlife and (or) humans. Their occurrence in aquatic systems depends largely on the characteristics of the watershed and land use within it. The PAH's, PCB's, and some of the chlorinated hydrocarbons and metals are by-products of industrial activities, and their presence in elevated concentrations in natural water would be an indication that the water was affected by industrial discharges. In lakes that are remote from point-source discharges, the primary source of these substances is atmospheric deposition. Other chlorinated hydrocarbons and some of the metals are derived from pesticides and herbicides, and they would most likely appear in aquatic systems that receive agricultural drainage. In still other systems, weathering or leaching of certain elements from rocks and soils in the watershed can produce unexpectedly high concentrations in receiving waters, even if inputs from industry and agriculture are minimal or nonexistent.

Figure 2. Gravity corer used to collect sediment samples in Geneva Lake.

Composition of Geneva Lake sediments

Characteristics of Geneva Lake sediments and concentrations of nutrients and metals found in the sediments are listed in table 1. Sediments from the three areas of the lake were nearly indistinguishable with respect to water content, organic content (loss on ignition), and calcium carbonate concentration. Total phosphorus, total nitrogen, aluminum, and zinc were measured in sediments from all three sites, and were present at lower concentrations in the Central Basin than in the bays. For arsenic, the distribution gradient was the opposite, with higher concentrations in the Central Basin than in the bays. This finding indicates that most of the arsenic in the sediments was not from recent urban drainage into the bays. Arsenic, extensively used as a herbicide for aquatic plant management, might have been deposited over a much longer time period, and during that time it might have become concentrated in the deep sediments.

Table 1 also provides sediment-quality criteria for arsenic, copper, and zinc. These criteria were developed from previous studies that identify concentrations above which detrimental effects on biota are frequently observed. Although each system has unique conditions that affect its responses to contaminants, the probability of biological effects increases substantially as concentrations exceed the published minimum standard levels. The absolute values of the concentrations are not as important as whether or not they are high relative to concentrations in other environments, and whether the constituents of interest are at concentrations that could produce biological effects.

The criteria cited in table 1 include Sediment Effect Concentrations (SEC's), based on toxicity data for Great Lakes sediment samples and two benthic species—*Hyalella azteca* and *Chironomus riparius*—commonly used for toxicity testing (Ingersoll and others, 1996). There are two Sediment Effect Concentrations: Effects Range-Low (ERL) and Effects Range-Median (ERM). Also cited are Canadian freshwater sediment quality guidelines based on data and spiked-sediment toxicity tests from the National Status and Trends Program (Canadian Council of Ministers of the Environment, 1999). Two types of Canadian freshwater sediment quality guidelines exist: Interim Sediment Quality Guidelines (ISQG) and Probable Effects

Table 1. Sediment characteristics and concentrations of nutrients, metals, and major ions in Geneva Lake sediments sampled 1996–1997. [Trace-metal data compared with Sediment Effect Concentrations (SEC's): ERL, Effects Range-Low; ERM, Effects Range-Median. Also compared with Canadian freshwater sediment quality guidelines: ISQG, Interim Sediment Quality Guideline; PEL, Probable Effects Level. All element concentrations based on dry weight. %, percent; --, no data; g/kg, grams per kilogram; mg/kg, milligrams per kilogram]

Characteristic variable and unit	Central Basin Mid-Lake	Williams Bay	Geneva Bay	SEC[1]		Sediment guidelines[2]	
				ERL	ERM	ISQG	PEL
Water content, %	89.3	80.8	84.2	--	--	--	--
Loss on ignition, %	13.3	13.3	14.0	--	--	--	--
CaCO3, %	25.1	23.4	26.9	--	--	--	--
Ca, %	22.2	--	--	--	--	--	--
TP, g/kg	0.78	1.61	1.48	--	--	--	--
TN, g/kg	8.1	15.8	14.9	--	--	--	--
Al, g/kg	7.9	17.6	13.4	--	--	--	--
K, g/kg	12.2	--	--	--	--	--	--
Fe, g/kg	0.9	--	--	--	--	--	--
Mn, g/kg	1.12	--	--	--	--	--	--
As, mg/kg	35.4	16.8	19.3	13	50	6	17
Cu, mg/kg	44	--	--	41	190	36	197
Zn, mg/kg	158	232	241	110	550	123	315

[1] Ingersoll and others, 1996

[2] Canadian Council of Ministers of the Environment, 1999

Figure 3. Ekman dredge used to collect sediment samples in Geneva Lake.

Levels (PEL). For both the criteria and guidelines, the lower level or threshold indicates where literature has shown biological effects just begin to appear, and the higher level above which literature has shown adverse biological effects are likely.

The data in table 1 indicate potential for concern with respect to the concentrations of arsenic, copper, and zinc in Geneva Lake sediments. All three elements were at levels exceeding the lower-level criteria (Effects Range-Low and Interim Sediment Quality Guidelines). Arsenic concentrations also exceeded the Canadian Probable Effects Level.

Synthetic organic compounds in the sediments

Concentrations of aromatic hydrocarbons (primarily PAH's) and DDT derivatives (DDD and DDE) found in Geneva Lake sediments are listed in table 2. For the group of most commonly known compounds, their concentrations are compared with those found in studies of two of the Great Lakes and with Canadian freshwater sediment quality guidelines.

A number of commonly used pesticides, including dieldrin, endrin, heptachlor epoxide, aldrin, endosulfan, lindane, and mirex, were not detected. Non-detection means that their concentrations were below the analytical detection limits, or minimum reporting levels, which are affected not only by analytical techniques and instrument capabilities but also by sample size, interfering substances in the sediment, and other characteristics of the sample. The minimum reporting level for the pesticides was approximately 3 ng/g (6 ng/g for endrin). Other nondetectable compounds included naphthalene, acenaphthene, quinoline, and nitrobenzene (the minimum reporting levels for these compounds was 50 ng/g), and polychlorinated biphenyls (PCB's, with a minimum reporting level of 170 ng/g). The absence of detections of these compounds does not necessarily mean that the compounds are not present; in fact, they could even be present at concentrations exceeding biological effect levels, because in some cases the minimum reporting level was higher than sediment-quality guidelines. Specifically, this is true for PCB's, heptachlor epoxide, and lindane in these samples.

A schematic representation of most of the data from table 2 is shown in figure 4. Again, the Canadian freshwater sediment quality guidelines for these compounds are shown for comparison. All PAH concentrations in Geneva Lake were well below Probable Effects Levels, but several of them were above Interim Sediment Quality Guidelines. The concentrations of the DDT derivatives were much closer to the Probable Effects Levels, and DDE actually exceeded the Probable Effects Level.

These findings with respect to synthetic organic chemicals are consistent with the land use in the Geneva Lake Watershed. The low concentrations of PAH's correspond to the absence of industry that could release this class of compounds in point-source discharges in the watershed. By contrast, DDT and its derivatives have a long history of persistence and widespread distribution in the environment, even though DDT applications have been discontinued for many years. These compounds are more likely to be associated with historical nonpoint-source runoff from agricultural fields and forested areas that are indeed dominant in the Geneva Lake Watershed. Hence, occurrence of DDT and its derivatives in the lake sediments at relatively high concentrations is not surprising.

Implications of contaminants in sediments

Importance of other environmental factors

Nitrogen and phosphorus stored in the bottom sediments (table 1) are a potential source of nutrients to the lake by internal loading. The extent to which this potential is realized depends to a large extent on the oxygen content and pH of the water in and above the sediments.

Anoxic conditions stimulate the activity of bacteria that reduce ferric iron and sulfates. Because much of the phosphorus in the sediments is sorbed to these compounds, phosphorus can be released under anoxic, reducing conditions. Moreover, anoxia produces an increased tendency for mobilization of phosphorus in the form of polyphosphates or colloidal organics. Nitrogen cycling is also sensitive to the oxygen content because nitrogen exists in several different oxidation states and species, including nitrate, nitrite, ammonia, nitrogen gas, and dissolved organic nitrogen. Denitrification (reduction of nitrate to nitrogen gas) by bacterial action can

Table 2. Aromatic hydrocarbons and chlorinated hydrocarbons detected in Geneva Lake sediments sampled July 17, 1997. [Canadian freshwater sediment quality guidelines are given where available: ISQG, Interim Sediment Quality Guideline; PEL, Probable Effects Level. All concentrations in nanograms per gram, dry wt.; e, estimate; --, no data]

Compound	Williams Bay	Geneva Bay	Lake Michigan[1]	Lake Superior[2]	Sediment guidelines[3]	
					ISQG	PEL
ANTHRACENE	14 e	14 e	12–55	--	47	245
BENZO(a)ANTHRACENE	45 e	44 e	18–162	28–65	32	385
d-BENZO(a,h)ANTHRACENE	<50	12 e	22–371	15–125	6	135
ACENAPHTHALENE	9 e	<50	0–21	--	7	89
FLUORANTHENE	130	110	129–496	36–153	111	2,355
BENZO(b+k)FLUORANTHENE	103	110	275–615	153–516	--	--
CHRYSENE	43 e	41 e	129–348	73–172	57	862
PHENANTHRENE	56	47 e	126–366	62–98	42	515
PYRENE	110	91	103–400	21–88	53	875
BENZO(a)PYRENE	53	52	80–268	32–64	32	782
BENZO(GHI)PERYLENE	45 e	47 e	143–302	41–216	--	--
PHENOL	15 e	17 e	--	--	--	--
DDD (*)	4–7	6–8	--	--	3.5	8.5
DDE (*)	9–13	12–15	--	--	1.4	6.8
2,6-DIMETHYLNAPHTHALENE	58	74	--	--	--	--
4HCYPENPHENANTHRENE	17 e	<50	--	--	--	--
9,10-ANTHRAQUINONE	37 e	39 e	--	--	--	--
9H-FLUORENE	3 e	<50	--	--	--	--
CARBAZOLE	13 e	<50	--	--	--	--
p-CRESOL	8 e	<50	--	--	--	--
IMIDENO123CDPYRENE	40 e	47 e	--	--	--	--
MESITOL	23 e	--	--	--	--	--
PYRENE, 1-METHYL	15 e	14 e	--	--	--	--

(*) sum of o,p' and p,p' isomers

Sources:

---

[1] Simcik and others, 1996

[2] Baker and others, 1991

[3] Canadian Council of Ministers of the Environment, 1999

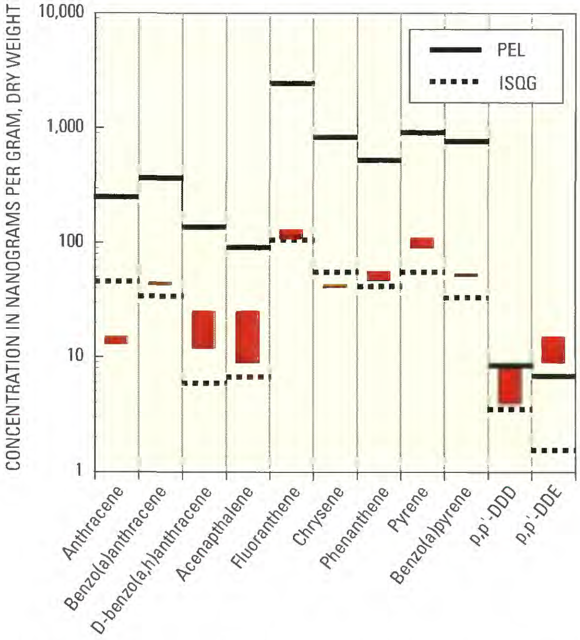

Figure 4. Concentrations of polycyclic aromatic hydrocarbons (PAH's) and DDT derivatives in surficial sediments of Geneva Lake, compared with Canadian freshwater sediment quality guidelines: Interim Sediment Quality Guidelines (ISQG) and Probable Effect Level (PEL) (Canadian Council of Ministers of the Environment, 1999). Bars show ranges from minimum to maximum concentrations reported (on log scale). If nondetectable, the concentration used is approximately one-half of the detection limit.

mobilize sediment-bound nitrate in oxic conditions, whereas formation of ammonia—also highly soluble and mobile—is favored in anoxic conditions.

The effects of pH changes on internal nutrient loading are variable, depending on the speciation of the nutrients present in the sediments. In general, nutrient mobility tends to increase if pH deviates significantly from neutral—either toward more acid or more alkaline conditions. Acidity increases the solubility of several common minerals and chemical precipitates that contain nutrients, such as apatite and ferric hydroxides. Highly alkaline conditions, on the other hand, can diminish nutrient sorption onto particulates, leading to nutrient releases even in oxic waters.

In Geneva Lake, the hypolimnetic zone (the deeper and cooler areas in temperature-stratified lakes) is commonly anoxic during the stratification period (June–October), but pH levels in this zone are usually only slightly alkaline (near 7.5). Relatively high phosphorus concentrations in the hypolimnetic waters (>100 µg/L) probably result from internal release associated with anoxia. In general, during the summer, this release does not stimulate algal blooms because most of the released nutrient does not reach the epilimnion or photic zone (shallow, warmer waters of a lake where light penetrates and algae are most abundant). However, under certain mixing conditions in the fall, this type of bloom stimulation is possible.

Potential effects of urbanization

Urbanization in the basin increases the likelihood that synthetic organic compounds and trace metals will be transported to the lake and accumulate in the lake sediments. Increased input of these constituents from urban stormwater runoff has been frequently documented. Compounds and elements commonly used in industrial and municipal applications include PAH's, some pesticides and herbicides, and some trace metals (arsenic, cadmium, chromium, copper, lead, and zinc).

Overview

The results of the analysis of the bottom sediments of Geneva Lake indicate that agricultural and municipal drainage from the watershed has produced elevated, and potentially problematic, concentrations of some elements and compounds in the lake's sediments. Moreover, continued development in the watershed could produce still further increases in inflow and accumulation of these compounds. Although the concentrations of a number of potentially toxic elements and compounds were found to exceed published criteria and guidelines for sediments, the actual effects on organisms are complicated by many interacting environmental factors, most of which have not yet been investigated in the Geneva Lake system. These factors include mechanisms of transfer through the food chain, chemical forms of the contaminants, and affinity for accumulation in biological tissue. The fact that total concentrations are elevated indicates little about actual toxicological effects on any biological species, but it serves as a signal that future investigators of contaminants in the lake may want to focus on such details as bioavailability, cycling within the ecosystem, and toxicology of these compounds.

References

Baker, J. E., S. J. Eisenreich, and B. J. Eadie, 1991, Sediment trap fluxes and benthic recycling of organic carbon, polycyclic aromatic hydrocarbons and polychlorobiphenyl congeners in Lake Superior, Environ. Sci. Technol., v. 25, p. 500–509.

Canadian Council of Ministers of the Environment, 1999, Canadian sediment quality guidelines for the protection of aquatic life: Summary tables. *in* Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

Fishman, M. J., J. W. Raes, C. N. Gerlitz, and R. A. Husband, 1994, U.S. Geological Survey approved inorganic and organic methods for the analysis of water and fluvial sediment, 1954–94: U.S. Geological Survey, Open-File Report 94-351, Denver, Colorado.

Ingersoll, C. G., P. S. Haverland, E. L. Brunson, T. J. Canfield, F. J. Dwyer, C. E. Henke, N. E. Kemble, D. R. Mount, and R. G. Fox, 1996, Calculation and evaluation of sediment effect concentrations for the amphibod *Hyalella azteca* and the midge *Chironomus riparius*, Journal of Great Lakes Research, v. 22, p. 602–623.

Simcik, M. F., S. J. Eisenreich, K. A. Golden, S.P. Liu, E. Lipiatou, D. L. Swackhamer, and D. T. Long, 1996, Atmospheric loading of polycyclic aromatic hydrocarbons to Lake Michigan as recorded in the sediments, Environ. Sci. Technol., v. 30, p. 3039–3046.

U.S. Environmental Protection Agency, 1983, Methods for Chemical Analysis of Water and Wastewater, U.S. Environmental Protection Agency, EPA-600/4-79-020, Washington, D.C.

Abbreviations

The following abbreviations are used in this publication: cm, centimeter; m, meter; km, kilometer; km^2, square kilometer; ha, hectare; µg/L, micrograms per liter; ng/g; nanograms per gram of sediment; g/cm^2/yr, gram per square centimeter per year.

Information

For information on this study or on other USGS programs in Wisconsin, contact:
District Chief
U.S. Geological Survey
8505 Research Way
Middleton, WI 53562
(608) 828-9901
http://wi.water.usgs.gov/

Authors: John F. Elder and Dale M. Robertson, U.S. Geological Survey; and Paul J. Garrison, Wisconsin Department of Natural Resources

Layout and illustrations: Michelle Greenwood, Aaron Konkol, and David Saad

Printed on recycled paper