Prepared in cooperation with U.S. Army Environmental Command

Assessment of Mercury in Sediments and Waters of Grubers Grove Bay, Wisconsin

Open-File Report 2022–1051

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

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Contents

Figures

Conversion Factors

U.S. customary units to International System of Units

Multiply	By	To obtain
	Length	
mile (mi)	1.609	kilometer (km)
	Area	
acre	4,047	square meter (m^2)
acre	0.4047	hectare (ha)
acre	0.4047	square hectometer (hm^2)
acre	0.004047	square kilometer (km^2)

International System of Units to U.S. customary units

Multiply	By	To obtain
	Length	
micrometer (µm)	3.937×10^{-5}	inch (in.)
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
	Volume	
milliliter (mL)	0.33814	ounce, fluid (fl. oz)
liter (L)	33.81402	ounce, fluid (fl. oz)
liter (L)	2.113	pint (pt)
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)
liter (L)	61.02	cubic inch (in^3)
	Mass	
nanogram (ng)	3.527×10^{-11}	ounce, avoirdupois (oz)
gram (g)	0.03527	ounce, avoirdupois (oz)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F = (1.8 \times °C) + 32.$$

Datum

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Supplemental Information

Concentrations for mercury species are reported in nanograms per gram (ng/g).

Mercury stable isotope measurements are reported in per mille (‰).

Sediment sampling depths are reported in centimeters (cm).

Abbreviations

IAEA	International Atomic Energy Agency
LOI	loss on ignition
MC–ICP–MS	multicollector inductively coupled plasma mass spectrometer
MDF	mass dependent fractionation
MIF	mass independent fractionation
MRL	Mercury Research Laboratory
n	number of samples
NIST	National Institute of Standards and Technology
P	probability
R^2	coefficient of determination
SE	standard error
SPM	suspended particulate matter
UR	upstream reference
USGS	U.S. Geological Survey
<	less than

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Abstract

Mercury is a global contaminant that can be detrimental to wildlife and human health. Anthropogenic emissions and point sources are primarily responsible for elevated mercury concentrations in sediments and waters. Mercury can physically move and chemically transform in the environment, resulting in biomagnification of mercury, in the form of methylmercury, in the food web and causing elevated mercury concentrations in upper trophic levels. The ability to measure total mercury concentrations in the environment has existed for several decades and makes it possible to detect hotspots that might exist because of ongoing or previous anthropogenic activity. However, recent (within the past 15 years) developments in mass spectrometry have made it possible to complete low level stable isotope analysis allowing for the determination of mercury sources—natural and anthropogenic—in the environment through "fingerprinting." Grubers Grove Bay in Lake Wisconsin, the focus area of this study, was determined to have elevated mercury levels even after multiple remediation efforts, resulting in its listing on the Federal list of impaired waters pursuant to the Clean Water Act. Adjacent to the bay is the former Badger Army Ammunition Plant, which manufactured ammunition for the U.S. Army during the early and middle 20th century, after which it was put on standby before being fully decommissioned. This study assesses mercury concentrations in the sediments and suspended particulate matter of Grubers Grove Bay, Wiegands Bay, and upstream sites, and in adjacent soils on the former Badger Army Ammunition Plant site. This study confirmed that mercury contamination exists in the sediments of Grubers Grove Bay even after dredging attempts by the U.S. Army. Additionally, using isotope ratios and a two-endmember mixing model, it was determined that soil from within Badger Army Ammunition Plant's former site contributed a substantial amount of mercury to the bay. This result was supported by an observed gradient of high to low mercury concentrations from the innermost (nearest Badger Army Ammunition Plant) to the outermost (farthest from Badger Army Ammunition Plant) part of the bay.

Introduction

Mercury is recognized as a global pollutant and an important contaminant to study because of its ubiquity in the environment, potential for long-range transport, and high toxicity towards humans and wildlife (Beckers and Rinklebe, 2017). Environmental mercury can be attributed to natural emissions (for example, volcanoes), anthropogenic emissions (for example, fossil fuel burning), or industrial point sources (for example, mercury catalyst waste, mercury mining; Driscoll and others, 2013; Blum and others, 2014). Past research determined that long-range transport of mercury results in elevated mercury concentrations, even in the most pristine environments, making it difficult to conclude that any environmental medium is completely free of mercury (Kang and others, 2016; Beckers and Rinklebe, 2017). Specifically, anthropogenic release of mercury into the environment from point sources has created hotspots, and transport from these locations has contributed to increased global mercury background levels compared to preindustrial levels (Beckers and Rinklebe, 2017; Eckley and others, 2020).

Mercury exists in different forms, which move, bind, and react differently in the environment. Determinants of mercury speciation and distribution in the environment are multifaceted. For example, total mercury and methylmercury in stream systems can vary with transport mechanisms (for example, atmospheric deposition, surface water runoff), water characteristics (for example, pH, dissolved organic carbon), and bed sediment characteristics (for example, grain size, organic content). Specifically, research has determined that total mercury can positively correlate with sediment and particulate organic content in freshwater systems because of mercury's high organic matter affinity (Sunderland and others, 2004; Marvin-DiPasquale and others, 2009; Nasr and Arp, 2017). Methylmercury also positively correlates with factors such as organic content in freshwater systems because organic matter is a substrate for microorganisms capable of methylating mercury (Krabbenhoft and others, 1999; Sunderland and others, 2004).

Methylmercury is of special concern because it is known to cause health problems such as impaired motor skills and brain development in wildlife and humans at lower doses than inorganic mercury (Ratcliffe and others, 1996). A primary pathway for methylmercury, the neurotoxic form of mercury, to reach humans is via fish consumption. Starting in anoxic environments of aquatic ecosystems, inorganic mercury is transformed to methylmercury by anaerobic microorganisms containing genes for mercury methylation (Hsu-Kim and others, 2013). Once formed, methylmercury readily bioaccumulates and biomagnifies within the food web, resulting in the highest concentrations of methylmercury in predatory species, including human-consumed fish, resulting in certain fish species to be a leading dietary source of mercury (Sunderland, 2007; Beckers and Rinklebe, 2017; Tsui and others, 2020).

Because of this high-risk exposure pathway and the health concerns related to methylmercury, fish consumption advisories are often put in place for mercury contamination (for examples, see the U.S. Environmental Protection Agency website: https://www.epa.gov/choose-fish-and-shellfish-wisely). In Wisconsin, waterbodies in both urbanized and remote regions have fish consumption limits in place because of elevated methylmercury in fish tissue (for examples, see the Wisconsin Department of Natural Resources website: https://dnr.wi.gov/FCSExternalAdvQry/FishAdvisorySrch.aspx).

Although total mercury and methylmercury concentrations are useful as basic contamination and risk diagnostic tools, they do not provide a robust understanding of mercury sources to the environment (for example, atmospheric deposition, industrial point source contamination, or nonpoint source runoff). However, advances in high-resolution mass spectrometry using a multicollector inductively coupled plasma mass spectrometer (MC–ICP–MS) have allowed measurements of stable isotopes of mercury, a useful tool for assessing mercury sources and cycling, at environmentally relevant levels.

Mercury has seven naturally occurring stable isotopes (mercury-196, mercury-198, mercury-199, mercury-200, mercury-201, mercury-202, and mercury-204) that can fractionate during chemical, biological, or physical reactions resulting in (1) mass dependent fractionation (MDF, reported in lowercase delta notation for mercury-202 as δ^{202}Hg), where the degree of separation is commensurate with the differences in isotopic masses, or (2) mass independent fractionation (MIF), which is observed in odd and even isotopes (reported in capital delta notation for mercury-199, mercury-200, mercury-201, and mercury-204 as Δ^{199}Hg, Δ^{200}Hg, Δ^{201}Hg, and Δ^{204}Hg, respectively; Blum and others, 2014; Tsui and others, 2020). As it is understood, MDF is observed with any biotic or abiotic processes (Blum and others, 2014). Odd MIF is primarily driven by the magnetic isotope effect and predominantly observed during the photochemical reduction or demethylation of mercury species (Blum and Bergquist, 2007). Even MIF is thought to take place during upper atmosphere processes, although the exact mechanisms are unclear (Chen and others, 2012; Fu and others, 2016).

Literature values from natural isotopic studies are sufficient to pair specific fractionation patterns with certain processes. For instance, it has been widely observed that industrial processes result in MDF with δ^{202}Hg between −1 and 0 per mille (‰) and usually near 0 ‰ for Δ^{199}Hg, Δ^{200}Hg, and Δ^{201}Hg (Eckley and others, 2020; Tsui and others, 2020). Using this information and mass balance calculations, isotope values can be compared between contaminated sites and reference sites to determine natural mercury sources and relative industrial mercury contribution (Eckley and others, 2020).

Site Description

Grubers Grove Bay, the site of this study, is a small (about 25-acre) bay in the downstream part of Lake Wisconsin, about 1 mile upstream from the Alliant Energy Dam in Prairie du Sac (fig. 1*A*). In 2003, Grubers Grove Bay was placed on the Federal list of impaired waters pursuant to the Clean Water Act (33 U.S.C. 1251[a]) because of elevated mercury levels in the sediment. The site is adjacent to the southwest corner of the former Badger Army Ammunitions Plant, near Baraboo, Wisconsin. Badger Army Ammunition Plant was operational during World War II, the Korean War, and the Vietnam War. In between these operational periods and after the Vietnam War until its closure in 1997, Badger Army Ammunition Plant was kept on standby. During its operational years, Badger Army Ammunition Plant produced single and double base propellants such as smokeless powder, rocket powder, and ball powder, which required the use of organics (for example, nitroglycerin), acids (for example, nitric acid, oleum), and other chemicals, many of which were produced onsite (Fay, 1985).

After the shutdown of the plant, organic chemicals related to ammunition manufacturing were discovered in local groundwater (U.S. Army Environmental Command, 2018). During monitoring of that contamination, the U.S. Army also detected elevated levels of mercury in and around Badger Army Ammunition Plant grounds, including in Grubers Grove Bay. Although the U.S. Army accepted responsibility for cleanup of mercury contamination, there is no reported use or disposal of mercury in any capacity at Badger Army Ammunition Plant, so exact causes of the contamination are unknown (Fay, 1985; U.S. Army Joint Munitions Command, undated). Despite dredging Grubers Grove Bay in 2001 and 2006, the most recent assessment in 2016 again revealed persistent high levels of mercury in the sediments of the bay (U.S. Army Environmental Command, 2018).

Purpose and Scope

The purpose of this report is to (1) present results for total mercury and methylmercury concentrations within Grubers Grove Bay and surrounding areas and (2) use stable isotopes to fingerprint mercury from the Badger Army Ammunition Plant site, Grubers Grove Bay, and upstream

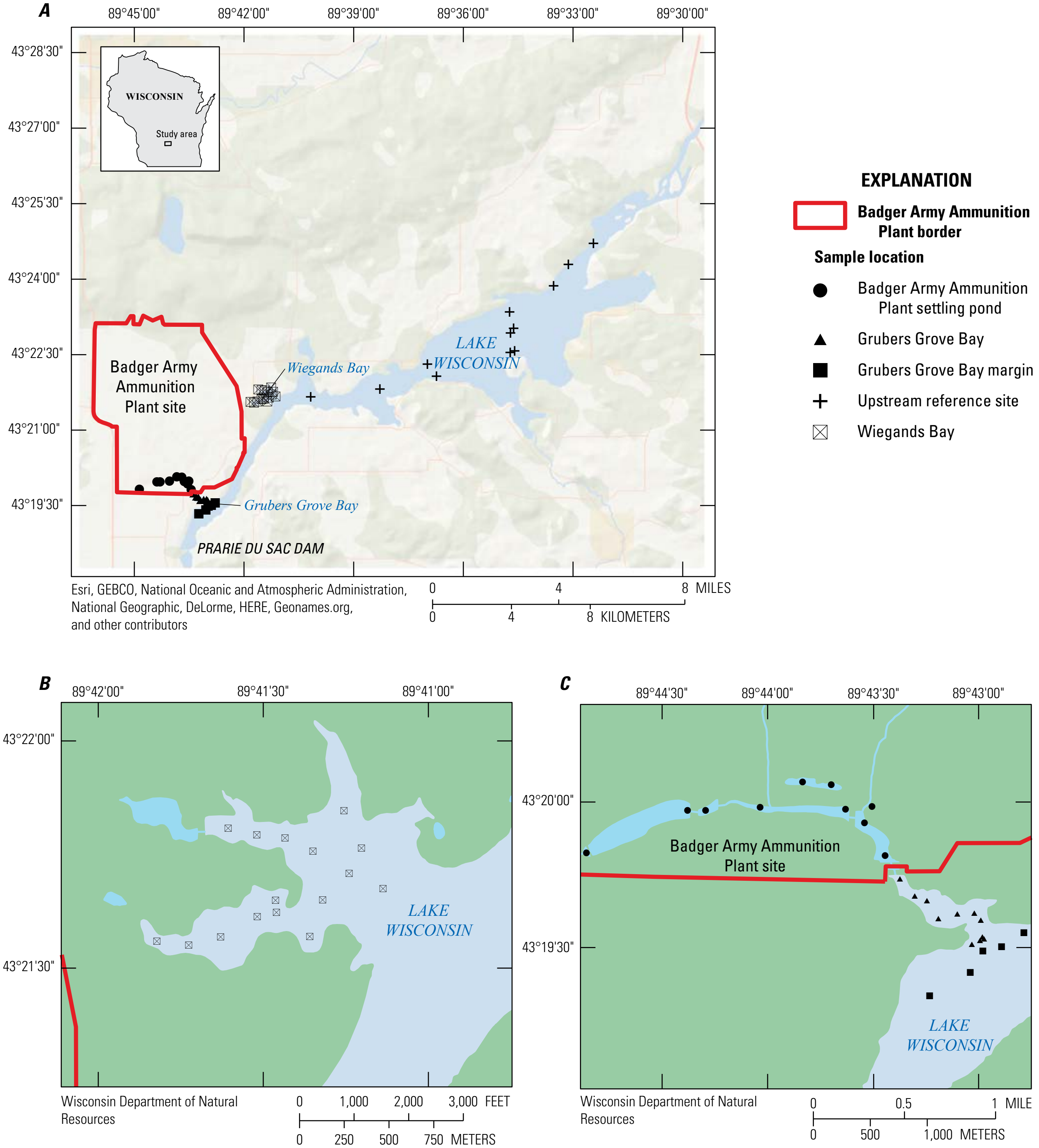

Figure 1. Location of sampling sites near the Badger Army Ammunition Plant study area, Sauk County, Wisconsin. *A*, location of sampling sites near the Badger Army Ammunition Plant study area; *B*, zoomed in view of the Wiegands Bay sampling locations; *C*, zoomed in view of the Badger Army Ammunition Plant settling ponds, Grubers Grove Bay, and Grubers Grove Bay margin sampling locations.

sites. Sediments, soils, and suspended particulate matter (SPM) were targeted to determine if contamination from Grubers Grove Bay was extending into Grubers Grove Bay margin—the margin between the bay and main channel of the Wisconsin River—and being resuspended into the overlying water column, allowing for transport away from the site. The study was further designed to assess the contributions of Badger Army Ammunition Plant mercury to sediments within Grubers Grove Bay to better inform the next phase of remediation at the site. Nongovernment organizations and the public have expressed vested interest in the successful restoration of the lands and water surrounding the previous Badger Army Ammunition Plant grounds, but there is a desire among stakeholder to define the extent of mercury contamination before further restoration (U.S. Army Environmental Command, 2018).

Methods

The following section discusses methods for site selection based on historic land use and mercury contamination, collection of sediments, soils and SPM at sites, analysis of samples, and statistics used to interpret data.

Sites

Samples were taken at five designated areas—one within Badger Army Ammunition Plant grounds and four within Lake Wisconsin. Global Positioning System coordinates and all data associated with this study are available in a U.S. Geological Survey (USGS) data release (Janssen and Krabbenhoft, 2019). Sampling sites within the lake were Grubers Grove Bay, Grubers Grove Bay margin (between Grubers Grove Bay and the channel), Wiegands Bay (a proximal reference bay), and open-lake locations in upstream Lake Wisconsin (upstream reference [UR] sites). The land sites (Badger Army Ammunition Plant) were chosen based on historical use and included four previous Badger Army Ammunition Plant waste stream settling ponds (numbered 1–4; fig. 1).

Collection

Samples were collected and processed by the USGS Mercury Research Laboratory (MRL) on May 28–30, 2019, using clean techniques (U.S. Geological Survey, 2006). For several locations, sediments and soils at multiple depths were collected. Duplicates were taken at two sites for sediments.

Particulate matter for isotopic mercury analysis was collected by filtering large volumes (18 to 36 liters per site) of raw water through an encapsulated membrane filter (Geotech High Capacity 0.45-micrometer filter) in the field (Janssen and others, 2021). SPM was kept on encapsulated membrane filters and frozen at −20 degrees Celsius (°C) until analysis.

Sediments were collected using a gravity corer with 90-millimeter diameter polycarbonate liners. The 0–5-centimeter (cm) interval of the sediment core (measured from the sediment surface) was sampled at all Lake Wisconsin sites. Additionally, at select Grubers Grove Bay and Grubers Grove Bay margin sites, deeper sections were collected in 5-cm increments to the maximum depth of the sediment core. Sediment and soil samples were stored at approximately 4 °C during field collection and transport, then frozen at −20 °C upon arrival at the laboratory. Sediment core sections were extruded into a clean plastic bag, homogenized by manipulation with gloved hands, and then subsampled into mercury-clean polypropylene jars.

Soil samples on the former Badger Army Ammunition Plant site settling ponds were collected by manual excavation. Although sites sampled were previously settling ponds, they were dry at the time of sampling, and all samples collected were classified as soils, not sediments. Vegetation was removed from the surface of the sampling area (about 2 cm deep), and a hole was dug with a stainless-steel shovel. From the exposed cross section of soil, samples were collected with a polypropylene scoop over depths of 0–12.7 cm and 12.7–25.4 cm (measured from the soil surface) and placed into polypropylene jars. Sediment and soil samples were stored at approximately 4 °C during field collection and transport, then frozen at −20 °C upon arrival at the laboratory.

Analysis

Total mercury and methylmercury concentration analyses were completed at the USGS MRL in Middleton, Wis. Sediment and soil total mercury concentrations were analyzed via atomic adsorption after direct combustion using a Nippon MA–2 mercury analyzer (U.S. Environmental Protection Agency, 2007). Methylmercury analysis for sediments, soil, and SPM was completed using a modified U.S. Environmental Protection Agency Method 1630 (U.S. Environmental Protection Agency, 1998). In short, an enriched isotope amendment was added to samples before distillation. Distillates were then ethylated with sodium tetraethylborate and analyzed via gas chromatography coupled to an inductively coupled plasma mass spectrometer (Thermo Scientific iCAP; Lepak and others, 2015a).

Quality assurance was incorporated throughout the analysis for all constituents. For all sample types, 1 in 10 samples were analyzed in triplicate for precision; analytical blanks were regularly incorporated to determine detection limits; and when possible, certified reference materials similar to the sample constituent were run every 1 in 10 samples to assess accuracy. Additionally, for samples processed and analyzed using wet techniques, 1 in 10 samples was spiked with analytical standard to quantify any matrix interference.

Published detection limits were 0.08 nanogram per gram (ng/g) for sediment methylmercury, 0.01 nanogram (ng) per filter for SPM methylmercury, and 0.07 ng per aliquot for sediment total mercury. Certified reference material recovery was between 98.2 and 104.9 percent (number of samples [*n*] =7, average=102.2 percent, standard error [SE] =0.84 percent) for sediment and soil total mercury analysis, and between 95.1 and 109.5 percent (*n*=6, average=100.7 percent, SE=2.1 percent) for all methylmercury analysis. All triplicate variation was less than 5 percent, and averages were 1.44 percent (*n*=5, SE=0.018 percent) for sediment and soil total mercury analysis and 2.85 percent (*n*=4, SE=0.77 percent) for all methylmercury analysis. Ongoing check blanks, quality control standards, and spike recoveries passed criteria previously set forth by the USGS MRL.

Mercury stable isotope measurements were made by the USGS MRL at the Wisconsin State Laboratory of Hygiene in Stoughton, Wis. Encapsulated membrane filters with particulate matter were extracted in 30 percent bromine monochloride at 55 °C for 5 days (Janssen and others, 2021), after which total mercury concentration was determined (appendix 1). Sediments and soils were digested in aqua regia solution (3:1 hydrochloric acid: nitric acid) at 90 °C for 8–10 hours followed by dilution with ultra-high purity water (Lepak and others, 2015b).

Samples too low in mercury for direct mercury isotope analysis were preconcentrated following purge and trap methods by Janssen and others (2019). In short, in a glass impinger, mercury (II) (Hg[II]) was reduced to elemental mercury (Hg[0]) with stannous chloride and purged with nitrogen gas onto custom built gold traps. Amalgamated mercury was thermally desorbed using a gradually increasing temperature profile (40 minutes, 550 °C maximum) into a 2-milliliter aliquot of 40 percent antiaqua regia (3:1 nitric acid: bromine monochloride). Recovery was determined as a ratio of oxidant trap concentration to original digest concentration, accepting more than 90 percent (*n*=9, average=93.8 percent, SE=0.57 percent).

Mercury stable isotope ratios were measured using an MC–ICP–MS (Thermo Scientific Neptune Plus). Solutions were introduced using stannous chloride reduction coupled to a custom gas liquid separator (Yin and others, 2016). Thallium (40 nanograms per milliliter; National Institute of Standards and Technology [NIST] 997) was simultaneously introduced to the gas liquid separator using a desolvating nebulizer (Apex-Q, Elemental Scientific) for mass bias correction during analysis. The MC–ICP–MS was tuned for optimal strength and stability (about 1 volt of mercury-202 per 1 ng/mL of mercury). Mercury isotopes were analyzed using standard-sample bracketing with NIST 3133 standards. Samples were matrix matched (that is, acid content) and mercury concentration matched to NIST 3133 standards. For every sample and standard, 135 ratios were collected for all the mercury isotopes of interest ($^{202}\mathrm{Hg}/^{198}\mathrm{Hg}$, $^{199}\mathrm{Hg}/^{198}\mathrm{Hg}$, $^{200}\mathrm{Hg}/^{198}\mathrm{Hg}$, $^{201}\mathrm{Hg}/^{198}\mathrm{Hg}$, and $^{204}\mathrm{Hg}/^{198}\mathrm{Hg}$). Outliers were rejected if they exceeded an SE of 2 for the average ratio value. A secondary standard (NIST reference material 8610, UM Almaden) was run every five samples at minimum to ensure external precision of isotope values. Certified reference materials for lake sediment (International Atomic Energy Agency [IAEA]–SL1), contaminated sediment (NIST 1944), and loam soil (European Reference Materials [ERM]-CC141) also were analyzed every 10 samples to ensure digest efficiency and produced values consistent with published literature (appendix 3, table 3.1). Uncertainty in sample measurements is represented by the second standard deviation of the corresponding certified reference materials. External reproducibility and accuracy of mercury stable isotope measurements were denoted by the SE of 2 for NIST reference material 8610 (0.01). Ratios were converted to delta notation and expressed as per mille (Blum and Bergquist, 2007):

$$\delta^{XXX}(‰) = \left[\frac{\left(\frac{^{XXX}\mathrm{Hg}}{^{198}\mathrm{Hg}}\right) sample}{\left(\frac{^{XXX}\mathrm{Hg}}{^{198}\mathrm{Hg}}\right) standard} - 1 \right] \times 1{,}000, \qquad (1)$$

$$\Delta^{XXX}\mathrm{Hg}(‰)=\delta^{XXX}\mathrm{Hg}-\delta^{202}\mathrm{Hg}(\beta), \qquad (2)$$

where

δ is the notation for MDF,
Δ is the notation for MIF,
XXX is the isotope of interest (202, 199, 200, 201, 204),
Hg is mercury, and
β is the mass scaling factor.

Calculations and Statistics

Statistical analysis was carried out using RStudio (1.4.1103; RStudio Team, 2021). Samples were spatially compiled to obtain averages with SE by site (Grubers Grove Bay, Grubers Grove Bay margin, Wiegands Bay, UR sites, and Badger Army Ammunition Plant settling ponds). To account for low sample numbers and nonnormally distributed data, Mann Whitney U tests were completed to compare values between each site. Significant differences for total mercury concentrations were determined using one-sided Mann Whitney U tests based on historical evidence that Grubers Grove Bay has elevated total mercury concentration compared to background levels. All other comparisons (that is, $\delta^{202}\mathrm{Hg}$) were done with two-sided Mann Whitney U tests because no historical evidence indicated that Grubers Grove Bay would differ in one direction for any other properties measured.

Estimates for source contributions were calculated using a mass balance equation:

$$\delta^{xxx}Hg_{SED}=f_{BAAP}\delta^{xxx}Hg_{BAAP}+f_{SPM}\delta^{xxx}Hg_{SPM}, \tag{3}$$

where

$\delta^{xxx}Hg_{SED}$	is the isotope value measured in the sediment;
f_{BAAP} and f_{SPM}	are the fractional contributions of Badger Army Ammunition Plant mercury and main river SPM mercury, respectively;
$\delta^{xxx}Hg_{BAAP}$	is the average isotope value of soils onsite at Badger Army Ammunition Plant; and
$\delta^{xxx}Hg_{SPM}$	is the average isotope value of SPM measurements.

Soils from the Badger Army Ammunition Plant site ($\delta^{202}Hg=-0.33$ plus or minus 0.16, $n=8$) were chosen as the industrial endmember because they are closely tied to the original contamination source from the plant. Upstream SPM isotope values ($\delta^{202}Hg=-0.80$ plus or minus 0.09, $n=9$) were chosen as the isotopic endmember for the greater Wisconsin River because these sediments would be the most likely material transported into Grubers Grove Bay from the river.

Results

The following section discusses results for total mercury, methylmercury, loss on ignition, mass dependent fractionation, and mass independent fractionation. Some sections are detailed further in the appendixes.

Total Mercury

Sediment total mercury concentrations in Grubers Grove Bay over depths of 0–5 cm ranged from 340 to 1,400 ng/g ($n=11$, average=570 ng/g, SE=103), and the concentration generally declined from the innermost site (closest to the historic Badger Army Ammunition Plant site) to the outermost sites (farthest from the historic Badger Army Ammunition Plant site and closest to the main channel; fig. 1*B*). The average total mercury concentration for Grubers Grove Bay sediment is significantly higher (probability [*P*] =0.0038, $P=0.0243$) than the average total mercury concentrations of 328 ng/g ($n=5$, SE=11) and 286 ng/g ($n=11$, SE=46) for Grubers Grove Bay margin and UR sites, respectively. The concentration also is greater than twice the average total mercury concentrations of 210 ng/g ($n=16$, SE=14) in Wiegands Bay (*P* much less than [<<] 0.001 (fig. 2*A*).

Sediment total mercury also was conserved at depth. Total mercury concentrations increased across depths of 5–45 cm from 340 to 640 ng/g and from 340 to 650 ng/g at two sampling points within Grubers Grove Bay and from 320 to 530 ng/g at one sampling point within Grubers Grove Bay margin (fig. 2*B*).

Soil total mercury concentrations in Badger Army Ammunition Plant settling ponds varied greatly, ranging from 9 to 8,243 ng/g ($n=13$, average=1,514, SE=670). Total mercury did not trend spatially with sample location in soils but was quite heterogeneous across locations.

Methylmercury

Here, we present the data for methylmercury in terms of percentage of methylmercury, rather than as raw concentrations, because of the number of factors on which methylmercury concentrations can depend. Sediment methylmercury concentration data are examined further in appendix 3.

Percentage of methylmercury was calculated as the ratio of methylmercury concentration to total mercury concentration. In sediments (0–5-cm depth), the percentage of methylmercury ranged from 1.1 to 1.2 percent ($n=3$, average=1.13, SE=0.03) in Grubers Grove Bay, from 0.6 to 0.7 percent ($n=3$, average=0.63, SE=0.03) in Wiegands Bay, and from 0.6 to 0.9 percent ($n=4$, average=0.68, SE=0.08) at UR sites and was 0.6 percent for the only Grubers Grove Bay margin measurement for 0–5-cm depth. Our results indicated a significantly higher percentage of methylmercury in Grubers Grove Bay than at Wiegands Bay ($P=0.0431$) and at UR sites ($P=0.0262$). At the two sites where samples were collected over a range of depths, the percentage of methylmercury decreased with depth.

Loss on Ignition

We used loss on ignition (LOI) as a surrogate for organic content in sediment. LOI was an average of 16.5 percent ($n=11$, SE=0.65) in Grubers Grove Bay, 16.4 percent ($n=3$, SE=0.48) in Grubers Grove Bay margin, 14.2 percent ($n=16$, SE=0.8) in Wiegands Bay, 13.1 percent ($n=11$, SE=1.7) at UR sites and 10.5 percent ($n=12$, SE=3.3) for Badger Army Ammunition Plant soils (fig. 2*C*).

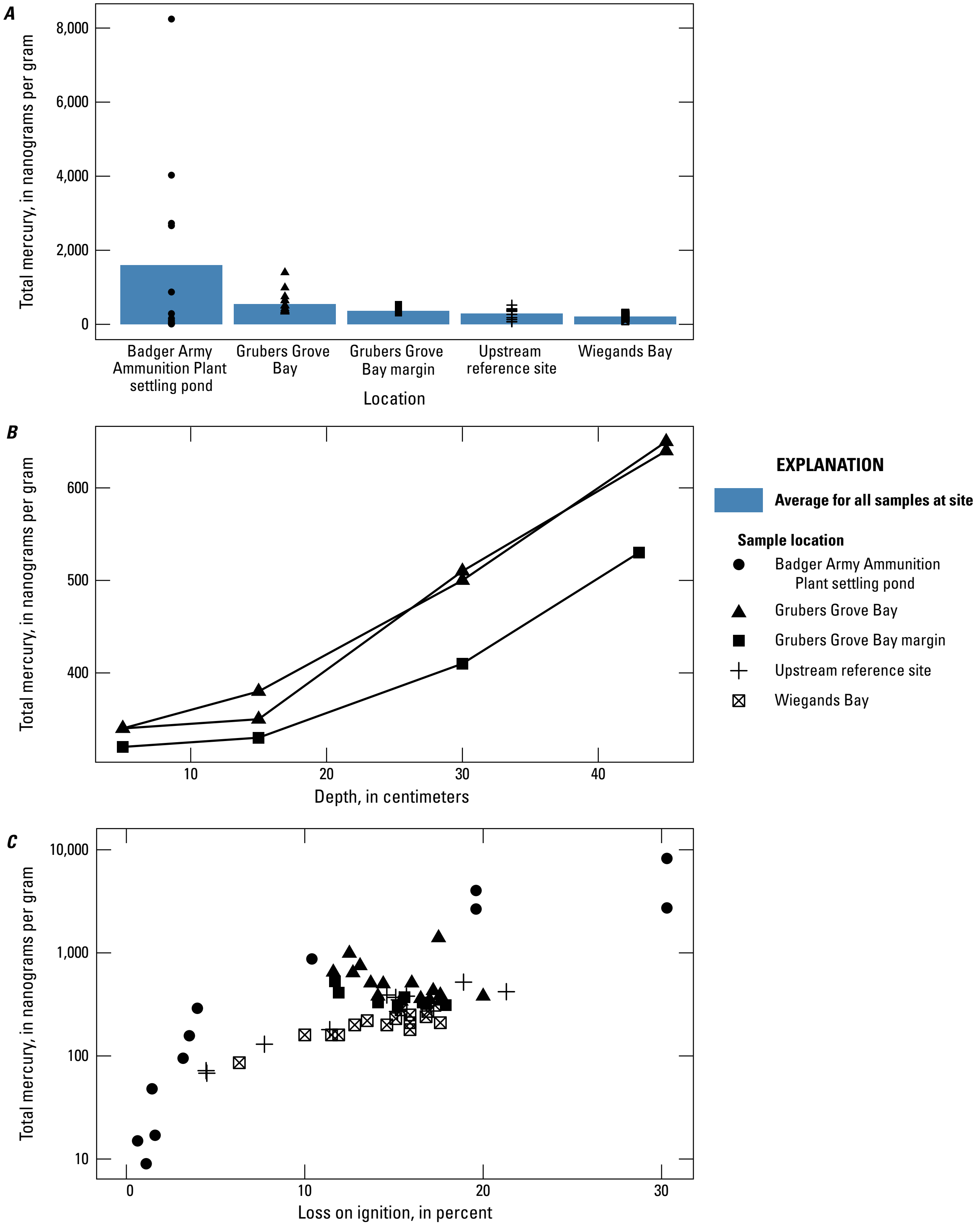

Figure 2. The relation of sediment and soil total mercury to site location, depth of sample, and percentage of loss on ignition. *A*, average sediment or soil total mercury for each location with individual sample point values; *B*, total mercury values over depths at two locations in Grubers Grove Bay and one in Grubers Grove Bay margin; *C*, total mercury plotted against percentage of loss on ignition for sediment or soil at all sampling points.

For UR, Wiegands Bay and Badger Army Ammunition Plant sites, there was a positive relation between LOI and total mercury (UR slope=25.96, coefficient of determination [R^2] =0.88; Wiegands Bay slope=14.96, R^2=0.69; Badger Army Ammunition Plant slope=190.16, R^2=0.76). Grubers Grove Bay and Grubers Grove Bay margin had a negative correlation between LOI and total mercury but with little and moderate correlation, respectively (Grubers Grove Bay slope=−34.44, R^2<0.08; Grubers Grove Bay margin slope=−26.65, R^2=0.69). Comparing sediment values, the combined range of LOI for Grubers Grove Bay and Grubers Grove Bay margin (11.6–17.9 percent) was smaller than the range for Wiegands Bay (6.3–17.6 percent) and UR sites (4.5–21.3 percent) and skewed towards higher values (fig. 2*C*).

Mass Dependent Fractionation Reported as δ Mercury-202, in Per Mille

Grubers Grove Bay sediments were statistically different from all other sites for δ^{202}Hg, in per mille ($P<0.05$ for all). However, *P* values for Grubers Grove Bay versus the Badger Army Ammunition Plant settling ponds and Grubers Grove Bay versus Grubers Grove Bay margin (P=0.0064, P=0.0031, respectively) are an order of magnitude larger than for Grubers Grove Bay versus Wiegands Bay and for Grubers Grove Bay versus UR sites (P=0.0004, P=0.0008, respectively). Grubers Grove Bay δ^{202}Hg (n=11, average=−0.57 ‰, SE=0.02) was more negative than the Badger Army Ammunition Plant settling ponds average (n=9, average=−0.33 ‰, SE=0.05) but more positive than the average of Grubers Grove Bay margin (n=6, average=−0.66 ‰, SE=0.02; fig. 3*A*), Wiegands Bay (n=13, average=−0.69 ‰, SE=0.02) and UR sites (n=10, average=−0.75 ‰, SE=0.04; fig. 3*A*). Where multiple depth samples were taken, the δ^{202}Hg values increased from surficial to at depth sediments (fig. 3*B*).

The average δ^{202}Hg value differed significantly between Grubers Grove Bay sediments (n=11, average=−0.57 ‰, SE=0.02) and Grubers Grove Bay SPM (n=4, average=−0.72 ‰, SE=0.02; P=0.004; fig. 3*A*). SPM in Grubers Grove Bay did not have a significantly different δ^{202}Hg value, in per mille, compared to SPM in Wiegands Bay or UR sites (P=0.093, P=0.180, respectively; fig. 3*A*). Average SPM δ^{202}Hg values for Wiegands Bay and UR sites were −0.83 ‰ (n=2, SE=0.01) and −0.90 ‰ (n=3, SE=0.01), respectively (fig. 3*A*).

Mass Independent Fractionation Reported as Δ Mercury-199 and Δ Mercury-200, in Per Mille

Sediments, soils, and SPM did not have Δ^{199}Hg or Δ^{200}Hg values exceeding detection thresholds (2SD measured for certified reference materials). The lack of these values indicates that photochemical and atmospheric transport processes were not prominently preserved in these matrices.

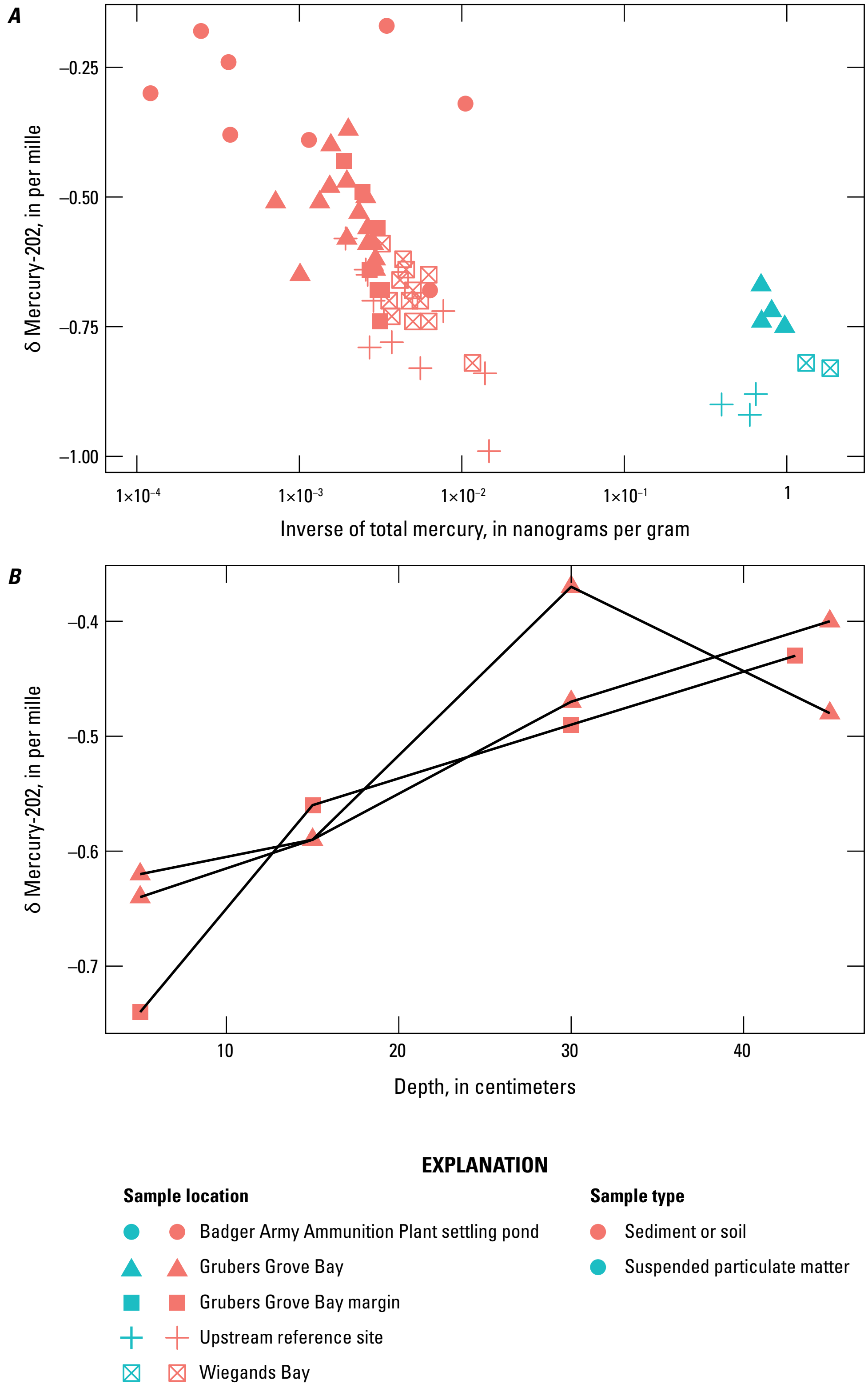

Figure 3. Mercury isotope data for samples taken at each of the sites. *A*, δ mercury-202 versus the inverse of total mercury for sediment soil or suspended particulate matter; *B*, subplot of δ mercury-202 at different depths for three sampling locations (two in Grubers Grove Bay and one in Grubers Grove Bay margin).

Discussion

Sediment total mercury concentration in Grubers Grove Bay is significantly higher than in the two reference sites (Wiegands Bay and UR sites). Total mercury also is significantly higher than in the adjacent Grubers Grove Bay margin area, and a clear gradient of high to low total mercury was detected from the innermost part to the outermost part of the bay. Soils adjacent to Grubers Grove Bay are elevated in mercury to a level indicating a land-based source of contamination. Highly variable total mercury concentrations within soils may be related to sampling of remediated and unremediated regions within the settling ponds, but specific site remediation information is not available to the authors. Therefore, the authors are unaware if sampling locations were within remediated or unremediated areas. It was noted that the highest concentrations were detected in pond 4, the closest pond to Grubers Grove Bay. The location of samples within Badger Army Ammunition Plant (that is, previous settling ponds) and mercury concentration detected indicate elevated mercury present in Grubers Grove Bay sediments could result from contemporary overland runoff from the Badger Army Ammunition Plant site. Furthermore, the isotopic mercury signature of Grubers Grove Bay sediments falls between the signatures of mercury within Badger Army Ammunition Plant and mercury from reference sites, indicating that the Badger Army Ammunition Plant source is still prevalent in surface sediments throughout Grubers Grove Bay despite previous remedial activity.

Grubers Grove Bay SPM δ^{202}Hg did not match that of the sediments in Grubers Grove Bay. Rather, isotope values indicate that SPM in Grubers Grove Bay is attributed to the influx of particulate matter from the Wisconsin River; therefore, sediments from Grubers Grove Bay are not being resuspended at a high enough rate to contribute substantially to mercury loads in SPM.

This work identified two potential endmembers for mercury within Grubers Grove Bay, soils from Badger Army Ammunition Plant and water column particulate matter from the Wisconsin River. A binary mass balance approach was used to describe the contributions of each of these sources to sediments within Grubers Grove Bay. Results confirmed that, on average across sampling locations, more than 50 percent of sediment mercury within Grubers Grove Bay were sourced from Badger Army Ammunition Plant mercury, but the contribution of this source declined approaching Grubers Grove Bay margin. Within Grubers Grove Bay margin, mercury from Badger Army Ammunition Plant was an average of 25 percent, with the higher proportion of mercury being contributed from riverine sources. It is noted, however, that in the deeper core samples from Grubers Grove Bay margin, more than 50 percent of the mercury was attributed to the Badger Army Ammunition Plant source. These results indicate that mercury from Badger Army Ammunition Plant was the most prominent historic source in Grubers Grove Bay margin sites and persists in deeper sediments despite previous sediment removal and influx of new particulate matter from the river. Because particulate matter deposition has lessened the prominence of mercury from Badger Army Ammunition Plant soils in surficial sediments (indicative of more modern mercury deposition), it seems mercury contamination from Badger Army Ammunition Plant is mostly contained within Grubers Grove Bay (fig. 4).

Alternate mercury sources including terrestrial and atmospheric deposits to the Wisconsin River were not determined in this endmember assessment of the system, but future efforts could assess the various contributions. These results highlight the extent of current mercury contamination in Grubers Grove Bay originating from Badger Army Ammunition Plant, however, more information is needed to determine if contamination is historic and remains due to previously failed remediation attempts to remove mercury from the bay or if mercury continues to be transported from Badger Army Ammunition Plant to Grubers Grove Bay even after successful sediment remediation.

Methylmercury abundance is important to consider for human and wildlife health. Sediment methylmercury concentrations were significantly different between Grubers Grove Bay, Wiegands Bay, and UR sites. However, direct comparison of Grubers Grove Bay methylmercury accumulation to UR sites is difficult because the sites do not represent similar conditions (that is, open, flowing water versus a protected bay). These different conditions could cause disparities in the organic matter deposition, the availability of electron acceptors, or the microbial community leading to more variable methylmercury concentrations at UR sites, despite lower total mercury concentrations (see appendixes 1 and 2, figs. 1.1 and 2.1). Grubers Grove Bay and Wiegands Bay share more similar water dynamics (that is, more stagnant water) than UR sites and are thus better suited for comparing methylmercury data. The sediment methylmercury concentrations observed in Grubers Grove Bay were significantly higher than methylmercury concentrations within Wiegands Bay. See appendixes 1 and 2 for more discussion of methylmercury concentrations.

Trends for percentage of methylmercury were noticeable across the sites. Grubers Grove Bay sediments had the highest percentage of methylmercury, indicating more favorable conditions to produce methylmercury in this region. Production of methylmercury can be driven by factors such as organic carbon, electron donors and acceptors (for example, sulfate and ferric iron species), microbial community composition, and the bioavailability of inorganic mercury (Hsu-Kim and others, 2013). A linear relation was determined between organic matter and methylmercury, indicating that organic matter is a driver for mercury methylation across sites. However, Grubers Grove Bay was not determined to have anomalously high organic matter in comparison to Wiegands Bay or UR sites, meaning it is not the only factor leading to the higher percentage of methylmercury in the sediments.

It has been documented that contaminated sites are commonly dominated by mineral bound and complexed mercury, resulting in a smaller fraction of bioavailable mercury. However, at least to a certain extent, the overall increase in

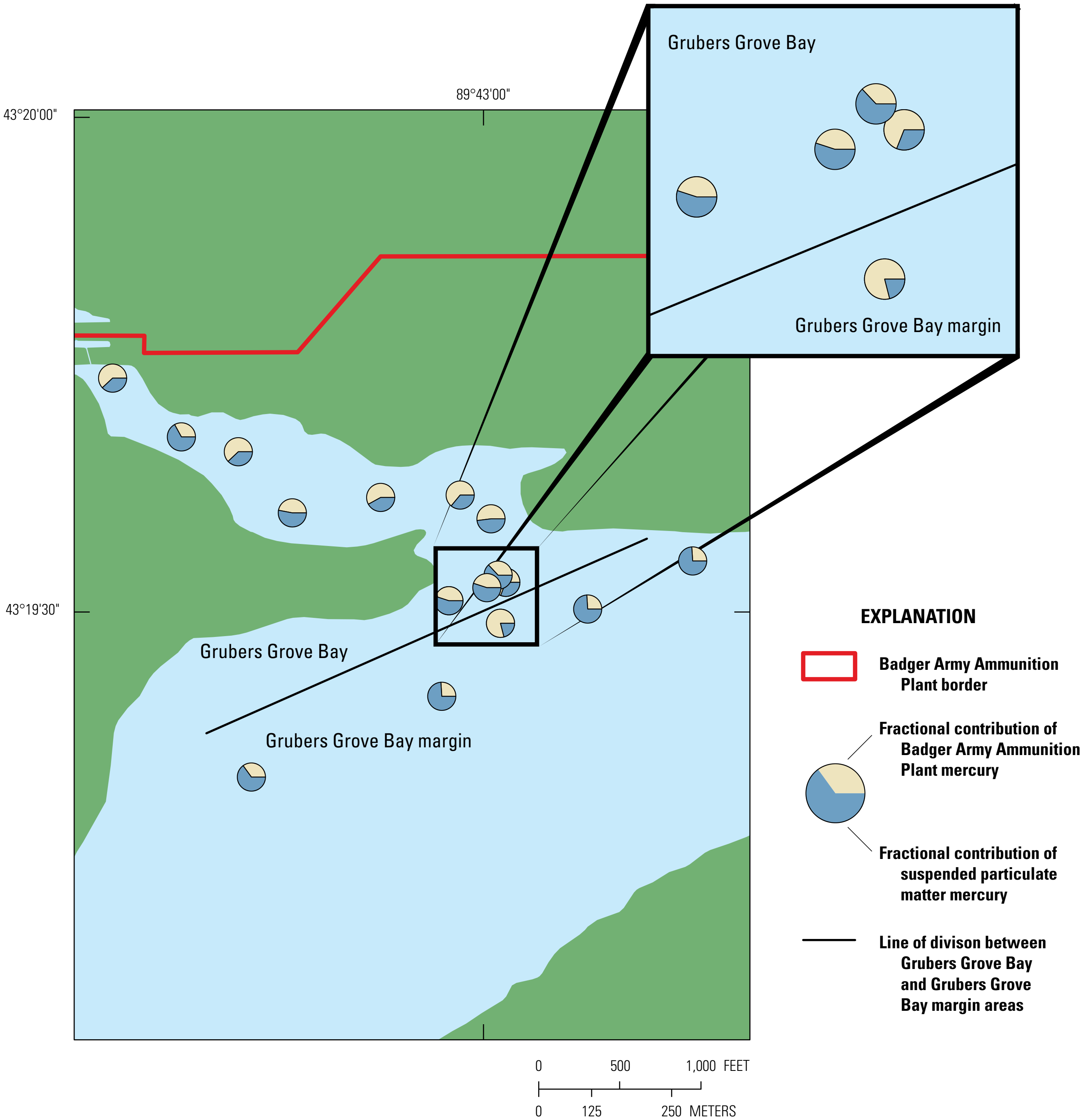

Figure 4. Grubers Grove Bay and Grubers Grove Bay margin sampling area with pie charts showing mercury source fractions for each sampling point.

total mercury due to contamination can inherently give rise to more total bioavailable mercury (Krabbenhoft and others, 1999; Kim and others, 2000; Marvin DiPasquale and others, 2009). Given that methylmercury is the bioaccumulative form of the chemical, there is a possibility that Grubers Grove Bay has a higher biological burden of mercury than other parts of the river. Follow-up investigation would help to fully assess the contribution of mercury contamination from Badger Army Ammunition Plant to the food web.

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Glossary

bioaccumulation The net accumulation of a substance, such as methylmercury, in an individual organism because of higher rates of accumulation than depuration.

biomagnification An increase in a substance in organism tissue over higher trophic levels in the food chain.

demethylation The conversion of methylmercury to inorganic mercury by the removal of methyl groups.

fractionation The uneven separation of isotopes during certain processes (for example, evaporation, demethylation).

methylation The conversion of mercury to methyl mercury—the organic form—by association with methyl groups.

trophic level/position Where an organism falls within a specified food web; for example, plants consuming raw nutrients are primary consumers (position 1), herbivores are secondary consumers (position 2), and so on.

Appendix 1. Suspended Particulate Matter Total Mercury and Methylmercury Data

Total mercury and methylmercury values were measured for suspended particulate matter (SPM). Total mercury values were calculated approximately from capsule filter digests before mercury isotope analysis. The amount of volume passed through each filter was between 18 and 36 liters. Methylmercury values were obtained from quartz fiber filters (nominal size 0.7 micrometer) used for SPM analysis by subsequent isotope dilution via distillation and an inductively coupled plasma mass spectrometer. SPM total mercury concentrations range from 1.03 to 1.44 nanograms per liter (ng/L; number of samples [*n*] =4, average=1.29, standard error [SE] =0.10) at Grubers Grove Bay, from 0.054 to 0.98 ng/L (*n*=4, average=0.732, SE=0.094) at Wiegands Bay, and from 1.55 to 2.52 ng/L (*n*=3, average=1.92, SE=0.03) at the upstream reference (UR) sites (fig. 1.1). Grubers Grove Bay SPM was significantly higher in total mercury than Wiegands Bay (*P*=0.0105) but not significantly more than the UR sites (probability=0.9831). Particulate methylmercury concentrations ranged from 0.06 to 0.08 ng/L (*n*=4, average=0.07, SE=0.004) at Grubers Grove Bay, from 0.05 to 0.07 ng/L (*n*=4, average=0.06, SE=0.004) at Wiegands Bay, and from 0.08 to 0.09 ng/L (*n*=2, average=0.09, SE=0.004) at UR sites.

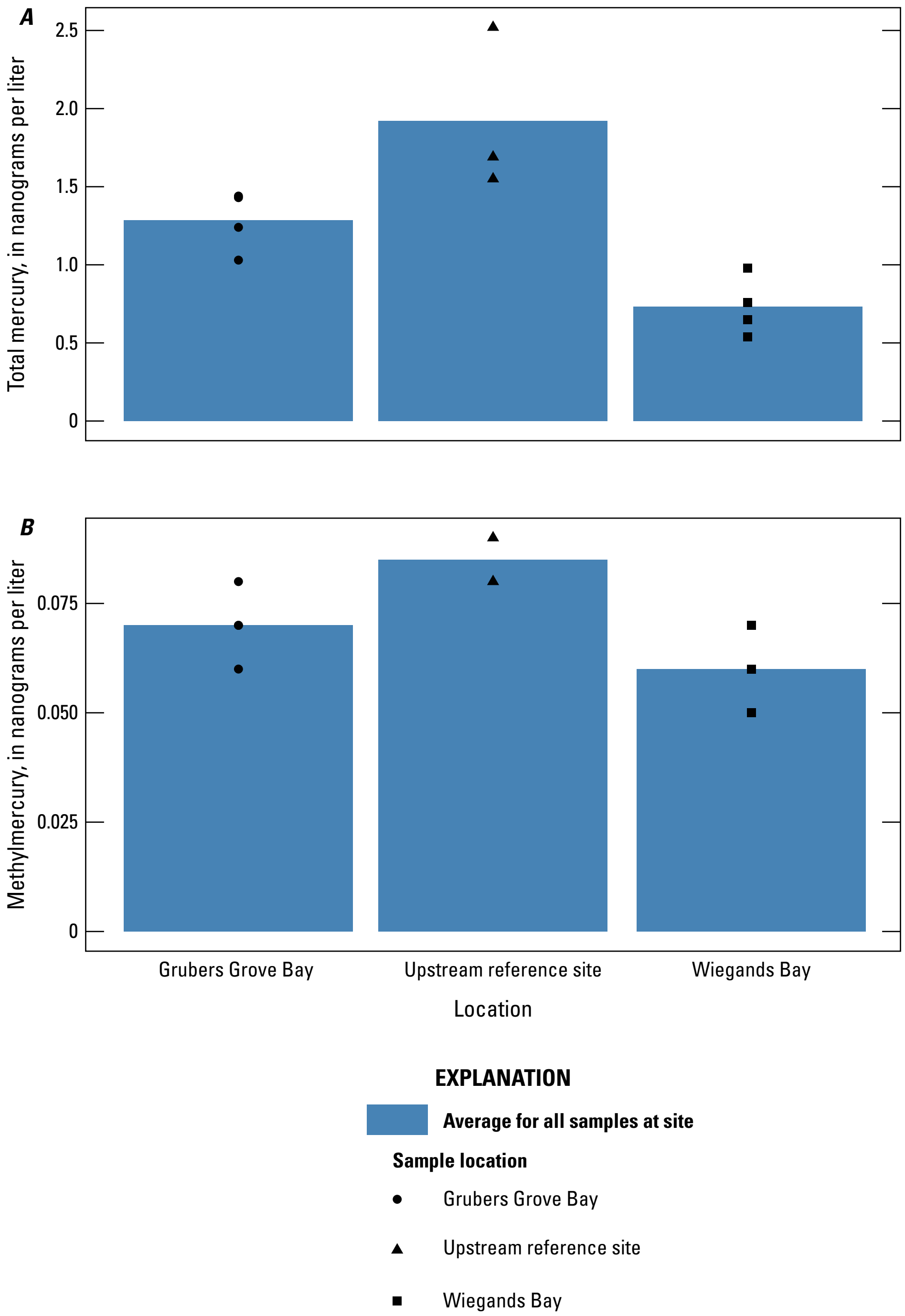

Figure 1.1. Average total mercury and methylmercury in particulate matter at available sites. *A*, total mercury; *B*, methylmercury.

Appendix 2. Sediment and Soil Methylmercury Data

Mass values of methylmercury can fluctuate with many factors, including microbe community, sediment characteristics, mercury speciation, and mercury pool size. The percentage of methylmercury, rather than mass of methylmercury, is described in the main report for those reasons. The concentration data are provided here for reference. Average concentrations of sediment methylmercury over 0–5 centimeters were 9.67 nanograms per gram (ng/g; number of samples [*n*] =3, standard error [SE] =3.357) in Grubers Grove Bay, 1.03 ng/g (*n*=4, SE=0.433) in upstream reference sites and 1.70 ng/g (*n*=1) for the only sample from Wiegands Bay (fig. 2.1).

Considering all depths, the concentration of methylmercury correlated strongly with percentage of loss on ignition at Wiegands Bay (slope=0.119, coefficient of determination [R^2]=0.966) and upstream reference sites (slope=0.108, R^2=0.99) but did not indicate any correlation at Grubers Grove Bay (R^2=0.001). Grubers Grove Bay margin (slope=–0.081) did not have sufficient samples to calculate an R^2 value (fig. 2.2).

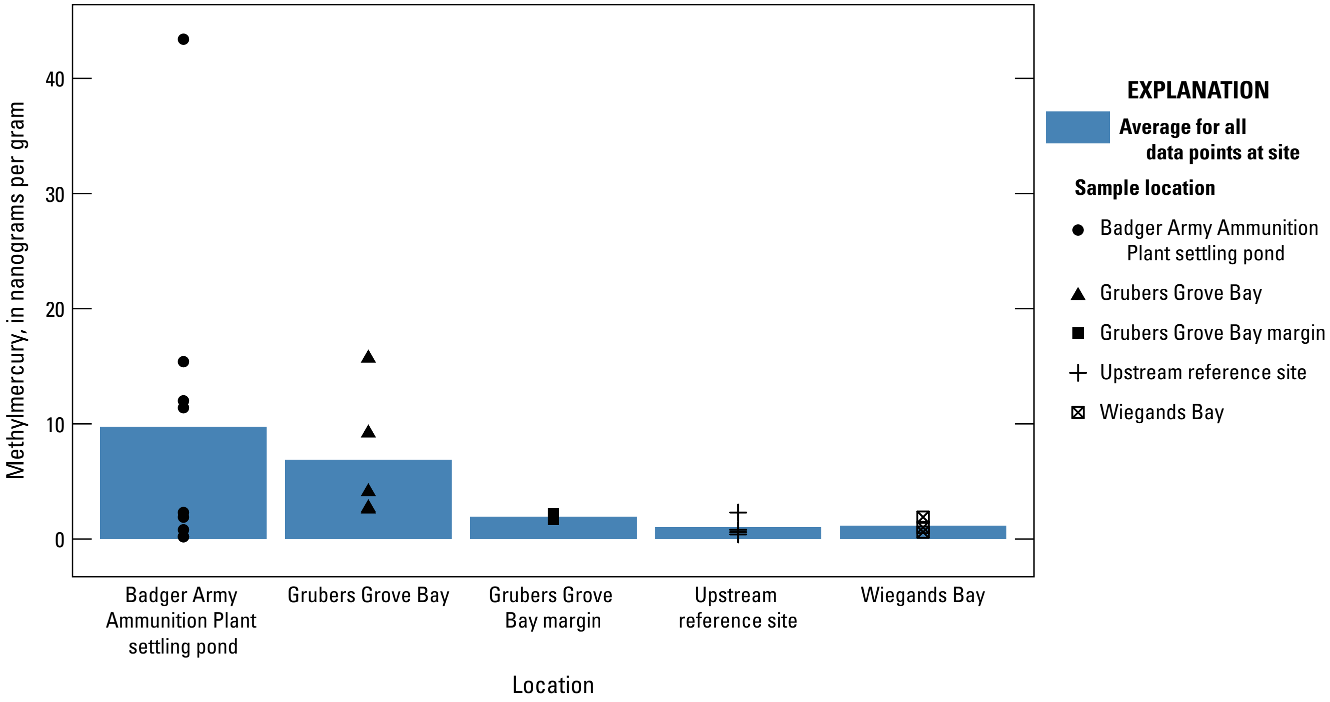

Figure 2.1. Average methylmercury in sediment and soils.

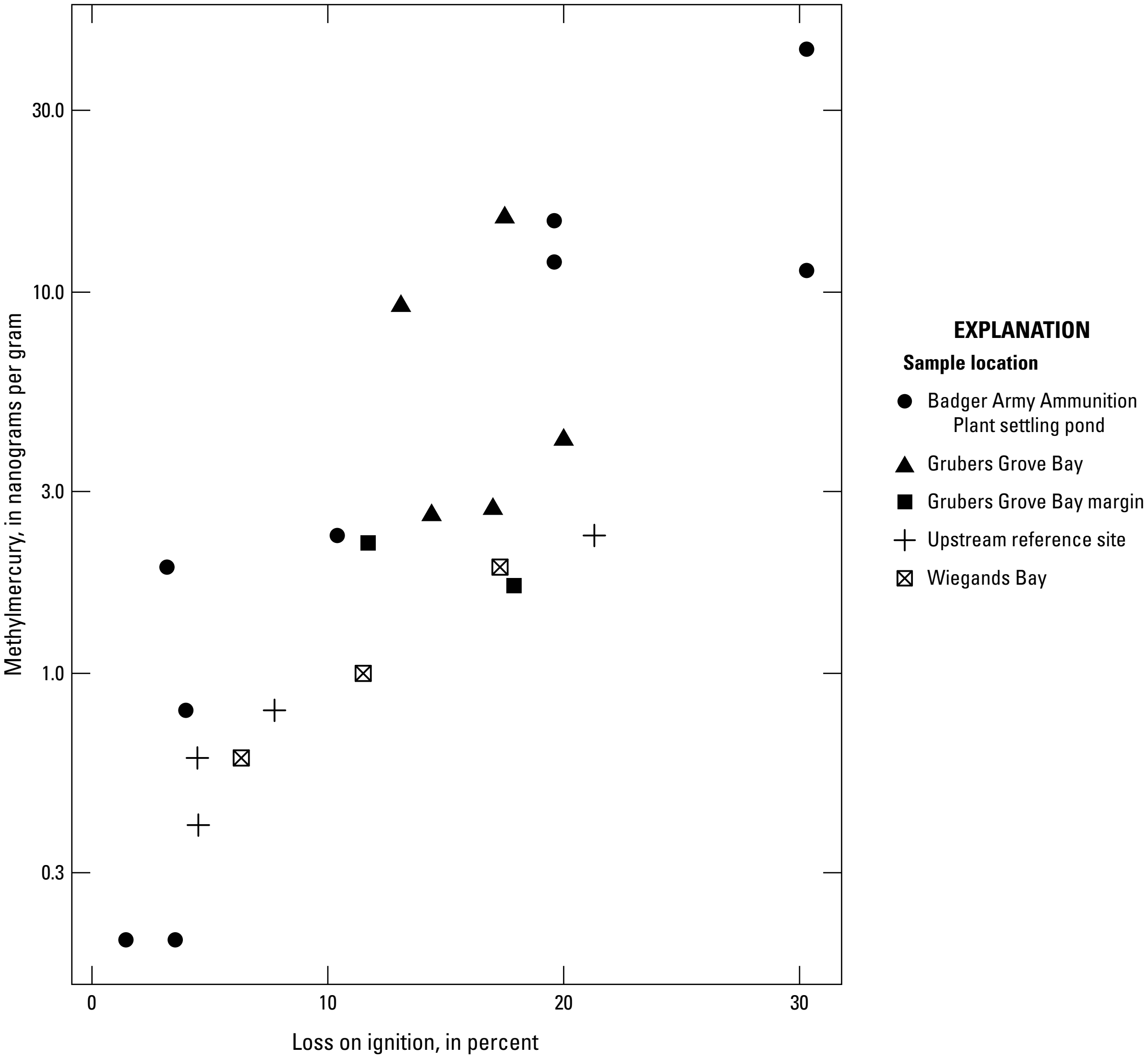

Figure 2.2. Methylmercury against loss on ignition for sediment and soils.

Appendix 3. Isotope Quality Assurance Results

Isotopes were analyzed using a multicollector inductively coupled plasma mass spectrometer. The quality assurance notes for the isotope analysis are provided in table 3.1.

Table 3.1. Quality assurance notes for isotope analysis via a multicollector inductively coupled plasma mass spectrometer.

[ID, identifier; δ, delta; ^{202}Hg, mercury-202; ‰, per mille; 2SD, two standard deviations from the mean; Δ, capital delta; ^{199}Hg, mercury-199; ^{200}Hg, mercury-200; ^{201}Hg, mercury-201; ^{204}Hg, mercury-204; *n*, number of samples; IAEA SL, International Atomic Energy Agency lake sediment; NIST, National Institute of Standards and Technology; ERM, European Reference Materials from the European Commission's Joint Research Centre; RM, reference material]

Reference material ID	Matrix type	δ^{202}Hg, ‰ (2SD)	Δ^{199}Hg, ‰ (2SD)	Δ^{200}Hg, ‰ (2SD)	Δ^{201}Hg, ‰ (2SD)	Δ^{204}Hg, ‰ (2SD)	*n*
IAEA SL-1	Sediment	−1.34 (0.07)	−0.16 (0.05)	0.03 (0.07)	−0.15 (0.04)	−0.06 (0.11)	3
NIST 1944	Sediment contaminated	−0.48 (0.01)	−0.02 (0.06)	0.00 (0.04)	−0.01 (0.06)	0.02 (0.01)	3
ERM CC141	Loam soil	−0.69 (0.15)	−0.10 (0.05)	0.00 (0.03)	−0.10 (0.06)	−0.01 (0.05)	3
NIST RM 8610	Aqueous-secondary standard	−0.55 (0.05)	−0.03 (0.05)	0.00 (0.05)	−0.04 (0.05)	0.00 (0.08)	25

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