J Paleolimnol (2008) 40:869–884
DOI 10.1007/s10933-008-9204-8

ORIGINAL PAPER

Arsenic contamination of lake sediments in Florida: evidence of herbicide mobility from watershed soils

Thomas J. Whitmore · Melanie A. Riedinger-Whitmore · Joseph M. Smoak · Keith V. Kolasa · Ethan A. Goddard · Richard Bindler

Received: 8 May 2007 / Accepted: 22 February 2008 / Published online: 26 March 2008
© Springer Science+Business Media B.V. 2008

Abstract Organic arsenical herbicides, which include monosodium methylarsonate (MSMA), have been applied to golf courses and lawns throughout Florida, USA, since the 1950s. These products convert rapidly to inorganic forms of arsenic (As) in soils and are mobilized readily. Leachates have been known to contaminate groundwater and surface waters, although past studies have not examined whether use of these products has led to significant As accumulation in lake sediments. We used paleolimnological methods to document the depositional history and inventories of total As in sediments and porewaters of Little Lake Jackson in Florida, which is adjacent to three golf courses. Six sediment cores, four of which were ^{210}Pb dated, showed porewater total As concentrations as high as 435 μg l^{-1}, and dry-sediment total As concentrations as high as 148 mg kg^{-1}. Approximately 537 kg of total As is present in >19,000 metric tons of sediment (dry mass), and an additional 18 kg of As is dissolved in 10.8×10^4 m^3 of porewaters. Total As content in surface sediments (mean = 47.3 mg kg^{-1}) exceeds the consensus-based sedimentary concentration for probable toxicity effects in freshwater benthic fauna. Surface and subsurface waters flow to the lake from topographically higher areas to the west, where golf courses and residential areas are located. Total As concentrations were elevated highly in monitoring wells and in a stream that flows between the golf courses and lake, but As was below detection limits in wells that were located at the distal perimeter of the golf courses. Subsurface and surface waters exit the lake towards topographically lower areas to the east. Nearly all As in sediments remains bound in the solid phase, indicating that As sedimentary profiles largely reflect depositional history. Sedimentary As concentrations are correlated strongly with aluminum and iron, which suggests that As was scavenged from lake waters during the past. Sedimentary As concentrations increased until the 1980s, then declined somewhat to the present time. Dissolved As was scavenged efficiently from the water column when hypolimnetic waters were oxygenated persistently,

T. J. Whitmore (✉)
Department of Geological Sciences, University of Florida, Gainesville, FL 32611, USA
e-mail: whitmore@ufl.edu

M. A. Riedinger-Whitmore · J. M. Smoak
Environmental Science, Policy, and Geography Program, University of South Florida-St. Petersburg, St. Petersburg, FL 33701, USA

K. V. Kolasa
Southwest Florida Water Management District, 2379 Broad Street, Brooksville, FL 34609, USA

E. A. Goddard
College of Marine Science, University of South Florida, St. Petersburg, FL 33701, USA

R. Bindler
Department of Ecology and Environmental Science, Umeå University, 901 87 Umea, Sweden

but after eutrophication led to a seasonally anoxic hypolimnion in the 1980s, apparently less As was co-precipitated, and more was lost to hydrological outflow. Arsenic accumulation in sediments might be common in areas where As derived from organic arsenical herbicide applications is directed by shallow water tables towards adjacent lakes.

Keywords Arsenic · Lake · Monosodium methylarsonate · Sediment · Florida · Contamination

Introduction

Monosodium methylarsonate (MSMA) was an active ingredient until 2006 in 44 turfgrass-management end-use products that were applied routinely to golf courses and lawns for weed control throughout the state of Florida, USA. Approximately 10% of the golf courses in the United States are located in Florida, and many of those golf courses are situated beside lakes or ponds (Ma et al. 2002). Because lake basins receive outputs from watersheds, toxic materials such as arsenic (As) can accumulate in lakes in quantities that pose substantive health or environmental risks. Many studies have addressed As accumulation in lake sediments from smelters, agriculture, and other sources (e.g. Crecelius 1975; Chen et al. 2000; Durant et al. 2004), but no studies have examined whether MSMA application to golf courses or lawns has led to As accumulation in lake sediments.

Arsenical herbicides have been applied to golf courses and to agricultural areas since the early 1900s. Lead and calcium arsenates were used for pest control on turf and on a wide variety of agricultural crops between 1900 and 1980. The U.S. Department of Agriculture recommended the application of 45–672 kg ha^{-1} yr^{-1} of lead arsenate to golf courses and lawns for the control of earthworms, grubs, and ants (Murphy and Aucott 1998; Chen et al. 2000). Lead arsenate usage peaked in the 1930s and the 1940s. Organic arsenical products for turfgrass and lawn applications were introduced in the 1950s beginning with disodium methylarsonate (DSMA). In the 1960s, MSMA became the leading form of organic arsenical herbicide on the market (Ma et al. 2000; U.S. EPA 2006). By the 1960s, lead arsenate usage had declined by 75% because of toxicity concerns and the availability of synthetic organic pesticides (Murphy and Aucott 1998). Lead arsenate application continued in a few regions of Florida until the 1980s, however, for pest control in grapefruit orchards (Solo-Gabriele et al. 2003).

An estimated 97% of Florida golf courses used MSMA (Ma et al. 2002), and the average Florida golf course applied 86 kg of As to soils each year in the form of MSMA (Solo-Gabriele et al. 2003). MSMA was applied to school fields, cemeteries, sod farms, and on private and public lawns in addition to golf courses (Ma et al. 2002). Application was in the form of an aqueous solution that contained approximately 1,350 mg l^{-1} of As (Solo-Gabriele et al. 2003). In 2001, 55 metric tons of MSMA products were sold in Florida for commercial and residential application, and by 2003, sales had increased to 85 metric tons (Solo-Gabriele et al. 2003). DSMA herbicide products had considerably less than 1% of the annual sales of MSMA products in the state of Florida. Beginning in 2006, MSMA sales in the United States and Canada were suspended pending a re-registration review of organic arsenical products because of groundwater contamination and other concerns (U.S. EPA 2006).

MSMA is transformed in soils and becomes oxidatively demethylated to inorganic As (Feng et al. 2005). Conversion rates are rapid and can result in complete demethylation, which makes differentiation between MSMA and inorganic As in natural environments unimportant for purposes of assessment or environmental regulation (Florida DEP 2002). Arsenic in MSMA-treated soils is mobilized readily, and dissolved As can contaminate groundwater and surface-water resources in adjacent areas (Ma et al. 2000, 2002; Cai et al. 2002). South Florida soils typically contain little clay or organic matter that might adsorb dissolved MSMA, and As concentrations consequently increase in shallow groundwater. MSMA applications that are consistent with manufacturers' recommendations can result in markedly elevated As concentrations in soils and groundwater. Soil As concentrations as low as 10 mg kg^{-1} can result in shallow groundwater As concentrations >50 μg l^{-1} (Florida DEP 2002), which is substantially higher than the 10 μg l^{-1} Maximum Contamination Level for As in drinking waters mandated by the U.S. Environmental

Protection Agency. Studies of 11 golf courses in south Florida showed mean total As concentration in soils of 69.2 mg kg^{-1} (Ma et al. 2000). Dissolved total As concentrations in shallow test wells on golf courses have been observed as high as 123 μg l^{-1} at tee sites, and 815 μg l^{-1} at herbicide mix-load sites (DERM 2002).

Golf courses are prominent sources of mobilized As because of high rates of herbicide application, frequent irrigation, and the porous nature of their soils. Most Florida golf courses are constructed using sand and soil constituents that have high infiltration rates, and they are underlain by gravel and drainage tiles (Ma et al. 2000). Approximately 1.9×10^6 m^3 of water are used to irrigate golf courses in Florida annually, with approximately equal quantities coming from groundwater, surface water, and from recycled sewage effluent (Ma et al. 2002). The long growing and playing season in Florida has led to more than twice the amount of herbicide application per golf course in Florida than is used on the average golf course in the remaining 49 states (Ma et al. 2000). Approximately 7,160 metric tons of As have accumulated in golf-course soils throughout the state of Florida (Solo-Gabriele et al. 2003). An additional 113 metric tons of As are dissolved in the state's surface waters, and 8,350 metric tons of As are contained in Florida's groundwater aquifer (Solo-Gabriele et al. 2003). Arsenic contamination of Florida's aquifers is a serious concern because groundwaters provide >90% of the state's drinking water supply (Florida DEP 2002).

Inorganic As occurs in several forms in soils, sediments, and water. Arsenate [As(V)] dominates in oxic conditions and has low solubility, whereas arsenite [As(III)] is more prevalent under anoxic conditions and has greater solubility. In oxic lake waters, As(V) co-precipitates with Al, Fe, and Mn (oxy)hydroxides to the sediments (DeVitre et al. 1991). Some As(V) in sediments can be converted to As(III) during reduction of Fe oxhydroxides, and As(III) can then migrate in porewaters towards the sediment/water interface. When overlying waters are oxic, dissolved As(III) in porewaters is likely to become bound again by oxidized forms of Fe and Mn at the sediment/water interface (De Vitre et al. 1991; Durant et al. 2004), but if overlying waters are anoxic, some As(III) can diffuse out of sediments (Ahmann et al. 1997).

We hypothesized that high As concentrations might be found in the sediments of lakes that are situated beside golf courses because of high MSMA application rates on golf-course soils, the well-documented mobilization of As to groundwaters, and the tendency for solutes exported from watersheds to accumulate in lake sediments. We selected Little Lake Jackson in south-central Florida for study because this lake is situated beside three golf courses, and previous studies demonstrated that turf applications of lime and fertilizer exerted considerable influence on water quality in the lake during the past (Whitmore et al. 2006). The present study examines recent As deposition in Little Lake Jackson, and it considers how arsenical herbicide application in the watershed might have contributed to high levels of As concentrations in sediments and porewaters.

Study site

Little Lake Jackson is a small lake (63 ha) located at 27°28′ N and 81°28′ W in Highlands County, Florida USA (Fig. 1). The lake lies within the city limits of Sebring, which was settled in 1913. The lake sustains stable thermal stratification between April and November of each year, and it is subject to wind-generated mixis during winter months. The watershed of Little Lake Jackson is relatively small (424 ha), and only 6.7 times the surface area of the lake. The largest portion of the watershed is located to the west and southwest of the lake (Fig. 1). Currently, 63% of the watershed is residential and 21% is recreational, including three golf courses and a 16-ha baseball/soccer/softball facility (Kolasa 1999).

Sebring Municipal Golf Course was constructed in 1926, and Harder Hall Country Club's golf course was built on the southwestern shore in 1958 (Fig. 1). Rapid residential development occurred along the southern and southwestern shores of the lake during the 1960s to 1980s. A third golf course, Harder Hall Executive Golf Course, was constructed south of Harder Hall Country Club in 1990. Sebring Municipal Golf Course was irrigated until the 1960s with water that was withdrawn from Little Lake Jackson through a canal. After the 1960s, the golf course was irrigated with alkaline (pH = 8.2) groundwater from deep wells that reach the limestone aquifer, and the canal was used to carry runoff water from the golf course to the lake.

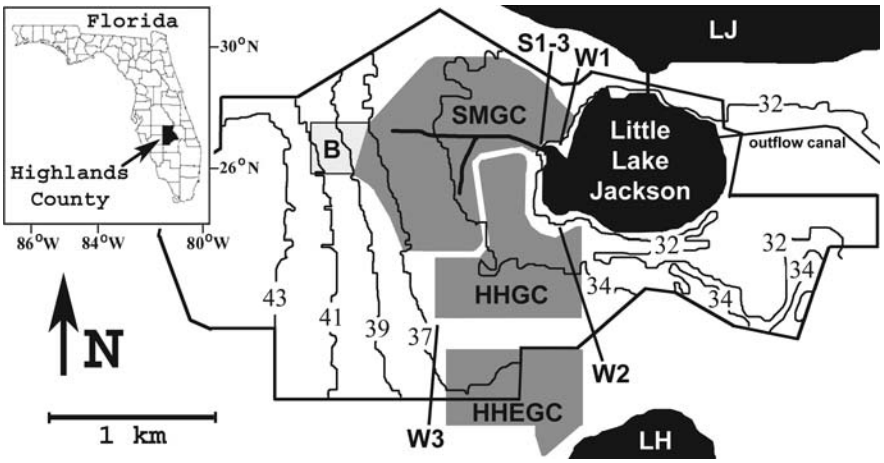

Fig. 1 Little Lake Jackson's watershed, and the location of stream and well sampling sites. Elevation of surface topography is shown in meters above mean sea level (amsl). Little Lake Jackson lies at 31 m amsl. Stream sampling locations are designated S1–3, and shallow monitoring well locations are designated W1, W2, and W3. The bold line surrounding watershed features approximates the watershed boundary. The dark line on Sebring Municipal Golf Course represents the stormwater canal that flows to Little Lake Jackson, and the Josephine-Jackson outflow canal is shown to the east of the lake. Abbreviations: LJ is Lake Jackson, LH is Lake Huckelberry, B is the baseball/soccer/softball complex, SMGC is Sebring Municipal Golf Course, HHGC is Harder Hall Golf Course, and HHEGC is Harder Hall Executive Golf Course

We asked Sebring Municipal Golf Course and Harder Hall Country Club whether they have applied MSMA and other organic arsenical products during the past. Sebring Municipal Golf Course indicated that for an extended period until 2006, it had applied MSMA products approximately three times per year in a manner that was consistent with herbicide manufacturers' recommendations. Sebring Municipal also reported that they used some DSMA herbicide products at times, and that they had applied somewhat less MSMA products for perhaps 3–5 years preceding 2006 as compared with their previous application rates. Harder Hall Country Club indicated that it also had applied MSMA products in the recommended manner during the past. Representatives at both golf courses reported that they have used no MSMA products since the U.S. EPA-imposed moratorium that began in the late summer of 2006 (U.S. EPA 2006).

Hydrological setting

Southwest Florida Water Management District (SWFWMD) evaluated the hydrological flow of surface and subsurface waters through the watershed and lake (Arnold and Richardson 1995; Kolasa 1997, 1999). Four sets of paired ground-water monitoring wells were installed in the western and southwestern parts of the watershed, with each pair containing one shallow well (~5 m deep) and one deep well (~11 m deep). Topographic slope of the ground surface declines approximately 12.3 m from the western edge of the watershed towards Little Lake Jackson on the east (Fig. 1). Water-table elevation declines 4.3 m between wells that are located at the western edge of the golf courses and the wells nearest the lake, which indicates that groundwater movement closely follows the downward slope of the land surface. The steepest water-table gradient occurs during the wet season, when soils are most saturated and the groundwater level is high throughout the watershed. The canal on the west side of the lake receives stormwater and seepage from a series of local ditches and canals that drain Sebring Municipal Golf Course and the immediate vicinity, and it represents the principal source of surface-water inflow to Little Lake Jackson (Kolasa 1999).

The eastern and southeastern portions of the watershed are an area of surface and subsurface drainage away from the lake. The lake's primary surface outflow was through a natural creek to a wetland on the east until the 1970s, when the Jackson-Josephine ouflow canal was constructed and a weir was installed. The lake has intermittent

surface outflow over the weir, as well as through a canal towards Lake Jackson on the north shore (Fig. 1) when water levels are sufficiently high (Arnold and Richardson 1995). A region of significant groundwater export from Little Lake Jackson occurs throughout the eastern and southeastern parts of the watershed, with average groundwater flow rates as high as 0.06 m^3 s^{-1} (Arnold and Richardson 1995).

Methods

We retrieved six sediment cores from the deep, central portion of Little Lake Jackson in January to June 2005 at water-column depths of 6.75–7.5 m (sites I–VI). Cores were collected with a 7-cm diameter, 1.83-m long polycarbonate piston corer (Fisher et al. 1992) from pre-selected sites (Fig. 2). Our previous study (Whitmore et al. 2006) showed that organic sediment deposits are focused in the central portion of the basin where water-column depth is >4.5–5 m, and that the depositional zone of the lake has an area of approximately 22×10^4 m^2.

Porewaters were extracted from wet sediments by centrifugation at 3,000 rpm. Sediment samples were freeze-dried then ground with a mortar and pestle. Organic matter content of sediment subsamples was assessed by loss-on-ignition at 550°C (Boyle 2004).

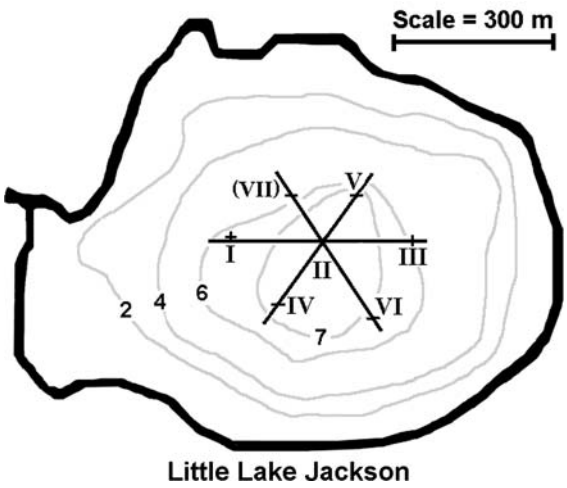

Fig. 2 The location of sediment coring sites I–VI in Little Lake Jackson. Approximate bathymetry contours are shown in meters below the mean water-surface level

Sediments initially were digested for total As analyses following U.S. Environmental Protection Agency (EPA) protocol 3050B for soils and sediments. Repeated digestions in our laboratory and in the Chemical Analysis Laboratory at the University of Georgia showed recovery efficiencies that varied between 40 and 80% as assessed by ICP-OES and ICP-MS. We concluded that As in sediments was bound too tightly in solid phase for effective use of EPA protocol 3050B. Sediment samples subsequently were analyzed at Waters Agricultural Laboratory in Camilla, Georgia using EPA method 7062 (U.S. EPA 1994a) for digestion of soils to assess arsenic content by atomic absorption spectrometry. Samples were digested with concentrated HCl and HNO_3 for 1 h at 95°C, then filtered with a Whatman™ Grade No. 1 (11-μm pore) filter. Total As content of digestates was measured with a PS Analytical Millennium Excalibur Analyzer. The minimum detection limit was 0.01 mg kg^{-1}. Precision was measured by three replicate readings on 10% of samples, and the average standard deviation for replicate samples was 0.15 mg kg^{-1}. Digestion efficiency was measured using three National Institute of Standards and Technology (NIST) Standard Reference Material 2702 samples within the sample run, and total As content of the NIST samples (mean = 45.02 mg kg^{-1}, range 44.46–45.75 mg kg^{-1}) demonstrated 100% recovery with respect to the certified As content of 45.3 ± 1.8 mg kg^{-1}.

Porewaters were acidified to 5% acidity with analytical grade HNO_3, then filtered with Millipore™ APFF (0.7-μm pore) and Whatman™ GF/A (1.6-μm pore) glass-fiber filters using a vacuum aspirator. Total As content of porewaters was measured with a Perkin–Elmer Optima 4300 Dual View ICP-OES at the wavelength of 188.979 nm, which showed greatest sensitivity and was free of spectral interference. The empirically determined Limit of Quantitation (LOQ) was 52.7 μg l^{-1} of total As and the Minimum Detection Level (MDL) was 15.8 μg l^{-1}. Porewater As concentrations were measured directly on the filtrates for cores I and III. For cores II, IV, V, and VI, we evaporated porewater filtrates to 1/3 of their initial volumes in a Thermo Electron Corporation Precision drying oven at 40°C, which effectively lowered the LOQ of the ICP-OES to 17.5 μg l^{-1} and the MDL to 5.3 μg l^{-1}. Porewater volumes were measured within 0.1 ml during this

evaporation procedure, which resulted in volume errors of less than 3%. We also used the ICP-OES to assay the total Fe, Al, and Mn concentrations in sediment digestates from cores I and IV.

Background, or pre-anthropogenic, As concentrations in sediments and porewaters were estimated from the mean of As values in the straight-line portion at the base of sediment cores. We estimated the inventories of recent anthropogenic (or excess) As in each core by subtracting the background As concentration from the measured concentration in each section higher in the cores to determine excess As concentrations. Porewater volume for each section was estimated with gravimetric analysis of subsamples and the known total volume of the sediment section. Excess porewater concentrations were multiplied by the volume of water in each section to obtain the mass of excess porewater As in each core section. Excess As concentrations per unit dry mass of sediments were multiplied by the dry mass of each corresponding section to obtain the mass of excess sedimentary As. Excess As masses were summed for each core to determine the cumulative mass of excess As in sediments and in porewaters for that core, and values were expressed on an areal basis.

Because sediment cores had approximate equal-area distribution within the depositional zone of the lake, we averaged excess As masses per unit area for all six cores to determine mean excess As content per unit area within the depositional zone. We estimated the total mass of excess As stored in sediments and porewaters within the lake by multiplying these mass-per-unit-area values by the approximate size of the depositional zone of the lake.

Lead-210 dates were obtained by direct gamma counting (Schelske et al. 1994) with an intrinsic germanium detector. Unsupported ^{210}Pb activity was estimated by subtracting ^{226}Ra from total ^{210}Pb activity. Sediment ages were calculated using the constant rate of supply model (Appleby and Oldfield 1983). We multiplied bulk sediment accumulation rates by As concentration values for each dated stratigraphic interval to obtain As accumulation rates.

Total As concentrations were measured in surface waters of the main stormwater canal at three sites that were spaced at approximately 15-m intervals near the edge of the Sebring Municipal Golf Course, about 90 m west of the lake (Fig. 1). Subsurface waters were collected from three sets of the shallow wells (~5–11 m deep) that were installed in the watershed west and southwest of Little Lake Jackson in 1995 by SWFWMD during their Ambient Monitoring Program study of the lake (Kolasa 1997). Well 1 is located just north of the stormwater canal and approximately 8 m to the east of Sebring Municipal Golf Course, between that golf course and the lake (Fig. 1). Well site 2 (Fig. 1) has two adjacent wells, 2A and 2B, that are situated approximately 8 m from Harder Hall Country Club's golf course, between that golf course and the southwestern shore of the lake. Well site 3 has two adjacent wells, 3A and 3B, that are located outside of the southwestern corner of Harder Hall Country Club, just west of Harder Hall Executive Golf Course (Fig. 1), and about 900 m distant from Little Lake Jackson. A small submersible pump was inserted into each well casing, and the well was purged for approximately 10 changes of water before samples were collected.

Stream and well samples were concentrated to 1/10 of their original volumes in a Thermo Electron Corporation Precision drying oven at 40°C. Concentrates were filtered through Millipore™ APFF (0.7-μm pore) and Whatman™ GF/A (1.6-μm pore) glass-fiber filters with a vacuum aspirator, then were acidified to 5% acidity with analytical grade HNO_3. A replicate water sample from Well A was concentrated to 1/3 of its original volume, then processed in the same manner. Total As content of filtrates was measured with the Perkin–Elmer Optima 4300 Dual View ICP-OES at a wavelength of 188.979 nm. Because of 10-fold concentration of these waters, effective LOQ was 5.3 μg l^{-1}, and the MDL was 1.6 μg l^{-1}. The effective LOQ of the 3-fold concentrated replicate sample was 17.6 μg l^{-1} and the MDL was 5.9 μg l^{-1}.

Results

Organic sediment deposits at each coring site were at least 1 m thick, with the exception of the core V site, which had approximately 60 cm of organic sediment. We could not retrieve a suitably long core from site VII because that site proved to be located in a steep-sloped region of transitional deposition.

Arsenic concentrations in dry sediments at the base of all sediment cores averaged 0.74 mg kg^{-1} (range 0.35–1.18), with the exception of core V,

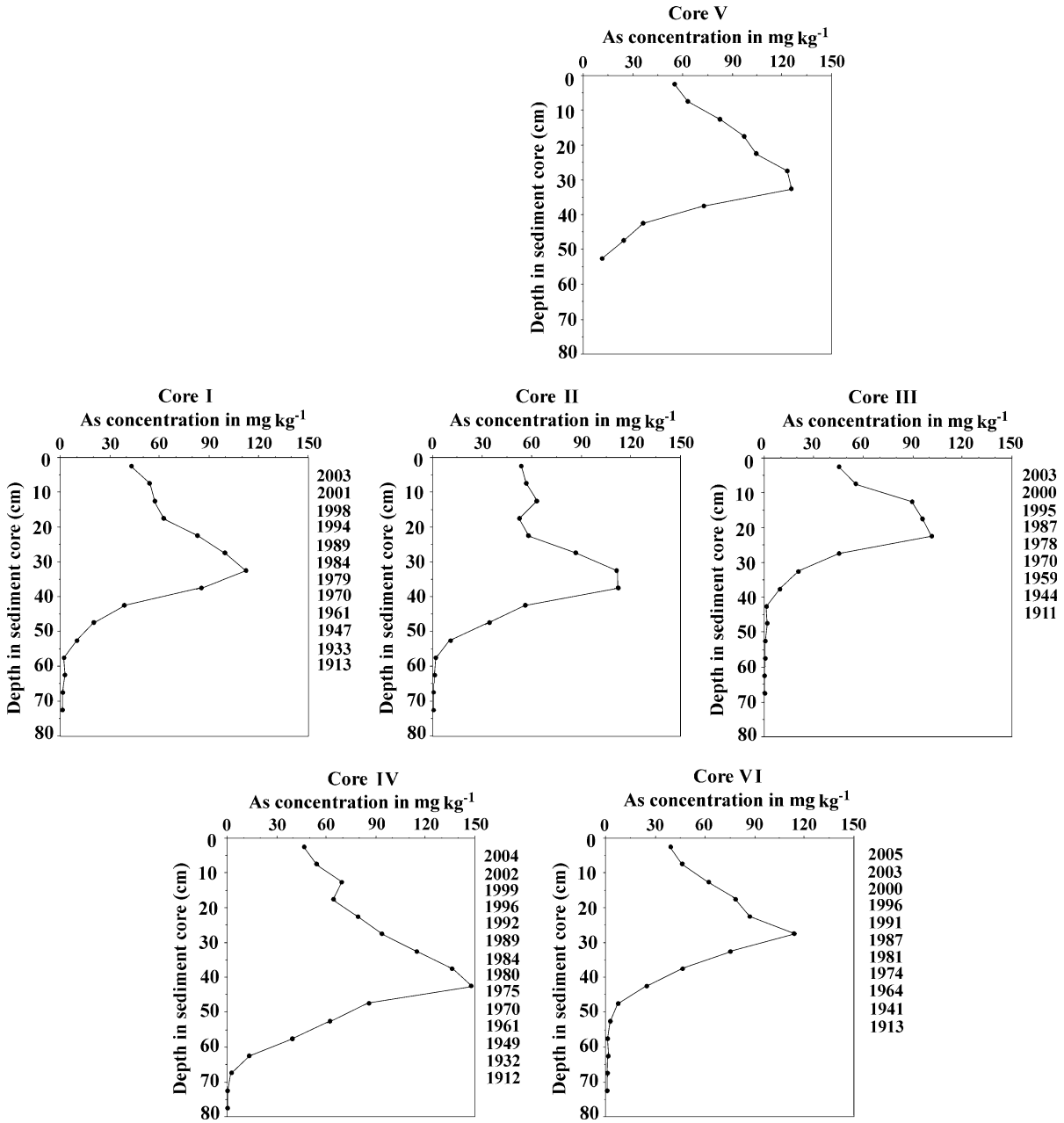

Fig. 3 Total As concentrations in dry sediments versus depths in the sediment cores. The core profiles in this figure are situated in a pattern that reflects their original relative positions in the lake

which had a truncated depositional history and showed a basal value of 11.4 mg kg^{-1} total As (Fig. 3). Sedimentary As concentrations increased rapidly in most cores after the 1940s (Fig. 3). The highest sedimentary As concentration (147.5 mg kg^{-1} total As) occurred in core IV in the 40 to 45-cm interval (ca. 1975–1980). The second-highest concentration (125.6 mg kg^{-1}) was in the 30 to 35-cm level of core V. Peak sedimentary total As concentration values were very comparable to each other in cores I, II, and III (range 112.2–113.9 mg kg^{-1}), but occurred at various depths in the sediment. Peak As concentrations occurred in the 30 to 35-cm interval of core I (ca. 1979–1984), in the 35 to 40-cm level of core II,

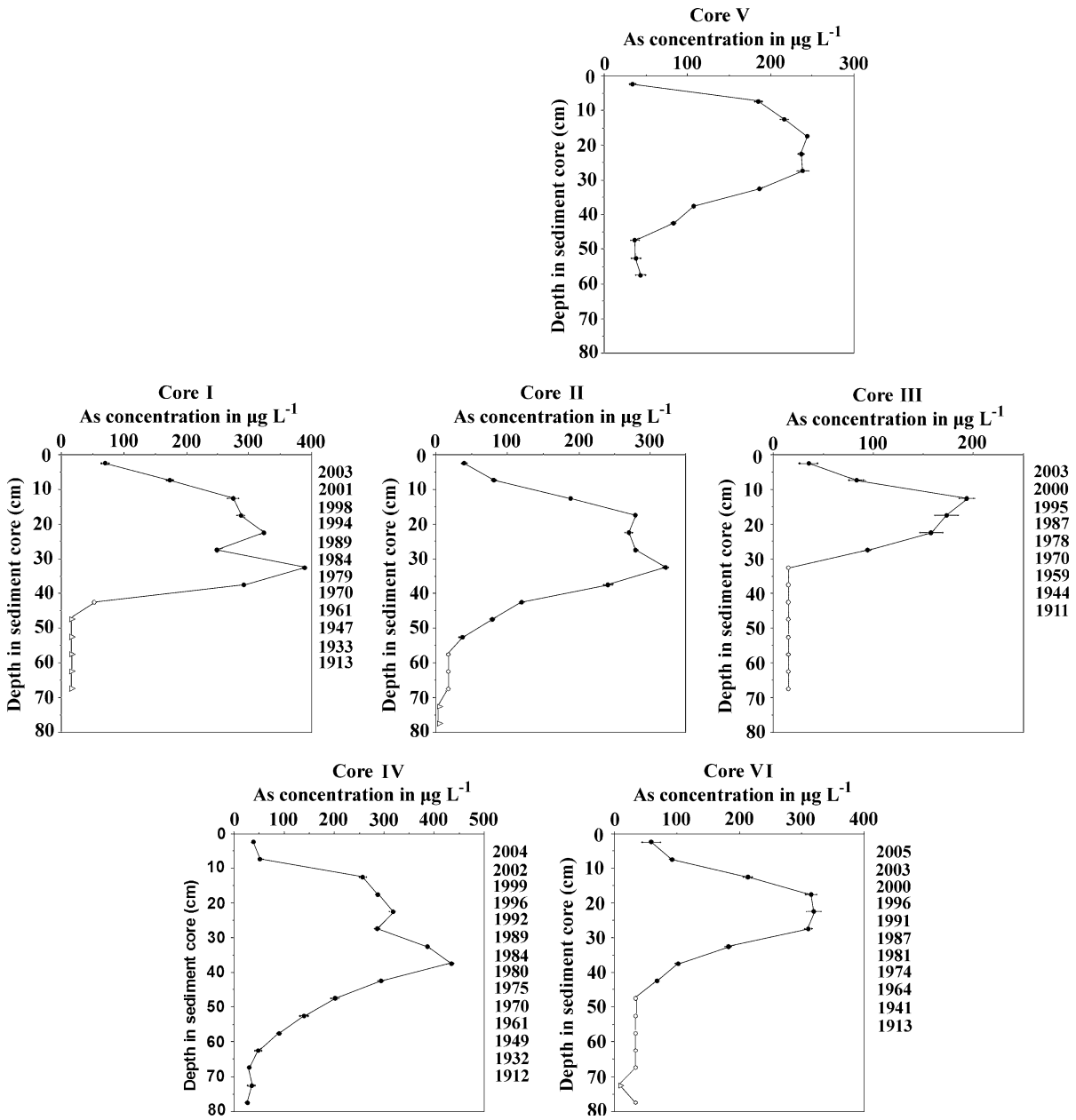

Fig. 4 Total As concentrations in porewaters vs. depths in the sediment cores. Error bars show ±1 standard error. Open circles denote values that are below the LOQ, and open triangles denote values that are less than the MDL

and in the 25 to 30-cm level of core VI (ca. 1986–1991). The highest peak in core III (101.3 mg kg^{-1}) occurred in the 20 to 25-cm level (ca. 1978–1987). Sedimentary As peaks in the four ^{210}Pb-dated cores, therefore, showed more correspondence in time than they did with respect to depth in sediments. In all six cores, sedimentary As concentrations declined from their peak values towards the tops of the cores (Fig. 3). Average sedimentary As concentration in the surface sediments was 47.3 mg kg^{-1} (range 39.0–53.5 mg kg^{-1}).

Total As concentration in porewaters was <17 µg l^{-1} at the base of cores I, II, III, and VI, and was 27 µg l^{-1} in core IV (Fig. 4). The baseline

concentration in core V was 44 μg l^{-1}, although this core had a shorter profile that lacked a baseline tail. Porewater As concentrations increased above the 40 to 50-cm levels (ca. 1960) in all sediment cores. The highest porewater As concentration (435 μg l^{-1} total As) occurred in the 35 to 40-cm interval of core IV. Cores I and II had peak porewater As concentrations >320 μg l^{-1}, and cores III, V, and VI had peak concentrations of 160–240 μg l^{-1} (Fig. 4). Porewater As concentration in the top 5 cm of cores II–VI averaged 36 μg l^{-1} (range 30–40 μg l^{-1}), but was distinctly higher in core I (70 μg l^{-1}).

Bulk sediment accumulation rates generally were constant throughout dated portions of the four ^{210}Pb-dated sediment cores, with an average of 61.1–63.4 mg cm^{-2} yr^{-1}. Exceptions were one sediment interval in cores I and VI, which each showed 107 mg cm^{-2} yr^{-1} accumulation, and one interval in core IV that showed 112.5 mg cm^{-2} yr^{-1}. Peaks in bulk sediment accumulation rates in the four ^{210}Pb-dated cores did not correspond in time with the peaks in sedimentary As concentrations.

Arsenic accumulation rates at the base of the four ^{210}Pb-dated cores (ca. 1912) ranged from 0.7 to 2.5 mg m^{-2} yr^{-1} (Fig. 5). Arsenic accumulated more rapidly in the middle portions of the sediment profiles, with peak arsenic accumulation rates of 85.9 mg m^{-2} yr^{-1} in core I, 63.4 mg m^{-2} yr^{-1} in core III, 122.3 mg m^{-2} yr^{-1} in core IV, and 96.2 mg m^{-2} yr^{-1} in core VI. Peak As accumulation rates averaged 57 times higher than the accumulation rates estimated for ca. 1912. Peak arsenic accumulations generally were synchronous, and occurred ca. 1979–1984 in core I, ca. 1978–1987 in core III, ca. 1975–1980 in core IV, and ca. 1986–1991 in core VI. After the periods of peak deposition, As accumulation rates generally declined in all four dated cores until the present time. Recent total As accumulation rates averaged 29.1 mg m^{-2} yr^{-1} (range 23.9–37.3 mg m^{-2} yr^{-1}), and were approximately 18 times higher than the total As accumulation rates for ca. 1912.

Excess total As inventory per unit area of dry sediment was highest at core site IV (3.97 g m^{-2}). At

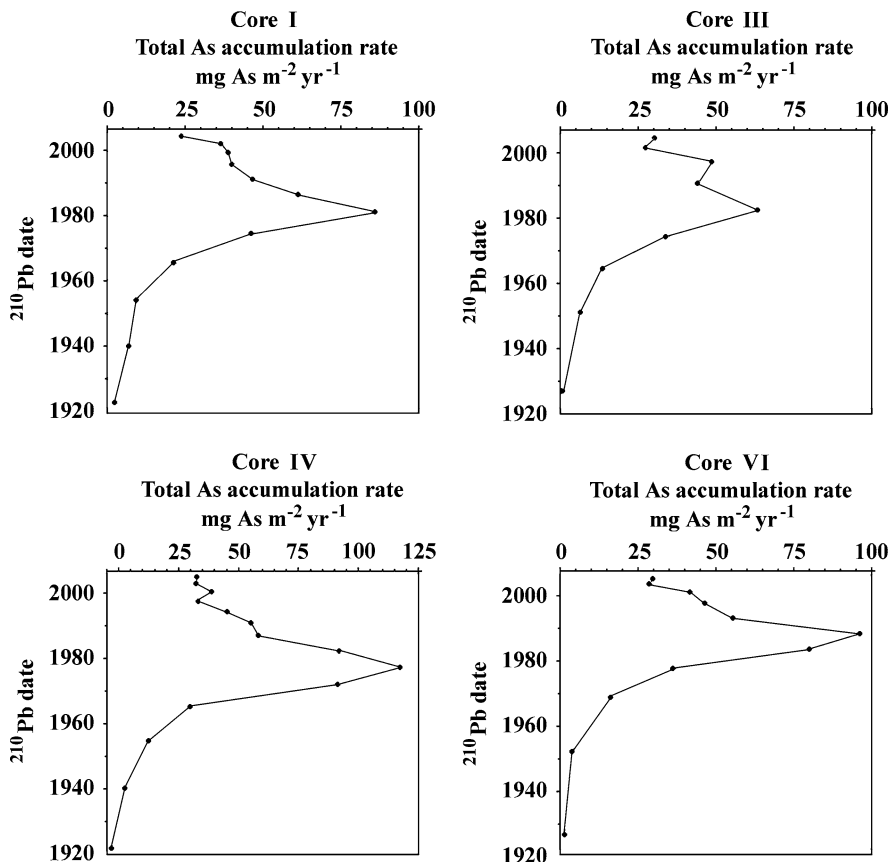

Fig. 5 Arsenic accumulation rates for the datable portion of the four ^{210}Pb-dated cores

Table 1 Total arsenic content of water samples from the stream and shallow wells

Sampling location	Total As content ($\mu g\ l^{-1}$)	1 SE ($\mu g\ l^{-1}$)	Depth for well samples (m)
Stream site 1	44.3	1.8	
Stream site 2	42.6	1.3	
Stream site 3	44.8	0.7	
Well 1	107.5	0.5	11.0
Well 1 replicate	115.4	1.4	11.0
Well 2A	26.5	0.5	11.0
Well 2B	17.0	1.4	5.5
Well 3A	Below MDL	–	5.5
Well 3B	Below MDL	–	9.5

The Minimum Detection Limit (MDL) for well samples 3A and 3B was 1.58 $\mu g\ l^{-1}$

sites I and V, excess As inventories in dry sediment were 2.20 and 2.65 g m^{-2}, respectively. Excess inventories were comparatively lower at sites II (1.96 g m^{-2}), III (1.83 g m^{-2}), and VI (2.02 g m^{-2}). Average excess dry-sediment As inventory per unit area from all cores was 2.44 g m^{-2}. We multiplied dry-sediment As inventory per unit area by the size of the central depositional zone (approximately 22×10^4 m^2) and determined that the total excess As inventory in dry sediment of Little Lake Jackson is approximately 537 kg of arsenic. The mean mass of affected dry sediment per unit area that contains this excess As was 86.7 kg m^{-2}. We estimate, therefore, that the total mass of dry sediment that is affected by excess As deposition in Little Lake Jackson is approximately 19,080 metric tons.

For porewaters, the excess As content ranged from 0.03 g m^{-2} (core III) to 0.19 g m^{-2} (core IV), with a mean excess As content of 0.08 g m^{-2} for all six cores. We estimated that the total excess As inventory in porewaters of Little Lake Jackson is approximately 18.2 kg of arsenic, which is dissolved in approximately 10.8×10^4 cubic meters of porewater.

In cores I and IV, sedimentary concentrations of total As and Al were highly correlated ($r = 0.94$, $r = 0.88$, respectively, both $p < 0.001$). Similarly in cores I and IV, sedimentary concentrations of total As and total Fe were highly correlated ($r = 0.79$, $r = 0.75$, respectively, both $p < 0.001$). These correlations suggest that much of the As in sediments is bound with oxides and oxyhydroxides of Al and Fe. Manganese was below the LOQ (0.02 mg kg^{-1}) for assessment by ICP-OES in all sediment samples, and consequently Mn oxides could not have been a significant solid-phase sink for arsenic.

Stormwater-canal samples, which were collected at three sites on 5 November 2006, showed dissolved total As concentrations that averaged 44 $\mu g\ l^{-1}$ (Table 1). SWFWMD collected three samples at the same sites on 13 November 2006 and reported similar dissolved As values (mean = 39.3 $\mu g\ l^{-1}$ total As, range = 37.4–42.8 $\mu g\ l^{-1}$), as determined by ICP-AES (U.S. EPA 1994b). SWFWMD subsequently measured dissolved total As concentrations on 14 February 2007 at these sites and reported a mean total As value of 36.1 $\mu g\ l^{-1}$ (range = 34.2–39.0 $\mu g\ l^{-1}$). At a point 30 m offshore from where the stormwater canal flows into Little Lake Jackson, SWFWMD measured dissolved total As concentrations of 10.2 $\mu g\ l^{-1}$ on 13 November 2006, and of 10.4 $\mu g\ l^{-1}$ on 14 February 2007.

Total As content of two water samples from well 1, which was located between Sebring Municipal Golf Course and Little Lake Jackson, averaged 111 $\mu g\ l^{-1}$ (Table 1). In wells 2A and 2B, which were located between Harder Hall Country Club's golf course and the lake, total As content averaged 21.8 $\mu g\ l^{-1}$. In wells 3A and 3B, which were located furthest from Little Lake Jackson on the southwestern corner of Harder Hall Country Club, the total As content was less than the Minimum Detection Level (<1.76 $\mu g\ l^{-1}$).

Discussion

Arsenic contamination in the lake and watershed

Total As concentrations in the sediments of Little Lake Jackson are high because of anthropogenic

activities in the watershed. Despite the small size of the lake, it contains approximately 0.56 metric tons of As in >19,000 metric tons of dry sediment and in 10.8×10^4 cubic meters of porewater. In the five cores that show pre-disturbance As concentrations at their bases, peak As concentrations average 212 times greater (range 95–428 times) than the background concentrations that were deposited prior to 1912. The ^{210}Pb-dated sediment cores show that maximum sedimentary total As concentrations were deposited in the 1980s. Modern sedimentary As concentrations average 81 times greater than background As concentrations that were deposited prior to 1912. Peak total As concentrations dissolved in porewaters range 16–43 times higher than the U.S. EPA (2002) Maximum Contamination Level for As in drinking waters (10 μg l^{-1} total As).

Test wells between the golf courses and the lake revealed total As concentrations that might pose health problems if shallow-well resources were used for potable water supply. Dissolved total As concentrations in the well between Sebring Municipal Golf Course and Little Lake Jackson were 10–11 times higher than the U.S. EPA drinking water standard of 10 μg l^{-1} total As. Total As concentrations in shallow wells between Harder Hall Country Club's golf course and Little Lake Jackson were approximately twice the U.S. EPA drinking water standard. Canal waters that flowed from Sebring Municipal Golf Course to Little Lake Jackson in November 2006 had dissolved As concentrations approximately four times higher than the drinking-water standard.

Conclusions about the source of arsenic

Arsenic contamination in Little Lake Jackson apparently was caused by past applications of organic arsenical herbicides, particularly MSMA. We base this conclusion on information about past sources of arsenic in the watershed and lake, on the hydrological relationship between the lake and potential sources, and on measurements of As in ground and surface waters that enter the lake.

Golf courses, recreational lawn fields, and residential lawns lie in close proximity to the lake and are large relative to lake size. Given average MSMA application rates on golf courses (Solo-Gabriele et al. 2003), there would have been >200 kg of As loading per year on the three golf courses in the Little Lake Jackson watershed. Recent nutrient-loading budgets for Little Lake Jackson suggest that residential areas potentially contribute a large portion of the annual nutrient loading to the lake (Kolasa 1999). In a similar manner, some portion of As loading might have originated from MSMA applications to residential lawns and to the baseball/soccer/softball facility.

Aside from the use of arsenical herbicides, we found no evidence of other large-scale As sources in the watershed during the past. There have been no herbicide applications for aquatic-plant management in the lake (Durant et al. 2004) that would account for significant As accumulation (Carl Smith, Highlands County Operations Department, Aquatic Weed Program, pers. commun.). Cattle farms that might have used As dips and chromated copper arsenate wood-treating facilities have been absent from the watershed. Land-use maps, aerial photographs, and historical records for the area show no evidence for significant agricultural activity during the past in the western and southern portions of the watershed. Agriculture was precluded to a large extent by poor drainage of local soils, which imposes moderate to severe limitations for cultivated, citrus, and pasture crops (Kolasa 1999). A portion of the watershed to the west and southwest remained as native scrub-oak community until recent housing development, and there is no evidence of past citrus agriculture in these areas. A small region of agriculture was present southeast of the lake during the 1950s, but that area lacked surface drainage to the lake, and was located where groundwater movement is directed strongly away from the lake towards the east and south (Arnold and Richardson 1995; Kolasa 1997).

Hydrological studies for the watershed show that the golf courses and residential areas to the south and west are the primary source for inputs of water and solutes to the lake (Arnold and Richardson 1995, Kolasa 1997, 1999). We measured high dissolved As concentrations in shallow test wells between the golf courses and the lake, but found undetectably low dissolved As concentrations in shallow wells that are opposite the lake and topographically higher than the golf courses. This indicates that golf courses were a prominent source for the As in groundwaters. High dissolved As concentrations in the stormwater canal that flows from Sebring Municipal Golf Course to the lake also suggest that this golf course was a significant source for As deposited in the lake.

Lead-arsenate herbicide applications to Sebring Municipal Golf Course and other lawn areas between the 1930s and the 1950s might have contributed to some early loading of As in Little Lake Jackson, although we have no specific knowledge that lead arsenates were used in this area during the past. The time of potential lead-arsenate usage precedes construction of Harder Hall Golf Course and Harder Hall Executive Golf Course, so those facilities would have had no history of lead-arsenate use. A greater amount of As loading would have occurred during the time period from the 1950s to the present, when organic arsenical herbicides were in use, and golf course and residential areas expanded.

Arsenic movement within the watershed and lake

Following demethylation of MSMA to inorganic As (Florida DEP 2002), rates of As release from soils probably were high in the watershed because of the nature of local soils and turfgrass treatments. Watershed soils are subject to saturation and continual lateral flow (Carter et al. 1989; Kolasa 1999), and high flow rates through soil facilitate arsenic leaching (Nikolaidis et al. 2004). Surface and subsurface waters are acidic, with considerable humic color from dissolved organic matter (DOM). In the presence of high DOM, particularly from peat soil amendments that are common on Florida golf courses, Fe and Al oxides can be released from soils by high molecular-weight DOM fractions, while As can remain dissociated from those colloid fractions but be transported through soils by DOM fractions of lower molecular weight (Bauer and Blodau 2006; Chen et al. 2006). Phophate dissociates As from the Al and Fe that bind it in soils (Alam et al. 2001), so fertilizer application on golf courses might have increased As release from soils. Sebring Municipal Golf Course, for example, applies 37 metric tons of N–P–K (20–10–10) fertilizer annually to fairways and greens. Arsenic mobilization might have increased because of carbonate, bicarbonate, and potassium loading that resulted from the liming of soils (Davenport and Peryea 1991; Murphy and Aucott 1998; Florida DEP 2002; Whitmore et al. 2006). Arsenic mobilization also might have been facilitated by bicarbonate ions in the hard groundwater that was used to irrigate Sebring Municipal Golf Course since ca. 1960 (Anawar et al. 2004).

Little Lake Jackson is particularly susceptible to receiving As that has been released from watershed soils. Hydrological studies show that surface and subsurface water movement in the watershed principally is from topographically higher areas on the west and southwest towards the lake basin. Impervious muck and sand lenses in soils create perched water tables, often 0.3–1.0 m below the ground surface (Carter et al. 1989; Kolasa 1999). When shallow water tables are present, MSMA usage leads to higher dissolved As concentrations in groundwater than would occur if soil permeability permitted greater downward percolation of dissolved As and progressive adsorption to soil particles (Ma et al. 2000, 2002; Cai et al. 2002; Florida DEP 2002). Shallow water tables in the Little Lake Jackson watershed direct dissolved constituents in groundwater rapidly towards the lake, particularly during periods of soil saturation (Kolasa 1999). The stream that drains Sebring Municipal Golf Course greatly facilitates the transport of dissolved As to the lake, and at times such as exceptional stormwater events, it might carry some As that is adsorbed to suspended sediment.

Subsurface waters can readily enter or exit the lake, depending upon hydrological flow patterns, through the large littoral zone that is composed almost entirely of coarse, highly permeable sands. Once subsurface and surface waters enter the lake, they are diluted by lake waters that are clear, alkaline, and low in DOM (Kolasa 1997; Whitmore 2006), and As mobility decreases. Sedimentary As is highly correlated with Al and Fe in Little Lake Jackson, which suggests that Al and Fe (oxy)hydroxides play important roles in scavenging As(V) from oxic lake waters to organic sediments in depositional areas of the lake (Peterson and Carpenter 1986; Schaller et al. 1997; Durant et al. 2004). Colloidal Al hydroxides that form under alkaline conditions adsorb dissolved orthophosphate and As(V) in lake waters and cause them to co-precipitate to sediments (Kopáček et al. 2000; Durant et al. 2004). Arsenic(V) bound to Al oxides is likely to remain stable and resistant to reduction to As(III) in sediments, even with persistent anoxia (Durant et al. 2004). Organic sediments are compact and rapidly deposited in Little Lake Jackson, and because interstitial flow rates are low in such sediments, small amounts of Fe reduction can lead to high porewater As concentrations, but negligible leaching of As (Nikolaidis et al. 2004).

Mechanism for the decline of As in sediments

Sedimentary As concentrations were influenced more by deposition than they were by remobilization. Peaks in sedimentary and porewater As concentrations lie 20–45 cm below the sediment–water interface, rather than in the top few cm of the profiles as would occur if As were being mobilized upwards in sediments (Belzile and Tessier 1990). Peaks in As concentrations show no correspondence with depth in sediments, but high correspondence in time, i.e. they are associated with sediments that were deposited in the 1980s. This close correspondence in time rather than depth in sediment indicates that the As peaks are not artifacts of mobilization, but rather that they reflect the depositional history of As during a specific period of time. Arsenic remains principally bound in the solid phase, and As concentrations are approximately 200 times greater in dry sediments than in porewaters for all samples. The stable binding of As in sediments also was suggested by the fact that large amounts of As remained refractory even after digestion attempts with strong acids using EPA protocol 3050B. The strong similarities between porewater and sedimentary As profiles indicate low interstitial flow rates, and low mobility of dissolved As in sediments (Nikolaidis et al. 2004).

Despite most sedimentary As being tightly bound in solid phase, As concentrations and accumulation rates decline in the top portions of all six sediment cores. Declines in As concentrations are evident particularly in porewaters, which decrease nearly to background concentrations in several cores. There are three explanations that might account for the recent declines of As in sediments:

1. Delivery of As from the watershed decreased because of less use of arsenical herbicides.
2. More As was mobilized out of sediments when eutrophication led to greater hypolimnetic anoxia and to greater reduction of Fe oxyhydroxides that bind As to sediments.
3. Less arsenic was scavenged from lake waters by Al and Fe when the lake became eutrophic and seasonal anoxia of hypolimnetic waters became established.

Decreased arsenical herbicide use is not consistent with the history of application in this watershed. Sebring Municipal Golf Course reported some reduced application of MSMA products during the last 3–5 years, but that would not account for the large decline in sedimentary As concentrations since the mid-1980s. Arsenical herbicide applications in the watershed might have increased, rather than decreased since the 1980s, because of the construction of Harder Hall Executive Golf Course. Remobilization of dissolved As out of sediments is not likely, for reasons addressed above. Consequently, we conclude that scavenging and sedimentation of As from overlying waters was reduced when seasonal anoxia became established in the 1980s, and that a greater proportion of dissolved As was lost from the lake through subsurface outflow.

The timing of sedimentary As decrease coincides with accelerated eutrophication and the establishment of seasonal hypolimnetic anoxia. Whitmore et al. (2006) documented eutrophication that began in the 1940s, as inferred from sedimented algal pigments, geochemistry, sedimented diatoms, and stable isotopes of sedimented organic matter. Cyanobacteria began to dominate after ca. 1970, and oscillaxanthin, a pigment specific to the Oscillatoriaceae, reached peak sedimentary concentrations ca. 1987. Presently, the dominant phytoplankton are all cyanobacteria, including *Oscillatoria*, *Lyngbya*, *Chroococcus*, and *Dactylococcopsis* in summer, and *Chroococcus*, *Anabaena*, and *Dactylococcopsis* in winter (Rutter 1995). Bottom waters have become persistently anoxic throughout the warm months of April through November (Kolasa 1997; SWFWMD unpublished data for 2004). In August of 2007, we measured a strong thermocline at approximately 3 m depth, and dissolved oxygen values that were saturated near the water surface, but declined rapidly to nearly 0 mg l^{-1} below 3 m depth to the base of the water column.

Efficiency of As scavenging by Al and Fe is reduced when hypolimnetic waters become anoxic because of eutrophication. Sohrin et al. (1997) documented increases in epilimnetic As and Fe concentrations in Lake Biwa that resulted from seasonal anoxia of hypolimnetic waters. Eutrophication, they concluded, increases the rates of reductive processes, and affects the concentration and speciation of As in hypolimnetic waters. Aluminum oxides have a strong sorptive affinity for As(V), but considerably less affinity for As(III) (Durant et al. 2004), so As scavenging by Al oxides would have been reduced greatly in Little Lake Jackson once the lake developed anoxic bottom waters

for approximately 7 months of the year. After onset of eutrophication, a greater proportion of the As entering Little Lake Jackson would have remained dissolved in the water column and been lost in the substantial subsurface outflow that exits the lake through permeable sands all along the eastern shore (Arnold and Richardson 1995).

Lake management implications

MacDonald et al. (2000) used a synthesis of toxicological studies to establish guidelines that predict when benthic organisms are likely to experience adverse biological effects from contaminant exposure in freshwater sediments. They defined the threshold effects concentration (TEC) for As in sediments as 9.8 mg kg^{-1} total As, below which toxicity was unlikely to occur, and the probable effects concentration (PEC) of 33.0 mg kg^{-1} total As, above which toxicity would occur the majority of the time. Total sedimentary As concentration in the surface sediments of all six cores from Little Lake Jackson (average = 47.3 mg kg^{-1}) exceeds the PEC for toxicity to benthic organisms. Consequently, As contamination in the sediments of Little Lake Jackson is likely to have adverse effects on the benthic fauna. The benthic macroinvertebrate assemblage in Little Lake Jackson has the lowest species diversity values and the second lowest species richness values among 26 lakes that were studied in Florida, which suggests that the lake is very degraded (Florida DEP 1994; Rutter 1995). Seasonal profundal anoxia might explain some of the depletion of benthic organisms, but sedimentary As concentrations also might affect the benthic fauna.

Accumulated toxic materials can pose problems when lake sediments are dredged. If sediment dredging were undertaken as part of lake-restoration efforts for Little Lake Jackson, the As content of dried sediment would substantially exceed Florida DEP's 2005 Soil Cleanup Target Level of 2.1 mg kg^{-1} of total As for residential soils or 12 mg kg^{-1} of total As for commercial and industrial soils. The large volume of contaminated water that would result from dewatering of sediments also could exceed the 10 μg l^{-1} As Maximum Contamination Level that is mandated for drinking waters (U.S. EPA 2002), which might further contribute to the As burden that is present already in the ground and surface waters of Florida (Solo-Gabriele et al. 2003).

Contamination of sediments from arsenical herbicides, particularly MSMA, might occur more commonly than is realized in Florida and in other regions where golf courses lie adjacent to lakes, especially where shallow water tables and surface waters direct runoff towards the lakes. Ma et al. (2002) estimate that 25% of Florida's approximately 1,400 golf courses are located near lakes or ponds, and 43% are located near multiple water bodies. Florida DEP (2002) has recommended that all hydrogeological conditions that are vulnerable to MSMA contamination should be identified. We suggest that future studies should better assess factors that predispose lakes to As accumulation from MSMA applications, and that associated toxicity risks for humans and the aquatic fauna should be investigated.

Acknowledgements We thank Keith Dominey at Waters Analytical Laboratory for technical support. Terrence Quinn provided use of ICP-OES equipment. Xuefeng (Bob) Wang, Clell Ford, and Charlotte Clayton helped with collection of sediment cores, and Monique Baughman helped with collection of stream and well samples. Todd Robbins assisted with sediment digestion and with ^{210}Pb dating. James Sickman, John Smol, and Mark Brenner provided helpful review of the manuscript. Partial support for this study was provided by the University of South Florida-St. Petersburg's Environmental Science, Policy, and Geography Program.

References

Ahmann D, Krumholz LR, Hemond HF, Lovley DR, Morel FM (1997) Microbial mobilization of arsenic from sediments of the Aberjona watershed. Environ Sci Technol 31:2923–2930

Alam MGM, Tokunaga S, Maekawa T (2001) Extraction of arsenic in a synthetic arsenic-contaminated soil using phosphate. Chemosphere 43:1035–1041

Anawar HM, Akai J, Sakugawa J (2004) Mobilization of arsenic from subsurface sediments by effect of bicarbonate ions in groundwater. Chemosphere 54:753–762

Appleby PG, Oldfield F (1983) The assessment of ^{210}Pb data from sites with varying sediment accumulation rates. Hydrobiologia 103:29–35

Arnold DG, Richardson DC (1995) Highlands ridge report. Southwest Florida Water Management District Engineering Section unpublished report. Brooksville, FL, 380 pp

Bauer M, Blodau C (2006) Mobilization of arsenic by dissolved organic matter from iron oxides, soils and sediments. Sci Total Environ 354:179–190

Belzile N, Tessier A (1990) Interactions between arsenic and iron oxyhydroxides in lacustrine sediments. Geochim Cosmochim Acta 54(1):103–109

Boyle J (2004) A comparison of two methods for estimating the organic matter content of sediments. J Paleolimnol 31:125–127

Cai Y, Cabrera JC, Georgiadis M, Jayachandran K (2002) Assessment of arsenic mobility in the soils of some golf courses in South Florida. Sci Total Environ 291:123–134

Carter LJ, Lewis D, Crockett L, Vega J (1989) Soil survey of Highlands County, Florida. U.S. Dept. of Agriculture, Soil Conservation Service

Chen CY, Sternberger RS, Klaue B, Blum JD, Pickhardt PC, Folt CL (2000) Accumulation of heavy metals in food web components across a gradient of lakes. Limnol Oceanogr 45:1525–1536

Chen ZR, Cai Y, Solo-Gabriele H, Snyder GH, Cisar JL (2006) Interactions of arsenic and the dissolved substances derived from turf soils. Environ Sci Technol 26(40):4659–4665

Crecelius EA (1975) The geochemical cycle of arsenic in Lake Washington and its relation to other elements. Limnol Oceanogr 20:441–451

Davenport JR, Peryea FJ (1991) Phosphate fertilizers influence leaching of lead and arsenic in a soil contaminated with lead arsenate. Water Air Soil Pollut 57–58:101–110

DERM (Department of Environmental Resources Management) (2002) Environmental quality monitoring at five municipal golf courses in Miami-Dade County. Final report, 159 pp

De Vitre RR, Belzile N, Tessier A (1991) Speciation and adsorption of arsenic on diagenetic iron oxyhydroxides. Limnol Oceanogr 36:1480–1485

Durant JL, Ivushkina T, MacLaughlin K, Lukacs H, Gawel J, Senn D, Hemond HF (2004) Elevated levels of arsenic in the sediments of an urban pond: sources, distribution and water quality impacts. Water Res 38:2989–3000

Feng M, Schrlau JE, Snyder R, Snyder GH, Chen M, Cisar JL, Cai Y (2005) Arsenic transport and transformation associated with MSMA application on a golf course green. J Agric Food Chem 53:3556–3562

Fisher MM, Brenner M, Reddy KR (1992) A simple, inexpensive piston corer for collecting undisturbed sediment/water interface profiles. J Paleolimol 7:157–161

Florida DEP (Florida Department of Environmental Protection) (1994) Lake bioassessments for the determination of non-point source impairment in Florida. Florida Department of Environmental Protection, Biological Section, Tallahasse, FL, 74 pp

Florida DEP (Florida Department of Environmental Protection) (2002) Environmental risks from the use of organic arsenical herbicides at South Florida golf courses. Florida DEP Website address http://fdep.ifas.ufl.edu/MSMA%20Dec%2027%202002.pdf. Accessed December 2007

Kolasa KV (1997) Little Lake Jackson water quality assessment. Unpublished report of Southwest Florida Water Management District, Brooksville, FL, USA, 33 pp

Kolasa KV (1999) Little Lake Jackson stormwater runoff analyses. In: Proceedings of the sixth biennial stormwater research and watershed management conference. Southwest Florida Water Management District, Brooksville, FL, USA, 14–17 September 1999, pp 41–59

Kopáček J, Hejzlar J, Borovec J, Porcal P, Kotorová I (2000) Phosphorus inactivaton by aluminum in the water column and sediments: lowering of in-lake phosphorus availability in an acidified watershed-lake ecosystem. Limnol Oceanogr 45:212–225

Ma LQ, Harris WG, Sartain J (2000) Environmental impacts of lead pellets at shooting ranges and arsenical herbicides on golf courses in Florida. Florida Center for Solid and Hazardous Waste Management Report #00-03, Gainesville, FL, 50 pp

Ma LQ, Cao RX, Hardison D, Chen M, Harris WG, Sartain J (2002) Environmental impacts of lead pellets at shooting ranges and arsenical herbicides on golf courses in Florida. Florida Center for Solid and Hazardous Waste Management Report #02-01, Gainesville, FL, 82 pp

MacDonald DD, Ingersoll CG, Berger TA (2000) Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Arch Environ Contam Toxicol 39:20–31

Murphy EA, Aucott M (1998) An assessment of the amounts of arsenical pesticides used historically in a geographical area. Sci Total Environ 218:89–101

Nikolaidis NP, Dobbs GM, Chen J, Lackovic JA (2004) Arsenic mobility in contaminated lake sediments. Environ Pollut 129:479–487

Peterson ML, Carpenter R (1986) Arsenic distributions in porewaters and sediments of Puget Sound, Lake Washington, the Washington coast and Saanich Inlet, BC. Geochim Cosmochim Acta 50(3):353–369

Rutter RP (1995) A bioassay of nine lakes in Highlands County, Florida with emphasis on the macroinvertebrate fauna. Florida Department of Environmental Protection Report, Punta Gorda, FL, 118 pp

Schaller T, Moor HC, Wehrli B (1997) Sedimentary profiles of Fe, Mn, V, Cr, As and Mo as indicators of benthic redox conditions in Baldeggersee. Aquat Sci 59:345–361

Schelske CL, Peplow A, Brenner M, Spencer CN (1994) Low-background gamma counting: applications for ^{210}Pb dating of sediments. J Paleolimol 10:115–128

Sohrin Y, Matsui M, Kawashima M, Hojo M, Hasegawa H (1997) Arsenic biogeochemistry affected by eutrophication in Lake Biwa, Japan. Environ Sci Technol 31: 2712–2720

Solo-Gabriele H, Sakura-Lemessy DM, Townsend T, Dubey B, Jambeck J (2003) Quantities of arsenic within the state of Florida. Florida Center for Solid and Hazardous Waste Management Report #03-06, Gainesville, FL, 153 pp

U.S. EPA (Environmental Protection Agency) (1994a) Method 7062 antimony and arsenic (Atomic absorption, borohydride reduction). U.S. Environmental Protection Agency

U.S. EPA (Environmental Protection Agency) (1994b) Method 200.7 (Revision 4.4): determination of metals and trace elements in water and wastes by inductively coupled plasma-atomic emissions spectrometry. U.S. Environmental Protection Agency

U.S. EPA (Environmental Protection Agency) (2002) The implementation guidance for the arsenic rule: drinking water regulations for arsenic and clarification to compliance and new source contaminance monitoring. U.S. Environmental Protection Agency Implementation Guide 816-K-02-018, 83 pp

U.S. EPA (Environmental Protection Agency) (2006) Organic arsenical herbicides (MSMA, DSMA, CAMA, and Cacodylic Acid), reregistration eligibility decision; notice of availability. U.S. Environmental Protection Agency, Federal Register Environmental Documents. URL: http://www.epa.gov/fedrgstr/EPA-PEST/2006/August/Day-09/p12905.htm. Accessed 29 March 2007

Whitmore TJ, Brenner M, Kolasa KV, Kenny WF, Riedinger-Whitmore MA, Curtis JH (2006) Inadvertent alkalization of a Florida lake caused by increased nutrient and solute loading to its watershed. J Paleolimnol 36:353–370