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Arsenic abundance and variation in golf course lakes

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1. Introduction

The use of monosodium methanearsonate (MSMA) on golf courses is a wide spread practice for weed control (Busey, 2004) and there is increasing interest in the fate of MSMA in the environment (Snyder and Cisar, 2002). As a result, public and private supply wells in the vicinity of golf courses may contain significant concentrations of arsenic (As), creating a potential environmental hazard. The United States Geological Survey investigated the water quality at several golf courses in central Florida, of which two were in Hillsborough County, and found elevated As concentrations (Swancar, 1996). Considering the potential magnitude of this problem, particularly in lieu of the new United States drinking water standard of 10 µg/L for As, surprisingly little scientific attention has focused on this potential problem. A thorough literature search produced

only a few peer-reviewed publications which addressed the occurrence of elevated As due to the use of MSMA (Busey, 2004; Cai et al., 2002; Cohen et al., 1999; Lewis et al., 2002, 2004; Ma et al., 2002; Swancar, 1996). None of those publications looked specifically at As concentrations in golf course lakes.

The U.S. Golf Association (USGA) database currently lists more than 16,100 golf facilities in the U.S. The exact number of U.S. golf courses that use MSMA is not known, but approximately 97% ($n=155$) of the golf courses surveyed in a recent study in Florida used MSMA (Ma et al., 2002). An evaluation of historical data for New Jersey, which hosts approximately 2% of all the golf courses in the U.S., concluded that up to 3.2 million kg of As per year were applied in New Jersey from 1920 to 1950 (Murphy and Aucott, 1998). While several studies investigated the problem of As occurrence in ground water, no systematic evaluation of As in surface waters on golf courses has

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apparently been published. Golf course lakes are of interest as they can constitute a pathway of preferential water recharge into aquifer systems (Upchurch, 1997). This is of particular concern in Karst terrains such as central Florida where sinkhole lakes are a dominant geomorphic feature. Lakes sediments readily scavenge As (e.g., Belzile and Tessier, 1990) and, therefore, affect both the concentration of As in the water column and As migration to ground water. However, changes in physico-chemical conditions in the sediment (e.g., redox, pH) may result in the release of adsorbed As and its potential migration into ground water (e.g., Pichler et al., 1999). Changes in basic water chemistry (i.e., major anions and cations) also play an important role. Large concentrations of phosphate, bicarbonate, silicate and possibly organic matter can enhance the desorption of As due to competition for adsorption sites (e.g., Smedley and Kinniburgh, 2002). Elevated concentrations of As in ground water are of concern to households, which rely on private wells for drinking water and to those entities responsible for providing safe drinking water.

The purpose of this study was to investigate As abundance and annual variation in golf course lakes at four golf courses in central Florida, focusing on the potential sources and sinks of this element, such as, ground water input, atmospheric deposition, seasonal variations and anthropogenic input. The evaluation of seasonal variations of concentration is necessary towards understanding As chemistry in a golf course environment, since the application of MSMA is typically higher during the growing season, causing a seasonal environmental marker.

2. Materials and methods

2.1. Description of study area

The four golf courses (B, C, R and RY) chosen for this study are located in Hillsborough County, Florida, exact locations in form of GPS coordinates are B: 28°03'09.35"N, 82°28'23.92"W; C: 28°04'19.29"N, 82°24'31.00"W; R: 28°01'11.55"N, 82°25'25.99"W; RY: 28°58'41.85"N, 82°33'26.42"W. All four courses had similar water usage characteristics and each used groundwater supplied by their own well(s). Strict water use guidelines, administered by the Southwest Florida Water Management District, set maximum monthly water withdrawals, which are higher during the predominantly dry season from October to April. The course R underwent extensive renovation the year prior to our study. Renovations included the re-shaping and dredging of lakes.

During the duration of this study, each of the golf courses applied the herbicide MSMA based on observation, e.g., the appearance of weeds in specific areas. Geology and hydrology underlying each of the golf courses is similar, namely a mantled Karst plain punctuated by many sinkholes. The mantle above the local Tertiary limestone is Quaternary marine sand underlain and occasionally interbedded with clays. The clay layer can act as a confining unit, typically breached at sinkhole lakes where direct connection between the surface and the Floridan Aquifer system may occur (Stewart and Parker, 1992).

2.2. Sample collection

Water samples from a total of 28 golf course lakes from 4 different golf courses were taken monthly over a one-year

period from February 2001 to January 2002. Samples were collected at the surface from the approximate center of a lake into 1-L Nalgene bottles and immediately transferred to the laboratory for chemical analyses. To test for the possibility of spatial variation in an individual lake, two of the larger lakes, C-1 and C-5, were sampled at two locations (i.e., C-1E and C-1W). Temperature and pH were measured in the field. Nine non-golf course lakes of comparable size in the vicinity of the studied golf courses and water from the Hillsborough River were sampled once in June 2001 for comparison. Based on As concentration in the water column and accessibility, sediment samples were collected from one lake per golf course (B-4, C-7, R-2 and RY-4). Sediment cores up to 70 cm in length were collected using a gravity driven corer mounted on a small boat. Each core was sampled at a 5 cm interval for As, Fe and Mn analyses.

2.3. Sample preparation and chemical analysis

Water samples were filtered through 0.45 μm membranes and kept at 4 °C until analyzed, usually within 24 to 72 h. Sample splits for cation analyses were acidified with HNO_3 . Total alkalinity was measured by titration with 1.6 N H_2SO_4 (Hach Company, 1997). Total arsenic was analyzed by hydride generation-atomic fluorescence spectrometry (HG-AFS) on a PSA Millennium instrument (Price and Pichler, 2005). A 2% solution of potassium iodide was used to reduce As(V) to As(III) prior to hydride generation. The anions F^- , Cl^- , NO_3^- , Br^- , NO_2^- , PO_4^{2-} and SO_4^{2-} were determined on a Dionex DX500 liquid chromatograph following the EPA 300 method. Bicarbonate concentrations were calculated from alkalinity titration values. The major cations Na^+ , Mg^{2+} , K^+ and Ca^{2+} , as well as, Fe and Mn were determined by inductively coupled plasma-emission spectroscopy (ICP-OES) following the EPA 200 method. Sediment samples were digested following the Kjeldahl method prior to ICP-OES (Fe and Mn) and HG-AFS (As) analyses. All analyses were performed at the University of South Florida Center for Water Analysis. Chemicals were trace metal grade or better. Instrument calibration standards were prepared from stock solutions purchased from SPEX and High Purity Standards. Based on duplicate samples (two per golf course) and the use of internal standards (every 10 samples) the analytical precision was estimated to be within 5% for each analysis. The charge balances (Σ Anions in $\text{meq/L} = \Sigma$ Cations in meq/L) for individual samples were better than 10%.

3. Results and discussion

3.1. Arsenic source

Total As concentration in all golf course lakes ranged from a minimum of 0.1 to a maximum of 124 $\mu\text{g/L}$. The lowest As concentration were generally seen in lakes from golf course R, which recently underwent complete renovation. The mean annual As concentration for all golf course lakes was 10.9 $\mu\text{g/L}$ ($n=336$); excluding golf course R this value increased to 13.3 $\mu\text{g/L}$ ($n=254$). Of the 24 lakes only 4 (R-3, B-3, R-1 and R-6) had mean As concentrations below 2 $\mu\text{g/L}$ (Table 1), which is considered to be the background As concentration in rivers, seawater, estuarine water, and lake water not affected by anthropogenic

Table 1 – Monthly variations of arsenic concentration from February 2001 to January 2002 for 28 golf course lakes in Hillsborough County in µg/L

Samples	Mean	Max	Min	Standard deviation	February	March	April	May	June	July	August	September	October	November	December	January
B-1	9.4	76.6	0.4	21.5	0.4	0.7	0.7	2.5	76.6	12.2	8.1	3.2	3.8	2.0	1.3	0.6
B-2	6.2	13.6	3.7	2.7	5.0	5.9	6.0	6.1	13.6	8.6	6.9	5.3	4.6	4.8	4.2	3.7
B-3	1.3	4.5	0.3	1.2	1.1	1.6	0.4	0.3	1.8	0.9	0.7	2.1	4.5	0.7	0.6	0.7
B-4	19.4	56.9	4.6	17.7	20.5	32.7	20.5	56.9	48.3	13.3	8.6	7.0	9.4	4.6	5.1	5.9
B-5	5.4	14.5	2.3	4.3	2.3	2.5	4.0	4.1	14.3	4.5	3.7	3.3	5.2	3.4	2.7	14.5
C-1E	2.0	5.7	0.7	1.4	0.7	0.8	1.6	1.4	5.7	3.2	2.4	2.2	2.5	1.3	1.7	1.1
C-1W	2.0	4.8	0.7	1.1	0.7	1.3	1.7	1.6	4.8	3.2	3.1	1.8	1.7	1.4	2.0	1.3
C-2	8.8	21.8	1.5	6.2	3.7	3.4	8.4	5.7	13.4	1.5	18.6	21.8	7.5	9.4	7.6	4.4
C-3	5.3	9.3	1.9	2.7	3.8	9.3	2.7	2.5	6.5	5.8	8.6	6.3	8.9	4.0	2.8	1.9
C-4	9.6	19.7	5.6	3.8	19.7	10.7	8.4	7.5	14.0	7.9	5.6	9.5	6.2	8.8	8.5	8.3
C-5N	7.1	9.2	4.7	1.6	5.5	5.5	4.9	4.7	9.1	7.7	8.4	9.2	7.8	8.2	8.1	6.1
C-5S	7.5	10.4	4.9	1.7	6.3	6.7	4.9	5.0	8.6	7.5	9.2	10.4	7.7	9.6	7.9	6.5
C-6	7.2	15.0	1.4	4.3	4.4	7.9	2.1	1.4	9.0	2.0	8.5	4.1	9.9	15.0	10.5	11.3
C-7	10.1	24.6	0.6	7.1	6.6	0.6	5.0	5.8	24.6	16.9	9.3	13.6	18.2	11.7	5.9	3.3
C-8	5.1	15.0	1.9	4.1	2.2	3.6	1.9	2.1	7.3	9.7	3.0	2.8	15.0	8.5	2.5	2.4
R-1	1.5	12.4	0.0	3.5	0.1	0.1	0.3	0.1	0.7	2.2	0.7	1.1	12.4	0.1	0.2	0.0
R-2	4.5	22.0	0.1	5.7	1.2	2.5	1.9	3.8	22.0	5.0	4.0	5.1	0.1	3.6	2.6	1.6
R-3	1.3	3.1	0.2	1.1	0.2	0.6	0.7	0.6	1.6	2.7	2.4	2.0	3.1	0.5	0.4	0.2
R-4	2.5	4.2	0.5	1.3	0.9	1.1	2.0	1.5	4.2	3.6	3.7	4.2	0.5	3.3	3.2	2.0
R-5	3.3	7.0	1.3	1.5	1.3	3.0	2.1	2.0	7.0	3.1	3.5	4.9	3.5	3.8	3.5	2.0
R-6	1.7	4.2	0.3	1.2	0.8	1.2	0.9	1.7	1.9	2.6	3.3	1.7	4.2	0.6	0.8	0.3
R-7	4.8	10.2	0.5	2.6	2.4	3.1	4.0	3.6	7.3	6.6	10.2	6.6	0.5	6.3	4.3	2.9
RY-1	65.7	124.3	19.8	27.6	19.8	57.1	40.3	56.7	124.3	59.2	83.0	85.6	73.2	89.8	57.8	41.5
RY-2	29.8	40.1	8.0	11.3	8.0	37.8	32.3	30.9	40.0	38.2	40.1	32.8	36.4	33.1	17.6	10.7
RY-3	2.4	7.2	0.3	2.2	0.3	1.4	3.2	0.9	1.9	2.7	6.2	2.6	7.2	1.1	0.7	0.5
RY-4	59.0	92.3	0.4	23.0	0.4	76.9	66.2	66.5	92.3	69.4	69.7	69.1	47.6	60.0	46.7	42.9
RY-5	3.4	7.2	0.6	2.1	0.6	4.1	3.7	1.6	3.3	3.4	7.1	4.5	7.2	3.0	1.9	0.9
RY-6	14.9	39.0	0.2	13.6	0.2	22.3	4.9	3.0	39.0	8.0	39.0	24.9	15.2	11.5	8.8	2.1
RY-7	15.3	32.7	2.1	10.2	2.1	16.0	7.0	5.8	32.7	20.5	30.8	23.7	15.8	15.9	8.9	4.3
RY-8	9.3	63.8	0.9	17.4	63.8	1.7	7.0	2.0	6.5	3.8	6.1	5.1	9.2	3.2	1.8	0.9

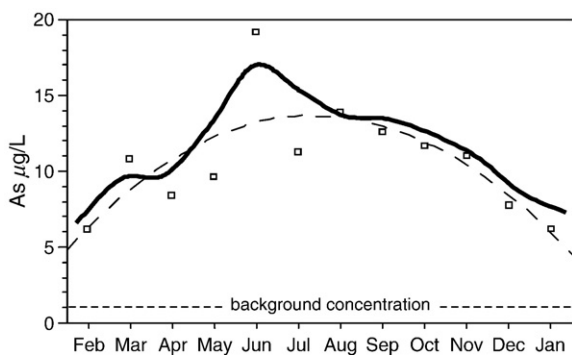


Fig. 1 – Yearly variation of average As concentrations for all 28 golf course lakes. Concentrations show some variation, but values are higher during late spring and summer. The solid black line represents the smoothed moving-average annual trend and the dashed line is a polynomial best fit. The background concentration of 1 µg/L is the mean of 9 water samples from comparable “non-golf course” lakes and the Hillsborough River in the same geographic area.

or unusual natural sources (Smedley and Kinniburgh, 2002). However, each of those four lakes exceeded 2 µg/L As at least twice during the course of the year (Table 1). Water samples from comparable “non-golf course” lakes and three locations along the Hillsborough River that were in the same geographic area as the golf courses showed a range of As concentrations from 0.2 to 2.4 µg/L with a mean of 1.0 µg/L ($n=9$). Only one non-golf course lake had a concentration above 2 µg/L. Although the concentrations of major anions and cations were comparable, mean annual concentrations of As in golf course lakes exhibited a 11-fold enrichment compared to the non-golf course lakes. The As concentrations in samples C-1E and C-1W and C-5N and C-5S were similar (Table 1), indicating that the lakes C-1 and C-5 were well mixed.

3.2. Arsenic variation

Total As concentrations varied substantially on all three levels of investigation: between golf courses, between individual lakes on a single golf course and between monthly sample collections (Table 1). The temporal variation of As concentration seemed to follow an annual pattern with the highest values observed during late spring and early summer (Figs. 1 and 2). To test for evaporative concentration of As the approach of Scanlon (1991) was employed and Cl, SO₄, Na and Ca were used as tracers to evaluate solute increase due to evaporation. No linear correlations, which are indicative for evaporative concentration, between As and any of the four tracers were observed for individual golf course lakes, whole golf courses or the whole data set (Fig. 3). The annual variation of anions and cations, as well as Fe and Mn in individual lakes were rarely beyond 10 to 20%, much lower than the variation of As (Table 1 and Fig. 1) and thus evaporative concentration, as a significant causative factor, appeared unlikely. Concentrations of As in water samples from the golf course irrigation wells, which draw water from the confined Upper Floridan aquifer, were below detection and in agreement with groundwater As values in central Florida (Jones and Pichler, 2007).

Thus, deep ground water can be excluded as the cause for the elevated As concentrations, implicating an increase in MSMA application as the remaining viable explanation.

Golf courses typically maintain records of the applications of fertilizer, herbicides and pesticides including the four golf courses that were studied. Although these records are not accurate enough to quantitatively evaluate MSMA input, they were sufficient to qualitatively estimate the amount and timing of MSMA applications. Based on the spray logs it was evident that most MSMA applications took place during the late spring and summer and that golf course RY used the most. Application of MSMA correlated with As concentration in the lakes, which were highest during late spring and summer, the prime growing season and that golf course RY showed the overall highest As values in its lakes.

Lake volume should be considered, because the larger a lake the harder it should be to affect its chemical composition. Lake volumes were calculated based on GIS data and field measurements of depth and compared to As data for June, December and the annual mean (Fig. 4). June was the month when As concentrations were generally highest, while December represents some of the lowest values. There was no apparent correlation between As concentration and lake volume (Fig. 4). The linear correlation coefficients (r^2) for As vs. annual mean, June and December were 0.06, 0.08 and 0.04, respectively. Nevertheless it is noteworthy that the largest lakes had the lowest As concentrations (Fig. 4). Hypothetically, it is surprising how little MSMA is needed to change the concentration of As in a lake. To change the As concentration by 1 µg/L in the biggest lake of our study, RY-3, which is approximately 70 m wide, 300 m long and 1 m deep (estimated volume = 2.1×10^7 L) only 21 g (2.1×10^7 µg) of As are needed. The manufacturer’s recommendation for MSMA application is approximately 7.5 to 15 mL of MSMA concentrate per L of water, which is the equivalent of 5.5 to 11 g of As per L. Thus the application of approximately 2 to 4 L of MSMA solution could hypothetically (assuming that all MSMA solution enters the lake) raise the As concentration in RY-3 by 1 µg/L. However, that all As applied to the golf course would reach the lake water is unlikely due to As accumulation in golf course soils (Cai et al., 2002).

3.3. Arsenic fate

The effective removal of As from golf course lake water was demonstrated several times during our study, since concentrations of As dropped dramatically from one month to the next (Table 1 and Fig. 2). Two possible mechanisms can be inferred to explain this drop in As concentration, (1) dilution by rain or groundwater and (2) adsorption/precipitation in lake sediments. The average concentrations of arsenic in uncontaminated rain from oceanic air masses in the northern hemisphere are around 0.02 µg/L and As concentrations in continentally influenced rain are expected to be in the range of 0.2–0.4 µg/L (Andreae, 1980). Thus addition of rainwater to golf course lakes is a mechanism that decreases As concentration via dilution. However, to account for some of the concentration changes several lake volumes would have to be added. For example, to account for the drop from June to July (approximately 76 to 12 µg/L As) in lake B-1 (Fig. 2) more than 4 lake volumes of rain would have to be added. Annual rainfall

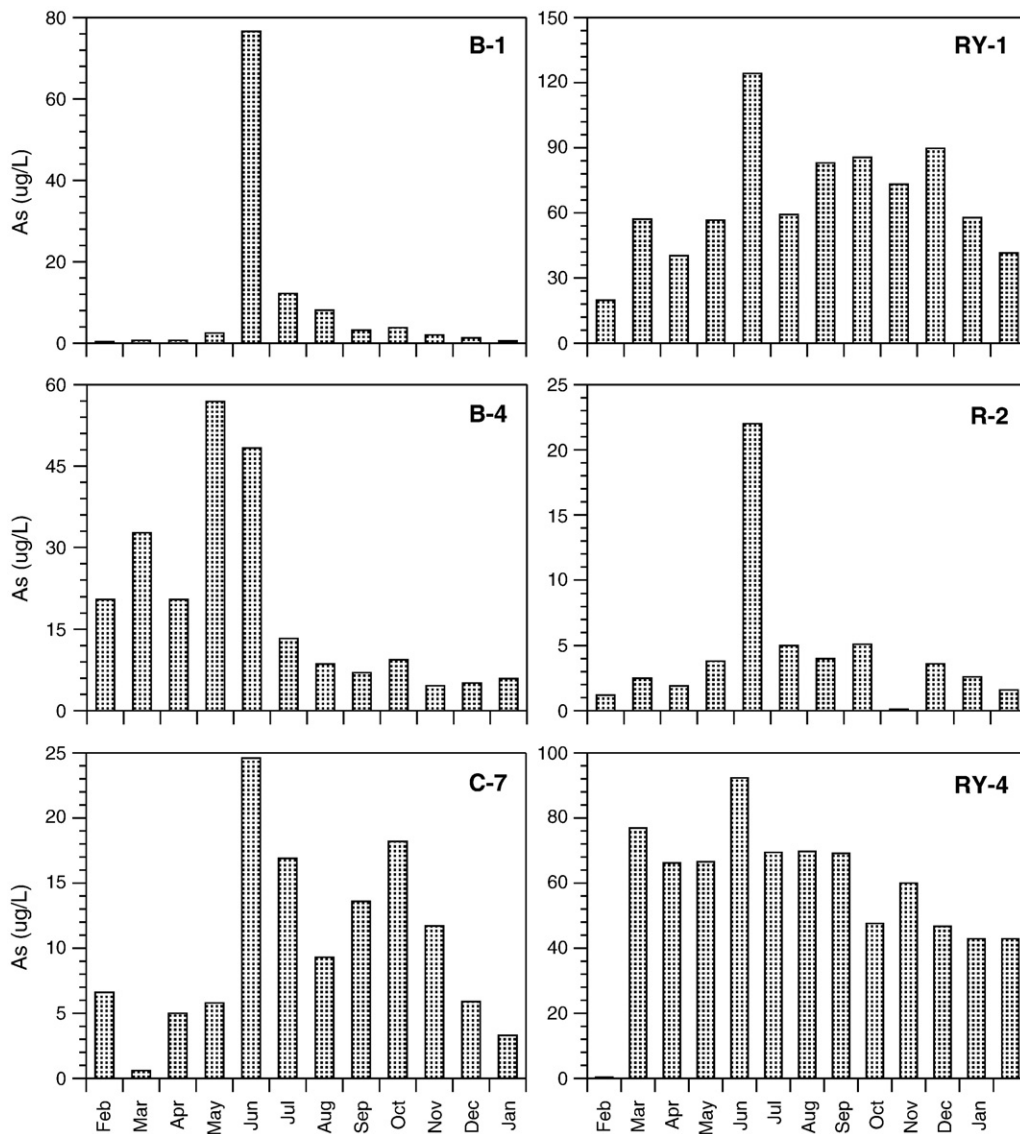


Fig. 2 – Monthly variation of As concentration for those golf course lakes highest in As and for those where sediment cores were taken (see Fig. 5).

in Hillsborough County is approximately 140 cm (55 in.), which represents roughly one lake volume for most of the lakes that were studied. While rainfall may have some part controlling the As concentration in the lakes, its role likely is minor.

The As concentration in lake water is often controlled by the presence of hydrous ferric oxide (HFO) in lake sediments, which has a high sorption affinity for As (Belzile and Tessier, 1990; De Vitre et al., 1991; Fortin et al., 1993). Azcue et al. (1994) for example, found As concentrations in Canadian lake waters affected by mining effluent similar to those not affected by mining effluent. Thus it is likely that HFO in golf course lake sediments play an important role in the cycling of As.

Except for lake R-2 the sediment cores, which were taken as part of this study all showed a distinct decline in As, Fe and Mn concentrations in the top 10–15 cm (Fig. 5). Fe and As were very well correlated in the top 15 cm (first three samples) in the lakes B-4 ($r^2=0.94$), C-7 ($r^2=0.99$) and RY-4 ($r^2=0.94$), while in R-2 there was no correlation ($r^2=0.33$). From a depth of 15 cm to the

bottom of the cores no correlation between Fe and As was observed ($r^2<0.3$ for all cores). Below 15 cm the concentrations of As, Fe and Mn elements were as expected for carbonate sediments in central Florida (Lazareva and Pichler, 2007; Price and Pichler, 2006), while above values were significantly higher. At approximately the same depth the cores changed in color from a brownish to a dark grey. Considering that the golf course lakes are well mixed (see above) and were generally less than 1 m deep, this indicates a change in physico-chemical conditions from oxygenated to oxygen depleted. Thus, the sharp drop of As and Fe concentrations below 10–15 cm can be explained by the existence of a redox boundary that affects the stability of hydrous ferric oxides. Above 10–15 cm HFO is stable as indicated by the high Fe concentrations in the sediment (Fig. 5) and As is retained due to sorption. The existence of Mn-oxyhydroxides is of limited importance, because concentrations of Mn are two orders of magnitude lower than those of Fe (Fig. 5).

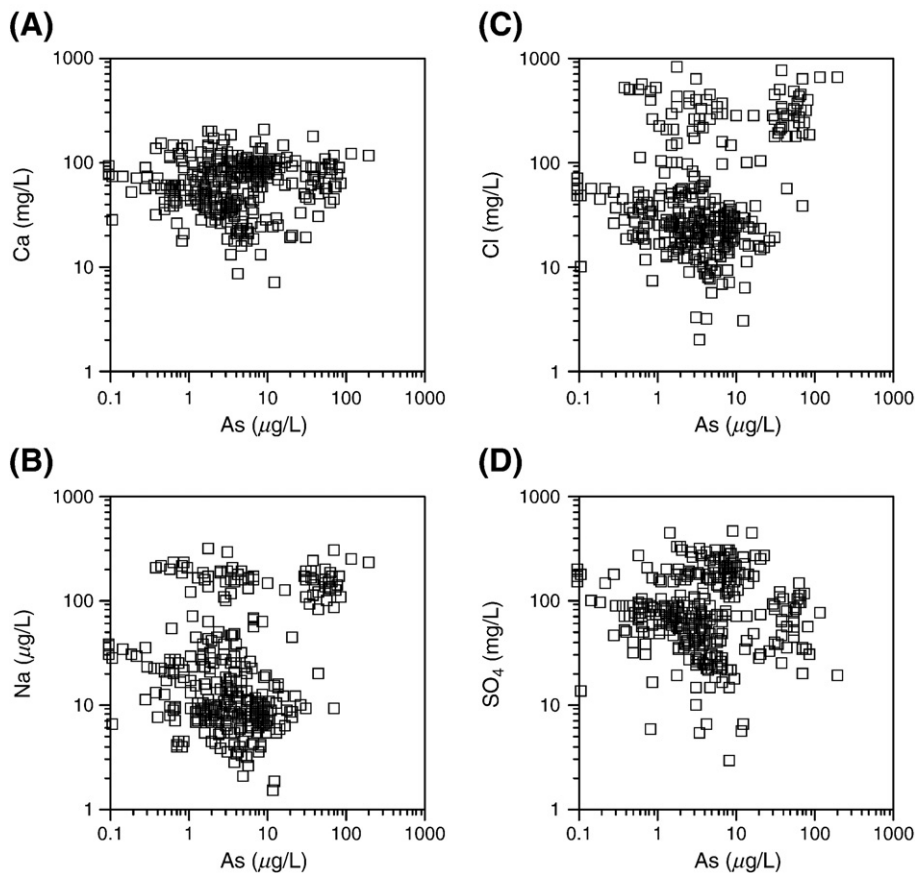


Fig. 3–Scatter plot of As concentration vs. Ca, Cl, Na and SO₄ for all 28 golf course lakes.

It is important to note that the golf courses lie within a karstic area characterized by cover-collapse sinkholes, minimal local relief and a shallow aquifer system. Because of the presence of cover-collapse features, lateral flow of shallow ground water is limited, resulting in a downward hydraulic gradient (Stewart and Parker, 1992). Thus, shallow ground water flows short distances until it either discharges into a surface water body or a sinkhole, through which it then

recharges the Floridan Aquifer (Stewart and Parker, 1992). Many of the golf course lakes are expressions of cover-collapse sinkholes and thus downward flow of lake water into the Floridan Aquifer is very likely. While As is evidently retained by HFO in the upper few cm of the lake sediments, below 10 cm there is no obvious retention. The drop in Fe, Mn and As concentrations indicates the presence of a redox boundary below which HFO is not stable anymore. Thus, once the loading capacity of the sediment is exceeded, As could pass through the upper 10 cm and migrate downward into the aquifer without any further retention. The actual loading capacity of the sediment with respect to As is difficult to evaluate, because As can be adsorbed by a variety of minerals. Nevertheless under oxygenated conditions and at a pH between 6 and 8 adsorption to HFO is likely strongest (Belzile and Tessier, 1990). Thus a good estimate of loading capacity can be generated by assuming that in the oxygenated zone of the lake sediment the entire quantity of Fe is present as HFO. Because of the importance of As/HFO associations in both natural and anthropogenic settings, there have been several detailed mineralogical studies, which demonstrated the large As sorption capacity of HFO, showing that sorption densities as high as 0.7 and 0.25 mole-As/mole-Fe can be obtained in coprecipitation and sorption experiments, respectively (e.g., Fuller et al., 1993; Raven et al., 1998). Natural As-rich HFO precipitates can attain sorption densities of up to 0.2 mole-As/mole-Fe (e.g., Berquó et al., 2007; Pichler et al., 1999).

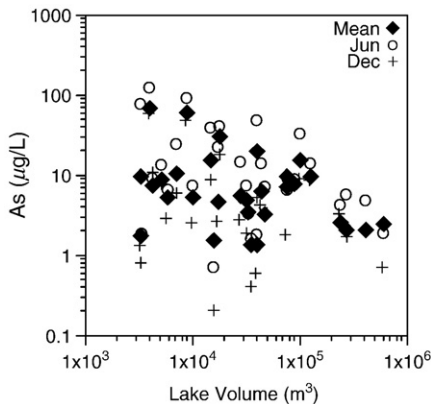


Fig. 4–Scatter plot of lake volume vs. As for the annual mean and the months of June and December, which represent high and low As concentrations, respectively. Individual linear correlation coefficients (r^2) are less than 0.1.

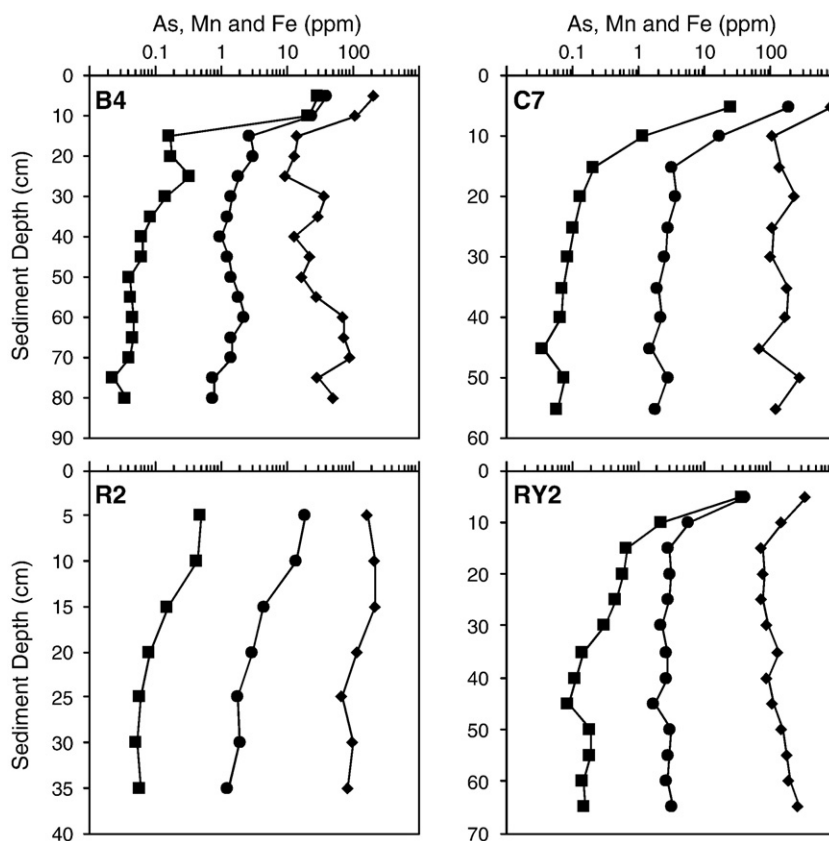


Fig. 5 – Concentrations of As, Mn and Fe vs. depth for the four sediment cores B-4, C-7, R-2 and RY-2. Squares (■) represent As values, circles (●) represent Mn values and diamonds (◆) represent Fe values (all in mg/kg). The values for As and Fe were divided by 10 for presentation purposes. The corresponding monthly variations in As concentrations in the lake water are shown in Fig. 2.

The mole-As/mole-Fe ratios in the top 10–15 cm of the lake sediments that were part of this study ranged from 0.003 to 0.220 with an average of 0.083, indicating that there is still substantial potential for the adsorption of As. It is noteworthy that lake R4 not only showed the lowest As concentrations in its water and sediment, but also the lowest mole-As/mole-Fe ratios, indicating that the renovation has reset the As accumulation in the sediments. Thus, at current conditions As should continue to accumulate in the upper 10–15 cm of the lake sediments. However, if redox conditions change (naturally or anthropogenically induced), solid-phase reduction of As(V) to As(III) may cause its release from the sediment. Under moderately reducing conditions ($E_h < 100$ mV) As(V) is reduced to As(III) in a matter of days or weeks and adsorbed As(V) is released as As(III) (Masscheleyn et al., 1991; Reynolds et al., 1999). The release of As can also occur via complete dissolution of the HFO. Kneebone et al. (2002) found that iron and arsenic concentrations in pore water from sediments of the Haiwee Reservoir in Olancho, CA increased greatly below 10 cm and were highly correlated with reductive dissolution of HFO.

4. Conclusions and outlook

Arsenic concentrations in the 28 golf course lakes were higher than those in comparable lakes not associated with golf

courses. Concentrations fluctuated on an annual basis and correlated positively with the application of MSMA. Values were highest during late spring and early summer, the growing season, followed by a sharp decrease during the fall and winter. This is likely a combination of dilution by rainfall, adsorption to lake sediments and, combined with decreasing MSMA applications. To confirm a potential escape of As from a golf course via downward migration into the Floridan Aquifer escape a more detailed study of lake sediments and sediment pore water will be necessary.

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