Distribution of Arsenic in Presque Isle, PA, Pond Sediments

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Grateful acknowledgement is made to the Pennsylvania Sea Grant Program, a Partnership of The Pennsylvania State University, The Commonwealth of Pennsylvania, and NOAA, which provided the funding which made this study possible.

November, 2001

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Executive Summary

A study was initiated of the occurrence of arsenic in pond sediments on the Presque Isle peninsula, Erie, PA, due to concerns expressed by citizens and due to occasionally high arsenic results in samples collected for other purposes by various government officials. Samples of pond and lagoon sediments were collected at thirteen primary sites and additional reference sites during the fall, 2000, and again in spring, 2001. Samples were collected such that the upper thin layer of sediments were collected separately from the underlying deeper sediments. Samples were digested and analyzed by atomic absorption spectrophotometry according to US EPA approved methods. Various quality control samples were also included to assure reliable results.

The probable effect concentration (PEC) for arsenic of 33.0 mg/kg was exceeded in the surface sediments at all 13 interior sites during fall testing. It was exceeded in all but one site during spring testing. For deep sediments, the PEC was exceeded in the fall at 9 sites and in the spring at 6 sites. Arsenic concentrations for fall sampling ranged from 36.9 mg/kg to 325.4 mg/kg for surface sediments and from 8.3 mg/kg to 206.3 mg/kg for deep sediments. Spring 2001 sampling revealed arsenic ranges from 17.5 mg/kg to 393.6 mg/kg for surface sediments and 3.6 mg/kg to 327.3 mg/kg for deep sediments.

When the results for both sampling seasons are combined and plotted, it is apparent that, without exception, surface sediments contained more arsenic than did deep sediments. These differences were more pronounced in the spring samples than in the fall samples. When surface and deep arsenic values are combined for the fall and compared with similar values for the spring, there are no significant differences at the 95% confidence level. However, several sites have quite higher concentrations in the spring than in the fall, while only a few have lower values in the spring. There appears to be a general trend, with numerous exceptions, for sites more distance from Gull Point to have higher arsenic levels.

The sediments of Presque Isle have high levels of arsenic and represent a likely threat to the aquatic ecosystem, based on widely accepted toxicity guidelines. These high levels most likely are due to a combination of natural processes which, over time, have resulted in a concentration of arsenic in surface sediments. That said, there is a possibility that human activities have contributed to a generally higher level of arsenic in the local environment, and that these secluded ponds and lagoons have acted as sinks and enrichment sites. This study has not attempted to document the risk to the ecosystem, but it is not unreasonable to speculate that elevated tumor incidence rates in Brown Bullhead bottom-dwelling fish and deformities in turtles and other reptiles often noted by area naturalists may be related to arsenic. This report also does not speculate about the need for remedial action, but suggests that further study be conducted to determine the appropriateness of such activities.

Introduction

A 1994 study conducted on the sediments of Presque Isle Bay, Erie, Pennsylvania, revealed the presence of heavy metals such as copper, cadmium, nickel, zinc and arsenic. Occasional high levels of arsenic in samples of Presque Isle sediments collected at various times has generated concern in certain members of the local community.

Presque Isle Bay was designated an Area of Concern (AOC) in 1991 by the US Department of State. The impairment of two beneficial uses of the bay, the presence of tumors in fish and restrictions on the dredging of sediments (due to contamination) warranted the designation, AOC (PADER, 1992).

Though no direct linkage has been established between any one pollutant and fish tumors, arsenic (inorganic) was placed in a "weight-of-evidence group A, human carcinogen" category by the US Environmental Protection Agency in 1991. Epidemiological evidence exists for the correlation of arsenic concentrations in drinking water to increased incidences of skin cancers (including squamous cell carcinomas and multiple basal cell carcinomas) as well as liver, bladder, respiratory system and gastrointestinal tract cancers. Occupational exposure has shown a direct linkage between arsenic exposure and lung cancer mortality (Lewis, 1998; Opresko, 1992).

The current study investigates the distribution of arsenic in the sediments of ponds and lagoons of Presque Isle State Park. Possible explanations have been offered for the sources, both natural and anthropogenic, and patterns of distribution of arsenic, both vertically and at various locations around the peninsula. Also, samples were collected in spring and fall, so that seasonal variations could be considered.

Background

Arsenic Mineralogy

Arsenic exists ubiquitously in rock, soil, dust, water, air and biological tissues. The element is a major constituent in over 200 minerals, ranging in concentrations from a few parts per million to percentage quantities. These arsenicals are classified as arsenates (60%), sulfides and sulfosalts (20%), with arsenides, arsenites, oxides, silicates, and elemental arsenic composing the remainder. Some common arsenicals are shown in Table 1. Arsenic is common in many mineral deposits of another dominant metal, such as pyrite, galena, chalcopyrite and less commonly, sphalerite. Arsenopyrite is the most abundant arsenic mineral (Thornton and Farago, 1997; O'Neill, 1990).

Table 1. Common Arsenicals.

Arsenates	Scorodite	$FeAsO_4 \cdot 2H_2O$
	Mimetite	$Pb_5(AsO_4).Cl$
Sulfosalts	Tennantite	$(Cu,Fe)12As_4S_{13}$
	Energite	Cu_3AsS_4
Sulfides	Realgar	AsS, As_2S_2
	Orpiment	As_2S_3
	Arsenopyrite	$FeAsS$
Arsenites	Trippkeite	$CuAs_2O_4$

Source: (Lippmann, 2000; Thornton and Farago, 1997)

Arsenic is generally uniformly distributed throughout major rock types. Most igneous rock possesses arsenic concentrations ranging from <1-15 mg/kg, with an overall average of 2 mg/kg. Sedimentary rocks, especially finer grained argillaceous rocks (shales, mudstones and slates) tend to contain much higher concentrations, ranging from <1-900 mg/kg. Arsenic is commonly found where iron or sulfide deposits exist. Arsenic has a propensity to bind to sulfur ligands and form precipitates. Consequently, arsenic precipitates of Fe and S may occur at elevated levels in sedimentary rock, in iron deposits and sedimentary iron ores, and in many mineralized areas. It is also in high concentration in manganese nodules. Arsenic has been shown to possess low organic affinities in various coal samples, though it was found in all organic fractions of the coal. Table 2highlights arsenic concentrations in various rock types (Kabata-Pendias and Pendias, 1984; O'Neill, 1990; Thornton and Farago, 1997).

Table 2. Arsenic in Major Rock Types.

Rock Type	[As] (ppm)
Magmatic Rocks	
Ultramafic Rocks (Dunites, peridotites, pyroxenites)	0.5-1.0
Mafic Rocks (Basalts, gabbros)	0.6-2.0
Intermediate Rocks (Diiorites, syenites)	1.0-2.5
Acid Rocks (Granites, gneisses)	1.0-2.6
Acid Rocks, Volcanic (Rhyolites, trachytes, dacites)	1.5-2.5
Sedimentary Rocks	
Argillaceous sediments	13.0
Shales	5.0-13.0
Sandstones	1.0-1.2
Limestones, dolomites	1.0-2.4

Source: (Kabata-Pendias and Pendias, 1984)

Arsenic in soil & sediments

Parent materials (underlying bedrock and weathered materials from other areas) are the primary sources of arsenic in soil. The process of weathering may free arsenic from rock in the form of arsenious acid and arsenic acid salts. Generally, soils contain higher levels of arsenic than rocks (Kabata-Pendias and Pendias, 1984; O'Neill, 1990). Unpolluted soils typically contain from 1-40 mg/kg of arsenic. Sandy soils and soils derived from granite may have lower concentrations while alluvial and organic soils may have much higher levels. The roasting of arsenic-containing sulfide ores and the burning of arsenic-containing coal leads to the emission of arsenic trioxide gas. The gas reacts with basic atmospheric oxides, such as alkaline earth oxides, to form arsenates that redeposit to the earth (Thornton and Farago, 1997).

Arsenic binds to ligands other than oxygen in soils, giving it stability when combined with a number of elements. In aerobic environments, ferric arsenate precipitates in soils. Soils containing the weathered products of pyrite have been observed to contain arsenic up to several hundred mg/kg via sorption to secondary iron oxides. Bauxites high in iron have shown As_2O_3 levels up to and above 500 mg/kg (O'Neill, 1990; Thornton and Farago, 1997).

Trivalent forms of arsenic tend to predominate in reducing soil conditions. However, the reduction of arsenate (+5) to arsenite (+3) is slow and soil levels may be under kinetic control. The pentavalent forms of arsenic acid (H_3AsO_4, $H_2AsO_4^{-}$, $HAsO_4^{-2}$ and AsO_4^{-3}) predominate at normal soil pH values of 4-8. Eh values of less than +300 mV at pH = 4 and –100 mV at pH = 8 (in the absence of complexing species and methylating organisms) tend toward the thermodynamic stability of arsenous acid (H_3AsO_3, $H_2AsO_3^-$ and $HAsO_3^{-2}$) of the trivalent oxidation state. Similar to the reduction of arsenicals in soils, the shift in oxidation state in aqueous systems is a slow process, and species that do not correspond to given Eh/pH values may be found (O'Neill, 1990; Thornton and Farago, 1997). Figure 1 summarizes arsenic speciation in soil under various combinations of redox potential and pH.

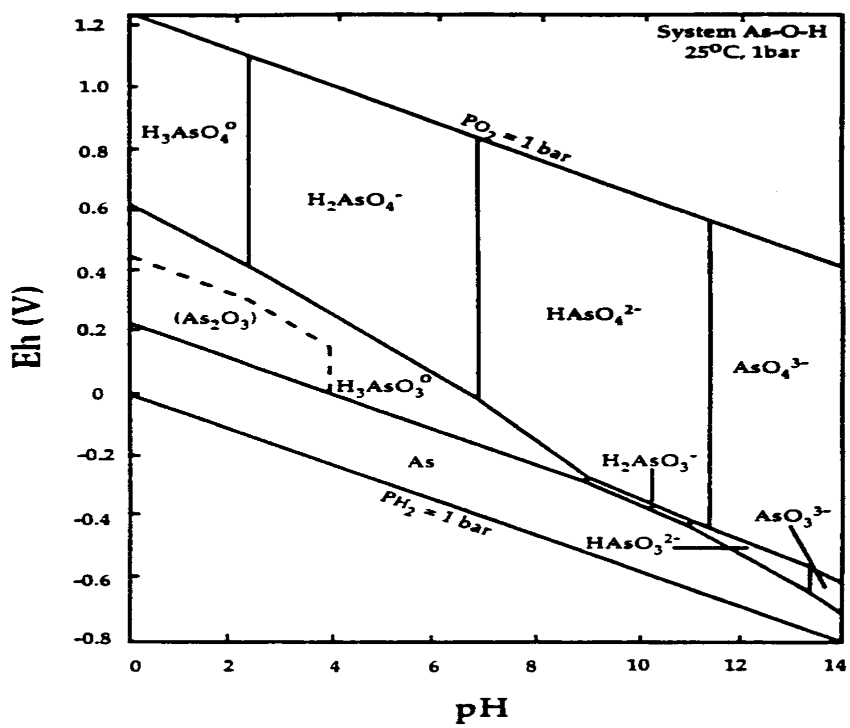


Figure 1. Arsenic stability diagram for 25°C, 1 atmosphere (Ringwood, 1996).

Inorganic arsenicals may also change oxidation states (solely or in combination with the inorganic processes described above) due to microbial activity. Resulting products under aerobic conditions may be monomethylarsonic acid ($CH_3AsO(OH)_2$), dimethylarsinic acid (or cacodylic acid, $(CH_3)_2AsO(OH)$) and trimethylarsenic oxide ($(CH_3)_3AsO$), and under anaerobic conditions, volatile and highly toxic and flammable methylarsine gases: trimethylarsine ($(CH_3)_3As$) and dimethylarsine ($(CH_3)_2AsH$). This biomethylation, however, depends on the microorganisms, soil conditions and arsenic species present.

Reducing conditions are shown to enhance arsenic mobility, while arsenic sorbed to soil particles in the unsaturated zone is unlikely to become desorbed. Arsenic sorbed to Fe and Al may become available if redox potential falls, with penta-valent arsenicals exhibiting a greater capacity for sorption than trivalent arsenicals. (Kabata-Pendias and Pendias, 1984; O'Neill, 1990). This may result in an increase in arsenic concentration in unsaturated soils over time.

Arsenic in Water

Unpolluted freshwater typically ranges from 1-10 μg/L of arsenic. Levels may increase to 100-5000 ug/L near areas of high sulfide mineralization and up to 35 mg/L in areas associated with hydrothermal activity. Under oxidizing conditions, arsenic exists in its pentavalent (arsenate) forms while under reducing conditions, (acidic or mildly alkaline), trivalent (arsenite) species dominate. The concentration of arsenic in solution may be controlled by co-precipitation with Fe, Ba, Co, Ni, Pb, and Zn. Also, arsenic sorbs to suspended particulate matter (Thornton and Farago, 1997; O'Neill, 1990).

Arsenic in Plants

The tissue of edible plants may contain low levels of arsenic, often at or below the limits of detection, when grown in arsenic-contaminated soils. Overall, however, arsenic uptake is specific to plant species. Plants grown in fine-grained soils (high silt, clay, and Fe/Al content) may contain less arsenic than when grown in coarse-grained soils (sands or sandy loams) with the same arsenic concentration. This may be due to the availability of arsenic as controlled by sorption to particle surfaces (O'Neill, 1990).

Though arsenic uptake rates vary widely among species, arsenic levels in terrestrial plants are generally lower than that of their soils. On the other hand, some aquatic macrophytes may accumulate arsenic levels similar to that of their sediments (over 1000 mg As/kg fresh weight have been observed) (O'Neill, 1990).

Carcinogenicity of Arsenic

The carcinogenicity of arsenic has not been conclusively established and its role in carcinogenisis has not been defined (Lippmann, 2000).

Epidemiological studies have shown inorganic As to be carcinogenic in humans. Elevated levels of arsenic in drinking water have been present in areas with cases of skin cancer, hyperpigmentation, and keratosis. Arsenic in drinking water and wine has been associated with liver angiosarcomas (Opresko, 1992). Other malignancies correlated with arsenic exposure include neoplasms of the lymphatic and hematopoietic tissues and cancers of the GI tract (Lippmann, 2000).

Pentavalent arsenic has been shown to inhibit host-resistance factors, possibly increasing the chances of developing cancer due to other agents. Inhibitions may also lie in DNA repair as trivalent arsenic has been shown to both diminish the action of the DNA ligase component of DNA repair and interfere with excision repair. Chronic exposure to arsenic has been theorized to deplete selenium concentrations in the body, thereby increasing cancer susceptibility (Lippmann, 2000).

Geology of Erie, PA and Associated Lake Erie

Erie, PA is located in the northwestern corner of the state and is bordered to the northwest by Lake Erie, with 47 miles of shoreline. Most of this shoreline consists of narrow beaches in front of 15 to 170 ft bluffs cut into Pleistocene and early Holocene glacial and lacustrine sediments atop Devonian shale bedrock. Streams draining northwestern PA have eroded overlying sediments down to the shale bedrock creating the majority of breaks in the nearly uniform bluff-face shoreline (Shultz, 1999) .

Major constituents of the upper bedrock are siltstones, sandstones and conglomerates. Four major glaciations dominated northwestern PA depositing what now overlays the bedrock in that area. Erie country is theorized to predominantly retain till of the late Wisconsin advance.

Shoreline erosion is widely variable as a function of weather patterns, lake levels and shoreline composition. Bluff erosion is dependent on wave activity and involves the removal of sediments within wave reach, acting to steepen the bluff face and leading to mass-movement and landslide processes.

Geology of Presque Isle State Park, Erie, PA

Presque Isle is a compound recurved sandspit peninsula that lies in Lake Erie. It is attached at its southwest end to the shore at Erie, Pennsylvania and proceeds northeastward from the shore to its tip. From attachment to the tip, referred to as Gull Point, the peninsula is approximately 10.1 km (6.25 miles) in length, with width varying from several hundred meters at its neck to 2 km (1.25 miles) at its widest point (DCNR-1, 1991; Kormondy, 1969; Shultz, 1999).

The underlying geologic structure of the peninsula is mainly derived from a large deposit of glacial till left atop the shale bedrock of the area approximately 13,000 to 14,000 years ago by glaciers of the Pleistocene period. Presque Isle's topical nourishment is largely sand derived from the deposition of eroded rocks along the lakeshore west of the peninsula, and transported northeastward by long-shore lake and wind currents. The bulk of these eroded particles originated from the bluffs of Ashtabula, Ohio, approximately 50 miles west of Erie. Sediment deposition continues to accrue at Erie, helping to form and maintain Presque Isle (DCNR, 1991; Kormondy, 1969; Shultz, 1999). Additionally, there is an annual program of beach nourishment. Mass addition of sand to the beaches has been performed by the US Army Corps of Engineers for a number of years. (DCNR, 1991; DCNR, 1999)

Pond and Lagoon Formation

Lagoons and ponds form in the shelter of the recurved sandspit as sand is moved to the northeast extension of the peninsula. Occasional storm wave activity curves the tip of the peninsula upon itself, forming an elliptical pond from the lake water that may extend up to 1.5 km in length and range from 50-75 m in width. Beach ponds form along the lakeside of the peninsula as storm wave activity creates sandbars high enough to section off a portion of lake water on the beach or provide a retention basin for rainwater. These ponds are elongate, running parallel to the beachfront, and seldom exceed 250 m in length or 20-40 m in width. While lagoon ponds may persist in contact with lake water for some years as they become sealed off, beach ponds are usually partitioned permanently from the lake when they form. Both types generally possess a uniform slope to the deepest point, seldom greater than 1 m in depth, lying in the center of the pond or eccentrically nearer to the lake. The pond floor is made up of partially decomposed organic detritus overlaying the sand bottom; depth varies with pond age with young ponds having little to no organic matter and older ponds possessing detritus depths up to 0.8 m.

As ponds age, both surface area and depth decrease due to the influx of windblown sediment and accumulating organic detritus. These reductions may be substantial, such that small ponds may have a lifetime of only a few years while large ponds may experience an overall reduction in size of up to 95% in 75 years. Rates of filling due to biomass are a function of eutrophication status. High nutrient levels result in faster filling rates with peak vegetation turnover and plankton density occurring in late July to early August. Physical factors such as lake levels influence vegetational filling as pond levels rise or fall in accordance to lake levels. Low water levels result in faster rates of peripheral vegetational encroachment (Kormondy,1969).

Methods

Age Estimation of Sampled Ponds

Approximate ages of Presque Isle's ponds can be determined by comparing old maps, using techniques such as tree corings or comparing pond stages of ecological succession to known patterns of development. Whereas map and successional stage comparisons are a good age indicator in the absence of specific tools, tree corings offer more specific results (Kormondy, 1969).

Pond ages were estimated for this study using a variety of sources. Some of the ponds used in the cited studies were also used in this study and the age estimates of those ponds are adjusted to the date of this study (Table 3). Kormondy listed two age estimates for Site 1, Ridge Pond, in his study, one at 200 years and the other at 250 years. Consequently, a range is given in the table.

Anecdotal evidence and various maps have also been used to estimate pond age for all ponds not listed in the above studies. Maps of the peninsula were obtained with publication dates of 1884 (Maguire), 1901, 1957 (USGS), 1990 (FWS) and 1999.

The West and East Settling Ponds, sites 6 and 7, were created around 1904 from two natural "Chimney Ponds" located at those sites (Walker, 2000). The Chimney Ponds are located on the 1884 map and are thus at least 117 yrs of age (Maguire, 1884) but it is difficult to estimate how old the settling pond sediments are. The West Settling Pond, site 6, retained a natural bottom while the East Settling Pond, site 7, had a cement bottom installed when it was built. Marina Lake, site 8, was dredged in 1956 (Walker, 2000).

An additional method used to estimate pond ages was based on the trend that the portions of the peninsula are older towards the neck and younger toward the tip. Using "Terrain Navigator" software (Maptech®, 1998), measurements were taken from site 15, the tip of Gull Point, thought to be the youngest area of the peninsula, to every other site on the map. Therefore, ponds with shorter distances to site 15 may be younger while those with longer distances may be older. These estimates are also presented in Table 3.

Table 3. Approximate Ages of Sampled Ponds Using Literature Sources, and Estimating by Distance from Peninsula Tip.

Site #	Identification	Research-Based Estimates (Years)	Calculation-Based Estimates (km from site 15)
1	Ridge Pond	232-282[a], 300[c]	2.7
2	Niagara Pond	> 117[e, b]	1.6
3	Unnamed, Gull Point pond	82[a]	1.1
4	Cranberry Pond	> 117[e, b]	3.7
5	Unnamed, just east of Horseshoe Pond	92[a], 100[c]	1.3
6	West Settling Pond, Natural Bottom	97[g]	5.9
7	East Settling Pond, Cement Bottom	97[g]	5.7
8	Marina Lake	45[g]	4.7
9	Duck Pond	100[b]-117[e]	4.6
10	Horseshoe Pond	> 117[e, b]	1.7
11	Boat House Pond	> 117[e, b]	2.7
12	Big Pond	> 117[e, b]	2.9
13	Long Pond	> 117[e, b]	3.5
14	Unnamed, newly formed pond, beach 11	10[f]-20	1.2
15	New Sand, tip of Gull Point shoreline	< 10[f]	0.0

[a] = Kormondy, 1969 [c] = Zagorski & Gance, 1971 [e] = Maguire, 1884 [g] = Walker, 2000
[b] = Lydecker et al., 1923 [d] = USGS, 1957 [f] = FWS, 1990

Sampling Locations

Samples were collected in the fall and spring. Fall sampling occurred from October 11-25, 2000 and spring sampling from April 5-12, 2001. Sites were numbered 1-15 (Figure 2) according to the order of sample collection in Fall 2000. For reference arsenic values, samples of shale bedrock were collected from nearby bluffs. Bluff sites are not shown in Figure 2 and are abbreviated hereafter as: Cascade Creek Shale (CCS), Mill Creek Shale (MCS) and Walnut Creek Shale (WCS). For all sites, a handheld Global Positioning System (GPS) unit was used to record the exact location of sediment sampling. Table 4 lists these sampling sites with their corresponding coordinates for Fall 2000 and Spring 2001. It should be noted that repeated GPS readings on different days in the exact same location varied as much as 8 seconds (n = 5) in latitude and as much as 6 seconds (n = 5) in longitude.

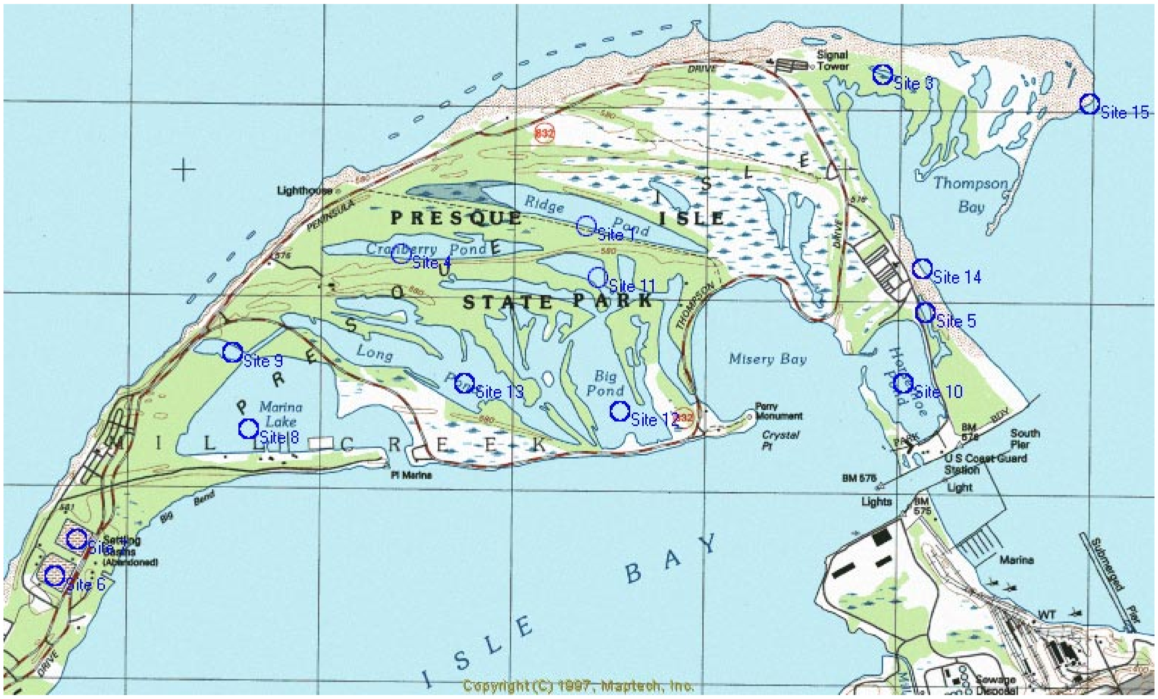


Figure 2. Map of Presque Isle State Park with Sampling Locations.

Sample Collection

Different methods of sample collection were employed depending on water depth. Sampling equipment also varied with respect to pond depth.

Shallow Ponds: A representative location in a given pond was determined by visual inspection to have typical depth and physical characteristics. Choosing a spot within arm's length, and undisturbed by the wading of the researchers, a 10 cm diameter Lexan core tube capped on one end was immersed on its side, down to the surface of the sediment layer. The lower lip of the corer's open end was immersed further, approximately 2-3 cm into the sediment, and pushed horizontally along the surface, effectively removing the top 2-3 cm of sediment. The open end of the corer was tilted upward to retain the surface layer of sediment, and the corer was removed from the water. The sample was placed in a 5 gal bucket. Two replicate surface sediment additions were added to the bucket and mixed. This mixture was allowed to settle for approximately 3-5 min inside the bucket. The water was decanted and the sediment was poured into the collection bottle, labeled and stored on ice.

Table 4. Sampling Sites, Names and Geographic Coordinates

Site #	Pond Identification	Latitude/Longitude Fall 2000	Latitude/Longitude Spring 2001
1	Ridge Pond	N 42.09.81 W 080.05.65	N 42.09.81 W 080.05.65
2	Niagara Pond	N 42.09.92 W 080.05.19	N 42.09.92 W 080.05.19
3	Unnamed, Gull Point pond	N 42.10.26 W 080.04.84	N 42.10.26 W 080.04.84
4	Cranberry Pond	N 42.09.77 W 080.06.82	N 42.09.77 W 080.06.82
5	Unnamed, just east of Horseshoe Pond	N 42.09.62 W 080.04.71	N 42.09.62 W 080.04.71
6	West Settling Pond, Natural Bottom	N 42.08.95 W 080.07.89	N 42.08.96 W 080.07.91
7	East Settling Pond, Cement Bottom	N 42.08.88 W 080.07.99	N 42.08.86 W 080.08.00
8	Marina Lake	N 42.09.31 W 080.07.36	N 42.09.31 W 080.07.37
9	Duck Pond	N 42.09.49 W 080.07.31	N 42.09.50 W 080.07.34
10	Horseshoe Pond	N 42.09.37 W 080.04.76	N 42.09.36 W 080.04.73
11	Boat House Pond	N 42.09.62 W 080.05.95	N 42.09.62 W 080.05.95
12	Big Pond	N 42.09.34 W 080.05.87	N 42.09.33 W 080.05.87
13	Long Pond	N 49.09.40 W 080.06.43	N 42.09.40 W 080.06.41
14	Unnamed, newly formed pond, beach 11	N/A	N 42.09.71 W 080.04.66
15	New Sand, tip of Gull Point shoreline	N/A	N 42.10.28 W 080.03.98
CCS	Cascade Creek Shale	N/A	N 42.07.52 W 080.06.63
MCS	Mill Creek Shale	N/A	N 42.05.59 W 080.04.25
WCS	Walnut Creek Shale	N/A	N 42.04.47 W 080.14.19

To obtain the lower sediments, the end cap was removed from a corer and an "egg crate" cap was placed on one end. Selecting another undisturbed part of the pond, the corer was pushed vertically into the sediment until resistance became limiting. Limiting resistance was encountered at depths of 20 to 35 cm below the surface. The core tube was then brought to the surface and the topmost layer was removed from the column by tilting the corer and allowing the topmost layer to pour out from the uncapped end of the corer, back into the pond. The remaining deeper sediment was added to a 5 gal plastic bucket. This process was repeated two times, resulting in three replicates. These replicates were then homogenized with a spade, placed into the sample bottle, labeled and stored in ice.

Deeper Pond and Lagoon Sediments: A small boat was used to travel to a representative area of the pond or lagoon. An anchor was dropped and the boat allowed to drift away from any disturbed sediment from the anchor. The Eckman dredge was lowered into the sediment, activated by a messenger, and redrawn to the surface with its captured sediment. The screens were removed from the dredge prior to remove the top 2-3 cm of sediment. This removal was performed using a plastic spade, and the top 2-3 cm was placed into the sample bottle. The deeper sediments were released from the bottom of the dredge and added to a 5 gal plastic bucket. Two additional replicate dredges were taken and added directly to the sample bottle for surface sediments, and to the bucket for deeper sediments. The surface sediment sample was labeled and stored in ice. The deeper sediments were mechanically homogenized with a plastic spade, a representative portion was bottled, labeled and stored in ice.

Pond Depth: Pond depth at the sampling sites varied from site to site and from fall to spring. Table 5 lists these depths at the various site locations for each sampling batch. Depth readings for sites 1-5, Fall 2000 (italicized in Table), were taken 10/27/01, 16 days after samples were collected; water depths were noted to have decreased significantly during that time. Depth readings for all other sites, batches 1 and 2, were taken at the time of sampling.

Shale Samples: Mainland bedrock (shale) samples were obtained from three different creek bed locations. From west to east, they were Walnut Creek (Fairview Township), Cascade Creek (City of Erie) and Mill Creek (City of Erie). Care was taken to extract unexposed shale along the water's edge by breaking away surficial shale and taking the shale from underneath. Shale samples were dried in an oven at 105^{o}C for one week. A ceramic mortar and pestle was used to grind the shale into finer particles. These particles were sieved through a #35 (500 μm) US Standard Testing Sieve.

Table 5. Pond Depths at Sampling Sites.

Site #	Pond Identification	Pond Depth (m) Fall 2000[1]	Pond Depth (m) Spring 2001
1	Ridge Pond	*0.15*	0.30
2	Niagara Pond	*0.13*	0.20
3	Unnamed, Gull Point pond	*0.03*	0.13
4	Cranberry Pond	*0.10*	0.41
5	Unnamed, just east of Horseshoe Pond	*0.01-0.03*	0.10
6	West Settling Pond, Natural Bottom	4.5	4.5
7	East Settling Pond, Cement Bottom	4.0	4.9
8	Marina Lake	4.02	3.26
9	Duck Pond	0.61	0.20
10	Horseshoe Pond	2.15	1.98
11	Boat House Pond	0.30	0.25
12	Big Pond	0.61	0.20
13	Long Pond	0.30	0.46
14	Unnamed, newly formed pond, beach 11	N/A	0.23
15	New Sand, tip of Gull Point shoreline	N/A	0.10

[1]Italicized depth readings were taken 10/27/01, 16 days after samples were collected.

Quality Control, Sampling: All sampling was done while stressing uniformity among sites. All sampling instruments were thoroughly rinsed between the sampling of upper and lower sediments and between sites to avoid cross contamination of samples. Sample bottles were washed with Alconox® detergent solution, rinsed with tap water, acid-washed for at least 24 h, and rinsed with deionized water prior to use. Field blank sand was acid-washed in dilute HCl solution for 14 days, rinsed with acetone and dried at 105°C for 7 days. In the field, sample bottles were topped off with site water to eliminate head space, tightly closed and placed in a cooler of ice as soon as possible after sampling.

Sediment Digestion and Analysis

EPA method 3050B was followed for digestion of sediment samples. This method, as described by EPA, is “not a total digestion technique for most samples” but “a very strong acid digestion that will dissolve almost all elements that could become ‘environmentally available’” (EPA, 1996). Acids employed were Trace Metal Grade by Fisher Scientific. The As stock standard was by Fisher Scientific. Sediment digestates were analyzed using a Perkin-Elmer AAnalyst 600 Graphite Furnace Atomic Absorption (GFAA) Spectrophotometer using a Perkin-Elmer Arsenic Lumina™ Lamp (Hollow Cathode), along with AA WinLab™ software (Perkin-Elmer Corp. 1996) and an 88 sample-capacity autosampler (Perkin-Elmer AS-800). It was determined that a 1:2 dilution was favorable for most samples and nickel nitrate produced more consistent results as a matrix modifier than did the palladium/magnesium mixture (both at 1:1 ratios).

Quality Control, Sediment Digestion: Typically, 3 matrix blanks, 8 duplicates and 1 triplicate were performed for purposes of quality control during the digestion procedure (Table 6). EPA method 3050B recommends a representative 1-2 g sample for digestion. Actual weights ranged from 1.73 - 3.53 g with a mean weight of 2.23 g. .

Table 6. Arsenic Concentrations of Quality Control/Quality Assurance Samples.

Sample Title	[As] mg/kg
Diluent Blank	<4.0
Field Blank 1	<4.0
Method Blank 1	<4.0
Nitric Acid Blank 1	<4.0
Nitric Acid Blank 2	<4.0
Field Blank 2	<4.0
Method Blank 2	<4.0

Statistical Distribution of Arsenic Concentration Values: Surface and deep sediment arsenic concentration values for Fall 2000 and Spring 2001 were found by the Shapiro-Wilks test to be log-normally distributed (Table 7). Therefore, non-parametric statistics were required for statistical comparisons. Thus, all paired arsenic concentration comparisons utilized the Wilcoxon signed-rank test and all unpaired arsenic concentration comparisons utilized the Wilcoxon rank-sum (Mann-Whitney) test (Minitab, 1995).

Table 7. Statistical Analyses Results pertaining to the Normal Distribution of Arsenic Data

	Shapiro-Wilks Test		Skewness
Arsenic Data Set	P-scores Non-Transformed Data	P-scores Log-Transformed Data	Non-Transformed Data
Fall 2000			
-Surface Sediments	0.0225	0.8445	1.51
-Deep Sediments	0.0096	0.7903	1.24
Spring 2001			
-Surface Sediments	0.0312	0.0888	0.35
-Deep Sediments	0.0019	0.2570	1.14

Results

Summary of Arsenic Concentration Results in Presque Isle Sediments

Arsenic concentrations for fall sampling ranged from 36.9 mg/kg to 325.4 mg/kg for surface sediments and from 8.3 mg/kg to 206.3 mg/kg for deep sediments. Spring 2001 sampling revealed arsenic ranges from 17.5 mg/kg to 393.6 mg/kg for surface sediments and 3.6 mg/kg to 327.3 mg/kg for deep sediments (Table 8 and Table 9).

Table 8. Arsenic concentrations in sediments collected during Fall, 2000.

Site #	Pond Name	[As] Surface Sediments (mg/kg)	[As] Deep Sediments (mg/kg)
1	Ridge Pond	60.8	8.3
2	Niagara Pond	131.0	40.7
3	Unnamed, Gull Point pond	74.4	18.2
4	Cranberry Pond	82.0	68.2
5	Unnamed, just east of Horseshoe Pond	154.5	41.2
6	West Settling Pond, Natural Bottom	49.0	30.6
7	East Settling Pond, Cement Bottom	211.9	148.9
8	Marina Lake	53.0	44.6
9	Duck Pond	325.4	206.3
10	Horseshoe Pond	36.9	27.5
11	Boat House Pond	180.7	193.9
12	Big Pond	75.0	71.7
13	Long Pond	90.6	71.5

Table 9. Arsenic concentrations in sediments collected during Spring, 2001.

Site #	Pond Name	[As] Surface Sediments (mg/kg)	[As] Deep Sediments (mg/kg)
1	Ridge Pond	59.5	3.6
2	Niagara Pond	309.9	27.0
3	Unnamed, Gull Point pond	73.8	10.2
4	Cranberry Pond	106.7	2.7
5	Unnamed, just east of Horseshoe Pond	266.1	17.4
6	West Settling Pond, Natural Bottom	363.9	236.6
7	East Settling Pond, Cement Bottom	64.7	37.4
8	Marina Lake	17.5	11.8
9	Duck Pond	359.5	188.4
10	Horseshoe Pond	37.2	23.8
11	Boat House Pond	285.5	237.7
12	Big Pond	113.6	109.4
13	Long Pond	393.6	327.3
14	Unnamed, newly formed pond, beach 11	5.4	4.3
15	New Sand, tip of Gull Point shoreline	4.6	N/A
CCS	Cascade Creek Shale	7.5	N/A
MCS	Mill Creek Shale	8.8	N/A
WCS	Walnut Creek Shale	15.5	N/A

When the surface layers of sediments for both seasons were averaged, the As concentration ranged from 5.4 mg/kg to 342.4 mg/kg. Similarly, average deep sediments ranged of 4.3 mg/kg to 215.8 mg/kg (Table 10).

Table 10. Mean Arsenic Concentrations for Surface and Deep Sediments when Fall 2000 and Spring 2001 values were combined.

Site #	Identification	Mean Surface [As] (mg/kg)	Mean Deep [As] (mg/kg)
1	Ridge Pond	60.1	5.9
2	Niagara Pond	220.4	33.9
3	Unnamed, Gull Point pond	74.1	14.2
4	Cranberry Pond	94.3	35.5
5	Unnamed, just east of Horseshoe Pond	210.3	29.3
6	West Settling Pond, Natural Bottom	206.5	133.6
7	East Settling Pond, Cement Bottom	138.3	93.2
8	Marina Lake	35.3	28.2
9	Duck Pond	342.4	197.4
10	Horseshoe Pond	37.0	25.6
11	Boat House Pond	233.1	215.8
12	Big Pond	94.3	90.5
13	Long Pond	242.1	199.4
14	Unnamed, newly formed pond, beach 11	5.4	4.3

Vertical Distribution of Arsenic in Presque Isle Sediments

When the results for both sampling seasons are combined and plotted (Figure 3), it is apparent that, without exception, surface sediments contained more arsenic than did deep sediments. These differences were more pronounced in the spring samples than in the fall samples, as illustrated in Figure 4and Figure 5 below.

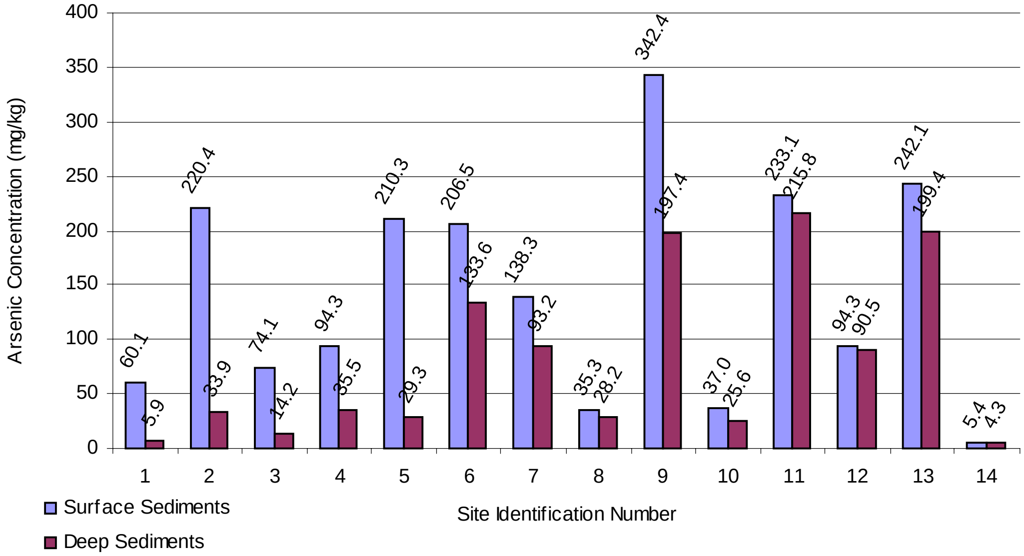
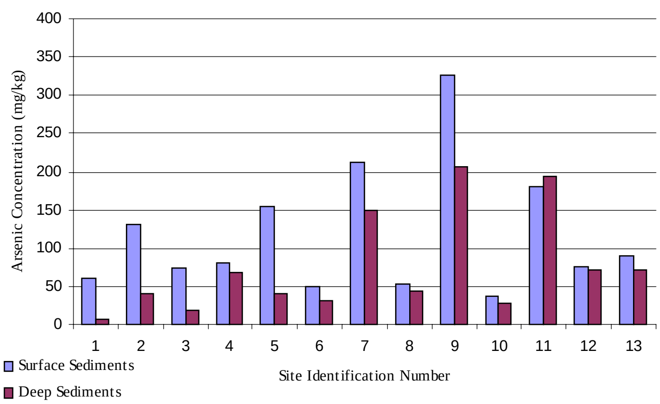


Figure 3. Plot of mean arsenic concentrations for surface and deep sediment layers.



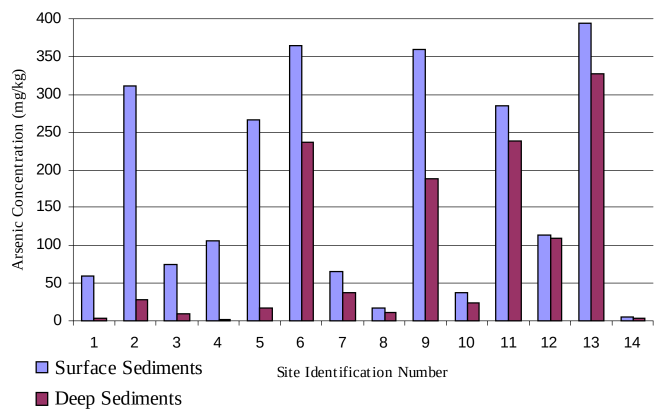


Figure 4. Fall arsenic sediment concentrations.

Figure 5. Spring arsenic sediment concentrations.

Seasonal Variation in Arsenic Concentrations

When surface and deep arsenic values are combined for the fall and compared with similar values for the spring, there are no significant differences at the 95% confidence level. However, as seen in Figure 6, several sites have quite higher concentrations in the spring than in the fall, while only a few have lower values in the spring. It may not be valid to simply average the results for surface and deep concentrations, since the deep value represents a much larger mass of sediment than does the top. A simple averaging would skew the result in favor of the surface arsenic concentration when that may not be representative of the value obtained if the samples were combined and homogenized.

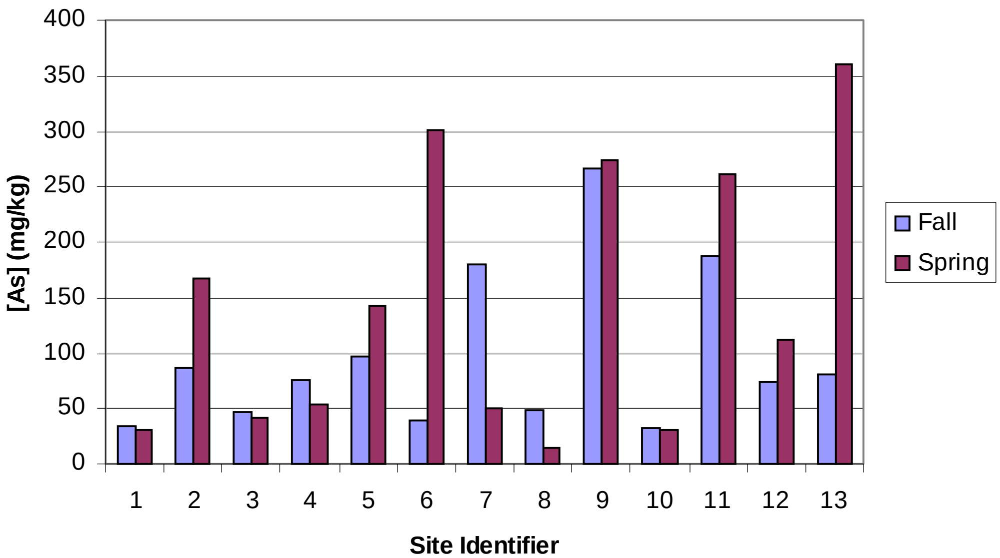


Figure 6. Comparison of arsenic concentrations in fall and spring when surface and deep values are averaged.

While averages of surface and deep concentrations are not significantly different from fall to spring, direct comparison of surface concentrations alone are moderately significant ($P = 0.065$). Surface sediments at eleven of the thirteen sampling sites had the same or increased arsenic concentrations in the spring compared to the fall while the concentration decreased at only two sites (Figure 7).

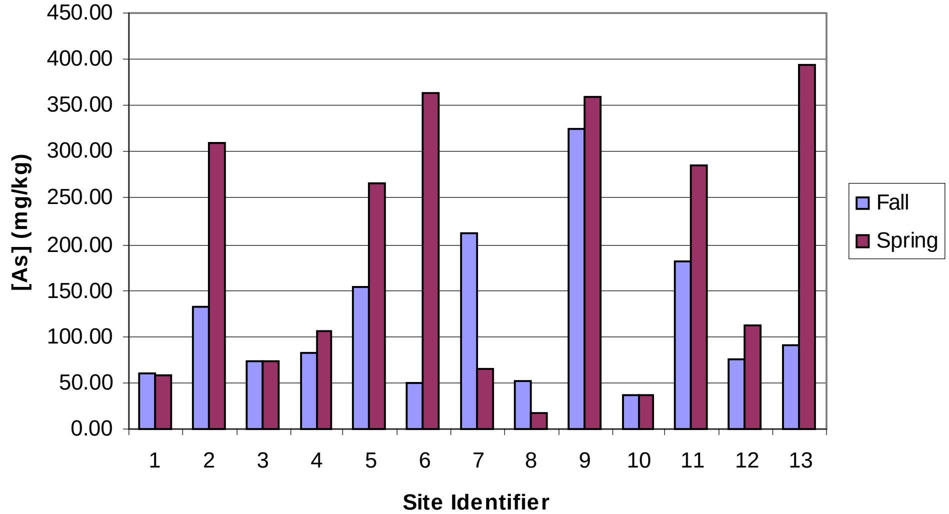


Figure 7. Comparison of values for fall and spring sampling of surface sediment arsenic concentrations.

Arsenic Concentration as a Function of Pond Age

Using site averaged arsenic concentrations, sites were arranged in descending order of literature-based ages. A rough bell-shaped curve was observed (Figure 8).

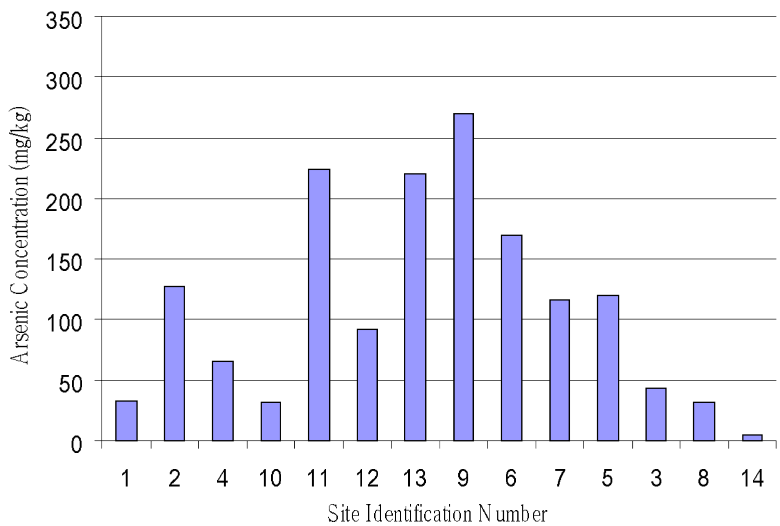


Figure 8. Sampling sites arranged according to age estimates, decreasing from left to right.

When the sites were arranged in decreasing order of distance from site 15, with numerous exceptions, a pattern of roughly descending arsenic concentrations was noted (Figure 9).

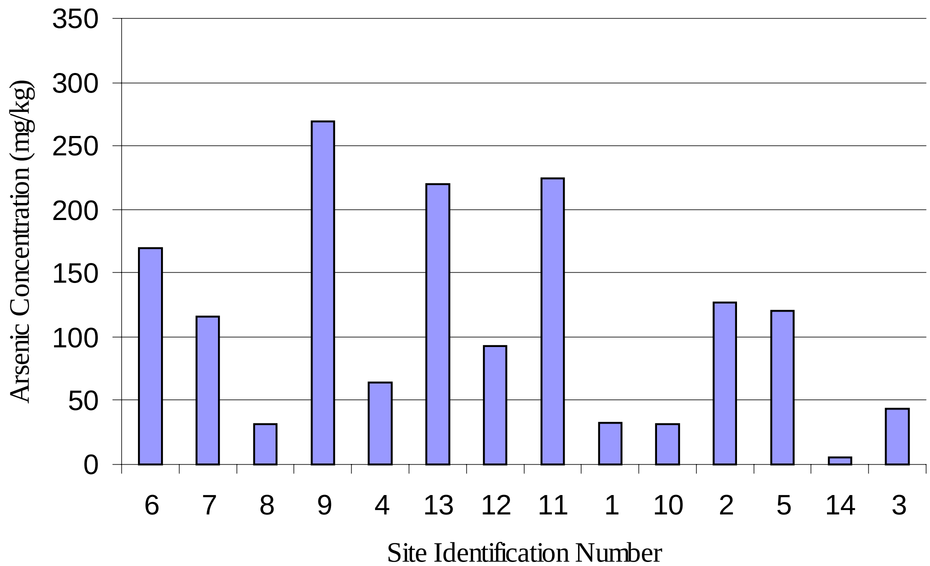


Figure 9. Sampling sites arranged according to distance from Site 15 (the youngest site), with greatest distance on the left.

Discussion

Arsenic Sediment Toxicity Values

Persaud et al. (1992),) reports a Lowest Effect Level (LEL) of 6.0 mg/kg for arsenic and a Severe Effect Level (SEL) of 33.0 mg/kg. Long and Morgan (1990) using a slightly different approach reported an Effects Range-Low (ER-L) of 33.0 mg/kg and an Effects Range-Moderate (ER-M) of 85.0 mg/kg. The New York Department of Environmental Conservation (NYDEC, 1999) concluded that sediment is moderately contaminated if the lowest criterion is exceeded and severely contaminated if both criteria are exceeded, i.e., LEL = 6.0 mg/kg and SEL = 33.0 mg/kg.

The USEPA (Ingersoll et al., 2000) refers to a Consensus-Based Probable Effect Concentration (PEC) derived from broad survey of literature values based on field and laboratory testing. The PEC is a level above which harmful effects are likely. The PEC for arsenic is 33.0 mg/kg.

The PEC for arsenic of 33.0 mg/kg was exceeded in the surface sediments at all 13 interior sites during fall testing. It was exceeded in all but one site during spring testing. For deep sediments, the PEC was exceeded in the fall at 9 sites and in the spring at 6 sites. At 6 of 13 sites, the ER-M of 85.0 mg/kg was exceeded in surface sediments in the fall, while it was exceeded at 8 of 13 in the spring.

When the measured values were divided by the PEC to obtain a toxicity ratio for the mean of fall and spring results (Table 11), it was observed that most of the surface samples exhibited arsenic concentrations more than double the PEC, and in some cases as much as six times the probable effects level (Duck Pond had over ten times the PEC).

Given the variability in the results from site to site, from surface to deep sediments, and from fall to spring, there may some uncertainty about the true arsenic concentrations. However, there can be little doubt that these sediments are severely contaminated with arsenic.

Table 11. Ratio of measured concentrations to PEC for surface and deep sediments.

Site #	Identification	Mean Surface: Ratio[1] Measured to PEC	Mean Deep: Ratio[1] Measured to PEC
1	Ridge Pond	1.8	0.2
2	Niagara Pond	6.7	1.0
3	Unnamed, Gull Point pond	2.2	0.4
4	Cranberry Pond	2.2	1.1
5	Unnamed, just east of Horseshoe Pond	6.4	0.9
6	West Settling Pond, Natural Bottom	6.3	4.0
7	East Settling Pond, Cement Bottom	4.2	2.8
8	Marina Lake	1.1	0.8
9	Duck Pond	10.4	6.0
10	Horseshoe Pond	1.1	0.8
11	Boat House Pond	7.1	6.5
12	Big Pond	2.8	2.7
13	Long Pond	7.3	6.0

[1] Mean of fall and spring concentrations divided by the probable effect concentration (PEC) for arsenic of 33.0 mg/kg.

Possible Arsenic Sources

Natural Sources of Presque Isle Arsenic: Shale samples taken from the Erie, PA, mainland near Presque Isle were found to contain arsenic at concentrations ranging from 7.5 to 15.5 mg/kg. The sample of sand taken from the youngest area of Presque Isle (Site 15- the tip of Gull Point) was found to contain 4.6 mg/kg (Table 12). Note that the concentration for Cascade Creek Shale is the average of two duplicates, one containing 5.9 mg/kg and the other 9.9 mg/kg.

Table 12. Arsenic Concentrations (mg/kg) of Erie, PA Shale Samples.

Site Identification	[As] (mg/kg)
Cascade Creek Shale	7.5
Mill Creek Shale	8.8
Walnut Creek Shale	15.5
Gull Point Sand (Site 15)	4.6

It is believed that Presque Isle was formed about 4,000 to 5,000 years ago from sediments transported to the current location by erosive forces. The major natural supplier of material to the peninsula has been the bluffs along the shore of Lake Erie to the west of Erie. Sand continues to move eastward along and across Presque Isle, nourishing beaches on the way and accumulating at Gull Point, the easternmost area of the peninsula.

As already noted, the arsenic concentration in Gull Point sand is relatively low. Sandy soils tend to possess lower arsenic concentrations due to their relative lack of organic material and low specific surface area available for sorption. Also, sand is imported onto Presque Isle for beach nourishment by the Army Corps of Engineers (ACOE) from various sources. Analysis of imported sands revealed a mean arsenic content of 10.9 mg/kg (Potomac-Hudson, 1991).

It may be that very fine suspended particles, derived from the City of Erie watershed, could be transported across Presque Isle Bay and enter interior peninsula waters via numerous inlets from the Bay. Once these transported particles have entered the quieter waters of the lagoons they would be likely to settle and become incorporated into the aquatic sediments.

Potential Anthropogenic Sources: The city of Erie, PA has historically supported a wide variety of industries, some of which have produced and do produce arsenic in their waste (i.e. foundry ash, coke-plant exhaust, the Erie wastewater treatment plant sludge incinerator (Potomac-Hudson, 1991)). However, the Presque Isle peninsula is now entirely occupied by a state park, and it is unlikely that in times past, solid wastes were trucked and dumped onto the peninsula. This possibility has not been investigated, however.

Information regarding air-deposited arsenic from point sources in Erie is lacking or at least conflicting. The Erie wastewater treatment plant sludge incinerator flue gas contains arsenic but pilot tests of its wet electrostatic precipitator, installed in 1989, showed reductions of 96.6-98.5% for all metal emissions (Potomac-Hudson, 1991). In January, 1996, solid material of an unknown origin was found on Presque Isle Bay ice by the county biologist. Samples were collected and showed 221 mg/kg of total arsenic. Similar samples were collected in subsequent years in similar locations on Presque Isle Bay but contained arsenic at <2.0 mg/kg (Wellington, 2001).

Concentration and Enrichment

The low levels of arsenic found in the sources of sediment transported to Presque Isle may be concentrated in the ponds due to bulk transport, such as the erosive forces of wind, water and storm activity, and due to geochemical transformations once on the peninsula. The leaching of arsenic is a function of the stability of its complexes with other elements, the electrochemical properties of those elements in complex with arsenic, the resulting complex's solubility, and the presence of clay minerals, organic matter, and iron and aluminum oxides. Also, biological activity includes uptake via plants, methylation due to microorganism metabolism and macroorganism ingestion and excretion. Thus arsenic imported at low levels to the peninsula by whatever means could be redistributed to areas of the peninsula other than the original site of deposition.

A propensity for incorporation and retention into aquatic sediments may have allowed Presque Isle's aquatic sediment levels to gradually increase in arsenic concentration over time. As previously discussed clay minerals, organic matter and the presence of iron and aluminum oxides have also been shown to increase retention and decrease leaching rates. Specifically for aquatic systems, inhibition of arsenic mobility is due to the presence and bonding potential of hydrated iron oxides and/or sulfides as well as arsenic's propensity to sorb to particulate matter in aquatic systems (O'Neill, 1990).

Vertical Distribution of Arsenic:

Surface sediments contained significantly higher arsenic concentrations than the adjacent deep sediments for most sampling sites in both Fall 2000 and Spring 2001 samples ($P < 0.05$). Comparisons were made using both paired (Wilcoxon sing-rank test) and unpaired (Wilcoxon rank-sum test) non-parametric mean tests (Table 13).

Table 13. Statistical significance of comparisons for surface and deep layers of sediments.

Data Set Comparison	P-score Paired	P-score Unpaired
Fall 2000 Sediments -Surface v Bottom	0.0037	0.0483
Spring 2001 Sediments -Surface v Bottom	0.0010	0.0346

Arsenic enrichment within surface sediments may occur as a function of the differing solubility of reduced versus the oxidized forms. Sediments deeper than the surficial 2-3 cm are generally anaerobic and thus reducing environments. Many reduced arsenicals have higher solubilities than their oxidized counterparts. Thus, diffusion would tend to transport dissolved arsenic toward the oxic surface layer. Once reaching the oxidized surface layer, sorption onto iron and/or aluminum oxides would occur as well as precipitation of oxidized arsenic compounds. This mechanism would tend to enrich surficial sediments and deplete arsenic from deeper sediments. Figure 10 illustrates this process.

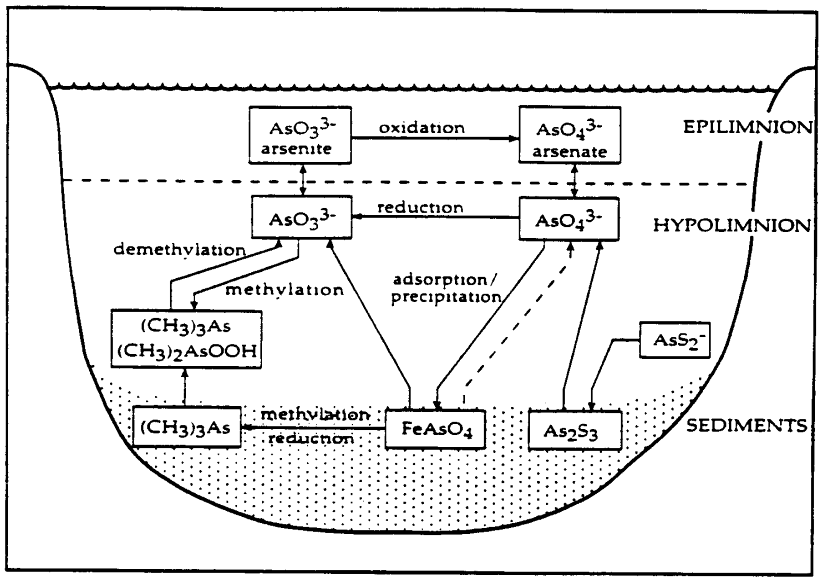


Figure 10. Arsenic Speciation and Cycling in an Aquatic Environment.

<u>Biological Transport</u>: It has been reported that some aquatic macrophytes may accumulate arsenic to levels similar to those of their sediments, with concentrations over 1000 mg As/kg fresh weight having been observed (Kabata-Pendias and Pendias, 1984; O'Neill, 1990). Sampling sites 1-13 possessed rooted macrophytes to some degree (with higher densities in shallower sites). It may be that macrophytic arsenic uptake through root systems would be from deep sediments. Subsequent death and decay of the plant tissues would result in a deposition of the residual arsenic on the surface of the sediments. This would result in a transferal of arsenic from deeper sediments to surface sediments.

<u>Microbial Volatilization</u>: Surface aquatic sediments tend to be aerobic due to proximity to the water-sediment interface so long as there is sufficient dissolved oxygen in the overlying waters. Deeper sediments tend to be anaerobic due to the absence of adequate oxygen replenishment. As previously discussed, inorganic arsenicals may be metabolized by microorganisms into volatile methylarsines (trimethyl and

dimethylarsines) under anaerobic conditions. Once formed, methylarsines would diffuse toward the surface and escape into the overlying water. In fact, low-temperature volatilization of alkylarsines is believed to be the largest natural emission source of arsenic to the atmosphere, estimated at 58% of the annual total estimate of 45,482 tons (volcanic activity is second with 38%) (Ringwood, 1996).

Sorption by Organic Matter: The maximum sorption of pentavalent arsenicals to humic material occurs at pH = 5.5. Optimal sorption of reduced (trivalent) arsenicals occurs at higher pH values. (Kabata-Pendias and Pendias, 1984; O'Neill, 1990). Since anaerobic deep sediments tend to be acidic due to the formation of fermentation by-products, it is likely that deep sediment organic matter would be less effective at retaining arsenic than would surficial organic matter.

Seasonal Variation in Arsenic Concentrations

Comparisons of seasonal data were made using both paired (Wilcoxon singed-rank test) and unpaired (Wilcoxon rank-sum test) non-parametric mean tests. The difference between fall and spring surface sediments was moderately significant (P = 0.0869) while the difference between fall and spring results for deeper sediments was not significant. Generally, surface sediment concentrations were higher in the spring than they were in the fall (fall mean concentration = 117 mg/kg; spring mean concentration = 188 mg/kg). In 11 cases out of 13, spring concentrations were equal or higher than in the fall.

This pattern may be the result of typical seasonal effects. At the end of the warm summer season, water overlying the sediments is likely to be depleted of oxygen due to higher microbial metabolic rates and lower oxygen solubility at higher temperatures. It is not unusual for eutrophic ponds to have hypolimnetic waters completely depleted of oxygen during the late summer/early fall. However, during the cold winter months, low metabolic rates and higher oxygen solubility in cold water typically result in higher dissolved oxygen concentrations and higher redox potentials in surface sediments. The increasing redox potential of the surface layer may have led to enhanced sorption and/or precipitation of arsenic.

Pond-Age Related Distribution of Arsenic

Regressions performed on various sets of arsenic data and age-related estimates failed to show any significant correlations. The accuracy and value of literature and anecdotal evidence for pond age are highly questionable. Because the peninsula has been a highly manipulated environment over the last number of decades, it is difficult to know the history of each pond and lagoon and thus properly interpret the arsenic concentration data as a function of *undisturbed* age. For instance, it is reported by park personnel and area citizens that certain of the lagoons were dredge in the mid-1900s. However, and while noting that it is not statistically significant, there does appear to be a general trend when sites are sorted by distance from Gull Point (the young tip of the peninsula), presented in Figure 9 and redrawn here.

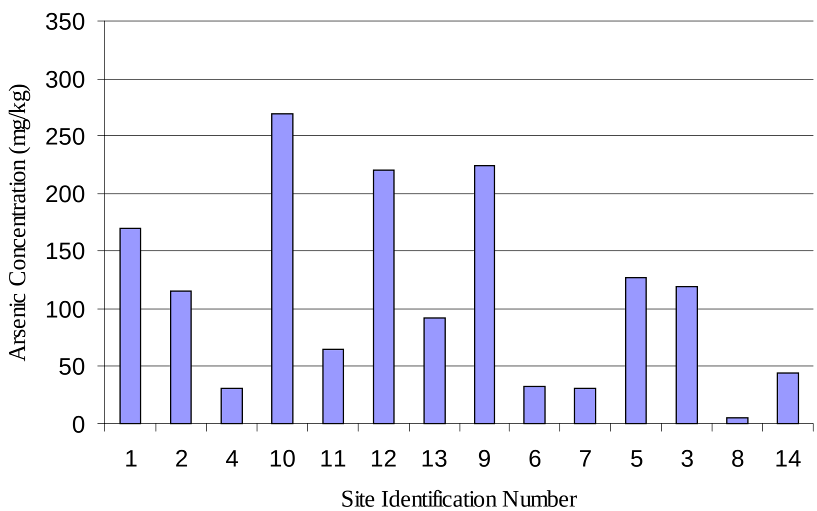


Figure 9 repeated. Sampling sites arranged according to age estimates, decreasing from left to right.

This pattern would suggest that older ponds do in fact have higher levels of arsenic in their sediments, and that some combination of processes may be responsible for an accumulation of arsenic over time.

Conclusions

The sediments of Presque Isle have high levels of arsenic and represent a likely threat to the aquatic ecosystem, based on widely accepted toxicity measures. These high levels most likely are due to a combination of natural processes which, over time, have resulted in a concentration of arsenic in surface sediments. That said, there is a possibility that human-related activities have contributed to a generally higher level of arsenic in the local environment, and that these secluded ponds and lagoons have acted as sinks and enrichment sites. This study has not attempted to document the risk to the ecosystem, but it is not unreasonable to speculate that elevated tumor incidence rates in Brown Bullhead bottom-dwelling fish and deformities in turtles and other reptiles often noted by area naturalists may be related to arsenic. This report also does not speculate about the need for remedial action, but suggests that further study be conducted to determine the appropriateness of such activities.

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