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COMMENTARY:
THE POCONO ENVIRONMENTAL EDUCATION CENTER – ENGAGING YOUNG SCIENTISTS, SUSTAINABILITY IN ACTION

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The Pocono Environmental Education Center (PEEC") is one of the largest residential environmental education centers in the US. It is an independent 501(c)(3) non-profit and the education partner of the National Park Service in the Delaware Water Gap National Recreation Area. For over 40 years, PEEC has focused on hands-on environmental science and sustainability education for 24,000 visitors per year from Pennsylvania, New Jersey and New York. PEEC sits in the midst of the Delaware Water Gap National Recreation Area and utilizes the natural and cultural resources of the Park's 77,000 acres as its outdoor classroom. PEEC's origins were to provide a hands-on residential outdoor environmental education experience for inner city students from Philadelphia, New York City and the urban centers of New Jersey, but in the ensuing years its role and its offerings have grown immensely.

PEEC's campus is the ultimate example of adaptive and innovative reuse. The Center has its origins as an old Poconos honeymoon resort that was seized under eminent domain, as part of the ill-fated Delaware River Tocks Island Dam Project. In 1972 PEEC's cabins and public buildings were repurposed as a residential environmental education center. Subsequent replacement and refurbishment of buildings has created a campus that combines the environmental best practices of the new and the creative reimagining of the old.

Figure 1. Visitor avtivity center/Dining hall

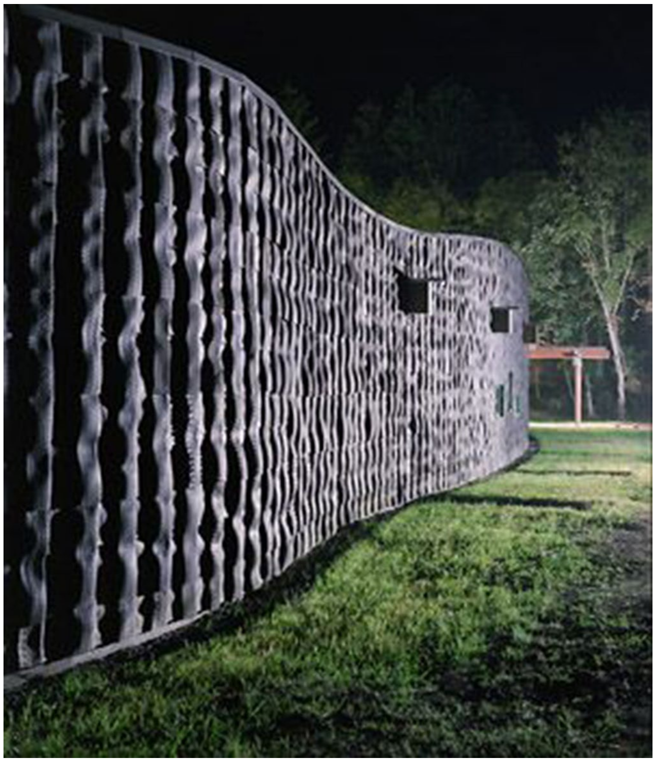

Figure 2. Reused tire wall

PEEC's award winning, passive solar dining hall (Fig. 1) was designed by renowned architect Peter Bohlin and features a wall of used tires (Fig. 2) pulled from the Delaware River, flanked by walls of glass, radiant floor heating and natural convection cooling.

In the main building, a no longer used indoor swimming pool was transformed into the EcoZone Exploration and Discovery Room (Fig. 3). It features a walk through beaver lodge and crawl though bat cave (Fig. 4) in the deep end of the pool; a life-sized climb-in bald eagle nest, and an authentic black bear skeleton (Fig. 5) magnetized for students to assemble--to name just a few exhibits.

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Figure 3. EcoZone Exploration and Discovery Room

The twin paradigms of the EcoZone are: i) to provide opportunities to explore places normally inaccessible to humans, and, ii) as a hands-on introduction to the resources to be explored in the National Park just outside. It is also a wet lab to promote further investigation as well as providing the most wondrous indoor teaching spaces for wildlife habitat studies. The EcoZone creates a sense of wonder, enhances the outdoor experience and provides a venue for deeper investigation.

Going forward, PEEC is continuing to innovate with architecture and adaptive reuse and incorporate these into the teaching process. PEEC has taken the position that campus

Figure 4. Inside the EcoZone bat cave

Figure 5. Magnetic buildable black bear skeleton

Figure 6. Old canoes used as raised vegetable beds, adjacent to a pollinator habitat

architecture is more than about providing classrooms and beds for 330 students. The design and function of the campus provides students with not only an appreciation for nature, but a fundamental understanding of the way their everyday decisions impact the environment and the sustainability of humans on the planet. Students also see concrete examples of what they, their parents, and their communities can strive to do to make a positive impact. PEEC's campus is part of all the lesson plans, from its vegetable garden in old canoes (Fig. 6), to its aquaponic / hydroponics system growing fish and vegetables, to its rain gardens integrated into its storm water management.

It demonstrates what is possible and what might be possible. PEEC and its buildings continue to be a laboratory for all the good that can be accomplished by human design – aimed at sustainability. Form not only follows function, but needs to engage, challenge and inspire.

PEEC is open year-round and offers environmental education, sustainability and recreational programs for every age student. Traditional pond and forest ecology classes, water and air quality programs, wildlife study, etc.., form the basis of PEEC's middle and high school residential programs. PEEC also has a summer research program for gifted science and math students (The Sci-Q Project), Delaware River based programs for urban young women (Women on the Water) and an organic gardening centered residential program for children and young adults with disabilities (Growing Green). PEEC has also added Art to the traditional STEM curriculum, turning STEM into STEAM. Specifically, for the past two years, with funding from the Geraldine R. Dodge Foundation, PEEC organized teacher training workshops focused on the math and science inherent in art and the natural world.

PEEC also organizes and implements specialized field research based programs for high school, college and graduate students. Last year PEEC collaborated with the University of Tennessee and Malcolm X. Shabazz High School in Newark to conduct an enzyme field research project. The research focused on understanding how bacteria acquire food by measuring protein-degrading enzymes. The enzymes measured had never previously been measured in freshwater. The enzymes are a key intermediate in the conversion of plant material into carbon dioxide (CO2) and therefore serve as a control on gauging the rate of global warming.

The keys to PEEC's many successful programs and research collaborations are its location within the Delaware Water Gap National Recreation Area and its amazing and varied partnerships. PEEC's wide variety of educational and research programs dovetail with the mission of the National Parks and PEEC has the staff and physical infrastructure to support this work. PEEC also has the ability to leverage the resources of the National Park Service, the Forest Service, as well as state wildlife and conservation organizations and local colleges and universities.

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MEGASPOROGENESIS AND MEGAGAMETOGENESIS OF CARDAMINE PARVIFLORA L. (BRASSICACEAE).

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ABSTRACT

***Cardamine parviflora*, "small-flowered bittercress", is a member of the Brassicaceae family. It is found throughout the eastern part of the United States and Canada. Flowering occurs from April through July. It has, as with all mustards, four separate sepals and four separate petals, six stamens, and one pistil with two united carpels. Each carpel has many ovules that start develop from the base of the ovary. Flowers were collected near Rocky Ridge County Park, York, PA and immediately fixed in FPA_{50}. At least 24 h later collections were serially dehydrated to 100% ETOH, and placed in Herr clearing fluid. A Nikon SMZ-U dissecting microscope was used for ovule removal and an attached DSFi1 Nikon digital camera was used to capture the images. Ovules, on the Raj slides, were viewed using a Nikon Eclipse 80i microscope with phase contrast to determine developmental stages and the attached Nikon digital cameras DS-Ri1 was used for image capture. Images of all stages of megasporogenesis and megagametogenesis were saved. A few morphological features determined from this study include are, ovules are campyloptropous, bitegmic and show Polygonum Type megagametophytic development. Developmental features reported here are compared with previous studies of *Arabidopsis thaliana* L. and *Draba verna* L. [J PA Acad Sci 87(3): 120-124, 2013]**

INTRODUCTION

"All plants can be regarded as accumulations of characters, and those which vary discontinuously in their expressions are the tools of classification. The practice of grouping like with like in a hierarchical system is systematics, but when an attempt is made for the system to express phylogeny as well as morphological agreement, the discipline is referred to as taxonomy" (Davis, 1966).

Davis also makes an excellent point about paucity of information taken from descriptive angiosperm embryology. Although this paper deals with female development, megasporogenesis and megagametogenesis, her point is further made that little attention has been given to male development in angiosperms. We agree and intend to continue our studies of *C. parviflora* L. and provide evidence for its microsprogenesis and microgametogenesis.

We also suggest that describing and giving names to morphological features represents a necessary beginning to these studies. Further, these studies should include, if possible, precise measurements of these descriptive features and further comparisons between and among those organisms being studied.

Cardamine parviflora L., a member of Brassicaceae, is a small plant known by its colloquial name of "Small-Flowered bittercress." *C. parviflora* is 1-3 dm tall and is usually found in upland soils. The wetland designation for *C. parviflora* is FACU[1]. The inflorescence is a raceme, the flower petals are white and the fruit is a silique (Rhoads and Block, 2007). There are four large stamens opposite each other, and two smaller stamens opposite each i.e., tetradynamous (Porter, 1967).

Using a clearing fluid to study sporogenesis and gametogenesis of both floral sexes was successfully accomplished by John Herr (Herr, 1971). Herr (1968) stressed the importance of noting and documenting any and all noticeable variation in megagametophyte development, and in particular variation in size of developmental stages that could be measured. In many cases, the study of ovules and female gametophyte development can be effectively accomplished with clearing techniques instead of the traditional paraffin embedding methods. The use of this clearing technique has greatly increased the ease and reliability of investigation of ovule and megagametophyte development as well as stamen and microgametophyte development.

Recent publications are not available that deal with ovule and megagametophyte development in *Cardamine*. To facilitate a comparison of findings reported here with those

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[1] U.S. Fish and Wildlife Service wetland codes. FACU or facultative upland species has a 1-33% probability of occurring in wetlands under natural conditions.

of close and distant related genera, the phylogenetic analysis reported by Couvreur et al. (2010) was consulted. The basis for this analysis was a mitochondrial marker, *nad4 intron1*. This marker was selected because of its slow evolving nature. The analysis shows that *Arabidopsis* and *Cardamine* are closely related, and this close affinity indicated *Arabidopsis* to be the best candidate for comparative purposes. A comparison of megasporogenesis and megagametogenesis in *C. parviflora* to the developmental features reported by Smith and Gilbert (1989) for *Draba verna* is appropriate, since the two genera are not closely related. Comparing development in *Cardamine* to that of a species more distantly related, viz., *Brassica campestris* L also seemed appropriate and is included in the current report (Smith and Lightner 1989).

The purpose of this study is threefold: (1) to assess the clearing technique on an untested genus within the Brassicaceae, (2) to report for the first time megasporogenesis and megagametogenesis of *C. parviflora*, and (3) to compare these developmental features with those reported for specific close and distant relative genera of *Cardamine*.

MATERIALS AND METHODS

The flowers were collected along Druck Valley road bordering Rocky Ridge County Park in Springettsbury Township, York, PA. Flowers in early to late stages of anthesis were placed in FPA_{50} (Formalin, Propionic Acid, and Ethyl Alcohol—50%) for at least 24 h and then transferred to 70% ethanol for storage. For the investigation, pistils dissected from the flowers in 70% ethanol were dehydrated in a series of 80%, 90%, 95%, and 100% ethanol for at least 10 minutes in each fluid. To assist in draining the previous concentration off, a watch glass over the opening of the container can be used. By leaving a small opening the liquid can flow out, and the buds will stay. From 100% ethanol the buds were transferred to Herr Fluid which consists of lactic acid, clove oil, phenol, chloral hydrae, and xylene in a 2:2:2:2:1 ratio by weight. After 24 hours in the Herr Fluid, the ovules were dissected from the ovaries and prepared for observation.

For observing the ovules, a modified Raj slide was made (Radford et al, p.231. 1974). With two cover glasses permanently attached about 5 mm apart with Canada balsam on the right side, the customized Raj slide is offset so that the flower buds can be dissected on the left side and transferred over the space between the two cover glasses which serve to support a cover glass placed over the 5 mm space. Usual protocol calls for size 0 cover glasses, but for this study it was seen that size 1 cover glasses were required to eliminate pressure on the ovules by the cover glass placed over the permanently attached support mounts. The thickness of the support mounts is determined by the size of the ovules being observed.

Ovules are dissected from the ovary in clearing fluid on the Raj slide. This is done using a specialized pick. Dissecting picks were made from wooden dissecting pins after their needles were replaced with minutien pins. A size 1, as opposed to the usual .20, minutien pin was used. To extract the ovules from the ovary, the pin is used to rip open the outer fleshy tissue. By prodding and scrapping the ovary with the pin more ovules can be removed. Once the dissection is complete, a cover slip of the same size is placed over the space between the support mounts. Time and patience are required to work with the Raj slide, and most problems can be overcome by trial and error.

The ovules were photographed using a Nikon Eclipse 80i phase contrast microscope equipped with a Nikon DS-Ri1 camera, and NIS Elements imaging software. Images were captured at magnifications indicated in the figure legend and by bars on the photographs.

OBSERVATIONS

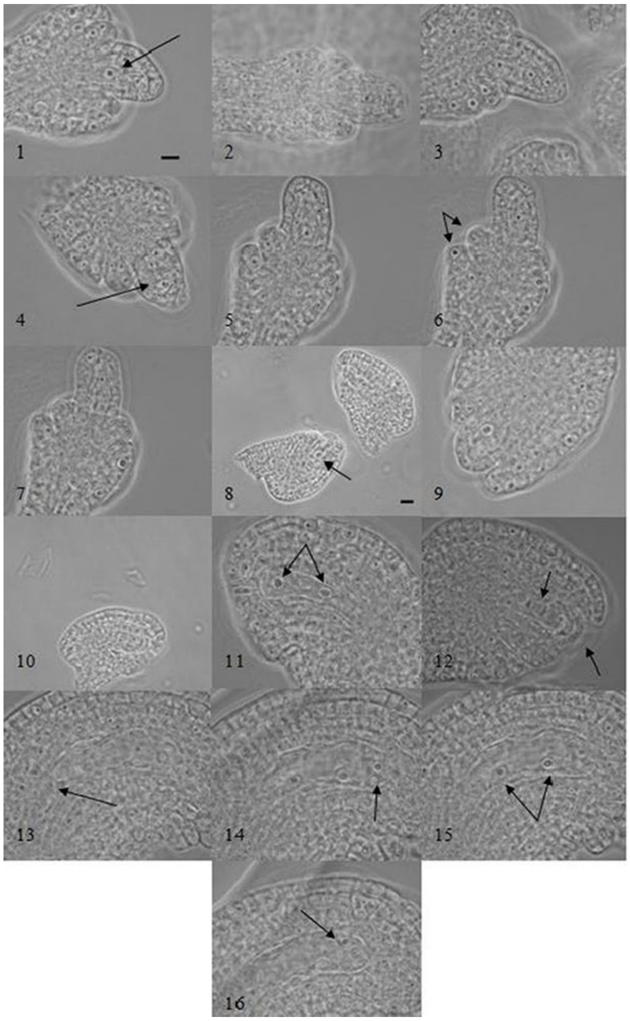
Ovule Development

As the *C. parviflora* ovary begins to grow, the first ovules can be seen emerging from the central placenta into each of the two carpels with the oldest ovule being at the base. When the ovary reaches its maximum growth the youngest ovule will be at the top. A particular stage of megasporogenesis or megagametogenesis near the base of the ovary would have a slightly younger stage near the top.

The nucellus is crassinucellate with two cells beneath the nucellar epidermis and the megasporocyte. The two integuments reach the level of the megasporocyte as the primary parietal cell completes an anticlinal division (Figs. 1, 2 the bar in 1 represents 10 microns for all figures except 8 and 10). The number of cells below the nucellar epidermis and the megasporocyte are never more than two and the one nearest the 4-nucleate megagametophyte represents a diminished remnant of the tetrad (Figs.11, 12).

Megasporogenesis

The out-of-focus shadow seen in some of the figures is a function of the clearing fluid's affect when the plane in focus has other cells in different planes slightly out-of-focus. The meiotic activity that characterizes the megasporogenesis development begins with the sporogenous cell swelling to sizes larger than the neighboring cells and having a nucleolus in its nucleus that is easy to detect.



All images were captured using oil immersion lens with phase microscopy. Magnification for all Figs. except 8 and 10 are 1,000X; Figs. 8 and 10 are 400X The bar in Fig. 1= 10 microns and applies to all Figs. except Figs. 8 and 10 and the bar in Fig. 8 = 20 microns for Fig. 8 and 10.

Fig. 1. Note the periclinally derived cells beneath the nucellar apex, parietal cells, and the enlarging MMC just below the single layer of parietal cells. Fig. 2. Another MMC, note the shadow affect resulting from the integuments surrounding the nucellus but out-of-focus. This is a result of the clearing fluid allowing light to penetrate throughout the width of the ovule. Fig. 3. This is a dyad forming just as the nucellus begins to arch back toward the placenta. Fig. 4. Dyad, note meiotic activity between two nuclei. Fig. 5. 6 and 7. Tetrad, three focal planes that capture the linear tetrad. Fig. 8. Functional chalazal spore. Fig. 9. Functional spore enlarged with other three spores nearly absorbed by the functional spore. Fig. 10. 2-nucleate stage megagametophyte with remnants of the other three spores not fully absorbed. Fig. 11. Further enlarged 2-nucleate stage. Note the complete coverage of nucellus by the integuments. Fig. 12 A 4-nucleage stage with a single nucleus at either end of the cell and the third and fourth nuclei still in meiosis II telophase. Figs. 13-16 same ovule. Fig. 13. Antipodals in focus at chalazal end of embryo-sac. Fig. 14.and. Fig. 15. Polar bodies in focus near center of embryo-sac and egg cell seen to the right of the polar bodies. Fig. 18. Synergids although seen in previous figs. are more clearly seen either side of the egg.

Megaspore Mother Cell (MMC)

The inner and outer integuments are discernible as the megasporocyte or MMC begins to enlarge (Fig. 1, 2). In the same figure the MMC and the cells toward the apex of the nucellus result from an archesporial cell having divided to form a primary parietal cell and a primary sporogenous cell. In this case the sporogenous cell becomes the MMC and anticlinal division of the primary parietal cell represents only one cell between the nucellar epidermis and the MMC. Technically this would be defined as a crassinucellate nucellus and a few stages later appear to be tenuinucellate.

Dyad

The dyad appears as though it is a MMC but cytokinesis has occurred and there are two cells and not one (Figs. 3, 4).

Tetrad

Inner and outer integuments become more noticeable as the dyad cells continue cytokinesis to form the tetrad with its four haploid cells thus ending megasporogenesis (Figs. 5, 6, 7 same ovule different focal planes).

Megagametogenesis

The chalazal cell of the tetrad becomes the functional megaspore with the other three spores being absorbed. The inner and outer integuments nearly reach the apex of the nucellus (Figs. 8, 9) The bar in Fig. 8 and Fig. 10 represents 10- microns.

2-Nucleate Stage

The outer integument away from the funiculus is beginning to overgrow the inner integument at the 2-nucleate stage. Also the campylotropous shape the ovule is to take begins to be noticeable (Fig. 10). Also the absorption of the non-functional spores of the tetrad as well as the single parietal cell is clearly observed (Fig. 11).

4-Nucleate Stage

The chalazal member of the 2-nucleate stage can be seen in mitotic telophase prior to division of the micropylar spore of the 2-nucleate stage. And, cells in the nucellar apex have yet to be fully absorbed by the developing 4-nucleate stage (Fig. 12).

Table 1. Comparison of early ovule development through megagametogenesis for *Cardamine parviflora*, *Arabidopsis thaliana*, *Draba verna*, and *Brassica campestris*.

Morphological Comparisons	***Cardamine parviflora*[1]**	***Arabidopsis thaliana*[2]**	***Draba verna*[3]**	***Brassica campestris*[4]**
Plant Size	1-3 dm[5]	1-4 dm	5-15 dm	3-9 dm
Inflorescence	Raceme	Raceme	Raceme	Raceme
Ovule Shape	Campylotropous	Campylotropous	Campylotropous	Campylotropous
Ovule Integuments	2	2	2	2
Archesporial Cells	1	1	1	1
Megasporocyte	Archesporial forms primary parietal and primary sporogenous cells	Archesporial[6] becomes megaspore mother cell	Archesporial forms primary parietal and primary sporogenous cells	Archesporial forms primary parietal and primary sporogenous cells
Megasporogenesis	Forms linear tetrad	Forms linear tetrad	Forms linear tetrad	Forms linear tetrad
Megagametogenesis	Polygonum Development	Polygonum Development	Polygonum Development	Polygonum Development

1 *C. parviflora* taken from this study.
2 *A. thaliana* descriptions taken from (Bowman 1994).
3 *D. verna* descriptions taken from (Smith, Gilbert 1989).
4 *B. campestris* descriptions taken from (Smith, Lightner, 1989).
5 Part of this study.
6 Taken from (Bowman 1994).

8-Nucleatge Stage

Figures 13-16 represent the same ovule at the eight nucleate stage. The antipodal nuclei (cells) (Fig. 13), the egg cell (Fig. 14), the polar cells (Fig. 15), and a synergid cell (Fig. 16) the nucleoli of both synergids can be seen flanking the egg cell (Fig. 14).

DISCUSSION

Megasporogenesis

Although megasporogenesis and megagametogenesis of *C. parviflora* has yet to be reported in the literature , development of the nucellus has been reported in a comparative study of five species of *Cardamine*. Line drawing illustrations of various stages of megasporogenesis and a few examples of megagametogenesis do not show all the stages for each of the five species. For example *C. pratensis*, *C. amara*, *C. hirsuta* and *C. sylvatica* developed various numbers from three-five archesporial cells that directly become the MMC and a few illustrations of dyads and tetrads developing from one of the multiple archesporial cells. One illustration of *C. impatiens* suggested a different pattern of development with a single archesporial cell becoming the MMC (Vandendries, 1912). Although not of any comparative value to this study, in *Cardamine chenopodifolia*, drawings and descriptions of microsporogenesis and microgametogenesis were discussed and illustrated (Gorczynski, 1935).

In this study of *C. parviflora*, the chalazal product of a hypodermal archesporial cell dividing results in the chalazal product of that division becoming the MMC. We did not see multiple archesporial cells and the single archesporial cell divided only once whereas the species mentioned above had multiple archesporial cells and they developed directly into the MMC. Therefore we describe the nucellus of *C. parviflora* as being crassinucellate but depending on the angle in which one views the apex of the nucellus, the nucellus may appear tenuinucellate. More precisely, as the ovule emerges from the placenta and the nucellus has but a few cells, the two integuments are discernible and found near the same level as the MMC. This is described as one of two types of tenuinucellate nucelli (Maheshwari, 1950, p. 59). Again, since at least one cell can be seen between the nucellar apex and the MMC we must call this a crassinucellate nucellus.

The meiotic cytokinesis of the single MMC results in a linear tetrad. This meiotic activity occurs before the two integuments grow beyond the level of the base of the tetrad. The Functional Spore of the tetrad is the beginning of the short life history of the angiosperm's haploid life history. It was the diploid ovule growing from the central placental of a 2-carpeled ovary, in this case, that provided the opportunity for this short-lived haploid life history that quickly becomes a new diploid in the form of a seed. The functional spore of this tetrad is the one nearest the chalazal end of the nucellus and once this is established the integuments are seen near the apex of the nucellus

Megagametogenesis

Since this is the first time the megagametophytic development of *C. parviflora* has been described and illustrated, there is nothing to compare to this study. However, starting with the beginning of what is classically known as the megagametophyte or haploid plant residing inside its diploid predecessor, all morphological features seen in this study will be summarized.

The functional spore absorbs the three sister spores and grows toward the apex of the nucellus. Before this functional spore begins mitosis, the outer integument away from the funiculus arches over the nucellar apex.

At the time of the 2-nucleate stage, the outer integument away from the funiculus has grown over the apex of the nucellus and the ovule is taking a campylotropous shape with the outer integument away from the funiculus is arching beyond the nucellar apex to nearly touch the other outer integument.

The ovule has nearly finished its arching process at the time of the 4-nucleate stage and very quickly becomes an 8-nucleate megagametophyte. This results in a Polygonum Type ovule development.

The two synergids as well as the egg and one polar body are seen at the micropylar end of the embryo-sac and the three antipodal cells and a second polar body are seen at the chalazal end.

As suggested earlier in this paper, a molecular phylogenetic study of Brassicaceae using the mitochondrial marker *nad4 intron1* concluded that, *Arabidopsis* and *Cardamine* to be the best candidates for comparative studies (Couvreur et. al. 2010). We suggested that other genera of Brassicaceae i.e., *Draba verna* and *Brassica campestris* should also be compared (Table 1). After a review of the four species of Brassicaceae seen in table 1, *Cardamine parviflora* and *Arabidopsis thaliana* are the smallest and nearly the same size while *Draba verna* and *Brassica campestris* are considerable larger plants. However, the only difference among the eight morphological categories for the four species compared was the megasporocyte. *A. thaliana* has its archesporial cell becoming the MMC directly while the other three species have archesporial forming a primary parietal and primary sporogenous cells with the latter becoming the MMC.

Future studies of this plant should be to continue studying embryogenesis as well as studies of the pollen development.

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THE INVASIVE NEW ZEALAND MUD SNAIL (POTAMOPYRGUS ANTIPODARUM) GROWS FASTER WHEN CONSUMING PERIPHYTON COMPARED TO DETRITUS

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ABSTRACT

Diet can play an important role in invasion success. The New Zealand mud snail (*Potamopyrgus antipodarum*) has invaded lakes and streams on four different continents. The snail has been established in the Laurentian Great Lakes since at least 1991 and has recently been discovered in stream habitats adjacent to the lakes. The purpose of this experiment was to examine the effect of a change in diet from a benthic diet of detritus to a diet dominated by periphyton on the growth rate of this snail. Juvenile snails were placed into one of four treatments: standard lab diet of *Spirulina*, benthic sediment (detritus), rocks with periphyton growth, or detritus and rocks with periphyton growth. The growth rate was determined after six weeks. The results demonstrated that diet greatly influences growth rate of *P. antipodarum* with a diet of periphyton resulting in the highest growth rate and a detritus diet resulting in the slowest rate. These results provide evidence that the movement of the snail into lotic waters where periphyton is in greater abundance in the Great Lakes region could result in faster individual and, possibly, population growth rates. [J PA Acad Sci 87(3): 125-128, 2013]

INTRODUCTION

Food quality can play an important role in the success of biological invaders (Tibbets et al. 2010) as it can influence individual growth rates, reproduction, and developmental rates (Dorgelo, et al. 2001), which in turn can influence invasion success. The New Zealand mud snail (NZMS), *Potamopyrgus antipodarum*, is an invasive species that has established populations in many locations worldwide including Europe, continental Asia, Japan, Australia, and the North America (Proctor et al. 2007; Alonso and Castro-Diez 2012). The populations in North America are divided into two groups based on the genetic structure and locations of introductions. One population that was first established in the late 1980's is located in the western United States and Canada (Proctor et al. 2007). The other population is found in the Laurentian Great Lakes where it was first discovered in Lake Ontario in 1991 (Zaranko et al. 1997) and has since expanded within Lake Ontario (Levri et al. 2008) and into Lakes Erie, Michigan, and Superior (Levri et al. 2007; Proctor et al. 2007). Invasive populations consist of asexual clones, at least three of which occur in North America (US1, US2 [=Ontario], and US3).

Population densities vary substantially between habitats and geographic areas. For example, in rivers and streams in the western United States densities vary from a few individuals per m^2 to hundreds of thousands per m^2 (Hall et al. 2006; Proctor et al. 2007), and the snail has been reported to have the highest secondary productivity ever reported for a stream invertebrate (Hall et al. 2006). In the Laurentian Great Lakes, densities have been found as high as 5600 individuals per m^2, but populations can be sparsely distributed and vary substantially in density (Levri et al. 2008). One of the primary concerns about the Great Lakes populations has been the possibility of the snail moving into lotic systems where greater densities and ecological impacts have been observed such as in the western US and Australia (Levri et al. 2008). One population of *P. antipodarum* was discovered in a New York stream in 2007 (Levri and Jacoby 2008), and another was discovered in another New York stream in 2011 (Levri et al. 2012).

P. antipodarum lives in a variety of habitats, which include freshwater, brackish water, shallow and deep waters, lotic areas, and on multiple substrates (Winterbourn, 1970). The snails primarily feed on detritus, algae, fungi and bacteria (Liess and Lange 2011). Benthic habitats are known to limit gastropod growth rates due to limited nutrient content (Stelzer and Lamberti 2002). The experiment reported here tests the hypothesis that a diet increasingly rich in periphyton will lead to an increase in individual growth rates of *P. antipodarum*. This experiment compared the growth rates of *P. antipodarum* Ontario clones taken from a stream emptying into Lake Ontario exposed to four different diets: a control using *Spirulina* powder (standard lab diet), detritus in benthic sediment, periphyton grown

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on rocks, and a mixed detritus and periphyton treatment. This experiment is relevant to the invasion potential of the snail in two ways. First, deep-water lake habitats (where the snail primarily exists in Lake Ontario) offer detritus to the snails as their primary food source, and periphyton content increases in stream habits. Thus if growth rates are higher in periphyton treatments, it could indicate a greater invasion potential in stream environments. Second, within streams there is variation in periphyton abundance due to the amount of sunlight that reaches the stream bottom. Anthropogenic disturbance could decrease riparian habitat and thus increase direct sunlight on the stream resulting in increased photosynthesis. Higher growth rate in periphyton treatments may also indicate a facilitative role of anthropogenic disturbance on the spread of *P. antipodarum*.

METHODS

We isolated Ontario clone snails from a New York stream near Lake Ontario (Levri and Jacoby 2008), and maintained the in the laboratory in 0.5 l plastic containers filled with water from a local stream. Instant Ocean was added to the water to achieve 3 ppt salinity. We fed the snails *Spirulina* powder ad libitum three days per week and acclimated them to the laboratory conditions for two weeks prior to the start of the experiment. We selected a total of 120 juvenile snails from the containers and isolated them in separate 200 ml plastic cups. These juveniles came from snails collected in the field, but the juveniles themselves were entirely lab reared. We used four different dietary treatments; *Spirulina* powder, detritus from sediment only, periphyton on rock only, and detritus from sediment plus periphyton on rock. We selected thirty snails for each of the four treatments ranging in size of 1.0-1.6 mm shell length. Prior to the experiment an analysis of variance was run on the initial lengths of the snails to ensure that a particular treatment did not have initially larger snails than others. We placed thirty juveniles individually in the plastic cups in each of the four treatments so that one snail was in each cup. We placed the cups in a cabinet without light exposure. This was to ensure that the sediment only treatment did not develop algal growth from natural or artificial light. We changed food and water every two weeks after the snails were measured.

The periphyton was grown on rocks that were placed in a plastic bin filled with stream water and located on a windowsill for two weeks. We estimated the surface area of the rocks measuring their diameter and by assuming that the rocks were spherical and calculating the surface area of a sphere ($SA=4\pi r^2$) for each rock measured. In an effort to keep the feeding surface areas of the rocks relatively constant, we used only the rocks with diameters ranging from 4.302 to 4.399 cm which resulted in estimated surface areas between 58.1 to 60.8 cm^2. For the sediment only treatment, we placed 11.6 g of sediment containing detritus in the bottom of the plastic cup. The sediment was taken from at least 5 cm below the surface of Spring Run stream on the Penn State Altoona campus and consisted of sand, silt, and organic debris. For the treatment with sediment plus rock, we cut the amount of sediment in half (5.8 g) and used rock sizes ranging from 28.5 to 30.2 cm^2. Thus, the amount of sediment and periphyton was reduced by half in the combined treatment. In all treatments, given the size of the snails, we provided more food than the snails could consume during the time of the experiment. We changed the sediment and rocks every two weeks during the experiment.

Over the six-week period, we measured the length of each of the 30 juvenile snails from the four different dietary treatments every two weeks. We determined the overall growth rate by taking the difference between the final size of the snails and the initial size of the snails and dividing that by the number of days in the experiment to get a per day growth rate. We utilized a one-way ANOVA using SPSS (IBM SPSS Statistics, v. 20) to compare the growth rates of the juvenile snails in the four different diet treatments and then performed pairwise comparisons using the same procedure to compare each treatment to each other. A Bonferroni correction was used to adjust the significance value for the number of tests. Thus with the five tests performed the critical P-value accepted as significant was 0.01.

RESULTS

The results showed significant differences in growth rates between snails in the four different diet treatments ($F = 54.7$, $df = 3$, $P < 0.001$; Figure 1) with average growth rates ranging between 0.025 mm/day (detritus treatment) to 0.048 mm/day (periphyton only treatment). A pair-wise comparison between each of the different treatments demonstrated that growth rates in each treatment were statistically significantly

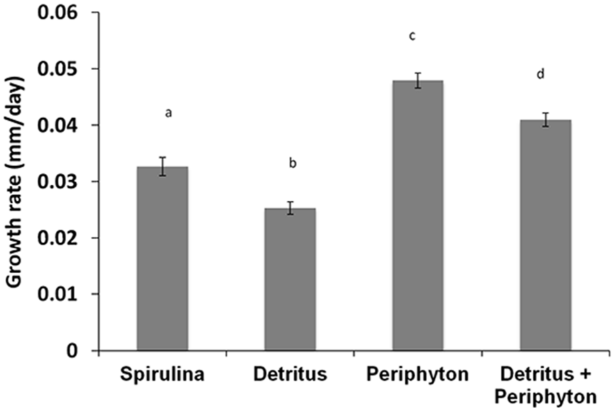

Figure 1. Growth rates of snails in the different diet treatments. Different letters above the bars indicate statistical significance. Error bars are standard errors.

different from each other (Table 1). The two treatments with periphyton included resulted in the highest growth rates.

DISCUSSION

Food quality can be determined by assessing growth rate of individuals (Dorgelo, et al 2001) and can affect population dynamics of an invasive species (Tibbets et al. 2010). In the invaded regions of the Laurentian Great Lakes, *P. antipodarum* is mostly found in silt-sand mixtures in relatively deep water below the photic zone of the lakes (Zaranko et al. 1997; Levri et al. 2008). Therefore, the mud snail's diet in these regions largely consists of detritus. The diet of the mud snail in invaded streams includes algal growth on rocks and other debris along with detritus.

The four different diet treatments resulted in significantly different effects on the growth rates of the snails. The periphyton-only treatment showed the highest growth rate of the snails with the periphyton plus detritus treatment also resulting in a higher growth rate than the control (*Spirulina*) or the detritus only treatments (Figure 1; Table 1). Thus, this study suggests that an increasingly periphyton-based diet similar to a stream will likely increase the individual growth rate in New Zealand mud snails compared to a detritus-based diet.

In addition, the periphyton-only treatment resulted in a greater growth rate than the periphyton plus detritus treatment. In this experiment, the amount of periphyton in both the periphyton-only treatment and the detritus plus periphyton treatment should not have been limiting for the snails. The slower growth rate of the snails in the detritus plus periphyton treatment was likely due to the smaller surface area of periphyton resulting in more time spent off of the rock with the periphyton. The increase in growth rate in the periphyton-only treatment may indicate that more time spent consuming periphyton results in higher growth rates than when consuming lesser amounts. This may demonstrate that an increase in periphyton growth in streams, such as that that may be found due to anthropogenic disturbance due to nutrient addition or a reduction in shading, will result in higher snail growth rates and possibly population growth rates.

Other studies have demonstrated that food quality influences New Zealand mud snail growth rates. New Zealand mud snails fed low quality algae had slower growth rates, matured later, and reproduced smaller brood masses compared to mud snails fed high quality algae (Tibbets et al. 2010). Thus, high algal quality or an increase in algal content in the diet could lead to high invasive potentials for the mud snails due to increased growth rate, high metabolism, increased reproduction, and early maturation.

The snails used in this experiment were derived from parents collected from a stream environment, thus the possibility exists that the snails were already adapted to a stream diet. However, the invasive populations of this snail are clonal, and this is the same clone as found in deep waters of Lake Ontario (where the stream populations likely derived from [Levri and Jacoby 2008]). It is not known how long the population has been in the stream because it was first discovered in 2007 (Levri and Jacoby 2008). Clonal species tend to evolve more slowly due to a lack of recombination. This population has also been through several bottlenecks in the past 120 years likely resulting in a significant loss of genetic diversity. The clone found in this stream was introduced to Europe in a founder event in the late 1800's, another founder event occurred in Lake Ontario within the last thirty years (Zaranko et al. 1997), and a third event occurred in establishing the population in this stream. Thus there is likely very little additive genetic variation in this population for any mechanisms of evolution to cause divergence, and the population in Lake Ontario and the stream are not likely to be very different genetically.

This experiment only measured individual growth rates, thus population growth rates under the different dietary conditions were not assessed. However, in most cases, higher individual growth rates lead to greater population growth rates because faster growth usually results in an earlier age at reproductive maturity. In addition, the sediment used in this experiment was of stream origin rather than lake origin, so it is very likely that the detrital composition differs from what is found at the bottom of a large lake. The sediment for this experiment was collected from sediment several centimeters deep in the stream, thus it was not likely to contain much if any recently grown plant or algal material. But it is possible that lake sediment could result in higher growth rates than stream sediment.

We originally expected that the sediment plus periphyton treatment would increase the growth rate of the snails more rapidly over a six-week period than any other treatment due to a more variable diet that includes primary production.

Table 1. Comparison of growth rates between the four diet treatments using pair-wise one-way ANOVA.

	Control (*Spirulina*)	Detritus	Periphyton
Detritus	F = 13.788	-	-
	df = 1	-	-
	P < 0.0005	-	-
Periphyton	F = 52.639	F = 173.039	-
	df = 1	df = 1	-
	P < 0.0005	P < 0.0005	-
Detritus + Periphyton	F = 17.050	F = 15.653	F = 92.911
	df = 1	df = 1	df = 1
	P < 0.0005	P < 0.0005	P < 0.0005

This outcome was not found in this experiment. It is possible that something in the detritus actually inhibits growth or periphyton is simply a much better quality of food source.

These results suggest that increasing periphyton content in the diet may increase the individual growth rates of New Zealand mud snails. If the detritus in our experiment is similar in quality to lake detritus, then our results may help to explain in part why population densities in the invaded ranges of North America tend to be higher in lotic systems compared to lentic, and it also suggests that anthropogenic disturbance may facilitate the invasion of this species. Taken together is seems probable that individual and population growth rates of the snail may increase as the population moves from the Laurentian Great Lakes into human-altered streams in the region.

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A SURVEY OF THE HEAVY METALS PRESENT IN THE SOIL OF A POTENTIAL URBAN GARDEN: A SERVICE LEARNING APPROACH

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ABSTRACT:

Eight soil samples were collected from a small urban land plot located at 1700 North Sixth Street Harrisburg, PA 17102 and the concentration of copper, nickel, zinc, and lead in existing soil was determined. The concentrations of these metals were compared to EPA standards to assess soil suitability for the development of a successful urban garden. Samples were prepared by acid digestion and then analyzed using atomic absorption spectroscopy (AAS). The concentration of copper was found to be 11 ± 4 mg/kg at the low end and 46 ± 25 mg/kg at the high end, nickel concentrations ranged from 11 ± 4 mg/kg to 20 ± 3 mg/kg, lead concentrations from 26 ± 1 mg/kg to 402+ mg/kg, and the zinc concentrations ranged from 30 ± 6 mg/kg to 216 ± 166 mg/kg. All concentrations, with the exception lead, were below the EPA recommended limits for heavy metals in home and vegetable gardens. This study also discusses the benefits of service learning for developing relationships between academic institutions and community partners as well as the role of Community Supported Agriculture (CSA) in urban areas. [J PA Acad Sci 87(3): 129-133, 2013]

INTRODUCTION

Various contaminants are found in soils and our study specifically focuses on heavy metals including lead, cadmium, zinc, copper, nickel, and mercury. These metals occur both naturally and as a result of human activities. Naturally occurring levels vary but are typically low and minimally absorbed by living systems, while concentrations generated from human activity tend to be higher and can be absorbed by plant matter at significant levels. For this reason it is important to know the concentrations of metals present both naturally and from anthropogenic sources in any area intended for the production of food for human consumption (Folstad et al. 2011).

Interest (and some concern) about metal contamination, particularly in urban settings, has grown in recent years and numerous studies have been performed in an effort to determine the extent to which these metals are harming the environment (USDA 2000; Brady and Weil, 1999; EPA 1993). Metal contaminants can be deposited into the soil which then can lead to contamination of groundwater and other natural waterways (Wilke et al. 1998) and plants grown for consumption can also absorb heavy metals from the soil, which can lead to contamination in food supplies (Fytianos et al. 2001). Consequently, it is important to be aware of these heavy metals in soil, particularly in an area slated for use in growing food for human consumption (Esbenshade and Schaeffer 2011). While these contaminants can be an issue in a variety of settings, they are of particular concern in urban gardens because higher levels of metal contamination are often found in urban areas due to the burning of fuels, presence of lead-based paints, and other industrial activities in the area. For example, increased concentrations of these metals often originate from smelters, high metal content sewage sludges, paint debris, and mining wastes, leading to phytotoxicity (Chaney et al.1984).

Currently over half of the world's population lives in urban areas (Guitart et al. 2012) and as urbanization continues to increase, fewer people produce their own food. This trend has increased the dependency on and consumption of imported foods and has led to rising concerns over the availability of a reliably consistent supply of fresh foods, a risk that disproportionately affects the urban poor. One response to these concerns on the local level has been an increase in the number of urban community gardens (Guitart et al. 2012). Community Supported Agriculture (CSA) is a way for consumers to support the local economy by buying local seasonal food from community gardens (Uribe et al. 2012). Not only are these gardens beneficial as sources for food, but they also promote community building and education (Guitart et al. 2012).

In order to provide education and leadership in the development of safe and healthy CSA projects, and as part of a college-wide initiative for service learning, we developed a laboratory curriculum in upper-division environmental chemistry that facilitates student and faculty engagement with local community partners. Our research here is centered on the analysis of soil at a potential site for an urban garden,

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which has the added benefit of being located across from an urban elementary school. As such, this particular project is informative to the scientific community and also beneficial for public education and local businesspeople committed to urban development. This kind of academic-community partnership is ideal for meaningful applied research as well as community service, engagement, and development.

In this study, we employ flame atomic absorption spectroscopy (AAS) to determine the concentration of four metals, copper, nickel, lead, and zinc, present in soil samples (Skoog et al. 1998). These metals are of particular importance in urban gardens because they can impact plant growth as well as be absorbed into the edible portion of the plant, resulting in an increased level of heavy metal ingestion in animals and humans (Fytianos et al. 2001; Hao et al. 2009).

Because of the potential health impact of ingesting heavy metals, it is recommended to sample the desired area before installing an urban garden. To adequately characterize a potential site for an urban garden, it is recommended that sampling be performed throughout the entire site enabling an accurate and comprehensive analysis of the area (Crozier et al.). Prior to analysis, digestion of the samples is necessary to release the metals from the solid soil matrix. Most frequently, acid digestion is implemented using various acids, most notably nitric acid. As the organic molecules dissolve in the solution, the metal atoms within the material are ionized and enter solution (Balcerzak 2002; Theory). After the digestion is completed, the concentration of the metal ions can be analyzed using AAS. Once the analysis is completed, the concentration of copper, lead, zinc, and nickel can be compared to EPA recommended concentration limits for a home garden (Electronic 1995).

MATERIALS AND METHODS

Sample Collection

Soil samples were collected from a small land plot located at 1700 North Sixth Street Harrisburg, PA 17102. Eight samples were collected using a soil probe with a diameter of ¾ inch, enabling extraction of approximately 8-12 inches of a vertical column of soil. A sample was taken at each of the four corners of the plot, along with four more samples taken from varying distances from the street to ensure a good representative collection of the entire site (Table 2, Figure 1). The latter were taken to determine what impact the proximity to the street has on the concentrations of metals in the soil.

Sample Preparation

Soil samples were air dried for 4-5 days prior to any analysis. Samples were ground to a fine powder using a mortar and pestle and filtered with a size 40 mesh to remove the larger, unwanted debris (Esbenshade and Schaeffer 2011). This ensured that the size of the soil particles was 420 μm or smaller. Samples were then air dried for an additional week for more thorough drying after filtration through size 40 mesh. Three replicate samples of approximately 1.0 gram were digested following EPA method 3050b. This involved the use of concentrated HNO3 and HCl, along with 30% H2O2 (EPA 1996). Samples were then gravity filtered using a Whatman 41 filter paper into a 100-ml volumetric flask where they were diluted with deionized water.

Analysis

Solutions were analyzed for copper, lead, nickel, and zinc using AAS. The instrument used was a Varian AA 240FS Atomic Absorption Spectrometer. This instrument used an air/acetylene flame in the absorbance mode; the wavelengths used for copper, lead, nickel, and zinc were 324.8 nm, 217.0 nm, 232.1 nm, and 213.9 nm respectively. Calibration curves, with standards ranging from 0.10 ppm to 5.0 ppm for each of the metals, were used to calculate the concentrations. From these concentrations, the concentration of metal in the original soil sample was calculated in mg metal/ kg soil material using the equation below. Following concentration determination, statistical tests were used to compare the concentrations among the various samples.

$$Conc_{soil} = \frac{(conc_{sample})(0.100L)\left(\frac{1000g}{kg}\right)}{mass_{sample}}$$

RESULTS

Figure 1 shows the location of the 8 samples taken within the boundaries of the potential garden. All metal concentrations, with the exception of lead, shown in Table 1, were below the EPA maximum levels for a home garden. The highest concentration of copper was found in Sample 5 at 46 ± 25 mg/kg; this sample was only 5 meters from the road and was outside the area of the plot intended for agricultural use. Within the garden, Sample 2 had the highest copper concentration at 44 ± 2 mg/kg. The EPA's recommended limit for copper concentration for home vegetable gardens is set at 1,500 mg/kg, well above any of our values (Electronic

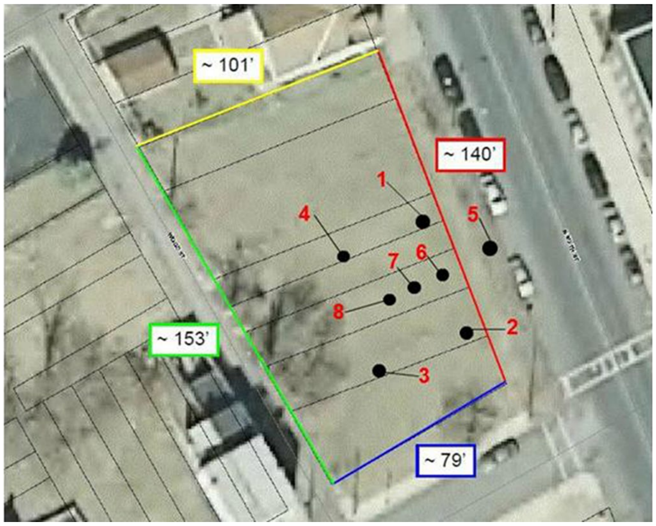

Figure 1. An aerial photo of the garden site of interest located at 1700 North Sixth Street Harrisburg, PA 17102. The site of each soil sample is depicted by the number corresponding to the values provided in Table 2.

1995).

Sample 5, as expected due to its proximity to the road, had very high levels of lead. One replicate had a concentration of 402 mg/kg while the two other replicates exceeded the calibration curve indicating that the lead concentrations were above 500 mg/kg. This was the only heavy metal tested that exceeded the EPA limits. It surpassed the limits in sites 2 and 3 within the garden, and site 5, outside the garden.

The EPA recommended limit for nickel in home gardens is 420 mg/kg. Nickel concentrations were all very low, the highest being only 20 ± 3 mg/kg in Sample 7. Zinc trends were similar to those of lead. Sample 5 was again the highest and Sample 3 was also significantly higher than the other locations with 216 ± 166 mg/kg. Samples 6 to 8 were not significantly different at the 95% confidence level.

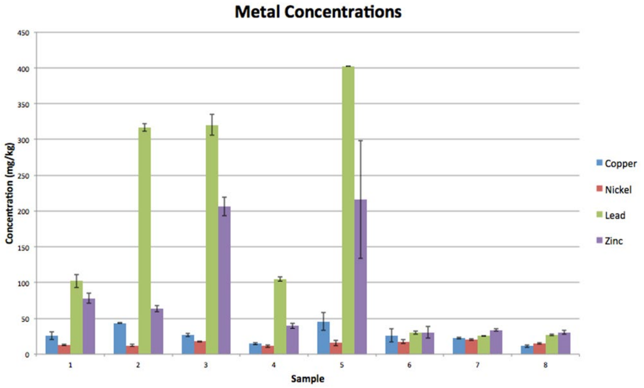

Figure 2. A bar graph comparing the concentration of each metal from each site of the garden.

DISCUSSION

There was a correlation between the distance from the road and concentrations of copper as Sample 5 had the highest concentration and Samples 6, 7, and 8 had lower concentrations respectively, the farther away from the street they were. A t-test was used to confirm that the concentration values between Samples 6 and 8 (sample 5 was excluded because it is not within the garden) are statistically different at the 95% confidence level indicating the differences in these values were caused by more than random error, possibly from decreasing proximity to the street.

Concerning Sample 5, the cause of high lead concentrations is most likely close proximity to the road and exposure to

Table 1. The concentrations in mg/kg of copper, nickel, lead, and zinc for each soil sample with a 95% confidence interval (N=3).

Sample	Cu Conc. (mg/kg)	Ni Conc. (mg/kg)	Pb Conc. (mg/kg)	Zn Conc. (mg/kg)
1	26 ± 11	13 ± 2	102 ± 17	78 ± 14
2	44 ± 2	12 ± 3	317 ± 8	64 ± 10
3	27 ± 5	18 ± 1	321 ± 23	207 ± 22
4	15 ± 3	11 ± 4	105 ± 6	40. ± 7
5	46 ± 25	16 ± 8	402+*	216 ± 166
6	26 ± 18	18 ± 6	30. ± 5	31 ± 16
7	22 ± 2	20 ± 3	26 ± 1	34 ± 3
8	11 ± 4.0	15 ± 2	27 ± 3	30 ± 6

*The concentration in sample 5 exceeded the calibration curve for 2 of the 3 replicates indicating a concentration higher than 500 mg/kg.

Table 2. The distance in meters of each soil sample relative to the street

Sample	Approximate Distance From Street (m)
1	10
2	10
3	23
4	23
5	5
6	10
7	15
8	20

contamination from leaded gasoline (Nichols 1997). The highest values within the garden for lead were Samples 2 and 3 with concentrations around the low 300s mg/kg, exceeding the EPA limit. For nickel concentrations, the data did not vary much across all of the sample locations and we saw no correlation between the distance from the road and nickel concentration. A t-test confirmed that the values between Samples 6 and 8 were not significantly different.

It is interesting to note that Sample 3 showed high concentrations for both lead and zinc and yet it is not as close to the road as Sample 2 is, thereby diverging from the typical trend of higher metals levels being measured with increased proximity to the road. Further information about the history of this lot could provide insight as to why this particular area showed an increase in metal concentration. All sites were below the EPA limit for zinc concentration in a home garden, which is set at 2,800 mg/kg.

It was determined that the concentrations of copper, nickel, and zinc, should not impede the development of a garden in the city of Harrisburg at this particular area. The highest levels obtained within the garden plot were 44 ± 2, 207 ± 22, and 20 ± 3 mg/kg for copper, zinc, and nickel respectively. All of these were below the EPA recommended limits for heavy metals in home and vegetable gardens. The high lead levels, however, may inhibit successful development of a garden at this site unless restorative efforts, such as the introduction of fresh soil, are undertaken. Major sources of lead include gasoline emissions, paint from older buildings, plumbing pipes, and other industrial processes. It is an accumulating and persistent contaminant, with serious health risks. Of particular concern is the exposure of young children and pregnant women to lead as it may result in behavioral and learning disabilities (Crozier et al.)

Most of the relative standard deviation values were within an acceptable range (~12% RSD) for this type of environmental analysis with the exception of a few, including the Sample 6 copper which had an RSD of 28.3% and sample five zinc with an RSD of 30.0% . The low overall RSD values indicate that our values within each sample are not highly variable and the trends observed based on sample location indicate that our results are likely to be representative of the metal concentrations throughout the plot. These results support the conclusion that the concentrations of copper, nickel, and zinc, in the soil should not impede the development of the plot as a community or urban garden in the city of Harrisburg. A more extensive sampling of the site could reveal a more comprehensive map of where the lead concentrations are highest.

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DISTRIBUTION OF ARSENIC IN PRESQUE ISLE STATE PARK POND SEDIMENTS

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ABSTRACT

A study of arsenic in pond sediments on the Presque Isle peninsula, Erie, PA, was conducted in 2000 and 2001 by Murnoch (2002) due to concerns expressed by citizens and various local officials. Samples of pond and lagoon sediments were collected at thirteen primary sites and additional reference sites for analysis of arsenic content during the fall, 2000, and again in spring, 2001. The probable effect concentration (PEC) for arsenic of 33.0 mg/kg-DW, an indication of the concentration above which adverse impacts on benthic organisms are expected to occur, was exceeded in the surface sediments at all 13 primary sites during fall sampling and in all but one site during spring sampling, with concentrations as high as 393 mg/kg-DW measured. For deeper sediments, the PEC was exceeded in the fall at nine sites and in the spring at six sites. Surface sediments contained more arsenic than did deeper sediments. These differences were more pronounced in the spring samples than in the fall samples. There was a general trend, with numerous exceptions, for sites closer to Gull Point (the geologically 'new' end of the peninsula) to have lower arsenic levels. While the source of the arsenic in the sediments of Presque Isle is unknown, these high levels are likely due to natural processes that, over time, have resulted in an enrichment of arsenic in surface sediments. A possible mechanism for this enrichment is proposed. This study has not attempted to document the risk to the ecosystem associated with elevated arsenic concentrations, but it is reasonable to speculate that there could be an adverse impact on some organisms. [J PA Acad Sci 87(3): 134-144, 2013]

INTRODUCTION

A study of arsenic in the sediments of ponds and lagoons of Presque Isle State Park was conducted by Murnoch (2002) to better understand the distribution of arsenic in the park. It has been known for some years that the arsenic level in groundwater within the park was higher than acceptable for drinking water purposes (Moore, 1994). This paper evaluates the data collected during that monitoring project and proposes a possible mechanism for the enrichment of arsenic in those sediments.

The Presque Isle peninsula constitutes most of the Presque Isle State Park which is near Erie, PA, located in the northwestern corner of the state and bordered to the northwest by Lake Erie (Figure 1). The lake's shoreline is characterized by tall bluffs up to 170 ft high. The bedrock in this area is Devonian shale overlain by Pleistocene and Holocene sediments deposited during glaciations and migration of the lake's shoreline. Four major glaciations dominated northwestern PA depositing the predominantly late Wisconsin glacial tills and lacustrine sediments that now overlie the bedrock (Shultz, 1999).

Figure 1. Northwestern shoreline of Pennsylvania on Lake Erie showing the City of Erie, PA, and the Presque Isle peninsula; reference sites for arsenic concentrations in shale bedrock are indicated (Google Earth 2013).

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Kormandy (1969) described Presque Isle as a "compound recurved sandspit peninsula". The peninsula (Figure 1) has a narrow neck at its southwestern end where it joins the lakeshore. The width of the peninsula increases to as much as two kilometers at its widest point and is about 10.1 km long from its southwestern attachment to its northeastern tip, known as Gull Point. (DCNR, 1991; Kormondy, 1969; Shultz, 1999).

It is believed that Presque Isle's existence is due to the deposition of glacial till deposited about 13,000 to 14,000 years ago by glaciers of the Pleistocene period (Shultz, 1999). Presque Isle's topical nourishment is largely sand derived from the erosion of bluffs along the lakeshore west of the peninsula, and transported northeastward by long-shore currents and wind. Sediment deposition continues to occur, helping to form and maintain Presque Isle (Shultz, 1999). Additionally, there is an annual program of beach nourishment performed by the US Army Corps of Engineers (DCNR, 1991; DCNR, 1999).

As sand and silt are moved northeasterly by lake currents and wind, the peninsula tends to grow in an easterly direction. As wave action causes the sand to deposit on the lee side of the tip, ponds and lagoons begin to form. Ponds also form if sandbars along the beach become isolated from the lake itself. These ponds, regardless of the formative mechanism, tend to be shallow, generally not exceeding about a meter in depth. (Kormondy, 1969).

Over time in a classic example of ecological succession, both surface area and depth of the ponds tend to become smaller and shallower as sediment and organic material accumulates. Kormandy (1969) estimated that small ponds may have a lifetime of only a few years, while larger ponds may experience an overall reduction in size of up to 95% in 75 years.

Over the years, a number of activities have modified the otherwise natural landscape of Presque Isle. Among other things, two settling ponds were created for use by the Erie Waterworks Authority. These two square ponds, used only briefly in the early 1900s, are discussed below. Additionally, a dredging activity in the 1950s created a marina (Marina Lake) and deepened and connected several lagoons (Walker, 2000).

Arsenic Geochemistry

Arsenic is present in most crustal material as well as in biological tissues. Arsenic is found in over 200 minerals. Arsenic can exist in aquatic environments and sediments as organo-arsenic compounds, and as inorganic arsenite, arsenate, sulfides, arsenides, and oxides. Arsenic is a trace contaminant of minerals such as pyrite, galena, chalcopyrite and less commonly, sphalerite. Arsenopyrite is the most abundant arsenic mineral (Thornton and Farago, 1997; O'Neill, 1990).

Arsenic is found in many major rock types (Kabata-Pendias and Pendias, 1984; O'Neill, 1990; Thornton and Farago, 1997). Igneous rock typically has arsenic concentrations ranging from <1-15 mg/kg-DW, while sedimentary rocks, often have concentrations from <1-900 mg/kg-DW.

In aerobic environments, arsenic can be retained due to precipitation of ferric arsenate or via sorption onto iron oxides, resulting in concentrations as high as several hundred mg/kg (O'Neill, 1990; Thornton and Farago, 1997). On the other hand, under reducing conditions and low pH, arsenic (III) tends to dominate as predicted in the stability diagram presented in Figure 2. While the speciation presented in the figure represents equilibrium conditions, kinetics often control the mix of species present since the conversion of arsenic (V) to arsenic (III) is relatively slow (O'Neill, 1990; Thornton and Farago, 1997). Microbial activity may also mediate changes in arsenicals. Typical products of aerobic methylation include monomethylarsonic acid, dimethylarsinic acid and trimethylarsenic oxide. Anaerobic microbial activity may lead to the formation of methylarsine gas (MacIntyre, 1994).

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

Arsenic Sediment Toxicity

Sediment quality guidelines represent effects-based tools for evaluating the potential effects of arsenic in sediments. 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), for marine and estuarine environments, 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 EPA refers to a consensus-based Probable Effect Concentration (PEC) (MacDonald et al., 2000; Ingersoll et al., 2000) derived from broad survey of literature values based on field and laboratory testing. The PEC is a level above which harmful effects are likely to be observed. The PEC for arsenic is 33.0 mg/kg.

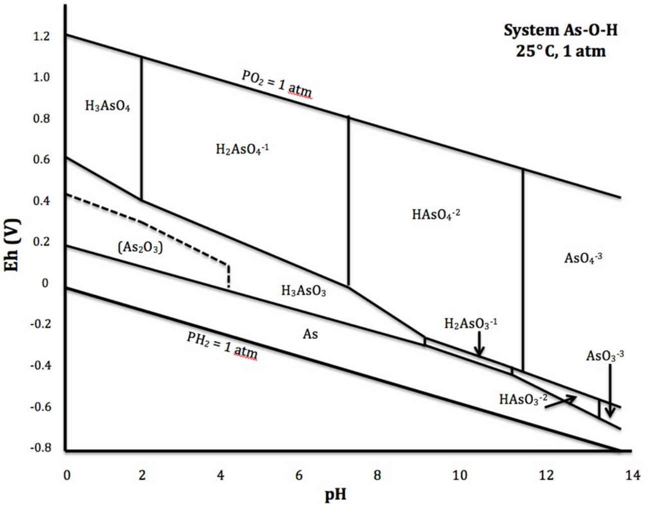

Figure 2. Arsenic stability diagram for 25 ^{O}C, 1 atmosphere (after Ringwood, 1996).

Figure 3. Presque Isle State Park with sampling locations; North is up (Google Earth, 2013).

MATERIALS AND METHODS

Sampling Locations

Sediment samples were collected by Murnoch in Presque Isle ponds, lagoons, and selected reference sites in the fall of 2000 and the spring of 2001 (Figure 3). Fall sampling occurred from October 11 to the 25th, , and spring sampling from April 5 to the 12th. For reference arsenic values, samples of new sand were collected from two sites around Gull Point, and shale bedrock was collected from nearby bluffs and streambeds. The bedrock sites are shown in Figure 1 and are abbreviated as: Cascade Creek Shale (CCS), Mill Creek Shale (MCS) and Walnut Creek Shale (WCS). For all sites, a handheld GPS unit was used to record the location of sediment sampling. Table 1 lists these sampling sites with their corresponding coordinates.

Sample Collection

Sample collection techniques employed by Murnoch varied depending on water depth and are summarized here.

Wadeable Ponds: A 10 cm diameter by 1 meter long Lexan tube capped on one end was immersed on its side and lowered to the surface of the sediment layer after it had been carefully clear of debris. The tube was used as a scoop by pushing it horizontally just under the surface, removing the top 2-3 cm of sediment. The open end of the tube was tilted upward to retain the collected sediment, and the tube was removed from the water. The sample was placed in a 5 gal bucket. This process was repeated two more times and the contents added to the bucket and mixed. This mixture was allowed to settle for approximately 3-5 minutes inside the bucket. The water was decanted and the sediment was transferred into the collection bottle, labeled, and stored on ice.

To obtain the deeper sediments, the end cap was removed from the tube and an "egg-crate" cap was placed on one end. Selecting an adjacent area, the tube was pushed vertically into the sediment to refusal. Refusal was typically encountered at depths of 20 to 35 cm below the surface. The tube was then extracted and the topmost layer was removed from the column by tilting the core tube and allowing the topmost layer to pour out from the uncapped end of the tube back into the pond. The remaining deeper sediment was emptied into a 20 L plastic bucket. This process was repeated two times, and the three grabs were then homogenized with a spade, and a subsample was transferred into the sample bottle, labeled, and stored on ice.

Non-wadeable Ponds and Lagoons: A small boat was used to travel to a selected location of the pond or lagoon. An anchor was dropped and the boat allowed to drift away from the anchor. An Eckman dredge was lowered into the sediment, activated by a messenger, and retrieved to the surface. The top 2-3 cm of sediment inside the dredge was removed using a small spade and was placed into a sample bottle. The deeper sediments were released from the bottom of the dredge and added to a 20 L plastic bucket. Two additional collections were made and the material obtained was added directly to the sample bottle for surface sediments, and to the bucket for deeper sediments. The deeper sediments were mixed with the spade, and a subsample was bottled, labeled, and stored on ice. Water depths at the sampling sites are provided in Table 2.

Shale Samples: Based on the assumption that shale bedrock was the original source of the pond sediments, shale bedrock samples were obtained from three locations as shown in Figure 1. Care was taken to obtain unexposed shale along the water's edge by breaking away surficial shale and taking the sample from underneath. Shale samples were

Table 1. Sampling sites.

Site #	Name	Latitude/LongitudeFall 2000	Latitude/LongitudeSpring 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 42.08.88 W 080.07.99	N 42.08.96 W 080.07.91
7	East Settling Pond, Cement Bottom	N 42.08.95 W 080.07.89	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	ns*	N 42.09.71 W 080.04.66
15	New Sand, tip of Gull Point shoreline	ns*	N 42.10.28 W 080.03.98
CCS	Cascade Creek Shale	ns*	N 42.07.52 W 080.06.63
MCS	Mill Creek Shale	ns*	N 42.05.59 W 080.04.25
WCS	Walnut Creek Shale	ns*	N 42.04.47 W 080.14.19

*ns = not sampled

dried in an oven at 105 °C for one week. A ceramic mortar and pestle was used to grind the shale into fine particles that were then sieved through a #35 (500 µm) US Standard Testing Sieve.

Quality Control, Sampling: All equipment was rinsed between the collection of upper and lower sediments and between sites to avoid cross contamination of samples. Sample bottles were washed in advance 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, and dried at 105 °C for 7 days. In the field, sample bottles were topped off with site water to eliminate head space, closed tightly, and placed in an ice chest as soon as possible after sampling.

Sediment Digestion and Analysis

EPA method 3050B was employed 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 arsenic standard solution was by Fisher Scientific. Sediment digestates were analyzed using a Perkin-Elmer AAnalyst 600 Graphite Furnace Atomic Absorption Spectrophotometer. Based on recommendations in the instrument's operating manual, nickel nitrate was found to produce more consistent results as a matrix modifier than did the palladium/magnesium mixture (both at 1:1 ratios).

Quality Control, Sediment Digestion: Quality control measues are described in greater detail in Murnoch (2002). Typically, three matrix blanks, eight duplicates and one triplicate were performed for purposes of quality control during the digestion procedure. EPA method 3050B recommends using a representative 1-2 g DW sample for digestion. Actual sample weights ranged from 1.73 - 3.53 g with a mean weight of 2.23 g. At least two replicate aliquots of each digestion solution were analyzed and mean values are reported.

Statistical Distribution of Arsenic Concentration Values: Surface and deeper sediment arsenic concentration values for Fall 2000 and Spring 2001 were found to be log-normally distributed using the Shapiro-Wilk test. Therefore, non-parametric statistics were required for statistical comparisons among sites. 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 2. Water depths at sampling sites.

Site #	Name	Water Depth (m) Fall 20001	Water 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	4.0	4.9
7	East Settling Pond, Cement Bottom	4.5	4.5
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		0.23
15	New Sand, tip of Gull Point shoreline		0.10

Age Estimation of Sampled Ponds

Pond ages as of the time of sampling were estimated using various sources of information. Some of the ponds studied by Kormondy (1969) were also used in this study and the age estimates of those ponds were adjusted to 2001. Published material and maps were used to estimate pond age as referenced in Table 3. Various maps of the peninsula were obtained and evaluated (Maguire 1884; USGS 1957; FWS, 1990).

The West and East Settling Ponds (Sites 6 and 7), also known as the Water Works Ponds, were created around 1904 from two natural "Chimney Ponds" located at those sites (Walker, 2000). The Chimney Ponds are shown on the 1884 map and are thus at least 117 yrs of age but it is difficult to accurately determine the age of the settling pond sediments. 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 constructed. Marina Lake (Site 8), was created by dredging in 1956 (Walker, 2000).

An additional method to estimate relative pond age was based on the assumption that the peninsula is geologically younger toward its eastern end (Gull Point). 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 distances are also presented Table 3.

RESULTS

Arsenic in Presque Isle Sediments

Arsenic concentrations found by Murnoch are presented in Table 4. For fall sampling, values ranged from 36.9 mg/kg-DW to 325.4 mg/kg-DW for surface sediments and from 8.3 mg/kg-DW to 206.3 mg/kg-DW for deeper sediments.

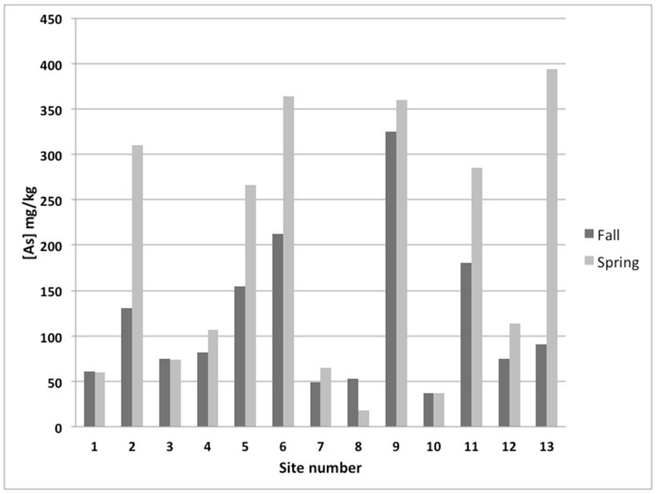

Figure 4. Arsenic concentrations (mg/kg DW) for surface samples from the fall and spring sampling.

Table 3. Age estimates of sampled ponds and distance from Site 15 (Gull Point).

Site #	Name	AgeEstimates (Years)	Distance from Site 15 (km)
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 b = Lydecker et al., 1923 c = Zagorski & Gance, 1971 d = USGS, 1957
e = Maguire, 1884 f = FWS, 1990 g = Walker, 2000

Spring 2001 sampling revealed arsenic concentrations from 17.5 mg/kg-DW to 393.6 mg/kg-DW for surface sediments and 3.6 mg/kg-DW to 327.3 mg/kg-DW for deeper sediments. With only one exception, surface sediments contained more arsenic than did deeper sediments.

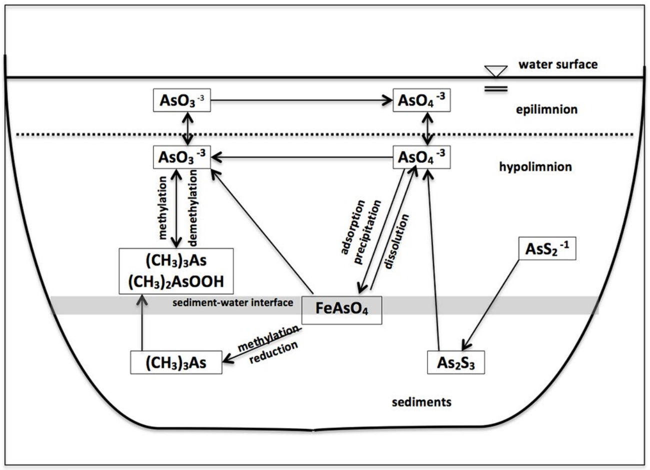

Figure 5. Arsenic speciation and cycling in an aquatic environment; after Ringwood, 1996.

DISCUSSION

Arsenic Sediment Toxicity

The PEC for arsenic of 33.0 mg/kg-DW was exceeded in the surface sediments at all 13 interior sites during fall sampling; the PEC was exceeded at all but one site during spring sampling. For deeper sediments, the PEC was exceeded in the fall at nine sites and in the spring at six sites. At six of 13 sites, the ER-M of 85.0 mg/kg-DW was exceeded in surface sediments in the fall, while it was exceeded at eight of 13 in the spring.

When the fall and spring values for each site were averaged and divided by the PEC, a PEC-Quotient was obtained (Table 5). Most of the surface samples had arsenic concentrations more than double the PEC, and in some cases as much as ten times the PEC (Duck Pond). For deeper sediments, a maximum PEC-Q of 6.5 was observed.

Possible Sources of Arsenic

Natural Sources of Presque Isle Arsenic: Shale samples taken from the mainland near Presque Isle were found to contain arsenic at concentrations ranging from 7.5 to 15.5 mg/kg-DW (Table 4). Samples of sand taken from the youngest area of Presque Isle (Site 14, a newly formed pond on Beach 11 and Site 15, the tip of Gull Point) were found to

Table 4. Arsenic concentrations in sediments collected during fall, 200, and spring, 2001 (mean of at least two replicates).

		Fall, 2000		Spring, 2001	
Site #	Pond Name	[As] Surface Sediments (mg/kg)	[As] Deeper Sediments (mg/kg)	[As] Surface Sediments (mg/kg)	[As] Deeper Sediments (mg/kg)
1	Ridge Pond	60.8	8.3	59.5	3.6
2	Niagara Pond	131.0	40.7	309.9	27.0
3	Unnamed, Gull Point pond	74.4	18.2	73.8	10.2
4	Cranberry Pond	82.0	68.2	106.7	2.7
5	Unnamed, east of Horseshoe Pond	154.5	41.2	266.1	17.4
6	West Settling Pond, Natural Bottom	211.9	148.9	363.9	236.6
7	East Settling Pond, Cement Bottom	49.0	30.6	64.7	37.4
8	Marina Lake	53.0	44.6	17.5	11.8
9	Duck Pond	325.4	206.3	359.5	188.4
10	Horseshoe Pond	36.9	27.5	37.2	23.8
11	Boat House Pond	180.7	193.9	285.5	237.7
12	Big Pond	75.0	71.7	113.6	109.4
13	Long Pond	90.6	71.5	393.6	327.3
	Reference Sites				
14	Unnamed, newly formed pond, Beach 11	ND	ND	5.4	4.3
15	New Sand, tip of Gull Point	ND	ND	4.6	ND
CCS	Cascade Creek Shale	ND	ND	7.5	ND
MCS	Mill Creek Shale	ND	ND	8.8	ND
WCS	Walnut Creek Shale	ND	ND	15.5	ND

ND = not determined

contain about 5 mg/kg-DW.

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 (DCNR, 1991; Kormondy, 1969; Shultz, 1999). The major natural source of material to the peninsula has been the bluffs along the Lake Erie shore to the west of Erie. Eroded material from those bluffs continues to move eastward along and across Presque Isle, nourishing beaches on the way and accumulating at Gull Point. Also, sand is imported onto Presque Isle for beach nourishment by the Army Corps of Engineers from various sources. Analysis of imported sands revealed a mean arsenic content of 10.9 mg/kg-DW (Potomac-Hudson, 1991).

Potential Anthropogenic Sources: The city of Erie, PA, has historically supported a wide variety of industries, some of which have produced and still 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 almost entirely occupied by a state park, and it is unlikely that solid wastes were 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, analyzed, and found to contain 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).

Table 5. Probable effects concentration quotients (PEC-Q) for surface and deeper sediments.

Site #	Name	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	8.7	5.8
7	East Settling Pond, Cement Bottom	1.7	1.0
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.

Seasonal Variation in Arsenic Concentrations

When fall surface arsenic values as a group were compared to values for the spring as a group, there was a significant difference ($P < 0.01$). As seen in Figure 4, all sites but three had higher concentrations in the spring than in the fall (spring mean concentration = 188 mg/kg-DW; fall mean concentration = 117 mg/kg-DW). When this same comparison was made for the deeper sediments, there was no significant difference ($P = 0.19$). In fact, eight of the sites had lower concentrations in the spring compared to the fall, while only five sites had increased concentrations.

This pattern may be the result of the changing temperature due to the seasons combined with geochemical processes. 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 essentially 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 higher redox potential of the surface layer may have led to enhanced sorption and/or precipitation of arsenic.

Vertical Distribution of Arsenic

Surface sediments contained significantly higher arsenic concentrations than the corresponding deeper sediments in both fall 2000 and spring 2001 samples ($P < 0.05$). Arsenic enrichment within surface sediments may occur as a function of solubility and sorption. Sediments deeper than the surficial 2-3 cm are generally anaerobic and, thus, reduced environments. Many reduced arsenicals have greater solubility than their oxidized counterparts. Thus, diffusion would tend to transport dissolved arsenic toward the oxic surface layer where sorption onto iron and/or aluminum oxides could occur, as could precipitation of oxidized arsenic compounds. This mechanism would tend to enrich surficial sediments and deplete arsenic from deeper sediments. Figure 5 illustrates this process for a hypoxic stratified lake (Ringwood, 1996).

Biological Transport: 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). Rooted macrophytes were present at sampling sites 1-13 with higher densities in shallower sites. Subsequent death and decay of the plant tissues might result in a deposition of the residual arsenic on the surface of the sediments, effectively serving as a pumping mechanism to move arsenic from deeper sediments to the surface layer.

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

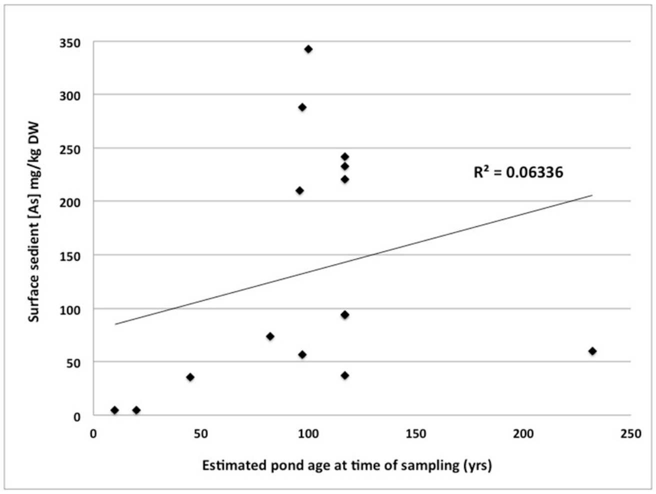

Figure 6. Plot of surface sediment arsenic concentration (mean of fall and spring) as a function of estimated pond age at time of sampling.

at higher pH values (Kabata-Pendias and Pendias, 1984; O'Neill, 1990). Since anaerobic deeper sediments tend to be acidic due to the formation of fermentation by-products, it is likely that deeper sediment organic matter would be less effective at retaining arsenic than would be surficial organic matter, adding to the likelihood of enrichment of the surface sediments.

Arsenic Concentration as a Function of Estimated Pond Age

The accuracy of historical evidence for pond age is questionable. Because the ponds and lagoons on the peninsula have been dredged and otherwise manipulated over the last hundred years, it is difficult to know the history of each pond and lagoon and, thus, difficult to know how to properly interpret the arsenic concentration data as a function of undisturbed pond age.

Nonetheless, mean of fall and spring surface arsenic values for each site were plotted against estimated pond age (Figure 6). While the regression line had a low coefficient of determination ($R^2 = 0.06$), generally, sediments from older sites contained more arsenic than younger sites. Similarly, when arsenic concentrations were plotted against distance from Gull Point (Figure 7) the coefficient of determination increased to 0.16 and a trend of increasing arsenic concentration with distance seemed a bit more convincing.

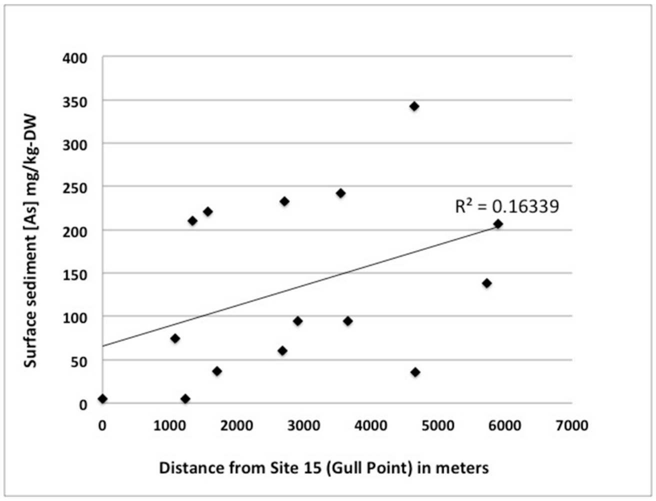

Figure 7. Plot of surface sediment arsenic concentration (mean of fall and spring) as a function of distance from Site 15 (Gull Point).

Concentration and Enrichment

If the nearby shale is the source of sediment in Presque Isle ponds, arsenic levels in surface sediments have become elevated by some mechanism. Within the sediments, the mass flux of arsenic is most likely a function of the speciation of the arsenic and the mobility of those species. Reducing conditions have been shown to enhance arsenic mobility and arsenic sorbed to Fe and Al may become available if redox potential decreases. On the other hands, pentavalent arsenicals exhibit a greater capacity for sorption than trivalent arsenicals (Kabata-Pendias and Pendias, 1984; O'Neill, 1990). The presence of organic matter and hydrated iron oxides have been shown to increase retention and decrease leaching rates (O'Neill, 1990).

Proposed Mechanism for Enrichment: The geochemistry of arsenic enhanced by a pumping mechanism might explain the unexpectedly high levels of arsenic in these sediments. The water level of Lake Erie is constantly changing due to long-term lake level changes and seasonal lake level changes as documented by NOAA at their water level monitoring stations (NOAA, 2013). Seiche effects have been documented to induce groundwater table fluctuations (Moore, 1994). These fluctuations, both long term and short term, might result in a pumping effect, driving water up and down through the pond sediments over long periods of time. Thus, soluble reduced arsenic in the anaerobic sediments could be forced up through the sediment-water interface and become oxidized. Oxidized arsenicals could then precipitate and/or become sorbed to iron oxides and organic matter in the oxic microzone at the surface of the sediments as water levels recede. During winter, the effect would be more pronounced than during the summer and fall since the presence or absence of oxidizing conditions just above the sediment surface would depend on temperature and microbial activity. This hypothesis will be tested in future work planned by the author.

CONCLUSIONS

The sediments of Presque Isle have high levels of arsenic and represent a likely threat to the aquatic ecosystem, based on widely accepted sediment quality guidelines. These high levels most likely are due to a combination of natural processes that, over time, have resulted in an enrichment 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 posed by arsenic-enriched sediments, but it is not unreasonable to speculate that some adverse effects are occurring.

ACKNOWLEDGEMENTS

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.

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RESEARCH NOTE:
A STUDENT-BASED INVESTIGATION TO ASSESS THE IMPACTS OF CHEMICAL DEICERS ON THE WATER QUALITY OF SPRING RUN STREAM IN ALTOONA, PENNSYLVANIA

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ABSTRACT

Students in an undergraduate independent study course at Penn State Altoona investigated the use and potential effects of chemical deicers on the water quality of the stream that runs through the campus. Spring Run supports a wild trout population and is a tributary of the Little Juniata River and a headwater stream for the Chesapeake Bay watershed. Students collected pre- and post- chemical deicer application water samples from Spring Run stream over four sampling dates. Water samples were analyzed for potassium (K^+), sodium (Na^+), dissolved oxygen, pH, chloride (Cl^-) and ammonia as nitrogen (NH_3^-). None of the parameters sampled exceeded the standard guidelines for the protection of aquatic life. However, this study found cause for future research, particularly as it relates to the concentration of chloride in stream water. Chloride exhibited significant increases in concentration between pre- and post-deicer application. With the exception of one sampling date, chloride concentrations (19.2-63.7 mg/L) fell within the range of concentrations found in streams in the northeast United States that have been contaminated by rock salt inputs. The learning outcomes and skill development objectives of this field-intensive experience were driven by the assumption that this type of field-based educational experience enhances student learning by contextualizing complex geographical processes better than a solely classroom-based experience. Through the research process students were exposed to working with field techniques, GPS, GIS, datasets and statistics. [J PA Acad Sci 87(3): 145-154, 2013]

INTRODUCTION

The application of solid and liquid chemicals, collectively known as deicers, to roadways have been widely used in colder regions of North America since the 1960s to maintain winter road safety and traffic mobility (Green et al. 2008, Fay and Shi 2012). The most commonly used deicer is rock salt, either as sodium chloride or calcium chloride. Rocks salts are effective up to a temperature of approximately -9 ^{o}C and are preferred for their natural occurrence, low cost and ease of storage and dispersal (Ramakrishna and Viraraghavan 2005). Acetate-based deicers have been used on winter roadways as an alternative to rock salts because they have been found to be less corrosive to automobile and roadway material (Fay and Shi 2012). Acetates, however, are slower acting and less effective in freezing rain, drier snowstorms and light traffic conditions in comparison to rock salt (Ramakrishna and Viraraghavan 2005). Acetate effectiveness also decreases below temperatures of –5 ^{o}C. The high cost of acetates (20 times that of salt) has hindered their wider application (Transportation Research Board 1991). The most commonly used acetate, calcium magnesium acetate (CMA), is a human-made powdered mixture of dolomite lime and acetic acid. Less commonly used on road surfaces are urea-based products. Urea is an organic compound, which degrades by hydrolysis to ammonia and then is converted to nitrate by soil microorganisms (Corsi et al. 2001).

In recent years, the use of deicers has grown as there has been a shift from reactive to proactive snow and ice control on winter roadways (Fay and Shi 2012). In urban and semi-urban areas, the increase in rock salt use is spatially correlated to the increase in impervious surfaces (Kaushal et al. 2005, Cassanelli and Robbins 2013). Approximately, 75-90% of applied deicing salts enter the roadside environment either directly dissolved in runoff and as splash or as aerosol deposition during application or plowing (Amrhein et al. 1992). The degree of percolation of dissolved salts into the soil depends on the soil permeability and moisture, with decreased infiltration when there is frost or frozen ground (Ramakrishna and Viraraghavan 2005).

The adverse impacts of elevated concentrations of deicers

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on the transportation infrastructure, automobiles and the environment have been well documented (see reviews in Fay and Shi 2012 and Green et al. 2008). In addition, the environmental impacts of rock salts include detrimental effects on groundwater, surface water and soil quality and aquatic habitats (Ruth 2003, Kayama et al. 2003, Meriano et al. 2009). Localized trends of increasing surface water salinity have been identified in the northeast United States (Kaushal et al. 2005). Elevated sodium concentrations have been observed to increase the growth of blue green algae stimulating nuisance algal blooms that deplete the dissolved oxygen in water bodies (Jones and Jeffrey 1992). The depletion of oxygen due to increased biochemical oxygen demand in receiving waters is also a byproduct of acetate degradation. The addition of acetate can potentially increase alkalinity and thus the pH of the surface water (Horner 1988). Both rock salts and CMA are associated with heavy metal mobility. Through soil cation exchange processes, heavy metals can be liberated from the soil (Jones and Jeffrey 1992) and the degradation of acetate produces bicarbonate ions that increase soil pH resulting in metal carbonate precipitation (Ramakrishna and Viraraghavan 2005).

Pedagogy

One of the hallmarks of the Environmental Studies Program at Penn State Altoona is the opportunity for student experiential learning in undergraduate studies. In addition to the primary goal of fostering ecological literacy in students, the curriculum is designed to help students develop an informed perspective on the natural world that can in turn “lead to purposeful action”. A key element of experiential learning is that student learning and knowledge gained occur as a result of being personally involved in this pedagogical approach (Hupy et al. 2005). One of the ways that this type of learning is achieved is through field work where students explore and apply classroom content in a specified research project. In addition to offering students a hands-on learning experience, the designing of field data collection procedures and data analysis lead to problem solving and critical thinking. Not only do students learn about the phenomena in a relevant setting, but they learn from the process itself (Hupy et al. 2005). As active participants in the learning process, the domain of concern for students is enlarged and they become more empowered concerning the subject matter (Simm and David 2002). Students are not only increasingly motivated towards academic inquiry, but the connection to the broader society is an integral part of community outreach and sets the stage for civic engagement (Walcott, 1999).

As part of an independent study course (Environmental Studies 496), two successive students (the second and third authors on this paper) investigated the impact of the use of chemical deicers on the water quality of the stream that runs through the Penn State Altoona campus. This course constituted field work accompanied by a research report outlining the physical characteristics of the landscape and an inventory and discussion of the chemical deicers used and the concentration of key water quality parameters in the campus stream.

A basic understanding of the transport and fate of each deicing material used is necessary to make informed decisions towards sustainable winter operations that are both environmentally and fiscally responsible. This article presents an outline of the process and the educational benefits of the research project as well as a discussion of the more important results for the study area. The research goal of the study was to provide a general assessment of the use and potential water quality effects of chemical deicers on the Penn State Altoona campus. The learning objectives were:

(i) *Conceptual*- understanding the chemistry of deicers.

(ii) *Procedural*- implementing field-based data collection.

(iii) *Mechanical*- performing required tasks accurately and completely.

(iv) *Contextual*- interpreting data in the context of the study landscape and the literature.

MATERIALS AND METHODS

Study Area

The study area is the Spring Run stream and its watershed in Blair County, PA (Figure 1). Spring Run is a tributary of the Little Juniata River and the Chesapeake Bay watershed. The stream is classified as a wild trout stream and supports a natural, reproducing population of brown trout (*Salmo trutta*) as well as a diverse community of macro-invertebrates (Pennsylvania Fish and Boat Commission 2011). On the Penn State Altoona campus, the stream has been modified by storm drains, erosion control measures and channelization. The watershed (137 km^2) is under mixed land use with 14% urban, 10 % agricultural, 67% forested. The largest municipality within the watershed is the city of Altoona with a population of approximately 46,000.

The average monthly temperature is 9.5 ^{o}C with July being the warmest month (mean of 21.4 ^{o}C) and January the coldest (mean -6.8 ^{o}C; Pennsylvania State Climatologist 2013). Mean annual rainfall is 1084.6 mm. Snowfall occurs from October through March, with the greatest monthly totals in January 241.3 mm (Pennsylvania State Climatologist 2013). The study was conducted over two study periods. For the October 2010-March 2011 period there was a total of 529.8 mm of rainfall and 911.9 mm of snow and/or ice (National

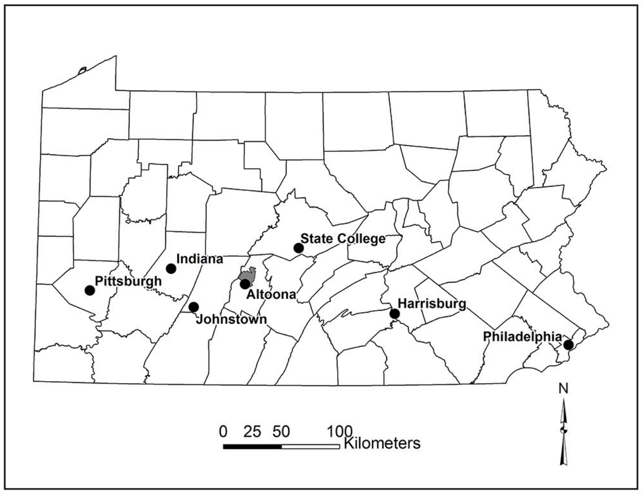

Figure 1. Location of the Little Juniata River Watershed, Blair County, Pennsylvania.

Climatic Data Center 2013). For the October 2012-March 2013 period there was a total of 479.3 mm of rainfall and 1366.5 mm of snow and/or ice (National Climatic Data Center 2013).

The study area is underlain by rocks of two geologic formations: the Brallier Formation (upper reach of the stream) and the Lock Haven Formation (lower reach of the stream). Both formations comprise shale and siltstone, with the Lock Haven formation also containing sandstone and limestone. The dominant soil association is the Berks-Brinkerton-Weikert Association with Berks-Weikert channery silt loams on steeper slopes (25-70%), Weikert channery silt loam on moderate slopes (3-15%) and urban-land Berks complex soils on gentler slopes and the floodplain (0-8%).

Spatial Data

Before the students could construct a water quality sampling plan, they needed to have an understanding of the spatial distribution of physical landscape features such as soils and hydrology as well as anthropogenic features including paved surfaces. The most efficient means to accomplish this task was through the use of Geographic Information System (GIS) software. Spatial data were acquired through the United States Department of Agriculture, National Resource Conservation Service (USDA-NRCS) Geospatial Data Gateway (National Land Cover Dataset 2006, hydrography) and the Penn State Institutes of Energy and the Environment's Pennsylvanian Spatial Data Access clearinghouse (soils, geology, county boundaries). All layers were projected to Pennsylvania State Plane South, North American Datum 83.

Field Data Collection

Through a literature review, students determined that water samples should be collected both upstream and downstream of the building used to store the deicers (Figure 2). The storage building is a simple roof over a stockpile of rock salts and acetate-based products (Table 1). With the limited budget and time available to the students, they determined that there would be a total of 10 sample sites from which water samples would be collected on two sampling dates for each study period (2010-2011, 2012-2013): one date prior to winter deicer applications and one date corresponding to a post-application melting event. It was hypothesized that the second sampling date would capture a 'flushing' event where deicers in the surface melt and those stored in soil and shallow groundwater aquifers would be transported into the stream due to the saturated conditions of the soil-groundwater system.

The students were responsible for doing field reconnaissance to determine the location of the 10 sampling stations. The sampling sites were located at 125 m intervals along the stream course; shorter intervals were necessary if access to the stream was impeded by fencing or other erosion control structures. The location of each sampling station was recorded using a handheld Geographic Positioning System (GPS) unit. The coordinates of the sampling points were input into a GIS to create a map (Figure 2).

The students conducted in person interviews with the supervisor of facilities and operations at Penn State Altoona to determine the type and quantity of chemical deicer used (Table 1). The active ingredients in the ice melt products included calcium magnesium acetate, potassium acetate and urea. The rock salt was sodium chloride and

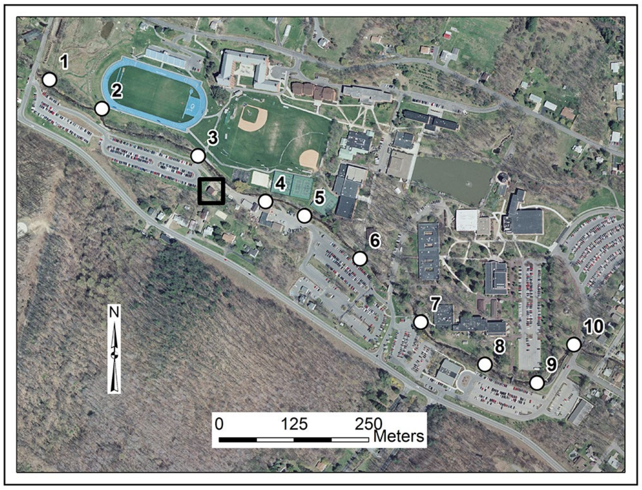

Figure 2. Location of the water chemistry sampling stations (numbers 1-10) on the Penn State Altoona campus. The location of the rock salt storage shed shown in the black box.

potassium chloride and was applied to all roadways and parking surfaces on campus. The ice melt products were used on the cement walkways. No other details of the winter maintenance program were available.

Based on the active ingredients of the chemical deicers used on campus, the students elected to determine the concentration sodium (Na^+) and chloride (Cl^-) as derivatives of rock salt dissolution, potassium (K^+) as a by-product rock salt and of acetate- based deicer degradation, ammonia as nitrogen (NH_3^-) as a by-product of urea breakdown and pH and dissolved oxygen as general water quality parameters. Since the stream alkalinity is naturally 'hard' (L.A.E. unpublished data), it would not be possible to determine if calcium (Ca^{2+}) and magnesium (Mg^{2+}) concentration in stream water was a by-product of deicer dissolution.

All samples were grab- sampled in 300 ml polyethylene bottles that were cleaned with a solution of Sparkleen detergent and tap water. Bottles were acid-washed with 20% H_2SO_4 and then triple rinsed with distilled water. Dissolved oxygen samples were collected so that no head space was left at the top of the bottle and the bottle was stoppered. Samples collected for the determination of potassium and sodium were acidified with 0.1 ml of concentrated nitric acid (HNO_3^-) to prevent microbial degradation. Collected samples were stored on ice and transported to the analytical laboratory within one hour of collection. All samples were analyzed by Fairway Laboratories, Altoona, Pennsylvania according to Standard Methods for the Examination of Water and Wastewater (SM) and Environmental Protection Agency (EPA) Methods (Table 2).

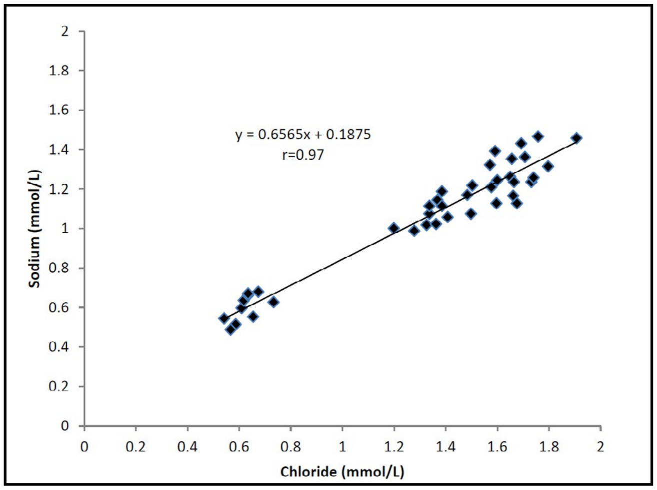

Figure 3. Correlation between the molar concentration of sodium and chloride ions in Spring Run stream water, Penn State Altoona campus, Blair County, Pennsylvania.

Table 1. The weight (metric tonnes) of deicer products used on the Penn State Altoona campus (Blair County, Pennsylvania) for the study period (2010-2013).

Deicing Agent	2010-2011 Weight (tonnes)	2011-2012 Weight (tonnes)	2012-2013 Weight (tonnes)
[1]Inferno Ice Melter®	26	10	30
[2]Green Premium Ice Melt®	21	7	20
[3]Pritts Ice Melt®	0	0	5
[4]Rock Salt®	267	112	172

[1] calcium magnesium acetate, potassium acetate, urea, sodium, sodium silicates, ethanol amines

[2] calcium magnesium acetate

[3] sodium chloride, potassium chloride

[4] sodium chloride

Statistical Analyses

Pearson correlation analysis was used to investigate whether the sodium and chloride concentration in stream water was indicative of rock salt contamination. The correlation coefficient (r) was used as a measure of the strength of the relationship. The test statistic (F) was used to determine whether there was a significant correlation between the two variables (sodium and chloride) at a significance of 99% ($\alpha = 0.01$)

The difference in stream chemistry for sodium, chloride and potassium for the pre- and post- application of chemical deicers was compared using a paired sample t-test assuming equal variance at a significance of 95% ($\alpha = 0.05$). All statistical analyses were performed using the Data Analysis Toolpak, Microsoft Excel 2010.

RESULTS

The molar equivalent of sodium and chloride were strongly correlated in stream water ($r = 0.97$, $P < 0.0001$, Figure 3). The molar ratio of sodium to chloride (Table 3) was less than one for the majority of the samples, with the exception of ratios greater than one for the November 2012 sampling date. For both sampling periods, there are clear seasonal differences in chloride concentrations with concentrations significantly higher ($P = 0.038$ 2010-2011, $P < 0.001$ 2012-2013) during the post- application melt events as compared to the pre-application sampling dates (Table 3). Similarly, there was a significant difference ($P = 0.0001$ 2010-2011, $P < 0.0001$ 2012-2013) between potassium concentrations for the pre- and post-application sampling dates, however the

Table 2. Analytical methods used to determine the concentration of sodium, chloride, potassium, ammonia as nitrogen, dissolved oxygen and pH in Spring Run stream water, Blair County, Pennsylvania.

Parameter	Analytical Method	Reporting Limit
Potassium	EPA[1] 200.7/4.4	0.100 mg/L
Sodium	EPA 200.7/4.4	0.200 mg/L
Chloride	EPA 300.0/.21	5.00 mg/L
Ammonia as Nitrogen	ASTM[2] D6919-03	0.100 mg/L
Dissolved Oxygen	SM[3]20-4500 O-G	0.100 mg/L
pH	SM20-4500H+B	

[1] Environmental Protection Agency Clean Water Act Analytical Methods
[2] American Society for Testing and Materials Analytical Methods
[3] Standard Methods for the Examination of Water and Wastewater

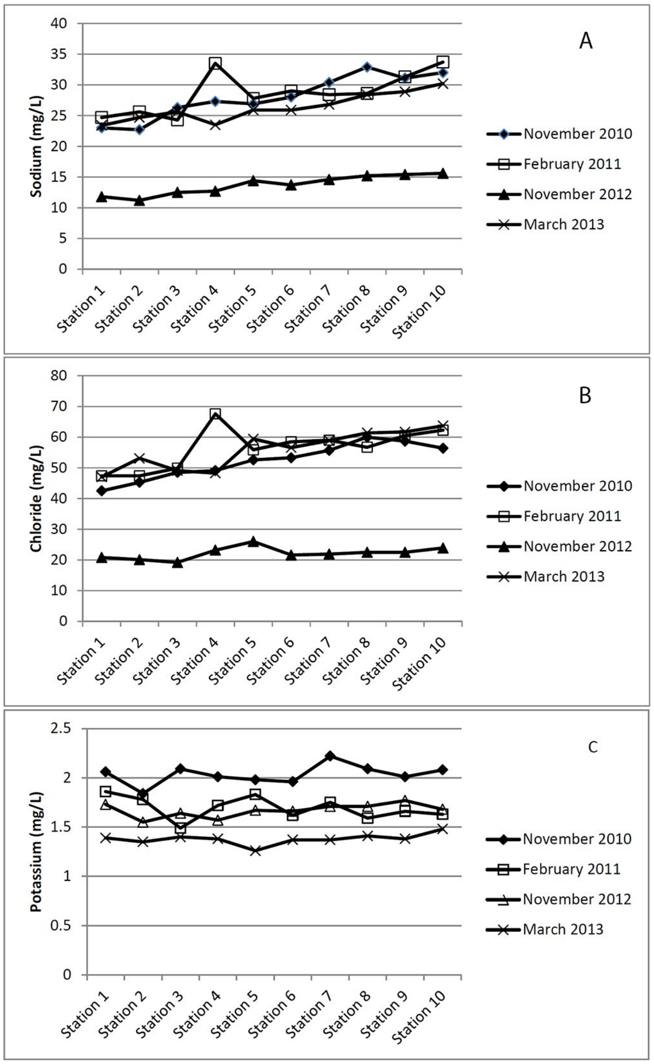

Figure 4. Sodium (A), Chloride (B) and Potassium (C) concentrations for stations 1 through 10 in Spring Run stream water, Penn State Altoona campus, Blair County, Pennsylvania.

concentrations were lower for the post-application dates (Table 3). For sodium, only the second sampling period (2012-2013) exhibited a significant ($P < 0.001$) increase in sodium concentration in stream water post-application.

Both sodium and chloride mean concentrations (Table 3) exhibited a much lower concentration for the November 2012 sampling date (sodium= 13.71 ± 1.56 mg/L, chloride= 22.71 ± 1.95 mg/L) compared to the other three sampling dates (sodium= 27.69 ± 3.16 mg/L, chloride= 54.88 ± 6.27 mg/L). In general, there was a trend towards increasing concentration of sodium and chloride with distance downstream, i.e. from Station 1 to Station 10 (Figure 4). The Environmental Protection Agency (EPA) does not consider sodium a contaminant in terms of aquatic life or drinking water. Waters with a concentration above 200 mg/L will taste salty (Environment Canada 2011). The EPA and Pennsylvania Department of Environmental Protection (PA DEP 2006) consider chloride as a secondary contaminant and set a limit of 250 mg/L. The concentration of chloride in Spring Run was well below this limit. The EPA and PA DEP do not have a water standard for potassium. The World Health Organization (WHO) has suggested a maximum concentration of 82 mg/L in drinking water (WHO 2009). The concentration of potassium (1.26-2.22 mg/L) in Spring Run for the two sampling periods was also well below this limit (Table 3). The concentration of potassium was comparable to the mean concentration (1.5 mg/L) in North American rivers (WHO 2009).

The pH values (Table 3) fell within the range (6.5-8.5) recommended for the protection of aquatic life (PA DEP 2006). The dissolved oxygen content of water is an indicator of a water body's ability to support aquatic organisms; daily values less than 4.0 mg/L threaten aquatic life (EPA 2006). Dissolved oxygen concentrations (Table 3) in Spring Run (10.5-13.1 mg/L) were above this guideline concentration for both study periods. The concentration of ammonia was below detection limits (<0.100 mg/L) at all stations for all sampling dates.

Table 3. The chemical analysis of sodium, chloride, potassium, pH and dissolved oxygen for all stream water samples collected in Spring Run, Blair County, Pennsylvania.

Collection Date	Station Number	Sodium (mg/L)	Chloride (mg/L)	Na:Cl (ratio)	Potassium (mg/L)	pH	Dissolved Oxygen (mg/L)
11/1/2010[1]	1	23.0	42.5	0.83	2.06	7.91	12.1
	2	22.7	45.3	0.77	1.84	7.91	12.5
	3	26.3	48.5	0.84	2.09	8.06	12.3
	4	27.3	49.1	0.86	2.01	8.22	12.5
	5	26.9	52.6	0.79	1.98	8.25	13.1
	6	28.0	53.3	0.81	1.96	8.18	12.6
	7	30.4	55.7	0.84	2.22	8.06	11.9
	8	32.9	60.0	0.85	2.09	8.15	12.2
	9	31.1	58.7	0.82	2.01	8.25	12.2
	10	32.0	56.4	0.87	2.08	8.05	11.6
2/18/2011[2]	1	24.7	47.4	0.80	1.86	7.46	11.8
	2	25.6	47.4	0.83	1.78	7.37	11.8
	3	24.3	49.9	0.75	1.49	7.41	11.9
	4	33.5	67.6	0.76	1.72	7.44	11.8
	5	27.8	55.9	0.77	1.83	7.37	11.9
	6	29.0	58.5	0.76	1.62	7.44	12.0
	7	28.4	59.0	0.74	1.75	7.47	12.0
	8	28.6	56.7	0.78	1.59	7.51	12.0
	9	31.3	60.5	0.80	1.66	7.53	11.8
	10	33.7	62.3	0.83	1.63	7.53	11.9
11/1/2012[1]	1	11.8	20.8	0.87	1.73	7.79	10.5
	2	11.2	20.1	0.86	1.55	7.75	10.5
	3	12.5	19.2	1.00	1.64	7.71	10.6
	4	12.7	23.2	0.84	1.57	7.73	10.6
	5	14.4	26.0	0.85	1.67	7.70	10.6
	6	13.7	21.6	0.98	1.66	7.90	10.6
	7	14.6	21.9	1.03	1.71	7.79	10.7
	8	15.2	22.5	1.04	1.71	7.82	10.6
	9	15.4	22.5	1.06	1.77	7.84	10.6
	10	15.6	23.9	1.01	1.68	7.83	10.5
3/22/2013[2]	1	23.4	47.0	0.77	1.39	7.85	11.4
	2	24.7	53.1	0.72	1.35	7.73	11.6
	3	25.6	49.1	0.80	1.40	7.51	11.7
	4	23.5	48.3	0.75	1.38	7.51	11.9
	5	25.9	59.4	0.67	1.26	7.61	11.9
	6	25.9	56.6	0.71	1.37	7.70	11.9
	7	26.8	58.9	0.70	1.37	7.65	12.0
	8	28.4	61.4	0.71	1.41	7.65	11.9
	9	28.9	61.7	0.72	1.38	7.72	12.0
	10	30.2	63.7	0.73	1.48	7.68	12.0
Mean		24.2	46.7	0.8	1.7	7.80	11.7
Standard Deviation		6.8	15.4	0.1	0.2	0.30	0.7

[1]Pre-application sampling date, [2]Post-application sampling date

DISCUSSION

A bivariate plot of sodium and chloride concentration forms a linear trend consistent with road salt (Jin et al. 2011). Natural background levels of sodium chloride are generally 1 mmol/L (Meriano et al. 2009). Our data show a regression line that is displaced from the sodium chloride dilution line, indicating that there may have been attenuation by soil and sediment adsorption (Figure 3, Ramakrishna and Viraraghavan 2005). The values less than unity may also indicate inputs from other sources such as septic systems or waste water treatment (Jin et al. 2011).

Although the chloride concentrations in Spring Run do not exceed the standard guidelines, the concentrations are above the average value of 8.3 mg/L for freshwaters in the United States (Demers and Sage 1990). Chlorides in freshwater streams and lakes generally range from 0 to 100 mg/L, with most concentrations lower than 20 mg/L (Fay and Shi 2012). With the exception of the November 2012 sampling date, our concentrations also fall within the range of concentrations found in other stream systems in the northeast United States that have been contaminated by rock salt inputs (e.g. Kelly et al. 2008, Jin et al. 2011). The November 2012 sampling date was preceded by a week of daily rainfall events, with 109 mm falling in the four days immediately prior to the November sampling date leading to more dilute conditions.

Other studies have also found similar seasonal differences in chloride concentrations in stream water attributed to road salt runoff, with the highest values between January and March (Kelly et al. 2012). The highest salt concentrations are associated with winter or spring thaw 'flushing events' with values in the 100s (Meriano et al. 2009) to 1000s (Environment Canada 2010) of mg/L being reported. The student hypothesis that post-chemical deicer application sampling of water would capture a 'flushing' of dissolved deicer contaminants in the stream was not supported for this study as our chloride concentration peaked at 67.6 mg/L. The limitation being that water samples were collected on one date at one time during a winter/spring thaw period. In order to truly characterize the rock salt inputs associated with such an event, time series stream water samples would need to be collected on both the rising and falling limbs of the hydrograph period. Studies have shown that runoff immediately following the first rainfall is the highest in deicer concentration; as time passes and additional rain or snowmelt occurs, the concentration rapidly decreases (Meriano et al. 2009, Fay and Shi 2012).

Further, year round sampling is necessary to assess the contributions of "reserve" supplies of chloride held in groundwater storage. Although shallow groundwater aquifers are susceptible to contamination and the short-term transport of pollutants to local surface water bodies, studies have shown that recharge of deeper groundwater aquifers can affect surface water bodies through groundwater baseflow over the longer term (Jones and Jeffrey 1992, Brown et al. 2011). This baseflow input creates a lag effect, whereby dissolved salt concentrations in surface water receiving bodies have been observed to have elevated concentrations of sodium and chloride during dry weather conditions (Kaushal et al. 2005, Perera et al. 2013). This lag effect can persist for decades (Kelly et al. 2008).

While there is no water quality guideline for sodium as it relates to the protection of freshwater aquatic life, concentrations as low as 5 mg/L promote optimum growth of algae and contribute to enhanced eutrophication and depletion of dissolved oxygen in surface waters (Ramakrishna and Viraraghavan 2005). The degradation of CMA can increase biochemical oxygen demand depleting dissolved oxygen in surface waters; however, several factors may mitigate this depletion. Dilution, absorption on soil particles, and microbial degradation (McFarland and O'Reilly 1992) can reduce the acetates that run off from paved surfaces during winter application. During spring thaw runoff, short periods of dissolved oxygen depletion in receiving waters may occur (Bang and Johnston 1998), however, in order to capture these short-term occurrences, more frequent monitoring of stream temperature and dissolved oxygen concentration is needed.

One of the by-products of urea breakdown is ammonia, a substance highly toxic to aquatic life at concentrations of 1 to 10 mg/L (Corsi et al. 2001). Our study results could not determine a presence or absence of ammonia as stream concentrations were below the detection limit. It may be that the ammonia hydrolyzed to ammonium or nitrogen was present as nitrate. Further testing of these latter two parameters is necessary to determine the impact of urea runoff to the stream.

While the present concentrations of potassium, sodium and chloride in particular are below thresholds of concern, the cumulative and long-term effects of deicer contamination of ground and surface waters on the Penn State Altoona campus warrants further research. This study provides baseline data from which both short-term salinization events and long-term loading rates can be determined. Additionally, we contribute site specific data. There is a scarcity of this type of site-specific data that is necessary to determine the spatial variability of these non-point source contaminants (Meriano et al. 2009). Watersheds, such as the one that drains Spring Run, with shallow soils covering hillslopes, are very susceptible to rock salt contamination (Jin et al. 2011).

Further study should include an analysis of the location and areal coverage of paved surfaces to determine the rate of application and potential source areas for runoff of chemical deicers. Additionally, the concentration of deicer runoff water is also a function of site-specific soil and microbial processes. An investigation of the soil cation exchange capacity and microbial pools is needed to determine the potential for storage of contaminants. Ultimately, a comparative watershed approach should be used and the water chemistry of Spring Run should be compared to the stream water chemistry of a comparable forested watershed with minimal deicing inputs in order to assess the contribution of chemical deicer runoff to the degradation of stream water quality.

We recognize that it is not practical to end the use of chemical deicers on the Penn State Altoona campus and in addition to the recommendations to decrease the use of deicers and to change the storage location of deicing products, we submitted a proposal to Operations management at Penn State Altoona to plant a native vegetated riparian buffer along sections of the stream adjacent to parking lots to decrease the amount of direct surface runoff to the stream. We received this funding and as part of another student research project, we have begun planting vegetated buffers across from the current deicer storage area. These buffers will provide a learning opportunity for students to study the ability of such buffers to mitigate the degradation of stream water quality by chemical deicer runoff.

This learning experience exemplified the key characteristics of a field-based learning experience as defined by Hupy et al. (2005): collection of data in an outdoor setting, practice of experiential learning, development of observational and analytical skills and responsibility for one's own learning. The specific activities that fulfilled the four learning objectives outlined at the outset of this paper included:

(i) *Procedural*-through pre-field work planning, the students developed a sampling scheme for water quality data collection that was both spatial and temporal in nature.

(ii) *Mechanical*-the students conducted in situ water sample collection and learned to accurately record analytical data and assess the limitations of the sampling technique.

(iii) *Contextual*-the students analyzed the data using statistical methods and discussed the study results within the context of the broader literature.

(iv) *Conceptual*-the synthesis of the overall study findings in the form of a research report demonstrated the students understanding of the chemistry of deicers.

The role of the instructors was to guide the learning process, allowing opportunities for students to take initiative, make decisions and ultimately to be accountable for the results. The GIS analysis provided both inquiry-based methods of learning and analysis tools for studying and exploring spatial geographic data. These analyses promoted more in-depth data explorations giving greater meaning to the work of the student researchers and providing technical skill development.

Through the research process students were exposed to working with field techniques, GPS, GIS, datasets and statistics. Students learned that data do not determine the interpretation of statistics patterns (O'Brien 2007) and it was only through a contextual understanding of the landscape and a conceptual understanding of deicer chemistry that their understanding of the subject was deepened as theory and practice became integrated (Haigh and Gold 1993). This understanding facilitates long-term retention of data and concepts and prepares students for their own fieldwork and research.

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