Final Report:

Monitoring and Assessment of Legacy Lead Contamination in the La Crosse River Marsh

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U.S. EPA Urban Waters Grant UW00E01025 Final Report

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INTRODUCTION:

Wetlands are ecologically threatened worldwide by habitat loss, damage and contamination from development, industrial discharge, urban and agricultural runoff, and other human activities. These biologically diverse and highly productive ecosystems provide vital habitat for aquatic plants and animals and serve as nurseries for larval insects, fish and amphibians. Wetlands also provide ecosystem services including filtration of water, degradation of organic wastes, and sequestration of inorganic and organic contaminants in plants and sediments (Peltier et al., 2003; Mitsch and Gosselink, 2000).

High levels of lead (Pb) found in many wetlands are often the result of Pb shot used in hunting and trap shooting activities. Millions of kilograms of Pb ammunition are discharged annually in the U.S., often with corresponding unintended consequences to wildlife and human health (Calvert, 1876; McAtee, 1908; Scheuhammer and Norris, 1996; Tranel and Kimmel, 2009; US EPA, 2005). Waterfowl poisoning through ingestion of Pb pellets prompted a ban in the U.S. in 1991 on the use of Pb shot over waterways. Pb shot breaks down in both terrestrial (Jorgensen & Willems, 1987) and wetland environments (Hui, 2002), but in wetlands, the hydric sediment potentially allows for greater migration of dissolved particles into surrounding sediments and the overlying water. The negative soil, water, and ecosystem effects of Pb can be particularly severe in wetland trap shooting ranges, where Pb shot densities of up to 370,000 pellets/m^2 have been measured (Clausen et al., 2011; Stansley et al., 1992). Because the dissolution of Pb shot and weathering into secondary Pb compounds can take up to 300 years (Jørgensen and Willems, 1987), former shooting ranges often leave a legacy of contamination long after shooting ceases, especially in wetland settings (Behan et al., 1979; Lund et al., 1991; Tsuji and Karagatzides, 1998).

Pb toxicity to both plants and animals is well documented. Divalent Pb (Pb^{2+}) displaces other essential divalent micronutrient ions such as iron, calcium and zinc that are necessary in cellular processes. This results in disruption of metabolic pathways and protein synthesis and changes in cell structure that can cause cell death (Company et al., 2008). Plants take up bioavailable Pb from the sediment or water through roots or leaves (Crowder, 1991; Sharma & Dubey, 2005). High concentrations of Pb in plant cells can cause loss of leaves and blackened roots (Sharma & Dubey, 2005), decreased rates of chlorophyll and protein synthesis and disruption of the electron transport chain and Calvin cycle (Patra et al., 2004). Animals are exposed to Pb through direct ingestion of Pb shot, ingestion of Pb dissolved in water, ingestion of Pb-contaminated food or particulate matter, or sorption of Pb to the surface of the organism. Sublethal effects of Pb on invertebrates include growth inhibition, developmental delays, morphological malformations, and neurological effects (Cohn & Widzowski, 1992; Gerhardt, 1994; Morley et al., 2003; Timmermans et al., 1992; Vermeulen et al., 2000). Vertebrates also exhibit sublethal effects of Pb toxicity, including delayed development and physical deformities (Berzins & Bundy, 2002; Stansley et al., 1997). Toxic effects of chronic exposure to Pb in fish include altered behavior (Rademacher et al., 2003), suppressed immune response (Eisler, 1988), degeneration of muscle and neurons, slowed growth and reproductive problems. High levels of Pb exposure can cause paralysis and death (Eisler, 1988; US EPA, 1976). Pb poisoning of waterfowl has been shown to cause anemia and muscular paralysis (Mudge, 1983), which compromises a bird's ability to forage, avoid predation and migrate (Bellrose, 1959; Clemens et al., 1975; Eisler 1988). Adverse effects of Pb in humans include learning difficulties, developmental delay, anemia, hearing loss, declines in mental functioning and memory loss, cardiovascular and kidney problems, and reproductive problems (CDC, 2015).

Trap Shooting in the La Crosse River Marsh:

The La Crosse River Marsh (LRM) is an urban wetland located within the City of La Crosse, Wisconsin. The LRM has been recognized for its high level of biological diversity in an urban setting (WI DNR, 1990) and is part of the larger 435 ha La Crosse River Valley wetland complex, situated on the southwestern border of Wisconsin at the confluence of the Mississippi and La Crosse Rivers along the Mississippi Flyway (Fig 1A). The LRM resides within the La Crosse River floodplain and is hydraulically connected to the La Crosse River and the Upper Mississippi River National Wildlife and Fish Refuge during periods of high water. During normal hydrologic conditions, the LRM study area is classified as a shallow to deep emergent marsh with open water and a few small islands, bordered to the south by a late-Wisconsin age sand and gravel glacial meltwater terrace escarpment (Knox, 1996). The local wetland plant community includes submersed (*Ceratophyllum demersum* and *Chara* spp.), emergent (*Sparganium eurycarpum*), and free-floating (Lemnacea) vegetation. The interspersion of open water and marsh vegetation attracts a wide variety of migrating waterfowl and wading birds, and provides habitat for fish including pike (*Esox lucius*), bluegill (*Lepomis macrochirus*), and bullhead (*Ameiurus melas*). The area is traversed by raised gravel trails and is heavily used for outdoor education and recreational activities including running, fishing, trapping and wildlife viewing (Moyer, 1989).

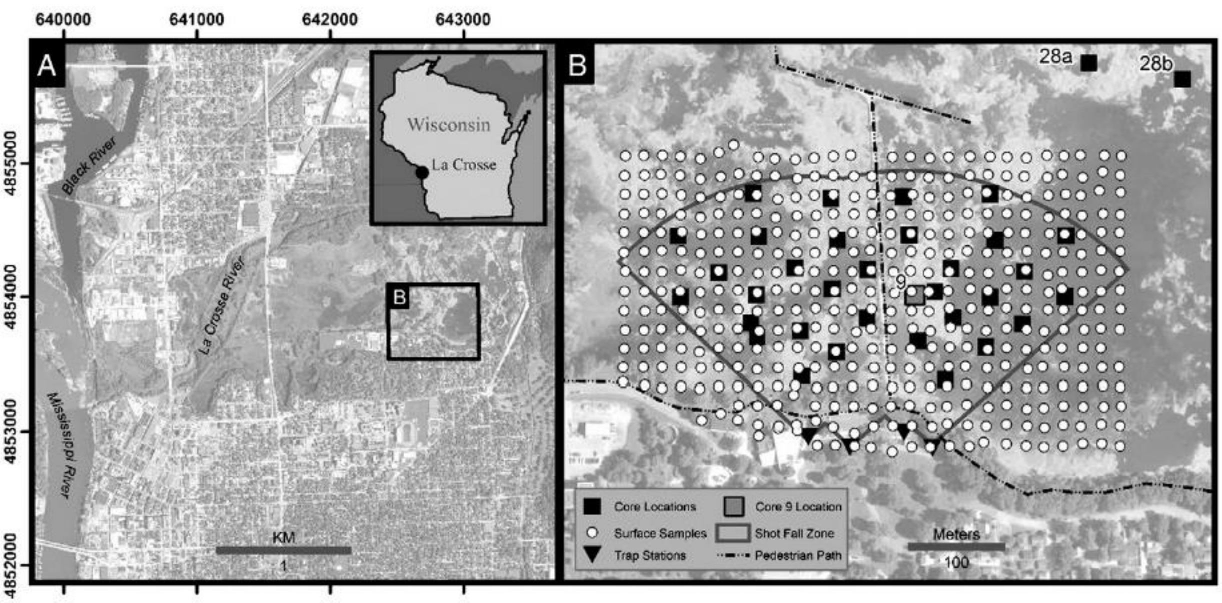

Figure 1. Maps of study location and sediment sampling sites. (A) 2010 aerial image showing the LRM study area and confluence of the La Crosse and Mississippi Rivers within the city limits of La Crosse, WI (inset map). (B) Study area showing former trap shooting stations, shot fall zone, and surface sediment sample and core sample locations collected by UWL. Sediment cores used to establish local background Pb concentration levels are labeled (28a, 28b) and shown in the upper right corner of Panel B.

The La Crosse Gun Club operated four trap fields overlooking a 15 ha section of the LRM from 1929 to 1963 (Fig. 1B). Large quantities of Pb shot were regularly discharged in the LRM until the City declined to renew the Club's lease in 1963. Work completed in conjunction with the WI DNR in the early 1990s found Pb shot densities as high as 41,600 pellets/m^2 (Fors, 1994). With the potential to negatively impact organisms throughout the wetland, and the frequent use of the site by humans, it is important to understand the fate of the legacy Pb.

We (UWL research team and WI DNR research team) utilized a collaborative approach to survey the LRM to better understand the extent to which Pb has mobilized physically, chemically and biologically within the LRM ecosystem, and to determine whether the contaminated sediments pose a toxicological risk. Parallel data was collected by researchers from the UWL and the WI DNR. Here we present the findings from our field and laboratory research in the context of the EPA Urban Waters Grant Objectives.

PROJECT OBJECTIVES:

Objective 1: Assess LRM biogeochemistry and sediment toxicity.

Subobjective 1.1: Analyze the physical and chemical characteristics of the marsh sediment and water.

An extensive study was conducted on the spatial distribution of Pb shot and Pb contaminated sediments in the LRM. The findings of this research helped shape the sampling design used in the subsequent research by UWL and the WI DNR. The following section summarizes our findings on the spatial distribution of Pb within the LRM sediments. See Appendix A for the full UWL sediment study published in *Science of the Total Environment* by Perroy, Belby, and Mertens (2014). See Appendix B for the full summary of WI DNR sediment results by Sullivan and Rasmussen (2012).

1.1.1: Assessment of Pb-concentrations and chemical characteristics of marsh sediments.

<u>UWL sediment sampling methods</u>: Field sampling was focused within a 300 x 520 m area in the potential shot fall zone located immediately to the north of the four former trap fields (Fig. 1B). Within this zone we established a 20 x 20 m grid for surficial (0-5 cm) sediment sampling and a 40 x 80 m grid for sediment cores (30-90 cm long), with denser sediment core collection occurring within the zone of expected maximum Pb shot. A total of 456 georeferenced surficial sediment samples were taken from the marsh using a Wildco hand core sediment sampler and 36 georeferenced deeper cores were collected using a modified Livingston (Bolivia) drive rod piston corer. Surficial samples were also collected from terrestrial sites along the pedestrian path bisecting the study area and the terrace surface adjacent to the form trap fields. Topographic and bathymetric data in the study area were collected using a Topcon total station to survey 2,072 points (5-12 m spacing) to create a 10 m resolution digital elevation model of the study site in ArcGIS.

Surficial and core sediment samples were dried and then lightly ground with a rubber-tipped pestle to pass through a 2 mm sieve. All observed Pb pellets were immediately removed, although fine fragments of shot may have passed through the 2mm sieve. Approximately 2.5 g of sediment from each sample was placed in a polyethylene cup with a mylar window film cover. All cups were X-rayed, and any observed intact Pb shot and shot fragments >0.5 mm were removed prior to XRF analysis.

Prepared sediment samples were subjected to X-rays for 60 seconds using a Bruker portable X-ray fluorescence TRACER III–V+ system. Raw detector counts were translated into quantified measures of near-total Pb elemental concentrations using a custom XRF calibration curve. The curve was calibrated using a subset of 48 LRM samples analyzed by XRF and then by ALS Chemex via ICP-AES following a nitric aqua regia digestion. An additional ten samples, analyzed by XRF and also sent to ALS Chemex for ICP-AES analysis, were held out of the calibration procedure and were used to validate the calibration model.

All undisturbed whole sediment cores were X-rayed to quantify Pb shot abundance and vertical distribution using a Varian medical systems A-192 X-ray tube at Gundersen Health System hospital in La Crosse. Digital radiographs for a given core were stitched together in Adobe Photoshop and a moving window was used to manually count Pb shot at a 2 cm interval. Shot was clearly identifiable in the cores. X-rays were taken for 8 cores from dual perspectives to test for consistency of shot counts, and shot was separated from cores 7a and 7b and counted manually for method verification.

Pb sediment values were assigned XYZ coordinates from the sample's GPS coordinates and bathymetric datasets and brought into MATLAB for spatial interpolation using the natural neighbor method. Raw shot count data from the sediment cores were scaled up to fit the modeled grid cell sizes. A map of total Pb shot was created by summing the scaled pellet data for each sediment core and interpolating the results across 2D space. A 'surface' 1 m^2 resolution 2D model of Pb concentrations was created using only samples from the upper 5 cm of LRM sediments. A 3D model (XYZ, 1 m × 1 m × 0.02 m) of Pb sediment concentrations was also created for the entire study area using data from both the upper 5 cm and the deeper sediment cores.

Organic matter content of core sediment was determined by loss on ignition at 550 °C. Analysis of sediment pH was completed using a 1:1 mixture of sediment to water. Sediment particle size was determined via laser diffraction on a Malvern Mastersizer 2000 following 24 h of dispersion in sodium hexametaphosphate solution.

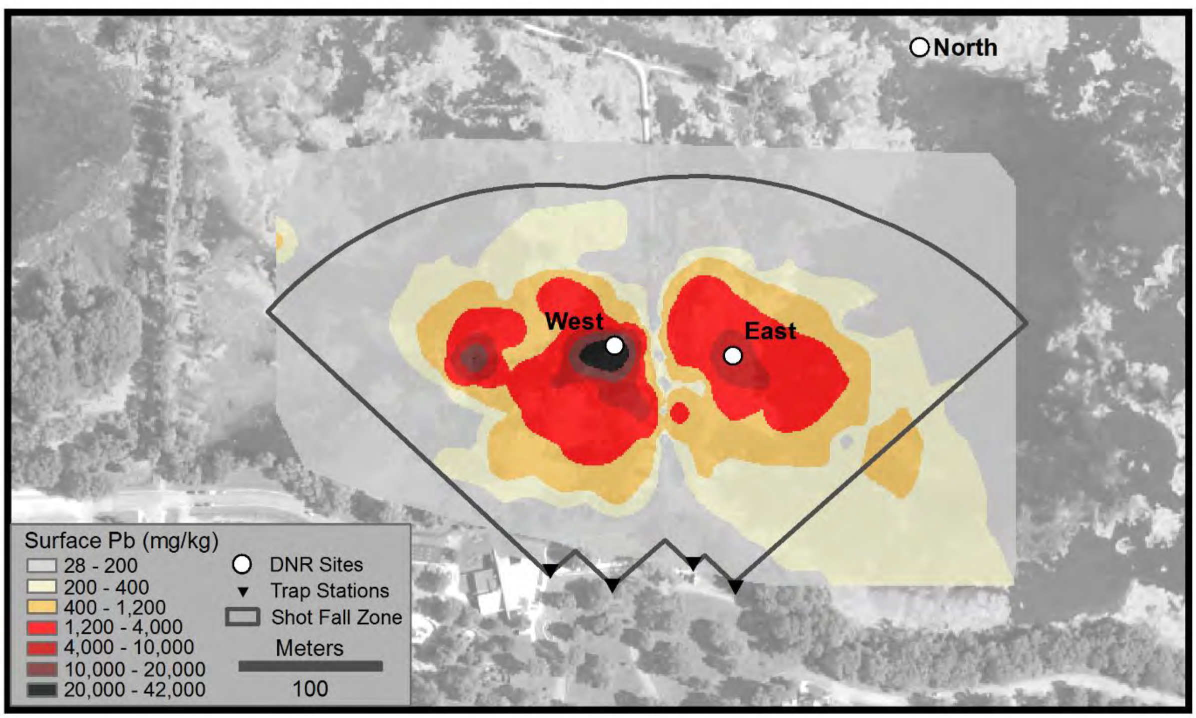

Figure 2. Location of WI DNR sampling sites on top of spatially interpolated surface (0-5 cm) Pb concentrations in LRM sediments.

Wisconsin DNR sediment sampling methods: The WI DNR collected bed sediments at three LRM monitoring sites (North, East and West) using a petite ponar (Fig. 2). An additional sample was collected at Lizzy Pauls Pond (Upper Mississippi River Pool 5) to serve as a reference. Several ponar grab samples were collected at each site and were placed into a large stainless steel bowl then mixed to obtain a composite sample. The sediment was then placed into lab-supplied sampling bottles for total volatile solids (TVS), total organic carbon (TOC), and Pb analysis. A small portion of the composite samples was placed into Ziploc bags for particle size analysis. The remainder of the sample (about 2 gallons) was placed into lab-supplied 5-gallon pails and secured with a cover. Chemical analysis and toxicity testing were performed by the Wisconsin State Laboratory of Hygiene (WSLH). Sediment particle size and pH analysis was performed by the University of Wisconsin Soil and Plant Analysis Laboratory.

Cylindrical glass sediment traps (500ml tall –ICHEM jars) were deployed at the North, East, and West locations in the LRM during April 5 to July 3, 2012 to provide a time-integrated sample for evaluating suspended sediments. The traps were deployed at the three depths within the water column (near surface, mid-depth and near the sediment-water interface). A vertical composite sample was obtained for each site by combining the accumulated sediment for each sampling depth at a site into a single sample prior to shipping to the WSLH for Pb, TVS, and TOC analyses. Another set of sediment traps were deployed at the North, East, and West locations from April 16 to July 17, 2013. These traps were all set at either 0.5 m above the sediment surface or mid-depth if the water was shallower than 1 meter.

Results: Pb concentrations in sediments

UWL sediment results: The elevation model of the study site shows distinct topographic differences between the east and west sides of the raised gravel path that bisects the study area (Fig. 3). With the exception of the deeper cut immediately adjacent to the raised path, the west side of the study area tends to be characterized by shallow depths and emergent islands during typical water levels. Depth on the east side of the raised path generally increases with distance from the berm.

Sediment in the shot fall zone is typical of a floodplain marsh. Surface sediment is characterized by flocculent silt with high organic matter content and low bulk density, transitioning to high bulk density silt and clay with lower organic matter content. Below this zone is a layer of sand, likely deposited during lateral migration of the La Crosse River. This general sequence is found throughout the study area, though intrusions showing abrupt changes in particle size and organic matter content were found in a number of the sediment cores. Sediment pH throughout the study area was generally acidic (mean = 5.6), ranging from 4.9 to 7.

A total of 1,351 sediment samples (surface, sediment cores and footpath) were analyzed for Pb concentration (Fig. 1). Sediment Pb concentrations in the cores sampled from the wetland ranged from a mean local background level of 51 mg/kg found in cores 28a and 28b located 150 m north of the potential shot fall zone to a maximum of 26,700 mg/kg found at a depth of 22 cm in Core 9 located 140 m north of the trap stations (Figs. 1 & 4, Table 1). Sediment Pb concentrations in the core data generally show peak values in association with peak shot counts 10–30 cm below the sediment surface, typically followed by a decrease to background levels at depth.

Surface sediment concentrations in the aquatic portion of the shot fall zone were highly contaminated, with 21.3% of the samples exceeding the EPA's soil contamination threshold of 400 mg/kg (Table 1). The highest surface sediment Pb concentrations corresponded with the region of highest shot counts and highest core Pb concentrations. All samples collected from the footpath that bisects the study area were below 400 mg/kg, with 84.7% below 130 mg/kg. Samples collected from the terrestrial surface adjacent to the former trap station sites all had Pb concentrations below 400 mg/kg. From the 2D and 3D interpolated models for Pb sediment concentrations in the LRM study area (Fig. 5, Table 2), it is estimated that 8.9 ha of surface sediment and 64,270 m^3 of total sediment exceeds the 130 mg/kg Pb probable effect concentration above which adverse biological effects in freshwater systems are expected to be frequent (MacDonald et al., 2000). It is estimated that the EPA's contaminated soil threshold of 400 mg/kg (US EPA, 2001) was exceeded across 3.8 ha of surface sediment and in 31,700 m^3 of total sediment.

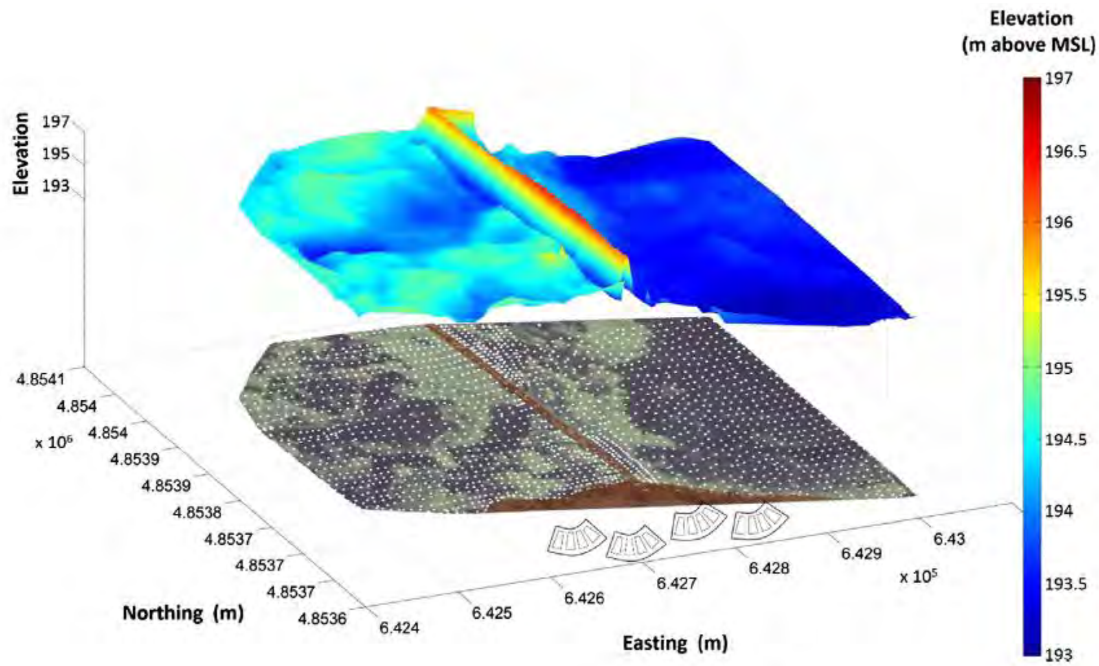

Figure 3. 3D model of study site topography created using total station survey points. Raised linear feature is a gravel path that splits the study area into west and east sections. Aerial photo with XY locations of total station survey points shown below 3D model. Brown shaded areas on aerial photograph signify dry terrestrial components of the study area; white symbols signify trap station locations. Projection is WGS 84 UTM Zone15, elevation in meters above mean sea level.

Pb shot was typically buried 10-30 cm below the LRM sediment-water interface. The greatest concentration of shot (51,154 pellets/m^2) was found in Core 9 in the center of the study area, 140 m north of the former trap shooting stations. All shot from cores 7a and 7b examined under a stereomicroscope had a pitted, irregular surface coated with a corrosion crust, and little to no unaltered metallic Pb visible on the surface. X-ray diffraction analysis indicates that Pb oxides (PbO) are the dominant decomposition products found in the shot crust, with lesser amounts of cerussite ($PbCO_3$) and shannonite ($Pb_2O(CO_3)$) present. The 2 cm increment Pb shot count data was summed for each core and used to create an interpolated map of total buried Pb pellets (Fig. 6). It is estimated that 4.2×10^8 Pb pellets, or 2.0×10^4 kg based on the average mass of shot recovered from cores 7a and 7b, remain in the LRM study area. No Pb shot was found on the pedestrian path or on the dry upland terrace immediately adjacent to the former trap station sites.

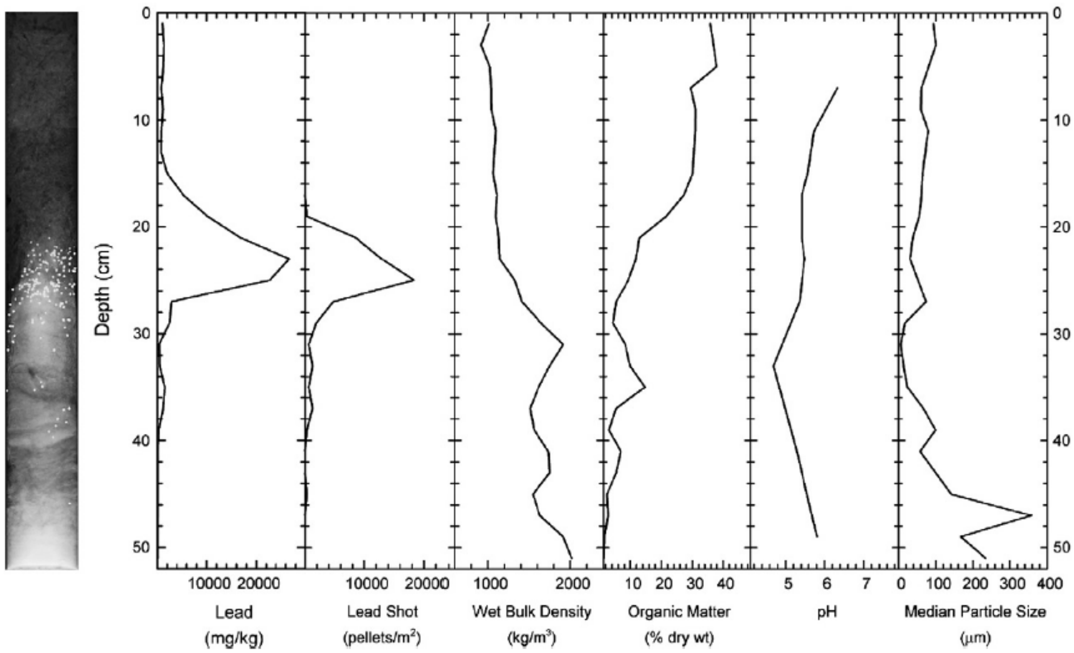

Figure 4. Representative sediment core dataset for Core 9. X-ray image at left shows location and abundance of Pb shot within the core (white dots).

Table 1. Summary of Pb concentration from surface and core samples. The number of samples (n) and the percentage of the total (%) are given for each category.

Lead mg/kg	**Shot Fall Zone Cores (2cm intervals)**		**Shot Fall Zone Surface Samples (0-5cm)**		**Shot Fall Zone Footpath Samples**		**Background Cores 28a & 28b (2 cm intervals)**	
	n	**%**	**n**	**%**	**n**	**%**	**n**	**%**
0-36[a]	232	28.0	12	3.0	28	38.9	7	14
37-130[b]	304	36.7	174	43.4	33	45.8	43	86
131-400[c]	110	13.3	129	32.2	11	15.3	-	-
401-1,200[d]	102	12.3	42	10.5	-	-	-	-
1,201-5,000	60	7.2	37	9.2	-	-	-	-
5,001-10,000	13	1.6	3	0.7	-	-	-	-
10,001-20,000	5	0.6	1	0.2	-	-	-	-
>20,000	2	0.2	3	0.7	-	-	-	-
Mean (ppm)	602		715		71		51	
Median (ppm)	53		52		40		47	
Max (ppm)	26,709		42,854[e]		288		80	
Min (ppm)	14		26		26		15	

[a] Threshold effect concentration below which adverse biological effects n are expected to be rare.
[b] Probable effect concentration above which adverse biological effects are expected to be frequent, identified in Wisconsin DNR's Consensus-Based Sediment Quality Guidelines.
[c] EPA hazard criteria for bare soils in residential play areas.
[d] EPA hazard criteria for bare soils in residential non-play areas.
[e] Outside of calibration curve maximum of 27,700 mg/kg.

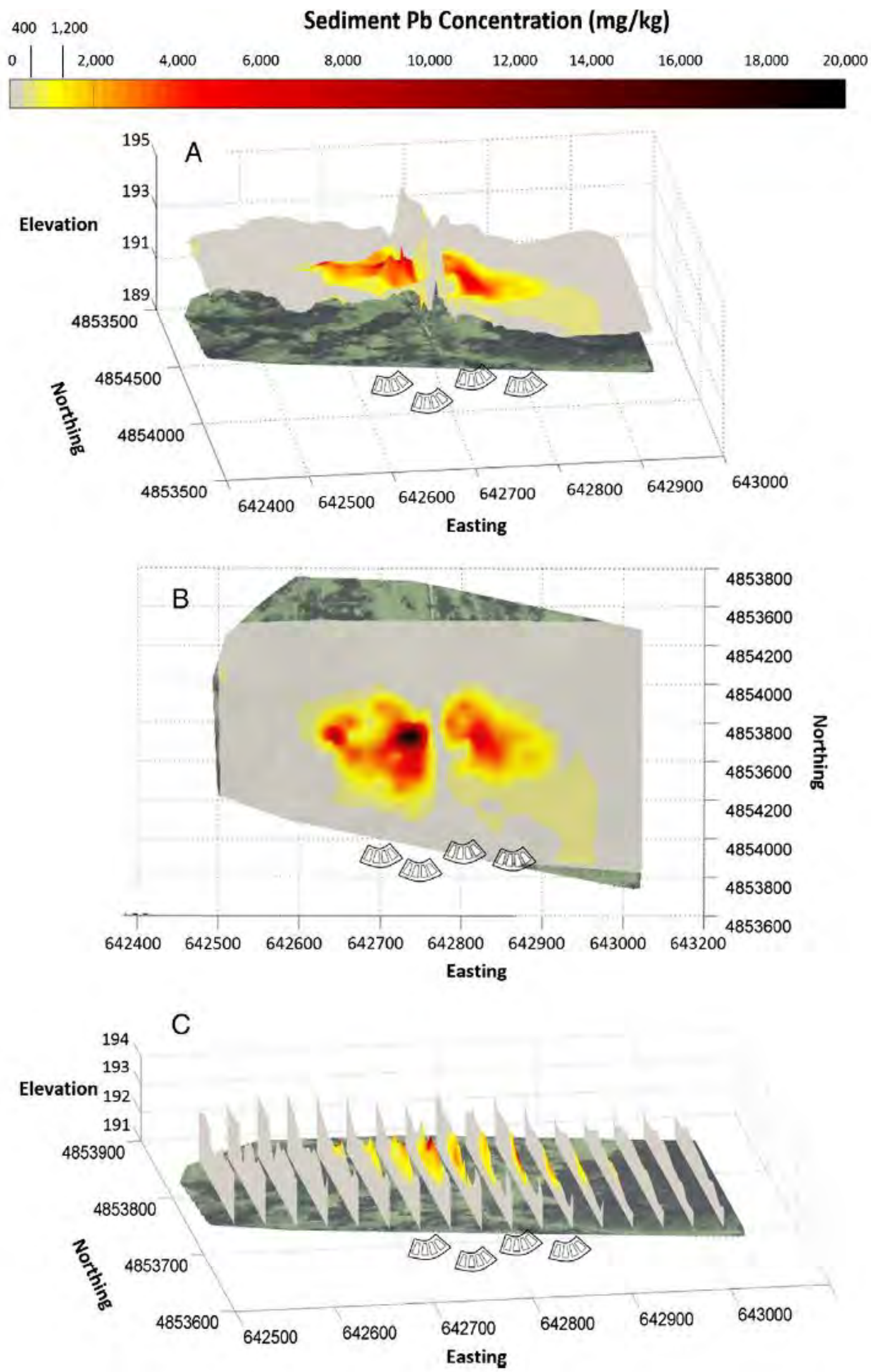

Figure 5. Spatially interpolated Pb concentrations in LRM sediments. (A) Oblique view depicting surficial (0-5 cm) sediment concentrations of Pb, draped over a 10 m resolution DEM; (B) top–down view of the same data as shown in Panel A; and (C) 2D slices through volumetric model showing spatial distribution of Pb contamination with depth. A 2010 aerial image and trap field locations are provided for reference.

Table 2. Pb modeling results from surface and core sample data at three different threshold limits.

Threshold Pb concentration (mg/kg)	Surface sediment estimate (hectares)	Volumetric estimate (m^3)
>1200	1.9	13,220
>400	3.8	31,700
>130	8.9	64,270

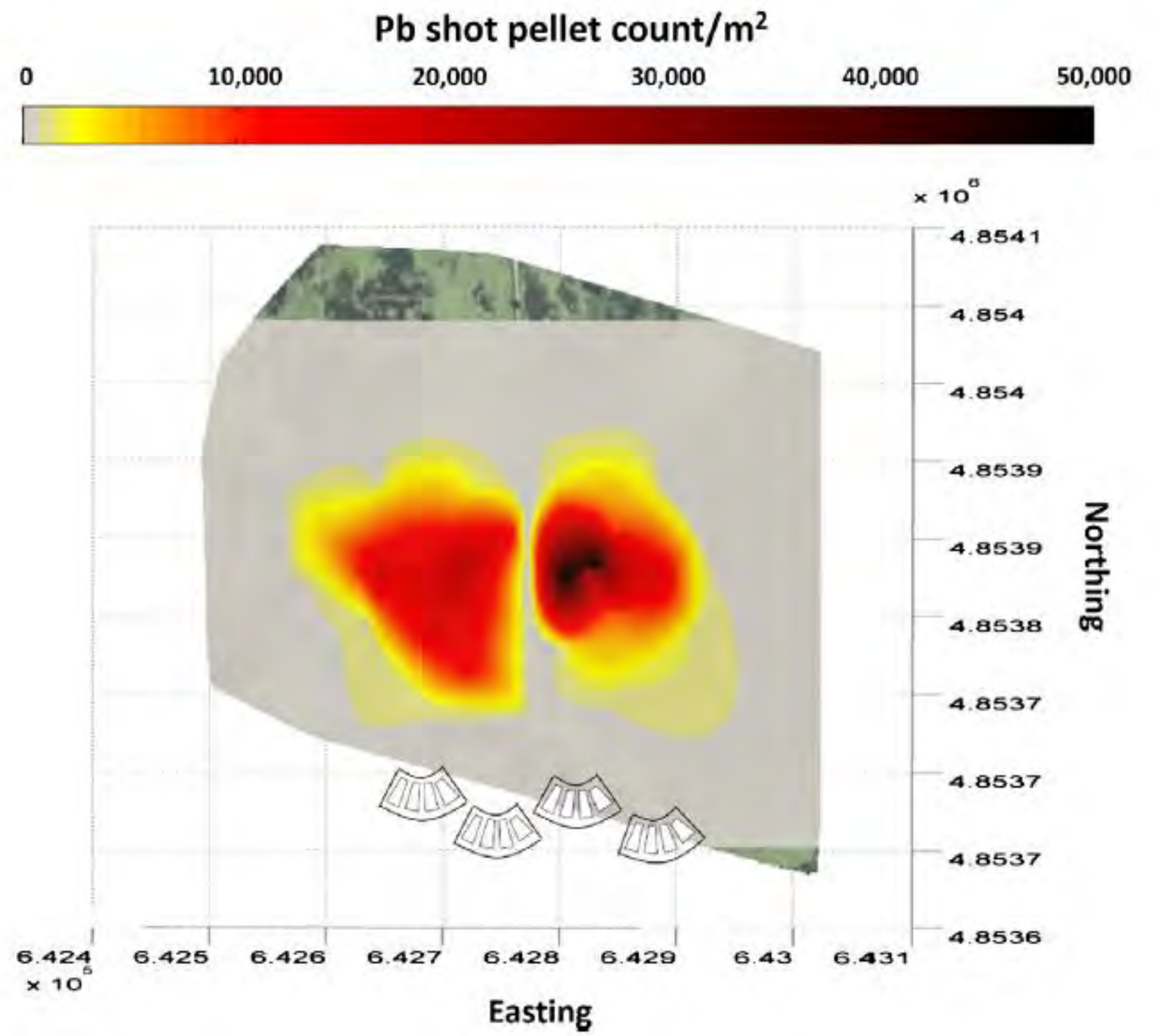

Figure 6. Top–down view of the total number of Pb pellets in LRM study area sediments per square meter. Trap station locations provided for reference.

<u>Wisconsin DNR sediment results:</u> Sediment from the LRM was silty with very high organic matter content as indicated by high TOC and TVS (Table 3). Sediment Pb concentrations in the LRM indicated moderate to very high Pb contamination (59 to 5,360 mg/kg) with highest levels reported at the East and West locations where maximum Pb shot fallout from the former trap shooting range would be expected. Pb concentrations at the East and West sites greatly exceeded the probable effect concentration of 130

mg/kg identified in the WI DNR's Consensus-Based Sediment Quality Guidelines. The North site had substantially lower Pb contamination, with concentrations exceeding the threshold effect concentration (TEC, 36 mg/kg) indicated in these guidelines. In contrast, bed sediment Pb concentrations from the reference site (Lizzy Pauls Pond) were low (11 mg/kg).

Sediment from the East site contained the highest level of Pb contamination (5,360 mg/kg) and this material had leachable Pb concentrations (TCLP analysis) slightly exceeding hazardous material classification (> 5 mg/L). The TCLP analysis is normally performed on contaminated material to help classify the material for disposal purposes and to provide an index of potential contaminant leaching. The testing was conducted at WI DNR to provide a cursory evaluation of Pb mobility and it should be recognized that this potential is strongly influenced by ambient conditions which may differ substantially from leaching conditions performed in a more controlled laboratory environment.

The sediment traps revealed very high Pb concentrations (2,670 to 3,660 mg/kg in 2012 and 1,290 to 1,590 mg/kg in 2013) at the East and West sites at locations where bed sediment Pb contamination was expected (Table 4). These concentrations were substantially greater than similar trap samples collected from the Mississippi River at Lock and Dam 3 and 4 during the spring of 2012, which had concentrations of 12 mg/kg at both sites. The trap samples deployed in the LRM contained sediment very high in organic matter as reflected in the TVS and TOC contents. Sediment traps in the LRM also accumulated more sediment at increasing water depths. It is suspected the bottom traps deployed during 2012 accumulated surficial bed sediment either due to sediment resuspension or entrainment of bed sediment as a result of the trap opening being below the sediment-water interface during the deployment period. The bed sediment at all sites was unconsolidated and flocculent in nature and resulted in some uncertainty in defining the depth of the sediment-water interface during trap deployment. The relatively shallow water depths during 2012 (0.15 to 1 m) suggests the trap samples were likely influenced by sediment mobilization due to wind-induced mixing or bioturbation of surficial sediment during the deployment period. The 2013 sediment traps were deployed approximately 0.5 m above the sediment surface, and it is believed the sediment Pb values from 2013 better reflect the suspended sediment concentrations because they were likely not influenced by bed sediment entrainment during deployment.

Table 3. Bed sediment results obtained for the LRM and Lizzy Pauls Pond. Samples collected by WI DNR in the LRM (North, West and East sites) on July 23 and Lizzy Pauls Pond on July 24, 2012.

Measurement	North Site	West Site	East Site	Lizzy Pauls Pond
Pb (mg/kg)	59	3820	5360	11
Pb TCLP[1] (mg/L)	*	2.01	5.13	*
Total Volatile Solids (%)	28.1	37.5	24.4	16.1
Solids (%)	13.2	11.7	16.6	16.4
Total Organic Carbon (%)	10.4	11.1	19.1	5.9
Sand (%)	19	23	11	3
Silt (%)	60	60	61	80
Clay (%)	21	17	28	17
pH	6.7	6.5	6.3	6.8

*No test performed because of low sediment Pb concentrations
[1]Toxicity Characteristic Leaching Procedure

Table 4. Water column sediment trap results for the LRM. Deployment periods: April 5 to July 3, 2012 and April 16 to July 17, 2013.

Measurement	North Site		West Site		East Site	
	2012	2013	2012	2013	2012	2013
Pb (mg/kg)	62	53.3	2,670	1,590	3,660	1,290
Total Volatile Solids (%)	27.3		41.8		32.3	
Solids (%)	7.4		5.7		6.9	
Total Organic Carbon (%)	8.59		14.2		8.8	

1.1.2: Pb level assessment in marsh water

UWL water sampling methods: Surface water and sediment pore water were sampled four times at five locations within the LMR during 2013-2015 to assess the mobilization of Pb from solid phases. The "control" site was located farthest from the trap shooting range where sediments had a Pb concentration <60 mg/kg, while the remaining four sites were adjacent to locations with high sediment Pb (Fig. 7).

Surface water and pore water samples were collected from a canoe, utilizing "clean techniques" that ensure non-contamination of Pb by the collection equipment or craft. At each site surface water was collected from the midpoint of the water column with acid-washed Teflon tubing and a peristaltic pump. One sample was pumped directly into a Teflon bottle to determine total Pb, and a second sample was filtered through an acid-washed in-line 0.45 µm polyethersulfone filter (Whatman Polydisc) to determine dissolved Pb. The Teflon bottles were shipped to the WSLH for Pb analysis by ICP-MS. Separate water samples collected from each site were analyzed for hardness by the WSLH.

Samples for sediment pore water were taken in the field by petite ponar and transferred using clean protocols into double-lined polyethylene bags for transport to the laboratory. Care was taken in the field to incorporate as little surface water as possible into the sediment grab sample, but a minimum of mixture (< 10% by volume) was likely. Pore water was extracted from sediment slurries by centrifuging in acid-washed 1-L polypropylene tubes at 8000 rpm for 10 minutes with a Beckman Coulter Avanti J-26C centrifuge. The centrifugate was then carefully decanted and filtered through a 0.45 µm in-line filter into a Teflon bottle for shipment to the WSLH. Pore water and surface samples that did not meet strict quality control standards during sampling are not reported in the results.

Surface water quality measurements (DO, pH, conductivity, turbidity and temperature) were collected at a depth of 15 cm throughout the three year study period using a Hydrolab Quanta. Data from sampling during the summer 2015 is presented here.

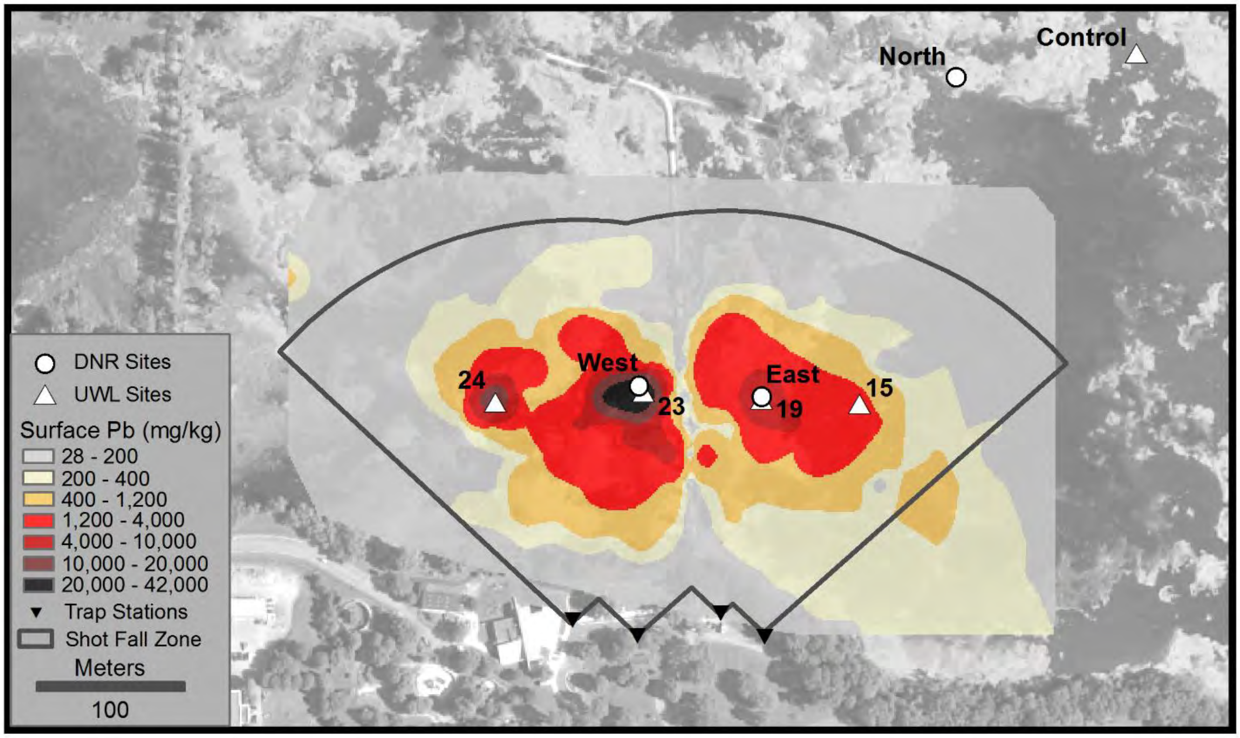

Figure 7. UWL and WI DNR water sampling sites. UWL sites were within 10 meters of the points shown on the map.

Wisconsin DNR water sampling methods: Surface water quality field measurements (DO, pH, conductivity, turbidity, and temperature) were collected 15 cm below the water surface at biweekly to monthly intervals from April to September 2012 at the North, East, and West sites in the LRM (Fig. 7). Water chemistry (nutrients, metals, chlorophyll a) samples were collected at the same three LRM sites and Lizzy Pauls Pond in late July and early August 2012 and coincided with sediment sampling or nutrient evaluations. A continuous dissolved oxygen and temperature logger was installed in the LRM (North Site) during July to September to document diurnal changes. Total Pb analysis was initially performed using atomic absorption (AA Furnace), which had a Pb detection level of about 1 ug/L. If Pb concentrations in the water samples were below detection using this method, then the lab was instructed to re-run the analysis on separate samples that were collected using low-level techniques followed by low-level Pb analysis (ICP-MS), which yield substantially lower detection levels (0.004 ug/L). This approach was followed to try to save on analytical costs. Water samples were also collected from the East site over 8 consecutive days in August 2013 and analyzed for total Pb by the WSLH to determine the average 4-day concentration, which is more appropriate for comparison to the chronic criterion.

Results: Pb concentrations in water

UWL water results: Field water quality measurements from the summer 2015 followed similar trends across the sites, though turbidity, pH, and dissolved oxygen had moderate variation across the sites within a given day (Fig. 8). Changes in weather and site depth, fetch relative to wind direction, and productivity likely explain variability across time and space. The surface water had a pH above 7 at all sites throughout the sampling period, with the lowest pH values typically found at sites 23 and 24 on the west side of the raised trail that bisects the study site. The marsh water is classified as moderately hard to hard (hardness values of 112-135 mg/L). The hardness values are consistent across the sites on a given day and have minor variability between the June 2014 and May 2015 sampling dates (Table 5). The hardness values are also consistent with the average value of 138.8 mg/L found by the WI DNR in August 2013.

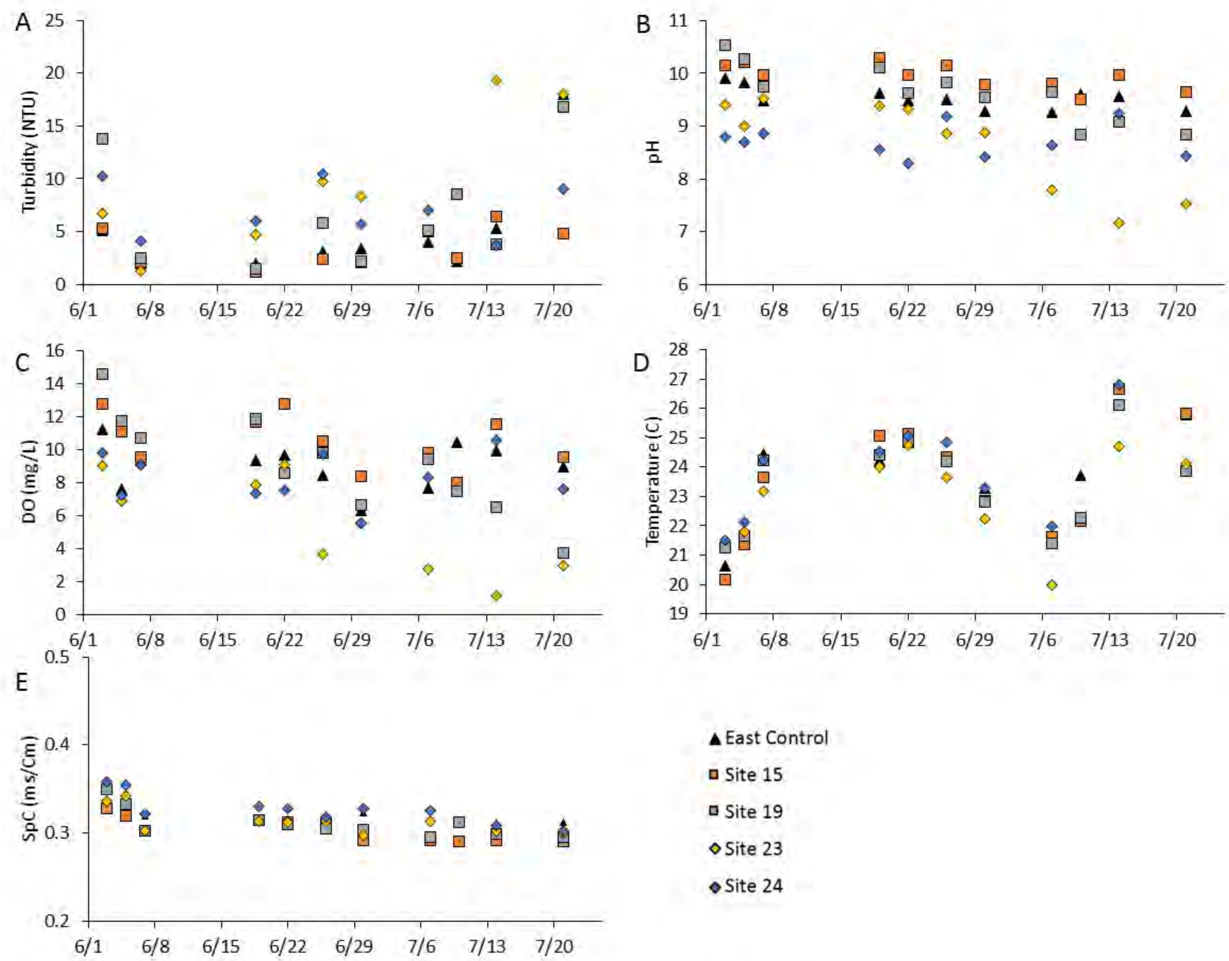

Figure 8. Water chemistry at LRM field sites collected by UWL during June to July 2015. (A) turbidity, (B) pH, (C) dissolved oxygen, (D) water temperature, and (E) specific conductance. Samples were collected by the UWL about 15 cm below the water's surface.

Total Pb concentrations in surface waters varied from 0.530 to 10.6 µg/L at the sampling sites, with the highest values generally found at sites with the highest sediment Pb levels (15, 19, 23, 24). Dissolved Pb in the surface water varied from 0.127 to 7.09 µg/L and was generally an order of magnitude lower than the total Pb measured at each site. The higher total Pb levels reflect the presence of Pb bound to suspended particulate matter in the water column. Pore water Pb levels varied from 0.443 to 409 µg/L, with the lowest levels occurring at the control site. The higher Pb concentrations in the pore water reflect the water's longer residence time adjacent to the solid phase Pb and the lower dilution of the interstitial water relative to surface water.

Acute and chronic Pb criterion are based on the WI DNR's surface water quality criteria guidelines, with harder samples having higher contamination thresholds. Because no hardness values are available for July 2013, the minimum hardness value sampled during three separate years by UWL and the WI DNR was used for this date to determine if samples exceeded the WI DNR's acute and chronic contamination criteria. Following this conservative approach, none (N=17) of the total Pb concentrations from the surface water exceeded the chronic criteria or the acute criteria.

Table 5. Water column Pb results for the LRM during four sampling periods.

Site ID	Date	Total (µg/l)	Dissolved (µg/l)	Pore (µg/l)	Hardness (mg/l)	Acute Pb Criterion (ug/L)	Chronic Pb Criterion (ug/L)
Control	7/11/13	1.62	0.451	1.48			
15	7/11/13	1.40	0.561	39.2			
19	7/11/13	1.41	0.343	108, 113, 233[a]			
23	7/11/13	5.90	1.35	275, 409[a]			
24	7/11/13	10.6	7.09				
Field Blank	7/11/13	0.0199	<LOD (0.0041)[b]	0.826			
Control	3/14/14		0.127				
15	3/14/14		0.392				
19	3/14/14		0.731				
23	3/14/14		4.17				
24	3/14/14		2.86				
Field Blank	3/14/14		0.0080				
Control	6/24/14	0.530	0.142	0.443	116	123	34
15	6/24/14	9.60	0.408	11.5	112	119	33
19	6/24/14	1.82, 5.56[a]	0.433, 0.460[a]	12.4, 6.60[a]	114	123	34
23	6/24/14	0.292	0.0630	84.2	125	133	37
24	6/24/14	1.01	0.206	110	120	128	35
Field Blank	6/24/14	0.0093					
Control	5/12/15	0.623	0.132	0.768	135	143	40
15	5/12/15	6.07	1.14	103	129	137	38
19	5/12/15	6.40, 10.5[a]	0.746, 0.881[a]	44.1	131	139	38
23	5/12/15	6.06	1.11	50.0	131	139	38
24	5/12/15	2.79	0.599	88.0	127	135	37
Field Blank	5/12/15	<LOD (0.0041)[b]					

[a]Multiple samples analyzed from same location.

[b]Limit of detection (LOD) for ICP-MS at Wisconsin State Laboratory of Hygiene

[c]Pore water sample collected on 7/11/14

<u>Wisconsin DNR water results:</u> Field water quality measurements (Fig. 9 and 10) indicated a substantial reduction in dissolved oxygen in the LRM in early July through early September 2012, and coincided with warm water and moderate to heavy aquatic vegetation growth. Dead and stressed game fish were found in the study area on July 3, 2012 and were likely a result of warm water and hypoxic to anoxic conditions. These conditions are not unusual for the LRM and fish kills have been reported in previous summers.

Total hardness values of 137 to 154 mg/L indicate the LRM has hard water (Tables 6 and 7). Nutrient concentrations in the LRM on July 23, 2012 indicated high to very high concentrations of total phosphorus (0.4 to 1.8 mg/L) and total kjeldahl nitrogen (2.9 to 11.7 mg/L). These concentrations were likely strongly influenced by sestonic material as reflected by relatively high turbidity levels, especially at the East and West sites, which had turbidity levels of 35 to 93 NTU. Total ammonia nitrogen concentrations were detected at all sites and were highest at the East and West sites in the LRM, 0.29 to 2.3 mg/L, respectively. It is suspected that these nutrient levels were strongly influenced by sediment disturbance or efflux from the sediments. Nitrite+nitrate-nitrogen (NO2+NO3-N) were not detected (<0.019 mg/L) at any site. This is commonly observed mid-summer in wetlands and backwaters along the Mississippi River and is related to reduced inflows of waters containing NO2+NO3-N, nutrient assimilation by plants and denitrification. Mid-summer field pH measurements revealed relatively low values (~6.5 to 7) at the East and West sites in the LRM in comparison to the North site or the reference site at Lizzy Pauls Pond (Tables 6 and 7; Fig. 9). The reason for this difference was not determined but may be an important factor influencing the Pb fraction in the dissolved versus particulate phase.

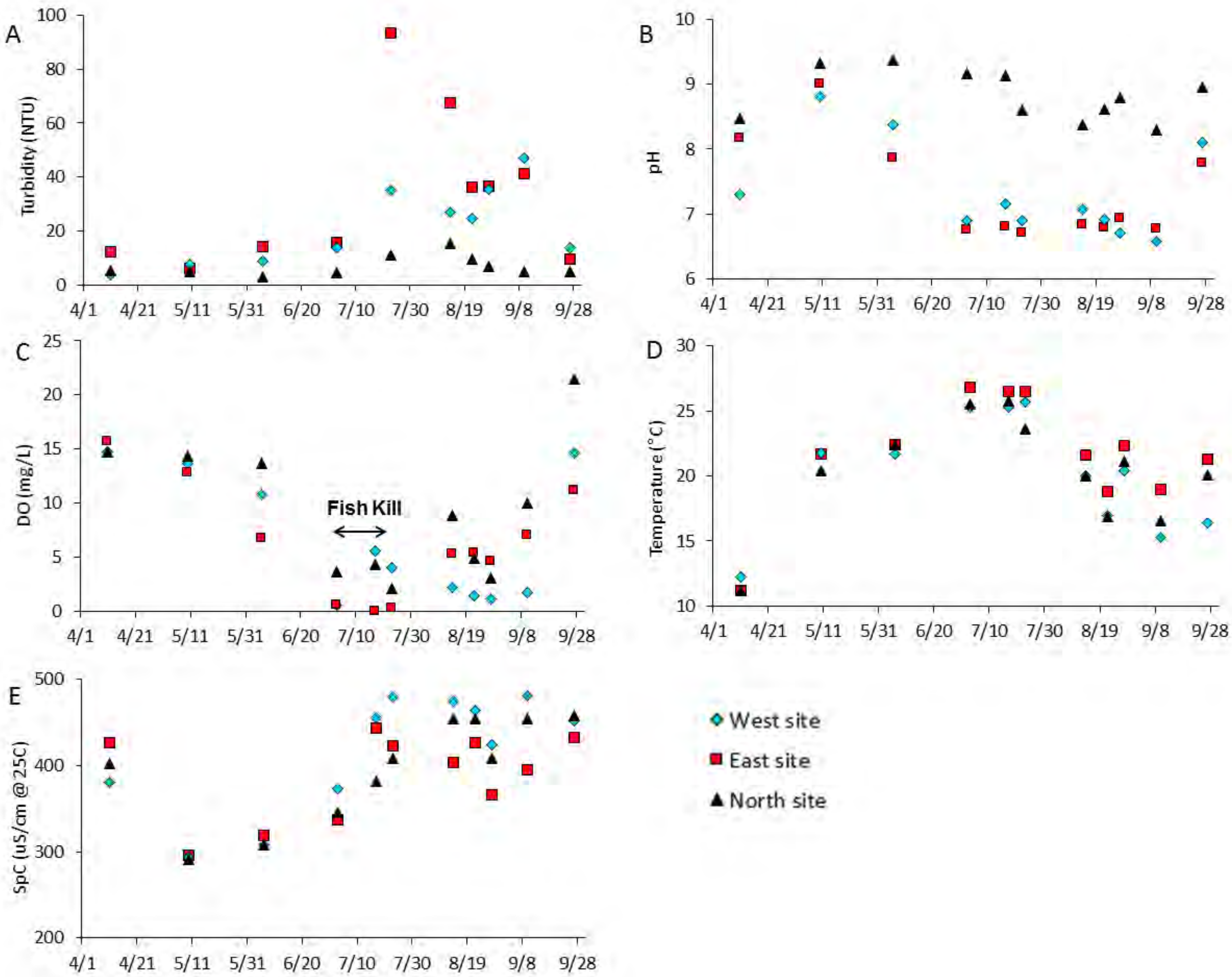

Figure 9. Water chemistry at LRM field sites collected by WI DNR during April to September 2012. (A) turbidity, (B) pH, (C) dissolved oxygen, (D) water temperature, and (E) specific conductance. Samples were collected by the WI DNR about 15 cm below the water's surface.

Total Pb concentrations in samples collected during July 2012 from the LRM ranged from 12.6 to 68.4 ug/L. The highest concentrations were present at the East and West sites, where bed and suspended sediments also revealed high Pb levels. The West site revealed an anomaly where the initial Pb result reported using atomic absorption method was <1 ug/L but the low-level analysis indicated 31.4 ug/L. The reason for this discrepancy was not established but may have reflected greater sestonic material in the sample collected for low-level Pb analysis. The highest total Pb concentration (68 ug/L) reported at the East site exceeded the chronic toxicity criterion when factoring in the total hardness of this sample (137 ug/L). Both the East and West sites had high to very high sestonic material in the sample as indicated by the high turbidity, 38 and 93 NTU, respectively.

Total Pb ranged from 7.93 to 28.7 ug/L (mean = 12.3) during the 8-day sampling period in August 2013. None of the eight samples collected exceeded the chronic or the acute criteria based on the water hardness measured over the same period (Tables 7 and 8). Total Pb concentrations were greatest at sites with the highest turbidity. The high water column Pb concentrations at these sites is likely strongly influenced by particulate material, especially if this material reflected mobilized bed sediment particles or detritus of plant material containing Pb.

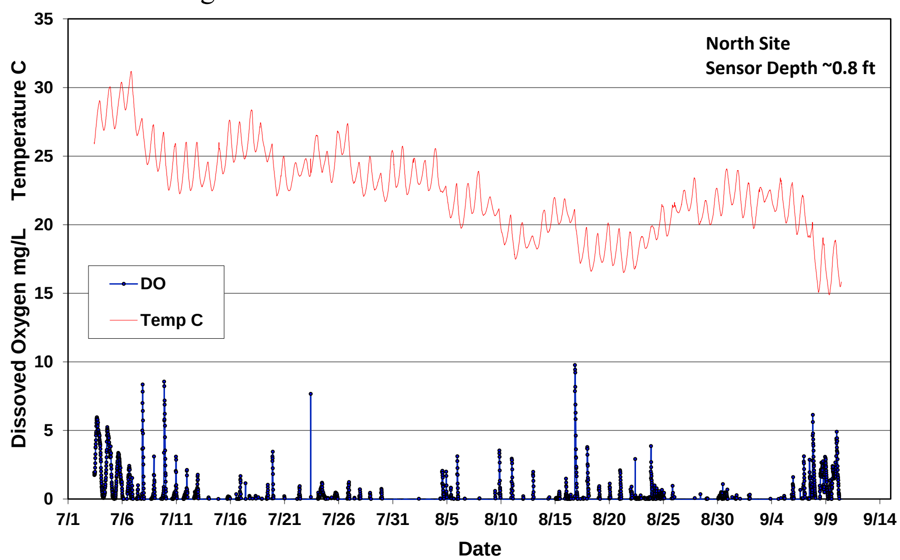

Figure 10. Continuous dissolved oxygen and water temperature monitoring results collected by WI DNR near the North site in the LRM in the summer of 2012.

Table 6. Field water quality and lab water chemistry results for the LRM and Lizzy Pauls Pond. Samples collected by the WI DNR in the LRM (North, West and East sites) on July 23, 2012 and Lizzy Pauls Pond on July 24, 2012.

Measurement	North Site	West Site	East Site	Lizzy Paul's Pond
Total Pb - AA Furnace (µg/L)	12.6	<1	68.4	<1
Total Pb – ICP-MS (µg/L)	*	31.4	*	0.0416
Total Calcium (mg/L)	26.9	26.7	27.6	20.5
Total Magnesium (mg/L)	19.5	21.4	16.7	21.5
Total Hardness (mg/L)	147	154	137	139
Dissolved oxygen (mg/L)	2.1	4.0	0.3	4.5
Temperature (C)	23.6	25.7	26.5	25.8
pH	8.6	6.9	6.7	8.3
Conductance (µS/cm)	409	480	423	281
Turbidity (NTU)	10.9	34.9	93.3	6.2
Total Kjeldahl-Nitrogen (mg/L)	2.94	4.15	11.7	0.90
NO3+NO2-N (mg/L)	<0.019	<0.019	<0.019	<0.019
NH3+NH4-N (mg/L)	0.079	0.292	2.33	0.060
Total Phosphorus (mg/L)	0.423	0.389	1.84	0.183
Dissolved Ortho-P (mg/L)	0.118	0.018	0.048	0.087

Table 7. Field water quality and lab water chemistry results for the East site of the LRM. Samples collected by the WI DNR 15 cm below the water surface between August 8, 2013 and August 13, 2013.

Date	Temp (C)	DO (mg/L)	Sp. Cond. (µS/cm)	pH	Turbidity (NTU)	Ca (mg/L)	Mg (mg/L)	Hardness (mg/L)
8/6/2013	23.6	6	341	7.50	8.0	28.6	14.7	132
8/7/2013	23.4	5.1	342	7.32	15.0			
8/8/2013	24.5	8.6	347	8.05	8.1			
8/9/2013	23.6	7.4	344	7.87	8.2			
8/10/2013	24.6	9.3	345	8.09	7.9			
8/11/2013	22.4	4.4	340	7.35	8.5			
8/12/2013	22.1	2.6	341	7.18	10.0			
8/13/2013	23.0	6.3	338	7.64	8.1	27.8	14.8	130
Average	*23.4*		*342*	*7.63*	*9.2*	*28.2*	*14.75*	*131*

Table 8. Water column Pb results for the East site of the LRM. Samples collected by the WI DNR 15 cm below the water surface between August 8, 2013 and August 13, 2013.

Date	Pb (µg/L)	Running 4-day Average Pb Concentration (ug/L)	Acute Pb Criterion (ug/L)	Chronic Pb Criterion (ug/L)
8/6/2013	12.9		139.8	36.6
8/7/2013	28.7			
8/8/2013	8.73			
8/9/2013	12.2	15.6		
8/10/2013	7.93	14.4		
8/11/2013	9.97	9.7		
8/12/2013	15.4	11.4		
8/13/2013	8.77	10.5	137.8	36.1
Average	*13.1*	*12.3*	*138.8*	*36.4*

Subobjective 1.2: Assess sediment toxicity of LRM using invertebrates and zebrafish as test organisms.

Given the high concentrations of Pb in the LRM sediments, we sought to determine whether they pose significant toxicological risk. We utilized several standard toxicity assays to determine risk to both invertebrates and vertebrates.

Wisconsin DNR Methods for measuring toxicity in invertebrates: Standard sediment toxicity assays were performed using larval midges (*Chironomus tentans)* and juvenile amphipod crustaceans (*Hyalella azteca*) to identify toxicity following exposure to LRM sediments (USEPA, 2001). All assays were run by the WSLH. Sediments were stored in the dark at 4ºC prior to testing. Homogenized sediments were placed in test beakers and tap water was added to each beaker at a ratio of 1:1.75 and acclimated to test temperature. After allowing the sediments to settle overnight, 10 organisms were randomly added to the test beakers containing artificial, reference (11 mg/kg Pb), and contaminated LRM sediments containing 59, 3820, or 5360 mg/kg Pb (8 replicates; N=80). Larval *C. tentans* and juvenile *H. azteca* were 10-11 days old on the day the test was initiated, and exposures lasted 10 days at 23 ± 1ºC with a 16 hour: 8 hour light:dark cycle. Overlying water was replaced twice daily and organisms were fed 1.5 ml Tetramin®

flake fish food mixture daily. Surviving organisms were recovered to determine mortality and ashed at 550°C to assess for growth by determining their dry weight.

<u>UWL Methods for measuring toxicity in fishes</u>: Standard sediment toxicity assays were performed using zebrafish (*Danio rerio*) to identify lethal and sublethal toxicity following exposure to LRM sediments; findings were compared with exposure to water soluble Pb (Pb nitrate: 0, 0.1, 0.2 or 0.4 mg/L). All experiments followed animal care protocols (7-13) sanctioned and accepted by UWL. Pilot studies identified that 0.25 g of sediment within 2 ml of zebrafish water allowed for limited observation of developing larvae, but did not induce toxicity to zebrafish from sediments alone. Homogenized sediments were mixed with buffered zebrafish water (pH 7) and were placed in 24-cell well plates (1ml). After allowing the sediments to settle overnight, zebrafish embryos were placed into the well (1 embryo/well) containing artificial, reference (10 mg/kg Pb), and contaminated LRM sediments containing low (269 mg/kg Pb), medium (4,463 mg/kg Pb) or high (12,520 mg/kg Pb) (24 at each concentration with 3 replicates; N=72). Fish were maintained at 28°C with a 14hr light, 10hr dark photoperiod without renewal or change of sediment solution. Mortality was used as the measure of acute toxicity, and surviving fish were moved to clean 24-cell well plates to assess sublethal toxicity.

A subset of larvae (8 representative fish from each assay; n=24) were evaluated for both neurological and morphological signs of sublethal toxicity. We utilized a C-start assay as a qualitative assessment of neurotoxicity as described by Hill et al., 2009. The C-start touch-response-assay involves administering a stimulus (touch) to larval fish, which initiates a standard response. After acclimating to the light of the microscope, the tail of the fish was touched with a pipet tip. The response of the larvae was scored on a scale from 0-3, with 0 being a normal C-start, 1 being a delayed C-start, 2 being an improper C-start (e.g., twitching) and 3 being no movement. Following neurological assessment, fish were immobilized in 2% methylcellulose, and lateral images were taken using a microscope-mounted camera. Developmental toxicity was assessed qualitatively by scoring individual fish for sublethal toxicity using a range from 0-3: 0 (healthy); 1 (mild toxicity, 1 endpoint), 2 (moderate toxicity, 2-3 endpoints) and 3 (severe toxicity, >3 endpoints) as previously described (King-Heiden, 2009). Lateral images were also used to quantify the number of visible gross abnormalities, and to assess growth (by measuring standard length). All observed toxicity was compared to Pb nitrate positive controls.

To determine whether observed toxicity following exposure to LRM sediments was due to Pb or something else within the sediments, we measured the relative expression of the gene ALA-D as a biomarker of Pb exposure. Pb is known to interfere with the production of red blood cells by altering the activity of the enzyme ALA-D (Heier et al., 2009). Here we measure the expression of this gene using quantitative RT-PCR. Fish were exposed to Pb nitrate, synthetic, or LRM sediments as described above. After 5 days, fish were euthanized and tissues stored in RNA later (Qiagen). RNA was isolated using Qiagen RNeasy kit, and cDNA synthesized using BIO-RAD iScript RT Supermix following manufacturer's instructions. qPCR was used to quantify ALA-D expression normalized to Elongation Factor 1 alpha.

<u>Results for toxicity assessment in invertebrates and fishes</u>: Toxicity assays utilizing amphipods were inconclusive due to high mortality in controls. LRM sediments were not toxic to larval midges, but did cause some mild toxicity in zebrafish larvae. See Appendix C for the report on WI DNR sediment toxicity tests. While acute exposure of zebrafish embryos to LRM sediments caused no significant increase in mortality (Fig. 11), we did observe signs of potential Pb toxicity in zebrafish larvae (Fig. 12).

Approximately 40-80% of zebrafish had signs of morphological and neurological toxicity following exposure to LRM sediments (Fig. 13). Sublethal toxicity was not dose-dependent (Fig. 14), and using expression of ALA-D as a biomarker of Pb exposure, appear to correlate with Pb exposure only at the medium contaminated sites (Fig. 14).

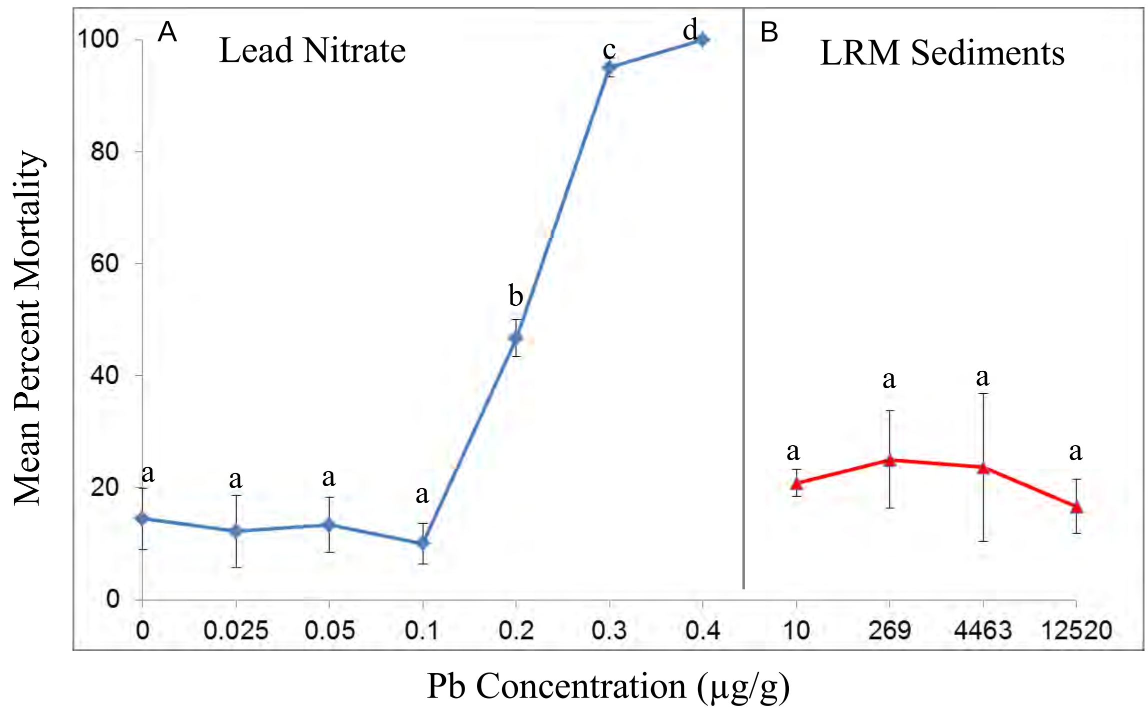

Figure 11. Cumulative mortality following exposure to Pb. Fish were exposed to waterborne $Pb(NO_3)_2$ (A) or sediments from the LRM (B) for 5 days. Letters denote significance.

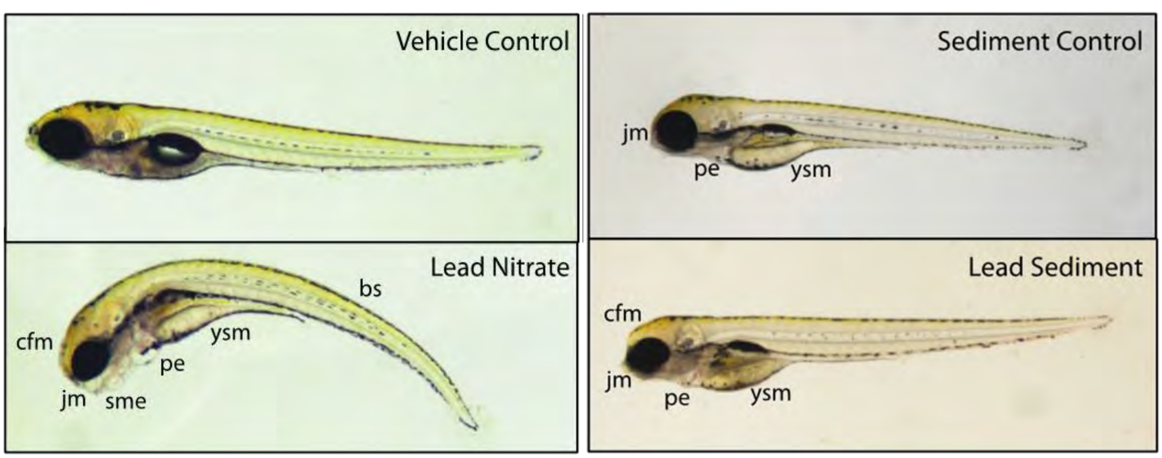

Figure 12. Representative micrographs. Zebrafish larvae exposed to waterborne Pb nitrate or sediments from the LRM for 5 days. Abbreviations: jm = jaw malformations; pe = pericardial edema; ysm = yolk sac malformations; cfm = craniofacial malformations; bs = bent spine.

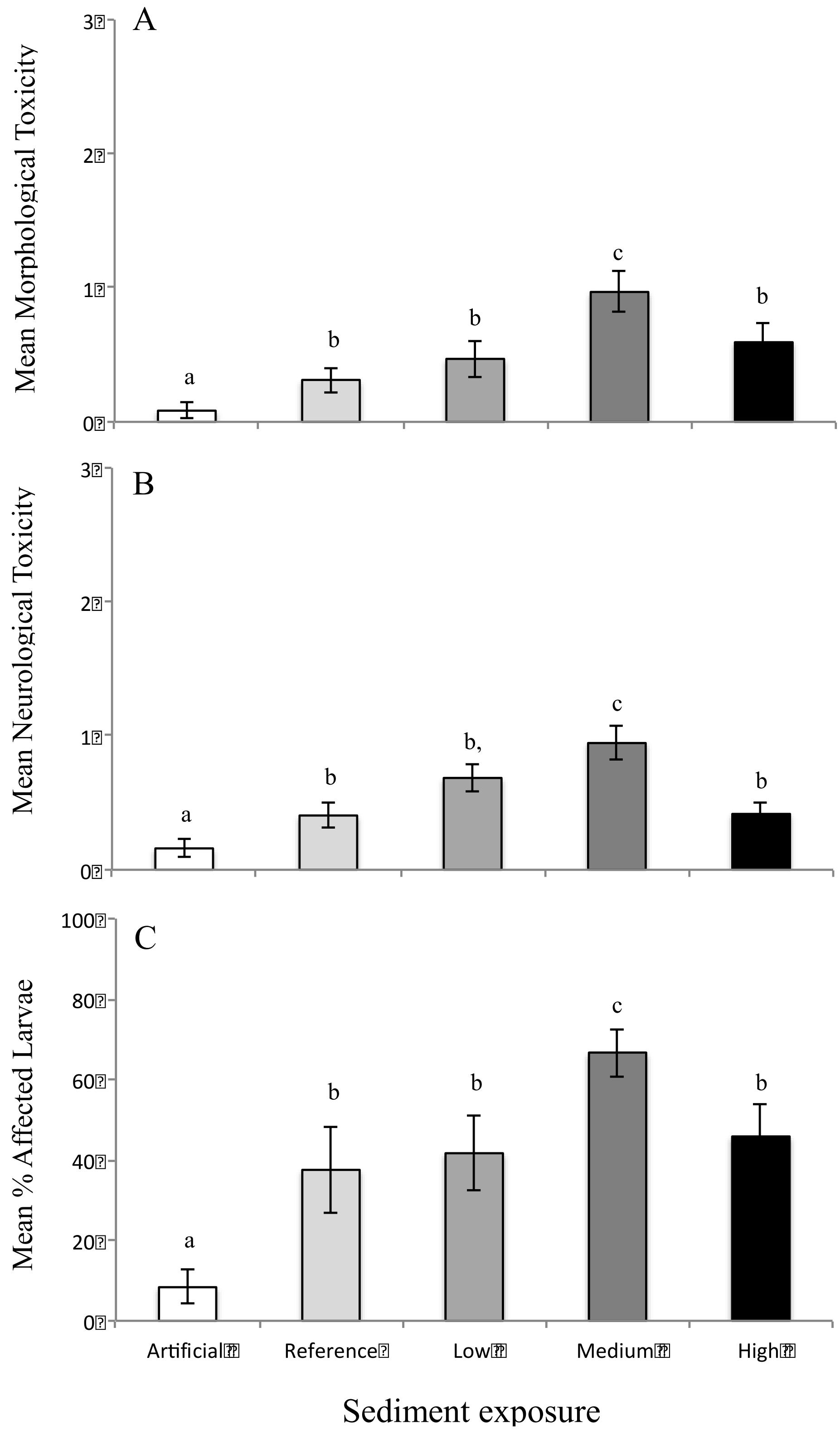

Figure 13. Sublethal toxicity following exposure to LRM sediments for 5 days. Impacts on (A) overall toxic response (B) neurotoxic response and (C) proportion of larvae affected. Letters denote significance.

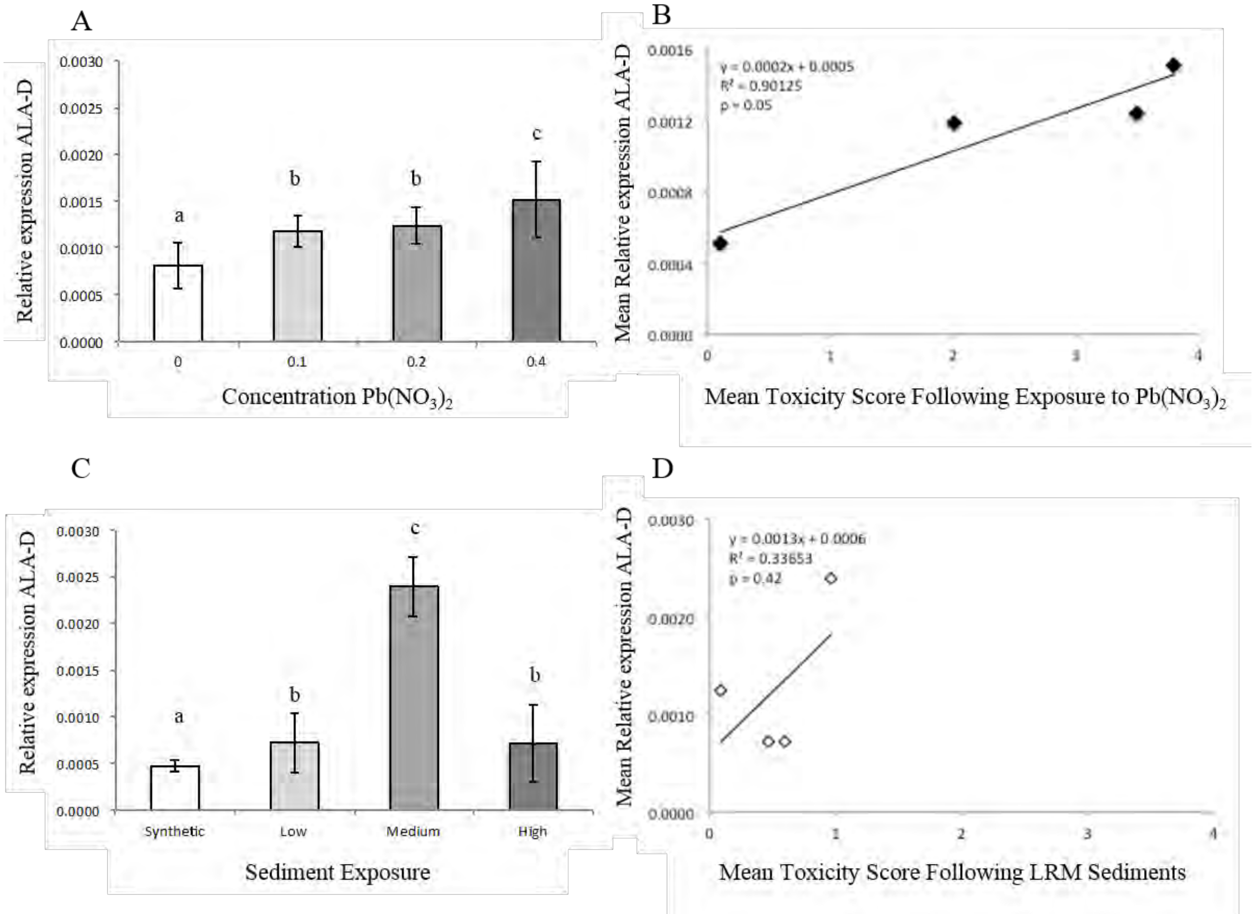

Figure 14. Toxicity attributed to Pb exposure. (A) Relative expression of ALA-D following waterborne exposure to $Pb(NO_3)_2$. (B) Linear regression of expression of ALA-D compared to observed general toxicity following exposure to $Pb(NO_3)_2$. (C) Relative expression of ALA-D following exposure LRM sediments. (D) Linear regression of expression of ALA-D compared to observed general toxicity following exposure to LRM sediments. Bars represent mean relative fold changes in expression of ALA-D is normalized to the expression of EF1. Letters denote significant differences.

Objective 2. Survey presence of Pb in the LRM biota.

Based on sediment Pb concentrations, we identified areas of varied contamination within the LRM to sample biota. Organisms at different trophic levels were targeted to delineate whether Pb from sediments is bioavailable and potentially transferring through the food web to wildlife and/or humans.

Subobjective 2.1: Measure Pb levels in LRM aquatic vegetation.

Methods for measuring Pb concentrations in aquatic vegetation: Duckweed (including *Lemna trisulca*, *Wolffia* sp., and *Lemna minor*) are small, fast-growing, floating, abundant aquatic plants found within water bodies throughout the U.S., including the LRM. Dissolved Pb and other heavy metals readily accumulate within duckweed from the water column, making it an ideal indicator for aquatic toxicity and water body impairment (Mohan and Hosetti, 1997). During July and August 2012 and September 2013, duckweed was sampled by UWL scientists from 19 locations distributed across a gradient of Pb levels within and outside the shot fall zone (Fig. 15). The WI DNR collected a duckweed sample from the LRM East site during August 2012. Samples were also collected by the WI DNR in August 2012 at a wetland in Stoddard, WI (Upper Mississippi River Pool 8) and Lizzy Pauls Pond (Upper Mississippi River Pool 5) to serve as references. The Stoddard site was located near Stoddard's former wastewater treatment plant disposal area, and low levels of localized bed sediment contamination exist at this site compared to the Lizzy Pauls Pond. For duckweed collection, a floating frame was placed over each site, and all floating material within the frame was collected using a 0.5 mm mesh stainless steel strainer (#35) and placed into a plastic tray. Non-duckweed material was discarded and the remaining sample was thoroughly rinsed with deionized water and spun dry. *Sparganium eurycarpum* (bur-reed), an emergent wetland plant commonly found in the LRM, was also collected by UWL during August 2012 from sub-aerially exposed sites on the west side of the trail that bisects the study area. All samples were analyzed for Pb at the University of Wisconsin Soil and Plant Analysis Lab via ICP-MS.

Figure 15. Location of UWL duckweed sampling sites. Sites are identified on top of spatially interpolated surface (0-5 cm) Pb concentrations in LRM sediments. Circle size is proportional to concentration of Pb in duckweed tissue (mg/kg dry mass).

<u>Results Pb in Duckweed:</u> Duckweed sampled at the East Site in the LRM by the WI DNR had a Pb concentration of 43.33 mg/kg (dry weight), while samples collected from Lizzy Pauls Pond and the Stoddard wetland had concentrations of <2 mg/kg and 5.76 mg/kg respectively. Duckweed collected by UWL ranged from <2 mg/kg at the control sites located outside of the potential shotfall zone to 268 mg/kg within the shotfall zone. Duckweed Pb levels generally increased with Pb concentration in the sediment (Fig. 16). Variability in this relationship is likely explained by the movement of the duckweed during low to moderate winds. *Sparganium* sp. Pb concentrations ranged from <2 mg/kg to 10.59 mg/kg,

with the highest value found where the sediment concentrations was greatest and the lowest value found north of the potential shot fall zone.

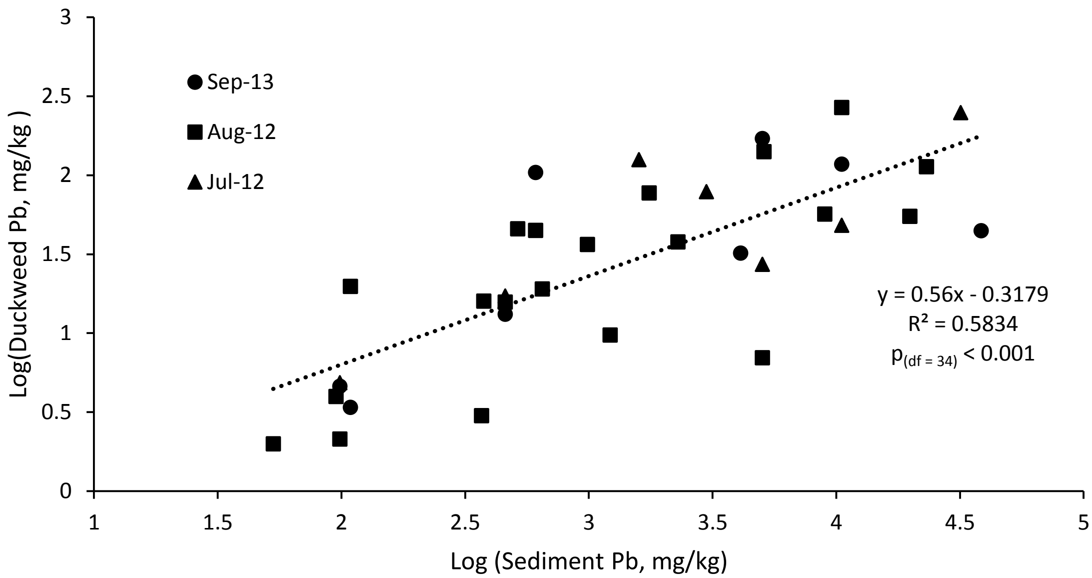

Figure 16. Pb concentrations in duckweed across contaminated sediments in LRM.

Subobjective 2.2: Measure Pb levels and malformation occurrence in LRM invertebrates.

Methods of invertebrate collection and determination of Pb content: Sites were visited between one and four times to collect the necessary number of invertebrate individuals to meet the mass requirement for tissue analysis. Dip nets were swept back and forth in the water column for approximately 45 minutes, with an attempt to minimize contact with the sediment. Only organisms within the water column were targeted, not organisms within the sediment. *Leptocerus americanus* made up >50% (and up to 80%) of the invertebrates collected across sites. It was selected as an indicator species and used to test for differences in Pb accumulation across sites with varied levels of Pb contamination in the sediments. *Leptocerus americanus* were collected at selected sites (Fig. 17) from the LRM during the months of May and June, 2012, using standard D-dip nets with 250 µm mesh. Due to the dry conditions in 2012, invertebrate sampling was focused in the east basin of the LRM.

Initial isolation of *L. americanus* made use of the animal's phototactic behavior. A light was positioned to shine through one corner of a clear plastic collection container, drawing the specimens to the lit corner where they could be removed en masse. Additional individuals were picked from the plants and debris with stainless steel forceps. The *L. americanus* specimens were placed in Petri dishes of distilled water for 24 hours in order to allow for clearance of the gut contents and the dishes were cleared of all extraneous dirt and debris with the aid of a dissecting microscope, micropipette and stainless steel tweezers. After 24 hours of gut clearance the *L. americanus* were frozen whole (bodies with cases). In preparation for processing at the WSLH frozen specimens were thawed and dried at 35°C for 48 hours. Aggregate samples (all individuals from a single site) were then ground manually with a ceramic mortar and pestle, weighed and placed in 60 mL plastic centrifuge tubes for shipping.

Pb analysis of the larval tissues was done at the WSLH's Ultra Trace Elements and Metals Testing Facility in Madison, Wisconsin using Krynitsky's nitric acid digestion protocol (Krynitsky, 1987) for recovery of metals from organic tissue. One-half gram of dried tissue is dissolved in concentrated nitric acid and 30% hydrogen peroxide, followed by Pb analysis with a Perkin Elmer 5300 Dual View Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) (WSLH EHD Metal Methods, 2013). Although Pb can exist in several different oxidation states (Pb^{2+}, Pb^{4+}), we used total Pb measurements in the tissues of *L. americanus* since the sediment Pb concentration in the LRM had also been measured as total Pb.

Collection of larval *L. americanus* was repeated in May of 2014 from sites at each level of contamination to analyze the partitioning of Pb between the bodies and cases. Specimens were processed as described above to clean the specimens and remove gut contents from the Pb analysis.

Emergence traps were set out in the LRM during the summer of 2013 to collect emerging adult aquatic insects, including *L. americanus,* in order to estimate the amount of Pb in the adult stage and to get an estimate of the total amount of Pb leaving the contaminated zone. The traps were placed at five of the same collection sites used for macroinvertebrate sampling, one site each in the control, low, and medium Pb level zones, and two sites in the high Pb level zone. The emergence traps are pyramid-shaped frames constructed of 2" diameter PVC pipe measuring $1m^2$ at the base that float on the surface of the water. They are covered with mesh net around all four sides to direct the emerging adults to a six centimeter hole at the apex of the pyramid which holds an inverted glass jar that screws into a collar attached to the trap. The traps were deployed and anchored in place for a period of four weeks, during which time the traps were emptied three times a week. Adult *L. americanus* were counted, dried, ground and weighed with the same protocol used for the *L. americanus* larvae.

The macroinvertebrate assemblage was collected at the same sites, at the same time and in the same manner used to collect *L. americanus* larvae (see above). Sampling efforts were unequal for different sites, so we used relative abundances within each site, as opposed to absolute abundances in our statistical analyses. Live macroinvertebrate samples were transported back to the lab in containers of marsh water where they were sorted from the aquatic plants, algae, and detritus and then preserved in 70% ethanol. After preservation the samples were sorted, identified and counted. Identification was accomplished with a dissecting binocular microscope and reference keys (DeWalt et al., 2010; Hilsenhoff 1995; Merritt & Cummins, 1995; Pennak 1989; Wiggins, 1977; Ward & Whipple, 1959). All organisms were identified to the level of family, with some being identified to genus and species, based on expertise. Relative abundances for each sample at the order and family level were then determined. The Shannon-Weiner Equation (H'), which incorporates both measures of species richness and evenness, was used to calculate diversity estimates at each site. Due to their extremely high abundance and preferential sampling, *Leptocerus americanus* were removed from the analysis to focus on the underlying diversity.

There were three replicates from the control, medium and high Pb levels, and two replicates from the low sediment Pb level. Analyses of variance was used to test how H' at the order level changed across contamination levels. In addition, the relative abundances (p_i) of each order were arcsine square root transformed to normalize the data and analyzed by using ANOVA to test variation between relative abundances across contamination levels.

Invertebrates were visually assessed for head, leg and abdomen malformations under a dissecting microscope. Anomalous morphologies for this study are defined as structures that are present that deviate from the normally observed morphology. Absence of body parts (antennae, limbs etc.) were documented but were recorded as damage rather than morphological anomaly.

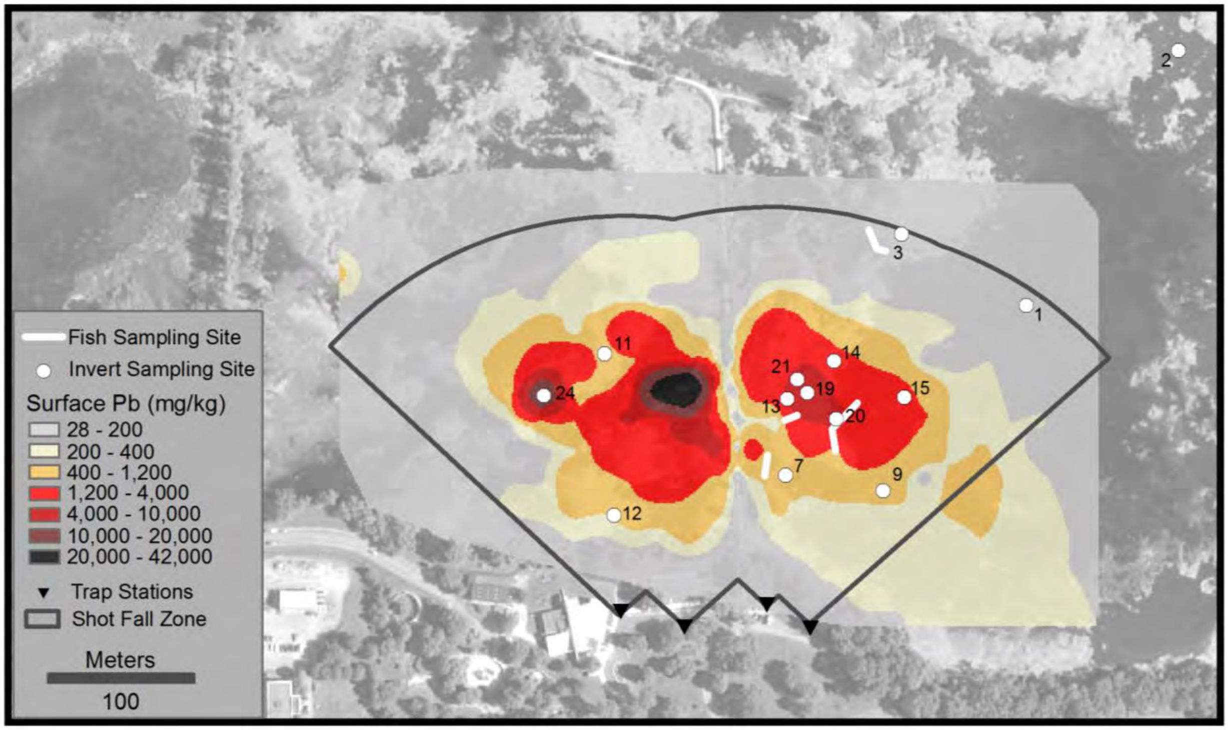

Figure 17. Map of the macroinvertebrate and fish sampling sites. Each white circle is a site from which macroinvertebrates were collected for Pb tissue analysis or for determination of diversity. Each white line represents location of Fyke nets used for fish sampling (adjacent to sites 3, 7, 13, 20).

Results Trichoptera Pb concentrations: There is a significant positive relationship between the concentration of Pb in the sediment and the concentration of Pb in the whole larvae (bodies and cases) of *L. americanus* ($R^2 = 0.696, p < 0.005$) (Fig. 18). Pb is being assimilated by this macroinvertebrate population at levels directly proportional to the concentration of Pb in the underlying sediment.

At sites where whole larvae were collected, bodies and casings partitioned from the same sites had positive relationships with whole body measurements. Pb was partitioned unequally between the cases and bodies (Fig. 19). Concentrations of Pb in larval cases of *L. americanus* were 11.93 ± 2.26 (SE) times higher than in the larval bodies (Pearson correlation = 0.91, two-tailed test for significance = 0.09). It is possible that this relationship is not linear and that at higher levels Pb concentration in the bodies reaches a threshold.

The Pb in the body of the *L. americanus* larvae is conserved throughout the process of metamorphosis and carried with the adult out of the water. This can be seen by the extreme overlap in Pb concentrations between larval bodies without casings and emergent adults (Fig. 19) ($R^2 = 0.92, p_{df3} < 0.01$). The ratio of Pb in the larval bodies versus the emerging adults is 0.91 ± 0.12, indicating that most of the Pb is conserved during metamorphosis.

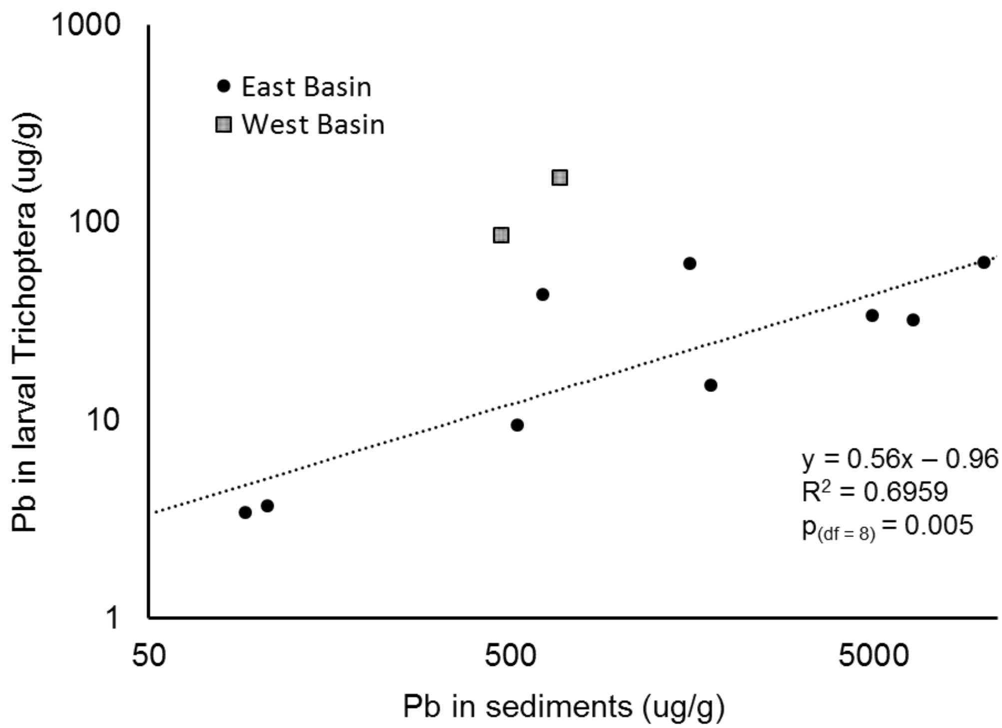

Figure 18. Concentration of Pb in larval *L. americanus* (Trichoptera) collected from the LRM.

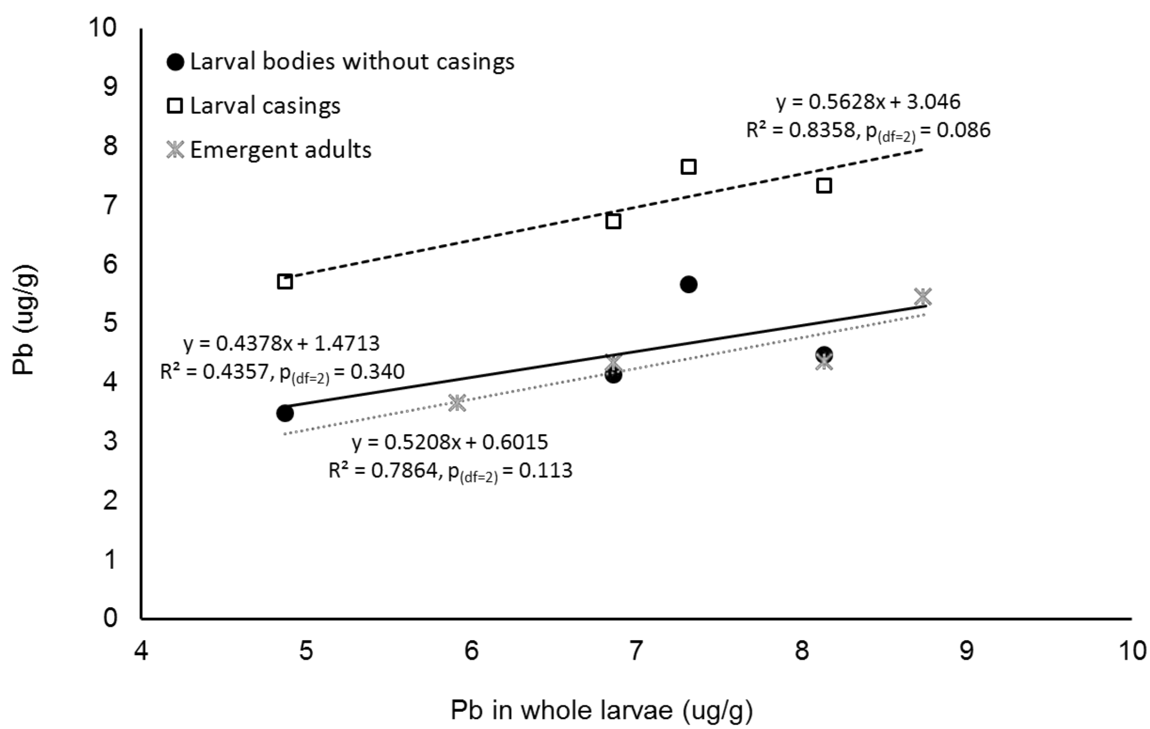

Figure 19. Concentration of Pb in bodies and casings of larvae, and in bodies of emergent adult *L. americanus* (Trichoptera) collected from the east basin of the LRM.

<u>Results of invertebrate diversity estimation and morphological anomaly</u>: There were seven orders and seventeen families of aquatic insects represented in the study area (Table 9). All seven orders were represented at all four levels of Pb concentration. Aside from *L. americanus*, the greatest proportions of aquatic insects in our samples were *Neoplea striola* (Heteroptera), *Caenis* (Ephemeroptera), Chironomidae spp. (Diptera) and *Enallagma* (Odonata). The Odonata were significantly less frequent in highly contaminated sediments (*p=0.037*), and small but noticeable trends existed for other orders (Fig. 20), which suggests differential sensitivities to Pb between the species of macroinvertebrates collected in the contaminated zone of the LRM. The proportion of Odonata at high Pb sites was 0.10 the proportion at the control sites, and both Ephemeroptera and Diptera decreased in relative abundance (0.5 to 0.33, and 0.10 respectively), from the low Pb contamination to the high Pb contamination. In contrast, proportions of Heteroptera were 3x higher at the high Pb level than at the low Pb level, while the proportion of Lepidoptera at the high Pb level was four times the proportion at the control Pb level. This does give a somewhat different picture of the macroinvertebrate community at the high Pb level than at the control Pb level, though orders Trichoptera, Diptera and Coleoptera have an inconsistent profile across the Pb sediment gradient.

Shannon diversity was similar across Pb sediment levels at both the order and family level (Fig. 21). There was no significant correlation between either diversity (*H′*) and bathymetric depth or diversity (*H′*) and macrophyte cover at the sites that were sampled.

Table 9. Aquatic insects collected from the zone of Pb contamination in the LRM.

Order	Suborder	Family	*Genus and species*
Ephemeroptera		Caenidae	*Caenis*
		Baetidae	*Callibaetis*
Odonata	Zygoptera	Coenagrionidae	*Enallagma*
	Anisoptera	Aeshnidae	*Anax*
		Cordulidae	*Epitheca*
		Libellulidae	*Erythemis*
Trichoptera		Leptoceridae	*Leptocerus americanus*
			Triaenodes
			Oecetis
			Ceraclea
Heteroptera		Belostomatidae	*Belostoma*
		Corixidae	*Trichocorixa*
		Notonectidae	*Notonecta*
		Pleidae	*Neoplea striola*
Diptera		Chironomidae	*spp*
		Ceratopogonidae	*spp*
		Syrphidae	*spp*
		Ephydidae	*spp*
		Syrphidae	*ssp.*
Coleoptera		Dytiscidae adult	*spp*
		Hydrophilidae	*spp*
			Hydrochus
			Berosus
Lepidoptera		Crambidae	*Parapoynx*
			Munroessa

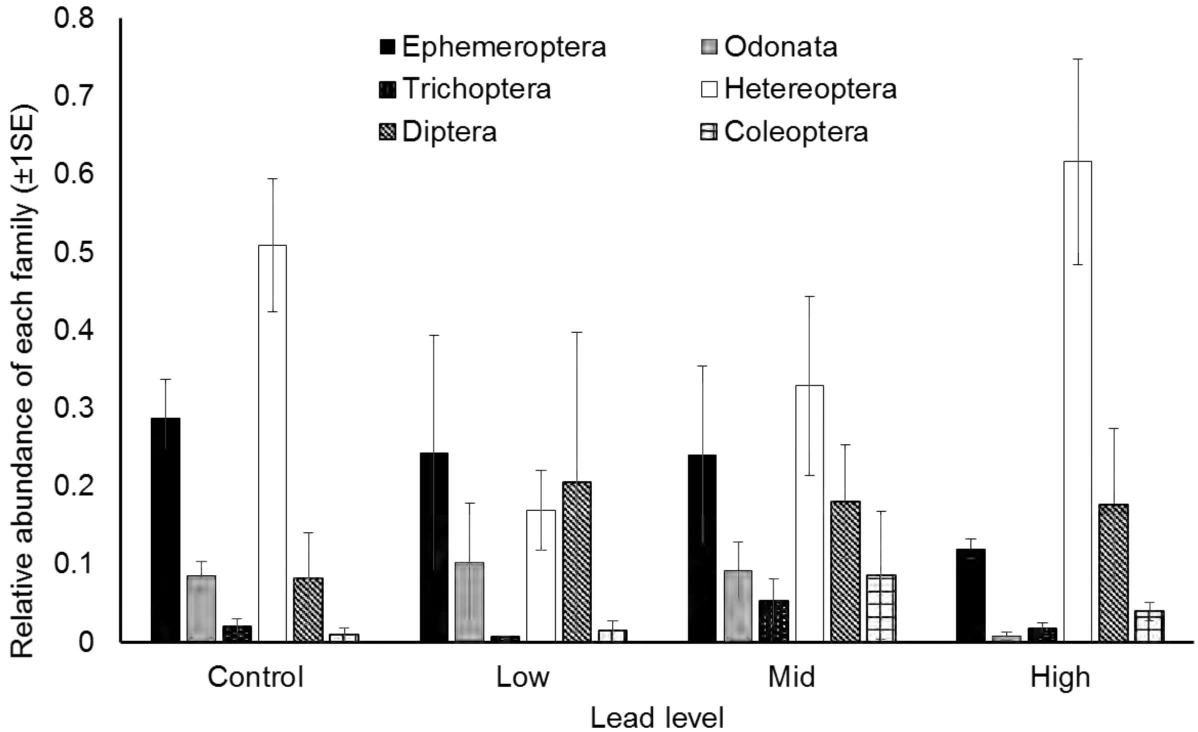

Figure 20. Relative abundance of invertebrate families across sites with varied Pb levels. Control (sites 1, 2 & 3) Low (sites 7 & 9), Mid (sites 14 & 15), High (sites 19, 20 & 21)

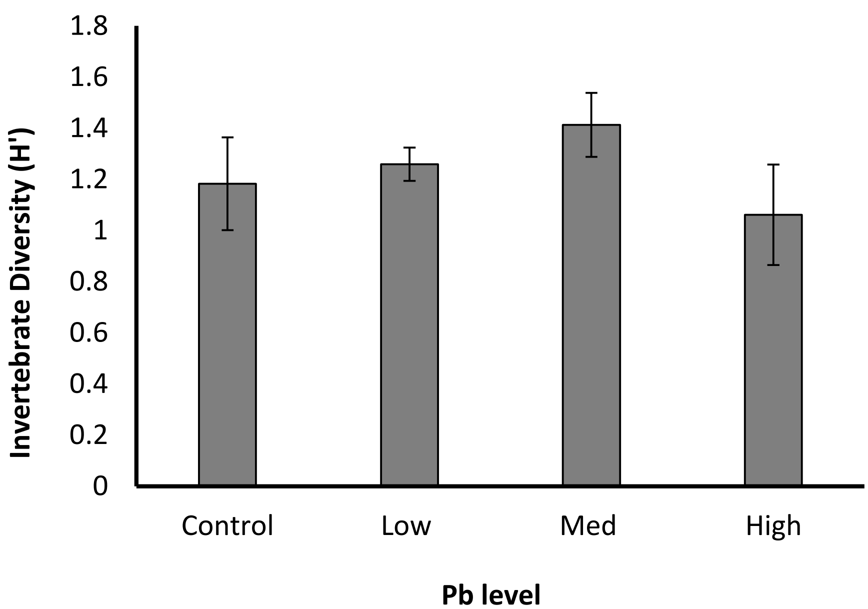

Figure 21: Shannon diversity index compared across sites with varied Pb levels.

Table 10. Anomalous morphology observed in macroinvertebrates collected across Pb concentrations in the LRM.

Site	Order	Family or Genus	n	# anomalies	description
1	Odonata	*Enallagma*	8	1	elongate left antennae
	Ephemeroptera	*Caenis*	237	2	bent antennae
	Trichoptera	Leptoceridae	341	0	
2	Odonata	*Enallagma*	3	0	
	Ephemeroptera	*Caenis*	37	0	
	Trichoptera	Leptoceridae	174	14	small bodied within cases
3	Trichoptera	Leptoceridae	12	0	
7	Ephemeroptera	*Caenis*	4	0	
	Trichoptera	Leptoceridae	11	0	
9	Odonata	Anisoptera	1	1	bent left antennae
	Odonata	*Epitheca*	1	0	
	Ephemeroptera	*Caenis*	99	0	
	Ephemeroptera	*Callibaetis*	4	0	
	Trichoptera	Leptoceridae	26	0	
11	Odonata	Zygoptera	7	1	elongate left antennae
	Odonata	Anisoptera	5	0	
	Ephemeroptera	*Caenis*	79	0	
	Ephemeroptera	*Callibaetis*	2	0	
	Trichoptera	Leptoceridae	8	0	
14	Odonata	Zygoptera	1	0	
	Ephemeroptera	*Caenis*	7	0	
15	Odonata	*Enallagma*	4	0	
	Ephemeroptera	*Caenis*	42	0	
	Ephemeroptera	*Callibaetis*	7	0	
19	Odonata	Anisoptera	1	0	
	Ephemeroptera	*Caenis*	20	0	
20	Ephemeroptera	*Caenis*	11	0	
24	Odonata	*Enallagma*	21	5	bent or elongate antennae
	Odonata	Anisoptera	4	0	
	Ephemeroptera	*Caenis*	224	0	
	Ephemeroptera	*Callibaetis*	76	0	

In close observation of the head, limbs, abdominal segments and filaments of the three major orders of macroinvertebrates, limited anomalies were observed (10/1477 *if we exclude small body size in the Leptocerus at site 2 which is likely a pre-molt observation*). The most common anomaly observed was asymmetry in the antennae of the Odonata, predominantly in the genus *Enallagma*. Observations included varied length or bent antennae, predominantly on the left of the head. Anomalies were observed in control regions as well as high Pb concentration regions. The highest number were observed at a high Pb site (24) in the West Basin of the LRM (Table 10). However, this site also provided the highest number of specimens for evaluation.

Subobjective 2.3: Measure Pb levels in LRM fish.

UWL Fish Collection & Determination of Pb Content: Survey sites were separated into four areas based on concentration of Pb within the surface sediments, and accessibility for fish collection: reference (0-200 mg/kg), low (400-1,000 mg/kg), medium (2,000-4,000 mg/kg) and high (4,000-8,000 mg/kg) Pb contamination (Fig. 17). All animal handling and euthanizing followed UWL's animal care protocols (7-12). Fish were collected under a State of Wisconsin Department of Natural Resources Scientific Collection Permit (form 9400-379). At each site there were at least three sampling areas where fish were captured with mini-fyke nets or a backpack electroshocker. We targeted fish from different trophic levels including: planktivores/zooplanktivores (golden shiners, *Notemigonus crysoleucas*), insectivores (bluegill, *Lepomis macrochirus*) omnivores (black bullhead, *Ameiurus melas*) and piscivores (northern pike, *Esox lucius*). See Table 11 for a summary of fish analyzed for total Pb content. Fish tissues were stored frozen and processed to determine Pb content in whole fish. Samples were analyzed by the WSLH to maintain consistency and appropriate quality control. Fish were shipped as whole specimens because metal types do not accumulate equally in muscle tissues compared to other body parts (e.g., liver, other vital organs and bones), resulting in a full specimen homogenization being the most accurate measure of Pb content (Wagner and Bowman 2003). Additional fish were collected in July 2015 to test Pb concentrations in the fillet portion to address the potential need for a consumption advisory. Fyke nets located at the highest Pb concentration sites in the east basin were used to collect 4 northern pike and 1 bluegill of catch size for fillet analysis. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used to measure Pb levels in all fish specimens, with results given as µg/g (mg/kg) Pb, wet weight.

Table 11. Summary of LRM fish survey. Number of whole body fish analyzed for Pb content from different survey sites within the LRM in summer 2012.

		Number analyzed per site			
Species	Number analyzed	reference	low	medium	high
Golden Shiner	7	4	0	1	2
Bluegill	16	4	4	4	4
Black Bullhead	13	4	1	4	4
Northern Pike	8	0	4	0	4

Wisconsin DNR Fish Collection and Determination of Pb Content: During August 2012 electrofishing was used to collect 21 fish, including 17 black bullhead and 4 bluegill, adjacent to the WI DNR's East site (Fig. 7). Whole specimens were composited based on species and size prior to analysis for Pb by the WSLH. For bullheads, there were 5 composite samples with 3 to 4 fish in each composite. For bluegills, there were 2 composite samples with 2 fish in each composite. The July 2012 fish kill resulting from reduced oxygen levels in the marsh limited the quantity and diversity of fish species collected by the WI DNR.

UWL Results: Pb content in surveyed fish: All fish analyzed contained detectable concentrations of Pb (Fig. 22), with generally higher levels found in whole body samples. Concentrations of Pb within whole fish were highly variable, indicating no significance between Pb among fish tissue and collection site ($P = 0.384$). Concentrations of Pb were only dependent on size for golden shiners regardless of collection site.

The bluegill fillet had a concentration of 0.127 ug/g. The pike fillets measured 0.102, 0.0838, 0.0523, and 0.0540 ug/g of Pb. All UWL fish Pb results can be found in Appendix D. Given the small sample size of our survey and the limited data we have regarding concentrations of Pb in edible portions of the fish, our findings suggest that further assessment of Pb content within game fish fillets is warranted.

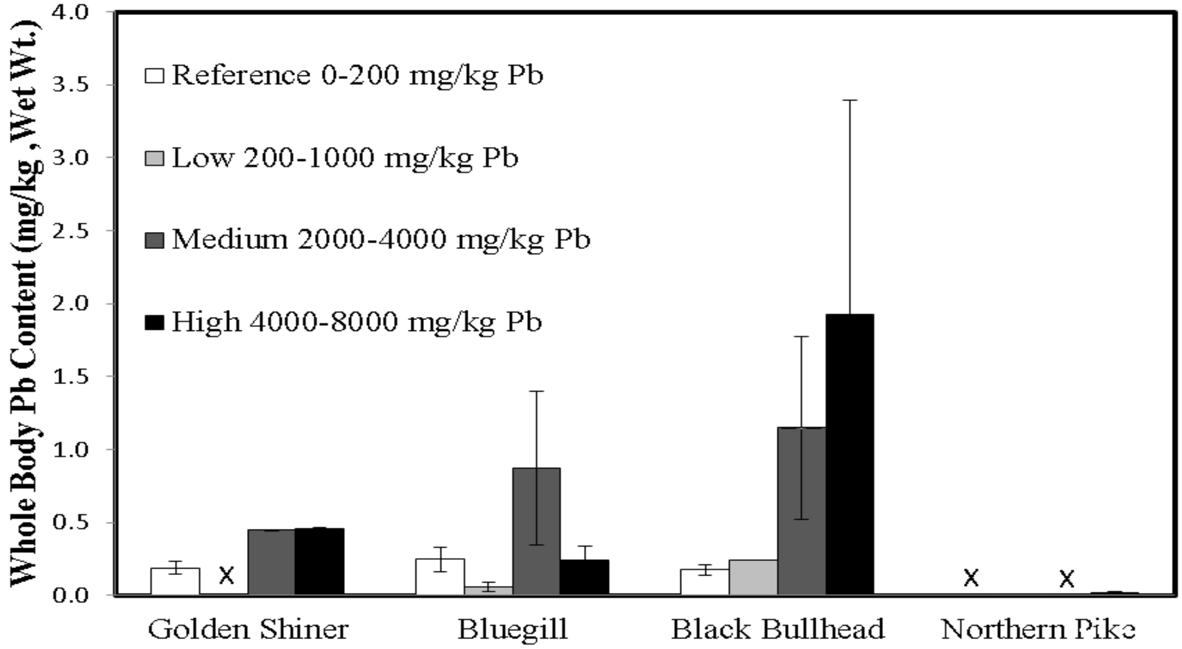

Figure 22. Concentrations of Pb within fish collected at different survey sites in LRM. Pb concentration within whole fish samples (mean ± SE) based on species and collection sites from the LRM, summer 2012. X denotes unavailable samples.

Wisconsin DNR Results: Pb content in surveyed fish: Similar whole specimen Pb levels were found for fish collected by the WI DNR and UWL within the Pb-contaminated area. Pb levels for the WI DNR composite samples ranged from 0.305 to 1.05 µg/g for black bullheads and from 0.176 to 0.826 µg/g for bluegill (Table 12).

Table 12. Concentration of Pb within composited fish samples collected from the LRM by WI DNR.

Species	# of Fish	Avg Length (cm)	Avg. Wet Wt (mg)	Unit Analyzed	Pb (µg/g, wet wt)
Black Bullhead	3	16.2	48	Whole Body	0.305
Black Bullhead	4	19.0	733	Whole Body	0.309
Black Bullhead	3	14.9	47	Whole Body	0.531
Black Bullhead	3	12.9	23	Whole Body	0.856
Black Bullhead	4	15.0	33	Whole Body	1.05
Bluegill	2	10.3	19	Whole Body	0.176
Bluegill	2	7.4	6	Whole Body	0.826

Objective 3. Increase Public awareness.

*Subobjective 3.1: Strengthen effective core partnership between UWL Research core and local regulatory agencies***.**

We have formed an effective collaborative relationship between the two research teams, and foresee future collaborative projects.

Subobjecive 3.2: Establish effective partnerships between UWL Research core, local regulatory agencies, and area non-profit (EcoPark) and community members with high investment.

Public Outreach Narrative: A thorough study of the transfer of Pb into LRM biota and the water was possible as a result of previous work by the WI DNR in the 1990s and the contaminant mapping efforts by Belby and Perroy prior to the EPA Urban Waters grant submission. The La Crosse Tribune and UWL Alumni Magazine published pieces in 2011 that highlighted the research being done in the LRM and the training opportunities involved with researching the contaminant. Wisconsin Public Radio - La Crosse (WHLA), WKBT News 8000, and Fox 25/48 also interviewed Belby and Perroy in 2011 about their research. By this time the WI DNR (John Sullivan and Kurt Rasmussen) had started a more intensive survey of Pb contamination in the LRM. At the time of grant submission, the WI DNR, the EcoPark (no longer in operation), and the City of La Crosse provided the UWL research team supporting letters of collaboration establishing the project as an opportunity to strengthen ties between research, education, management and public entities that would be involved with conservation decisions and outreach.

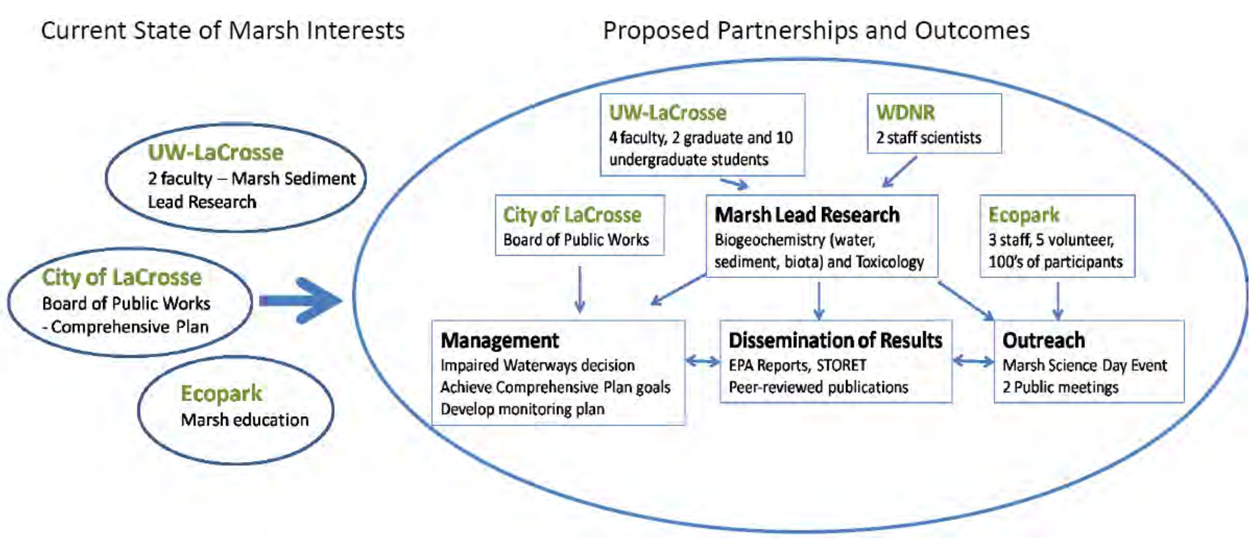

Figure 23. Partnerships and outcomes identified in the EPA Urban Waters Grant proposal.

After receiving EPA funding in May 2012, a number of news agencies picked up on the news release. Television and interviews were aired in August 2012 on local and regional channels including, Fox 25/48, WKBT News 8000, and WXOW News 19, and WIZM Radio. The La Crosse Tribune also published a follow up piece entitled 'UWL Researchers hunt for Pb in marsh continues'. The publicity surrounding the project painted the collaborative nature of the project and highlighted the UWL student training aspects.

During the data collection and compilation period of the research, presentations were given at multiple local, regional and international forums to promote awareness of the findings to research and management communities (see list of presentations in Appendix E). The first WI DNR report was submitted by John Sullivan in November 2012 and followed up by an oral presentation by Sullivan at the Water Quality Technical Section Meeting at the Upper Mississippi River Conservation Committee in Fairport, IA. From 2012 – 2015 there have been 43 total oral or poster presentations on various aspects of the grant objectives; 13 at national or international conferences, 20 regional presentations and 10 local presentations. Many of the presentations were co-authored and presented by UWL graduate and undergraduate students. There have also been two Master's theses and numerous undergraduate research projects that have resulted from and contributed to the project. Nearly all students involved in the Pb contamination research have gone on to secure fulltime jobs in environmental consulting or resource management with government agencies, or have enrolled in graduate school. In addition to the funding provided as part of the EPA Urban Waters Grant, an additional $79,864 ($39,250 student research grants; $40,614 faculty grants) in research funding was obtained between 2010 and 2014 in support of Pb research in the LRM (Appendix F).

Collaborators (City of La Crosse, WI DNR, and UWL) met on October 27, 2014 to discuss findings and to plan for presentation of findings to the La Crosse Board of Public Works. The public meeting with the Board of Public Works took place February 2, 2015. Belby presented both WI DNR and UWL collected data regarding the LRM and fielded questions. The meeting included discussion of findings in the context of remediation and monitoring needs. Since this was a preliminary report of findings the outcome was to take no immediate action and to revisit recommendations pending the comprehensive report. This meeting also included discussion of planning for two signs to be produced that educate the public on Pb in the LRM and the LRM ecosystem in general.

One of the farthest reaching outreach events that was a product of the proposal included development and recruitment of participants to add a scientific component to the annual Earth Day Event that takes place at the Myrick Center (formerly the EcoPark) and adjacent Myrick Park near the LRM. We originally planned to have an independent science in the marsh event. As plans developed, it became clear that publicity and participation of the broader public would be greatly increased by pairing with the existing sustainability event that has a built in reputation and that annually reaches thousands of community attendees of all ages. Our contribution to the Earth Fair Event included a science section where the WI DNR, the US Geological Survey's Upper Midwest Environmental Center, and the US Fish and Wildlife had interactive educational display booths. The UWL Mycology Club and UWL River Studies Center also contributed activities, with assistance from Peggy Donnelly of the US EPA. Research posters were presented at the event by six graduate students from UWL to share findings from local research efforts, and the posters included two on the Pb contamination in the LRM. Jim Nissen (retired US Fish and Wildlife Service's La Crosse District Manager of the Upper Mississippi River National Wildlife Refuge) and Colin Belby gave oral presentations open to the community, one on Pb in waterfowl and one on the LRM contamination. The science section received an estimate of >300 visitors (youth to adult) within a 6 hour period. Belby also co-led a walking tour of the marsh that included a discussion of past trap shooting activities and Pb contamination. The science section participation of the Earth Fair Event has extended beyond the scope of the grant and continues as planning develops for the Spring 2016 Earth Fair.

In collaboration with graphic designers contracted by the EPA, Belby, Gerrish, King-Heiden, Sullivan (retired WI DNR), and Giblin (WI DNR) developed text and imagery for producing a sign to educate the public on the legacy of Pb deposition in the LRM and the current state of contamination (Appendix G). An additional general sign was developed on the value of wetlands (Appendix H). Input on the Pb contamination sign was contributed by the City of La Crosse Board of Public Works during the development. Upon finalization of the sign, the Board of Public Works and the Board of Park Commissioners approved the content and placement of the Pb contamination sign in the LRM adjacent to a trail that is frequented by the public. The general sign on the value of wetlands will be shared with WisCorps, located in the former EcoPark building, and will be visible to the members of the public that participate in their environmental education activities. This process was a strong collaboration between UWL researchers, WI DNR and the City of La Crosse toward presenting scientific information, conservation and human impacts in a light that is not overly alarmist but educational. Signs are set for placement during the Spring of 2016.

Timeline of Outreach:

Fall 2011:

- Lang K. *Researchers study Pb concentration in river marshes*. UWL Alumni Magazine. url: http://lantern.uwlax.edu/researchers-study-Pb-concentration-in-river-marshes/

May 2012:

- EPA Grant notification

August 2012:

- Stories on: WPR La Crosse Regional Studio, WIZM radio, Fox 24/48, WKBT News 8000, and WXOW News 19
- Anderson P. 2012. *UWL Researchers' hunt for Pb in marsh continues*. url: http://lacrossetribune.com/news/local/UWL-researchers-hunt-for-Pb-in-marsh-continues/article_66b6bcb4-ecdd-11e1-b8f1-001a4bcf887a.html

Oct. 2014

- City of La Crosse, WI DNR, and UWL initial discussion of findings and sign planning.

Feb 2015

- City of La Crosse Board of Public Works meeting. Presentation by Belby.

April 2015

- Earth Fair Event:
    - Collaborative interactive Science Center with USGS (local amphibians and fishes), Fish and Wildlife Services (furs and wildlife station), UWL Mycology Club (fungal activity and specimens), UWL River Studies Center and EPA (invertebrate exploration).
    - Two presentations on Pb in Myrick Marsh. (1) *Pb Shot Problems in Waterfowl* - Jim Nissen Former La Crosse District Manager for the Upper Mississippi River National Wildlife and Fish Refuge; (2) *Pb Contamination in the Marsh* - Colin Belby, Ph.D. River Studies Center, UWL
    - Student posters: (1) *Management of refuge riparian wetland for wildlife benefits promote water quality ecosystem services; (2) Invasion of the faucet snail; (3) Effects of roadways in wetlands on dragonfly and damselfly communities; (4) Pb mobilization from Myrick Marsh by aquatic insects; (5) Moss animals? Marine invertebrates that are invading local watersheds; (6) The effects of fly ash on municipal solid waste*

Fall 2015:

- Completion of Marsh Signage:

- Presentation of Pb contamination sign and approval at Board of Publics Works open meeting and Board of Park Commissioners open meeting.
- AN UNINTENDED LEGACY: Trapshooting and Pb Pollution in the La Crosse River Marsh
- La Crosse River Marsh

CONCLUSIONS AND FUTURE DIRECTIONS:

Summary of Findings

The goal of this research was to establish a baseline monitoring program to identify areas of concern related to Pb-contaminated sediments within the LRM. To this end we have worked with the Wisconsin DNR to complete extensive sampling of sediments, water, aquatic vegetation, fish, and macroinverebrates within the marsh. We have also assessed the toxicity of the Pb-contaminated marsh sediment to fish and invertebrates. A summary of our findings as they relate to potential impairment of the water body and transfer of Pb from the sediment to other parts of the ecosystem is provided in Table 13.

An estimated 20,000 kg of Pb shot remains within the marsh sediment, typically buried below 10-30 cm of organic rich silt. An estimated 3.8 hectares of the LRM contains surface sediment that exceeds the EPA criteria of 400 mg/kg for contaminated soils and 8.9 hectares exceed the WI DNR criteria of 130 mg/kg for probable effects on biota. Terrestrial sites in the study area where most human activity is focused (e.g. gravel pedestrian trail and Myrick Park) were not found to have soil Pb levels above the EPA criteria of 400 mg/kg.

Pb is transferring from the sediment to the water column, though the effects appear to be limited based on our data. The water had elevated levels of total and dissolved Pb relative to the control sites, with the highest levels generally found above the most Pb-contaminated sediments. Of the 28 surface water samples collected and analyzed for Pb, one exceeded the WI DNR's chronic criteria and none exceeded the acute criteria. None of the running average 4-day surface water Pb concentrations exceeded the WI DNR's chronic criteria. Low concentrations of dissolved Pb in the surface water indicates that most of the water column Pb is associated with suspended particulate matter. This is supported by the high Pb levels found in suspended sediment traps placed within the former shot fall zone and by the correlation between total Pb and turbidity.

Duckweed in the LRM had elevated Pb levels relative to control sites, with the highest levels generally found above the most Pb-contaminated sediments. Research has shown that Pb levels in duckweed is dose dependent and in highly contaminated waters Pb bioconcentrates to levels several orders of magnitude above what was found in the LRM duckweed samples (Kaur et al, 2010; Debusk et al., 1996; Zayed et al., 1997). While we did not examine LRM duckweed for signs of toxicity, research indicates Pb-induced toxicity occurs at dissolved Pb concentrations above that found in the LRM water column (Kaur et al, 2010; Sobrino et al., 2010; Saygideger et al., 2013)

All invertebrate and fish samples from the marsh had measurable Pb. In fish, higher levels were generally found in whole fish samples than fillets. In 1995 the USGS sampled primarily carp and bass from river shorelines and backwaters within the Mississippi River Basin and they found a maximum concentration of 0.69179 µg/g out of the 159 whole fish composite samples analyzed (Schmitt, 2002). This concentration was exceeded in 3 of 7 composite fish samples collected from the LRM by the WI DNR and 5 of 49 individual whole fish samples collected by UWL. Unlike the USGS survey of the

Mississippi River Basin, the LRM fish samples did not include carp or bass. Only a limited number of fillets (n=5) from LRM fish were analyzed, and the WI DNR and US EPA have no known consumption guidelines based on Pb concentrations in fillets.

Our data suggests that Pb from contaminated LRM sediments do not pose a significant toxicological risk following acute exposure. We observed minor toxicity to developing zebrafish, and that toxicity is likely due to factors other than, or in addition to, Pb exposure. Contaminated LRM sediments posed no toxicity to invertebrates. Few malformation were observed in invertebrates sampled from the LRM, and there was no correspondence with sediment Pb levels.

Table 13. Summary of Pb study results and comparison to contamination criteria or samples collected from uncontaminated sites when available.

	Max in LRM Study Area	Max at LRM Control Sites	Regional Values	Contamination Criteria
Surface Sediment (mg/kg)	42,854[a]	59	11[b]	36[c] 130[d] 400[e]
Core Sediment (mg/kg)	26,709	83	47[f]	36[c] 130[d] 400[e]
Sediment Traps (mg/kg)	1,590[g]	62	16[h]	NA
Total Lead Surface Water (µg/l)	68.4	12.6	0.0416[b]	33[i] 119[j]
Dissolved Lead Surface Water (µg/l)	7.09	0.451	NA	NA
Dissolved Lead Pore Water (µg/l)	409	1.48	NA	NA
Fish Fillet (µg/g)	0.127	NA	NA	NA
Whole Fish (µg/g)	6.3	NA	0.69179[k]	NA
Invertebrate Body (µg/g)	170	3.4[l]	NA	NA
Duckweed (µg/g)	268	<2	<2[b]	NA
Invertebrate Toxicity	No toxicity observed	NA	NA	NA
Fish Toxicity	Mild toxicity observed	NA	NA	NA

[a] Value outside of calibration curve maximum of 27,700 mg/kg.
[b] Sample collected from Lizzy Paul's Pond in Upper Mississippi River Pool 5.
[c] Threshold effect concentration below which adverse biological effects are expected to be rare (WI DNR, 2003).
[d] Probable effect concentration above which adverse biological effects are expected to be frequent (WI DNR, 2003).
[e] EPA hazard criteria for bare soils in residential play areas (US EPA, 2001).
[f] Sample collected from Mississippi River Pool 8 backwater lake (Belby 2009).
[g] From samples collected in 2013 that were not influenced by bed sediment entrainment during deployment.
[h] Sample from Mississippi River Pool 8 sediment trap (Sullivan and Moody 1996).
[i] Chronic Pb criterion based on minimum hardness value of 112 mg/l observed in LRM (WI DNR, 2010).
[j] Acute Pb criterion based on minimum hardness value of 112 mg/l observed in LRM (WI DNR, 2010).
[k] Mississippi River Basin composite sample from USGS BEST database of primarily carp and bass (Schmitt, 2002).
[l] Invertebrate collected at site 1 (figure 17) located immediately beyond potential shot fall zone.

Waterfowl Mortality in the LRM

Waterfowl mortality associated with direct ingestion of Pb pellets can be a serious problem in aquatic environments or adjacent terrestrial areas receiving high accumulations of Pb shot. This problem is widespread and was documented in Wisconsin by Trainer and Hunt (1965) who summarized Pb poisoning of waterfowl during the period from 1938 to 1963. Pb poisoning was reported for geese, ducks and swans, and problem areas were concentrated in the counties of south central Wisconsin. There were no cases reported in La Crosse County during the period of activity at the La Crosse Gun Club. Trainer and Hunt found that a high concentration of birds at a site, a high concentration of Pb shot in surface sediments, and a solid sediment surface were particularly important when assessing the potential for Pb poisoning in geese.

Waterfowl mortality has been directly associated with trap shooting ranges at Lake Geneva, Wisconsin in 1992 (USEPA, 1994) and at Nahant Marsh, Davenport, IA in 1994-1997 (USFWS, 1998). In both situations, Pb poisoning was directly associated with the consumption of Pb pellets by waterfowl. EPA-mandated clean-up actions occurred at both locations under the Superfund Program largely as a result of these waterfowl mortality problems.

While the assessment of waterfowl mortality was not an objective of our grant, steps were taken to begin to understand if it is occurring in the LRM. Current and retired wildlife managers that worked for the Wisconsin DNR and US Fish and Wildlife Service at La Crosse were contacted to determine if they were aware of any waterfowl mortality problems for the LRM for the period from 1990 to 2015. The Coulee Region Humane Society in Onalaska, WI was also contacted because they are the regional center for receiving injured wildlife needing rehabilitation. There were no reports of injured or ailing waterfowl that were believed to be impaired by Pb ingestion.

A direct assessment of the presence of ailing or dead waterfowl in the LRM was made by canoe on twelve occasions from April 28 to November 2, 2015. The surveys started just north of the trap shooting range and proceeded along the shoreline and emergent vegetation. Surveys were conducted at different times of the day ranging from 8:00 a.m. to 7:00 p.m. An emphasis was placed in the eastern portion of the Pb-fallout zone where waterfowl use by geese and ducks were commonly observed, especially during spring and fall migratory periods. In addition, Canada goose nesting or loafing areas in the marsh were searched for ailing or dead geese. The marsh trails near the trap shooting range were also walked two to three times a week throughout 2015, each time scanning the trail area and open water for impaired or dead waterfowl.

The 2015 field surveys did not reveal any obvious signs of ailing or dead waterfowl. This is not to say that Pb-related mortality was not occurring. Rather, signs of this problem where not apparent at the site. It is possible that due to presence of soft organic sediment in the La Crosse Marsh, the Pb pellets have settled into the sediment and are not readily available to waterfowl. This would suggest the zone of legacy Pb pellet contamination has a low potential for contributing to Pb pellet-related mortality problems in waterfowl.

According to Jim Nissen, former Upper Mississippi River Fish and Wildlife Refuge La Crosse District manager, the lack of sick or dead birds reported by the public does not mean Pb-poisoning is not happening in the marsh (personal communication, March 11, 2016). Without an established process to contact agencies if a member of the public found a sick or dead bird, it likely would not have been reported. While the trail system throughout the study site and surrounding marsh receives extensive year-round use by the public, few people are directly in the marsh or the emergent vegetation where the sick birds are likely to be scattered. Human-caused disturbance created by traffic on the trails could also have caused the sick birds to seek cover from the trails, and affected birds are typically difficult to find. Sick birds and carcasses can also be quickly removed through predation or by scavengers. If mortality is occurring in the LRM it is likely to be affecting a few birds at a time, though this could add up to a large number of birds over several years.

Future Pb-Contamination Research Needs in LRM

The goal of our research was not to perform a full ecological risk assessment for the La Crosse River Marsh but rather to establish a baseline monitoring or surveillance program to identify regions of concern related to Pb-contaminated sediments identified within the mash. While the data collected for our study will go a long way towards informing whether and where site remediation may be needed, a more comprehensive ecological risk assessment is likely required. In addition to conducting a thorough review of our data, we recommend taking the following actions prior to making a recommendation on remediation:

- For our study we primarily analyzed whole body Pb concentrations in LRM fish because of the food web implications. Because humans typically consume only the fillet portion of the fish, we recommend completing a more comprehensive analysis of fillets for fish commonly caught in the marsh for consumption. While the occurrence of fishing in the study area is poorly understood and likely much lower than the nearby La Crosse and Mississippi Rivers, community members were frequently observed fishing from the pedestrian trail that bisects the study area and the observation platform immediately north of the study area. The culvert located adjacent to the highest Pb-contaminated sediments is one of the more popular fishing sites in the LRM, and evidence of ice fishing was also observed on the east side of the trail above the Pb-contaminated sites.
- While field surveys for moribund and dead waterfowl were initiated in 2015, it is recommended that a procedure be developed for the public to report sick or dead waterfowl. It is also recommended that a thorough field investigation for signs of Pb-poisoned waterfowl be undertaken. As was done in Nahant Marsh, this would include thorough and frequent coverage of the study of the marsh using well-trained retrieving dogs because the severely poisoned birds often isolate themselves in protective cover. Chapter 43 of the USGS National Wildlife Health Center's *Field Manual of Wildlife Diseases: General Field Procedures and Diseases of Birds* should be consulted for a thorough description of field signs associated varying stages of Pb-poisoning in waterfowl.
- For this study we found elevated levels of Pb in larval *Leptocerus americanus*, but we did not study how this may be affecting the food web when the adult aquatic insects emerge from the marsh. We recommend using tree swallows to evaluate the extent and effect of Pb exposure on wild bird populations living near the LRM. Nesting boxes built near the study site will attract the swallows, and they feed on emergent aquatic insects near their nesting sites. Tree swallows have been used to assess Pb contamination in aquatic systems, and comparative data on Pb levels in swallows exits for multiple sites across the U.S. (Custer et al., 2006; Custer, 2011). Researchers Christine and Thomas Custer from the USGS Upper Midwest Environmental Sciences Center in La Crosse, WI developed protocols for carrying out this type of study and may be able to provide guidance.
- Our study focused on Pb contamination associated with trap shooting. Soil and sediment contamination may also result from polycyclic aromatic hydrocarbons (PAH) compounds associated with clay trap targets. Targets are composed of ~70% dolomitic limestone and 30% pitch, which historically has been coal tar or petroleum. While modern targets are often produced with reduced or no-PAH compounds, the age of the targets used at the La Crosse Gun Club suggests they likely contain high PAH levels from coal tar pitch (Lobb, 2006). Soils containing

elevated levels PAHs at the Nahant Marsh shooting range were removed as part of that site's cleanup (Tetra Tech, 2006). Clay target fragments and intact targets are expected to land 50 – 90 meters from the target throwing stations (Lobb, 2006). In the LRM clay target fragments litter the slope leading down to the shoreline, and intact targets were encountered while coring the LRM sediment. Due to the abundance of targets in and adjacent to the LRM that have been breaking down for 50+ years, we recommend determining PAH levels in the soil and sediment within the target fall zone.

Appendices I, J, and K also contain relevant information related to ecological risk assessments performed at the former gun club ranges in Lake Geneva, WI and Nahant Marsh in Davenport, IA. Additional details on these, and other cleanups that have occurred throughout the country, were not readily available. It should also be recognized that no two sites are the same with regards to ecological risks from past trap shooting activities.

Potential Disturbances Associated with Sediment Removal

Remediation efforts at the former shooting range in Nahant Marsh involved excavation of Pb- and PAH-contaminated soil and sediment. While it is not known what specific methods were used to remediate the Nahant Marsh site, the following concerns were identified for the Nahant Marsh as part of the ecological risk assessment, and they are directly relevant to the LRM should remediation be required there.

- The Pb-contaminated LRM sediment primarily consists of highly flocculent organic rich silt. Currently the zone of contaminated soil is relatively well-confined, indicating minimal lateral movement has occurred since the start of trap shooting. Depending on methodologies used, the potential exists for sediment removal to redistribute the fine fraction of the Pb-contaminated sediment beyond the current zone of contamination.
- The contaminated sediments are primarily confined to the organic-rich silt. Removal of the Pb-contaminated silt may expose the underlying sand substrate, which may be less suitable for some wetland plant and animal species.
- Deepening the wetland through substrate removal may permanently alter the wetland community. The study area currently has high topographic heterogeneity (Fig. 3). Depending on the extent of sediment removal, habitat heterogeneity may be reduced, leading to reduced species diversity. It may be possible for sediment removal to be done in a way that maintains or increases topographic variability.

Summary of Grant Outputs

The combined research conducted by UWL and WI DNR scientists has enabled us to achieve the desired outputs of this EPA funded research, including: (1) Identifying areas of concern related to Pb contamination in the LRM; (2) Improving our understanding of the LRM water quality as it relates to Pb toxicity; (3) Developing outreach educational activities and presentations for residents of La Crosse; and (4) Developing a partnership between the WI DNR, the UWL research core & River Studies Center, and the City of La Crosse.

We have also achieved the major outcomes identified in our original proposal, including (1) Gaining knowledge and developing baseline conditions about the potential risks that the Pb-contaminated sediments pose to wildlife and the community; (2) Engaging and educating residents, community decision makers, and state and federal agencies about these potential risks; and (3) Providing the necessary water quality data for the WI DNR to make an Impaired Waters decision. It is our hope that our efforts will lead to continued monitoring of water quality within the LRM, strengthening of partnerships between the WI DNR, UWL, and the City of La Crosse with regards to the LRM, and long-term community interest in maintaining the environmental health of this ecologically and culturally important urban wetland.

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Appendix A

UWL Journal Article on Lead Mapping in LRM

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Mapping and modeling three dimensional lead contamination in the wetland sediments of a former trap-shooting range

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HIGHLIGHTS

- We mapped 3D Lead contamination in the wetland sediments at a former shooting range
- X-ray fluorescence & imaging allow rapid and inexpensive quantification of contamination
- Highest Pb contamination levels were typically found 10-30 cm below sediment surface
- We report high-resolution volumetric contamination estimates at various action levels
- Our mapping and modeling techniques can be readily applied to other contaminated sites

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ABSTRACT

Legacy lead (Pb) contamination from sport shooting activities is a well-known hazard. Assessing the risk this contamination presents to the environment and public health requires a detailed understanding of its spatial distribution, yet our knowledge in this area is limited, especially for wetland shooting ranges. In this study, we analyzed 1351 sediment samples from 456 surficial (0–5 cm) locations and 38 sediment cores (0.3 to 0.9 m) to quantify the three dimensional spatial distribution of Pb contamination in an urban wetland at the site of a former trap shooting range located in southwestern Wisconsin, USA. Non-destructive X-ray images of the sediment cores were used to quantify Pb shot abundance and burial depth. Surficial and core sediment samples were processed and analyzed for total Pb content via X-ray fluorescence (XRF) analysis. X-ray and XRF results were interpolated to create a three-dimensional model of Pb shot density and sediment concentration across the study area. Over 31,000 m^3 of sediment surpassed the US Environmental Protection Agency's contamination threshold of 400 mg/kg Pb, with a maximum calibrated value of 26,700 mg/kg Pb occurring near the center of the expected shot fallout zone. Shot densities of >50,000 pellets/m^2 were found in the shot fallout zone, primarily 10–30 cm below the sediment surface. X-ray image analysis and XRF analysis of sediment cores provide an accurate and inexpensive technique for rapidly mapping Pb contamination associated with gun clubs and hunting; these findings will benefit environmental contamination studies and remediation efforts at active and abandoned shooting ranges worldwide.

1. Introduction

1.1. Lead shot in the environment: History, impacts and importance

With >100,000 current and former shooting ranges worldwide (Darling and Thomas, 2003; Sorvari, 2011) and millions of kilograms of Pb ammunition discharged annually in the US, Pb contamination from shooting activities is a widespread problem, with corresponding unintended consequences to wildlife and human health (Calvert, 1876; McAtee, 1908; Scheuhammer and Norris, 1996; Tranel and Kimmel, 2009; US EPA, 2005). Detrimental effects of environmental Pb shot contamination on wildlife include behavioral changes, impaired reproduction and death (Abel et al., 2007; De Francisco et al., 2003; Kendall et al., 1996; Mateo et al., 2001; Newth et al., 2012; Stansley et al., 1997). These and other negative soil, water, and ecosystem effects can be particularly severe in wetland trap shooting ranges, where Pb shot densities of up to 370,000 pellets/m^2 have been measured and dissolution and weathering rates may be greatly accelerated under acidic conditions (Clausen et al., 2011; Stansley et al., 1992). Increased regulation, particularly under the Clean Water Act and the Resource

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Conservation and Recovery Act, has led to dramatic improvements in levels of Pb contamination in active shooting ranges (US EPA, 2005). However, because the dissolution of Pb shot and weathering into secondary Pb compounds can take up to 300 years (Jørgensen and Willems, 1987), former shooting ranges often leave a legacy of contamination long after shooting ceases, especially in wetland settings (Behan et al., 1979; Lund et al., 1991; Tsuji and Karagatzides, 1998).

Despite growing concern about health risks of lead exposure in human and wildlife populations, gaps remain in our understanding of the spatial distribution of Pb contamination in and around outdoor shooting sites, particularly in wetlands. Existing studies for upland ranges typically rely on sparse transect data with highly limited sample numbers ($n = 12$ to 235) (Cao et al., 2003; Clausen and Korte, 2009; Craig et al., 2002; Duggan and Dhawan, 2007), with similar numbers for wetland ranges (Hui, 2002; Tsuji and Karagatzides, 1998). While these studies highlight the magnitude of Pb contamination in shooting range settings, their depictions of the geography of contamination are incomplete.

Our objective was to create a high resolution three-dimensional (3D) dataset and model of Pb contamination in the wetland sediments of a former trap shooting range in an urban setting to better understand the spatial distribution of Pb throughout the sediment and the possible risks this contamination presents to the local wildlife and community. This study is novel in three important ways. First, by taking advantage of X-ray fluorescence (XRF) analysis, a non-destructive and rapid technique for quantifying the total elemental composition of materials, our study sample size ($n = 1351$) is approximately two orders of magnitude greater than those previously reported. This large sample size allows us to model and visualize the 3D distribution of Pb contamination at a very high spatial resolution. Second, the urban wetland setting allows us to better understand the impact of Pb shot contamination in a poorly-studied but ecologically critical zone. Third, because trap shooting at the wetland site ended 50 years ago, we are able to document the redistribution and long-term fate of this legacy contaminant. The methods developed here can be applied at other former and current shooting ranges to guide biological and ecological sampling and remediation efforts.

1.2. Study area

This work was conducted at the former site of the La Crosse Gun Club, a 15 ha section of the La Crosse River Marsh (LRM) located within the city limits of La Crosse, WI (Fig. 1). The LRM is part of the larger 435 ha La Crosse River Valley wetland complex, situated on the southwestern border of Wisconsin at the confluence of the Mississippi and La Crosse Rivers along the Mississippi Flyway. The LRM is part of the La Crosse River floodplain and is hydraulically connected to the La Crosse River and the Upper Mississippi River National Wildlife and Fish Refuge during periods of high water. Surface water sources to the LRM study area include Miller Coulee Creek, a 290 ha drainage basin east of the study area with an ~150 m local relief, and numerous urban storm sewers on the southern shoreline. During normal hydrologic conditions, the LRM study area is a shallow to deep (0–2 m) emergent marsh with open water and a few small islands, bordered to the south by a late-Wisconsin age sand and gravel glacial meltwater terrace escarpment (Knox, 1996). The contact between these two landscape units is marked by an east–west footpath near the southern edge of our sampling grid (Fig. 1B). The local wetland plant community includes submersed (*Ceratophyllum demersum* and *Chara* spp.), emergent (*Sparganium eurycarpum*), and free-floating (Lemnacea) vegetation. The interspersion of open water and marsh vegetation attracts a wide variety of migrating waterfowl and wading birds, and provides habitat for fish including pike (*Esox lucius*), bluegill (*Lepomis macrochirus*), and bullhead (*Ameiurus melas*).

The La Crosse Gun Club operated a four station trap-shooting range on the terrace surface overlooking the LRM from 1929 to 1963, and hosted state and national trap-shooting championships. Large quantities of Pb shot were regularly discharged into the LRM until the city declined to renew the Club's lease in 1963, due to resident complaints and a growing urban population (Godfrey, 1990). In 1952, Pb shot was salvaged from the LRM sediments, but few details regarding the salvage operation are available. Trap-shooting continued for another decade with no additional recovery efforts documented. A previous study on Pb shot abundance in the LRM found a maximum of 41,600 pellets/m^2 within the expected fallout zone,

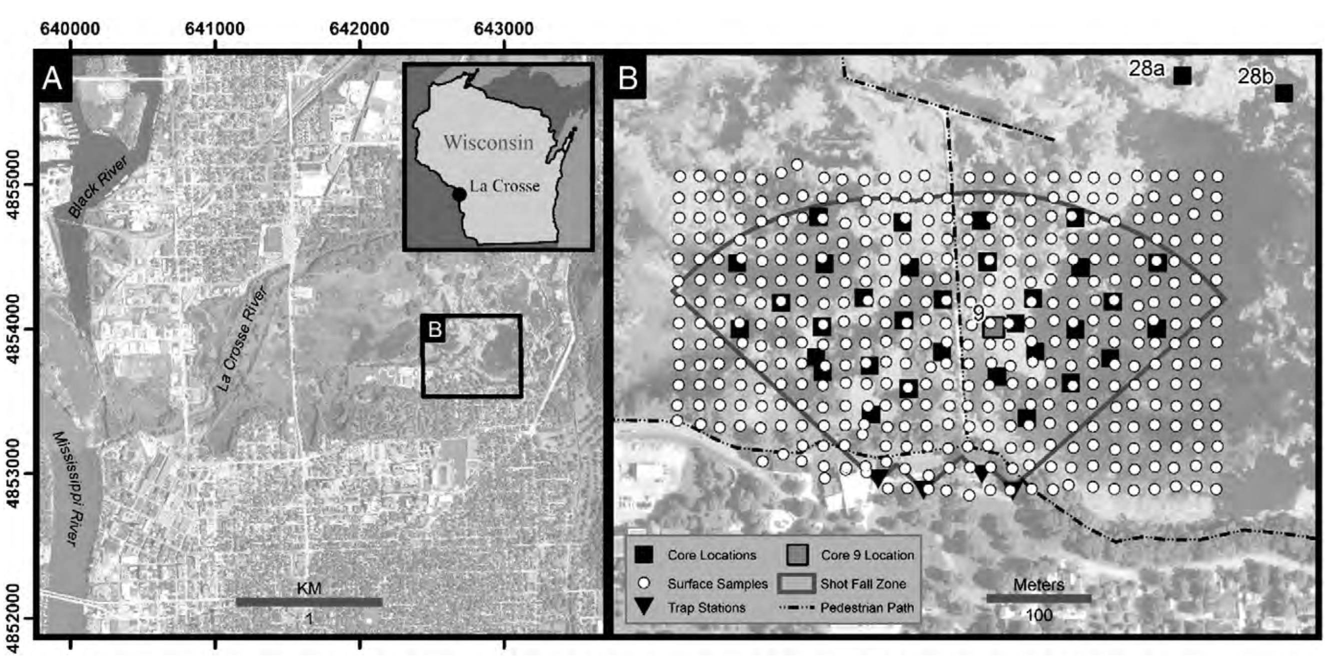

Fig. 1. (A) 2010 aerial image showing the La Crosse River Marsh study area and confluence of the La Crosse and Mississippi Rivers within the city limits of La Crosse, WI (inset map). (B) Study area showing former trap shooting stations, shot fall zone, and surface sample and core sample locations. Sediment cores used to establish background Pb concentration levels are labeled (28a, 28b) and shown in the upper right corner of Panel B.

but did not look at Pb levels within the sediment (Fors, 1994). Supernumerary antenna malformations in Corduliidae (dragonfly) specimens collected within the LRM shot fallout zone were also observed prior to this study, and hypothesized to be linked to high Pb exposure (R. Haro, UW — La Crosse Biology Department, pers. com.).

Today the LRM is a city park, nature preserve, and complex open water habitat recognized for high levels of biological diversity in an urban setting (WDNR, 1990). The area is traversed by numerous raised gravel paths and is heavily used for outdoor education and recreational activities including running, fishing, trapping and wildlife viewing (Moyer, 1989). The gravel path bisecting the study area is approximately 1 m above the LRM water surface during normal low water conditions, and only becomes inundated during large floods on the La Crosse or Mississippi Rivers.

2. Material and methods

2.1. Field methods

2.1.1. Sample design

The maximum Pb shot travel distance at trap shooting ranges is 180–300 m, depending on shot size (US EPA, 2005). Based on this travel distance, historical aerial photographs of the four former trap stations, and data from a preliminary sample transect, we selected a 300 × 520 m sampling area to encompass the potential shot fall zone (Fig. 1B). We established a 20 × 20 m grid for surficial (0–5 cm) sediment sampling and a 40 × 80 m grid for sediment cores (30–90 cm), with denser sediment core sampling occurring within the zone of expected maximum Pb shot fallout (100 to 200 m from the trap stations). Sampling sites were located in the field using a Trimble 6000 GeoXH handheld GNSS receiver and actual sampling positions were recorded for 120 s and differentially corrected to decimeter accuracy.

2.1.2. Sediment sample collection

Surficial (0–5 cm) samples (n = 456) were collected from the aquatic sites (elevation < 195 m) using a Wildco hand core sediment sampler with a 5 cm diameter plastic liner, either from a modified cataraft or on foot depending on water depth. Flocculent surface sediment was allowed to settle in the liner before the upper 5 cm was extruded with a baster and a PVC collar. Samples were transferred into plastic bags and returned to the University of Wisconsin — La Crosse (UWL) for processing. Surficial samples were collected from terrestrial sites (elevation > 195 m) along the pedestrian path and on the terrace surface adjacent to the former trap station locations using a trowel. Pathway samples were collected from both the surface (0–5 cm) and shallow pits (5 cm increments, maximum depth of 25 cm) immediately along both sides of the path.

Longer sediment cores (30–90 cm) were collected in the aquatic areas from the cataraft using a modified Livingston (Bolivia) drive rod piston corer with a 3.175 cm radius polycarbonate core barrel. Length of sediment cores was highly variable depending on the depth to sand found beneath the overlying flocculent silts and organics throughout the study area. The flocculent sediment–water interface was secured using sodium polyacrylate absorbent (Zorbitrol) prior to capping the cores. Cores were transported to UWL and stored upright in a refrigerator at 5 °C prior to processing.

2.1.3. Bathymetric and topographic data

Topographic and bathymetric data in the study area were collected to model the three-dimensional distribution of Pb within the LRM sediments. A Topcon total station was used to survey in 2072 points (at a 5–12 m spacing) to create a 10 m resolution digital elevation model (DEM) of the study site in ArcGIS (Fig. 2). A survey pole with a 0.3 m diameter disk foot was used to minimize penetration into soft marsh sediments at submerged or excessively wet sites. Survey positional control was provided by 5 differentially geo-referenced control points distributed throughout the study area.

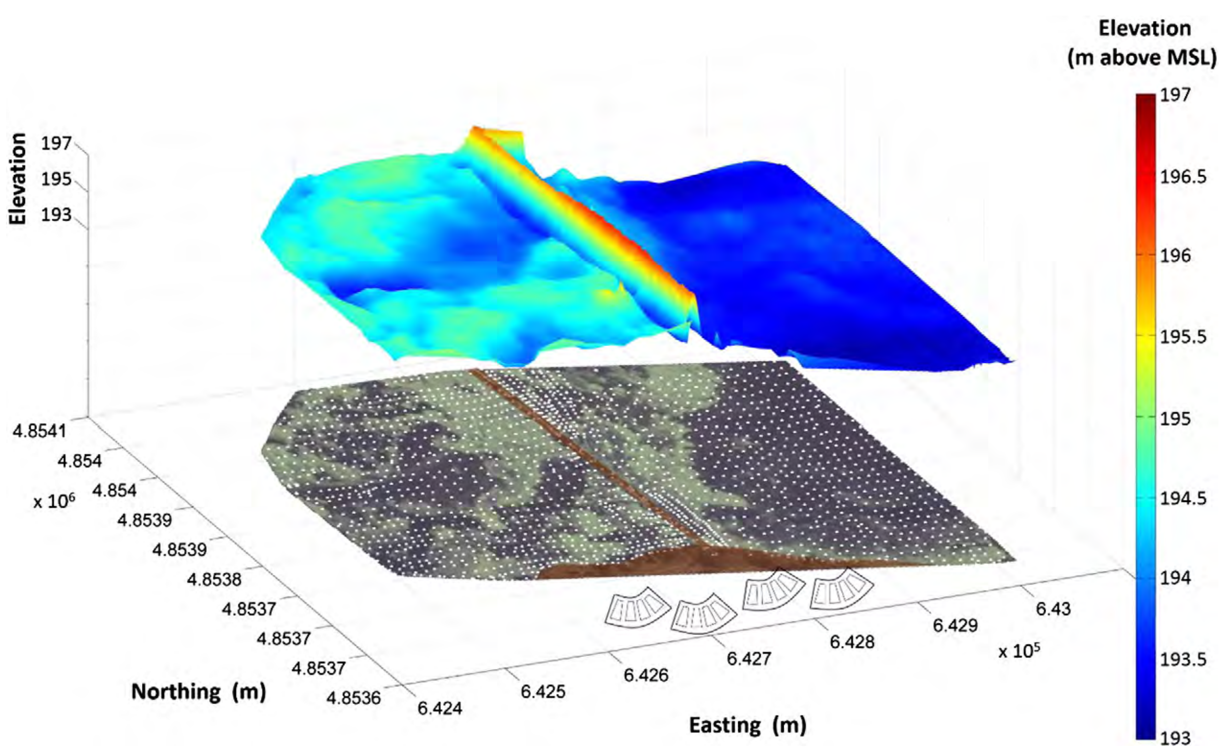

Fig. 2. 3D model of study site topography created using 2072 total station survey points. Raised linear feature is a gravel path that splits the study area into west and east sections. Aerial photo with XY locations of total station survey points shown below 3D model. Brown shaded areas on aerial photograph signify dry terrestrial components of the study area; white symbols signify trap station locations. Projection is WGS 84 UTM Zone15, elevation in meters above mean sea level.

2.2. Laboratory methods

2.2.1. Sample preparation

Of the 36 cores presented, 28 were X-rayed at Gundersen Health System (La Crosse, WI) prior to initial core description at the University of Minnesota Limnological Research Center. High resolution (10 pixels/mm) color images were acquired by a Geotek Geoscan-III and wet bulk density was measured by gamma ray attenuation on a Geotek multi-sensor core logger. The cores were split lengthwise; working halves were returned to UWL and sub-sampled at a 2 cm interval. Both surficial and core sediment samples were dried at 65 °C for 48 h. Dried samples were lightly ground with a rubber-tipped pestle to pass through a 2 mm sieve and all observed Pb pellets were immediately removed. Fragments of shot present in the marsh sediment at the time of sample collection or introduced during sediment grinding passed through the 2 mm sieve. Approximately 2.5 g of sediment from each sample was placed in a polyethylene cup with a mylar window film cover. All cups were X-rayed, and any observed intact Pb shot and shot fragments >0.5 mm were removed prior to XRF analysis.

Organic matter content of core sediment was determined by loss on ignition at 550 °C (Heiri et al., 2001). Analysis of sediment pH was completed using a 1:1 mixture of sediment to water (USDA, 2004). Sediment particle size was determined via laser diffraction on a Malvern Mastersizer 2000 following 24 h of dispersion in sodium hexametaphosphate solution (Sperazza et al., 2004).

Whole cores 7a and 7b (located ~24 m east of Core 9, Fig. 1B) were sub-sampled at a 2 cm interval and shot was manually separated from the wet sediment (i.e. its size was not altered by grinding the sediment). The recovered shot was thoroughly rinsed with deionized water, dried at 65 °C, and individually weighed. The diameter was measured at three locations with a digital caliper. The corrosion crust visible on the recovered shot was removed by ultrasonification and analyzed via X-ray diffraction on a Siemens D500 with a Cu X-ray source to determine the dominant weathering products (Jørgensen and Willems, 1987).

2.2.2. XRF analysis

XRF spectrometry is a method for detecting and quantifying element distributions within virtually any type of sample without destructive pre-treatment steps (Kalnicky and Singhvi, 2001; Palmer et al., 2009; Van Greiken and Markowicz, 2001). Although not as sensitive as wet chemistry techniques such as inductively coupled plasma-atomic emission spectrometry (ICP-AES), XRF spectrometry has several advantages including cost, speed, ease-of-use, and portability (US EPA, 2007). A growing number of studies have successfully used XRF spectrometry to analyze heavy metal contamination, illustrating its utility for rapid assessment of the extent and spatial distribution of metals in soil (Argyraki et al., 1997; Dao et al., 2013; Drake et al., 2003; Hürkamp et al., 2009; Vanhoof et al., 2004; Weindorf et al., 2012).

Prepared sediment samples were subjected to X-rays for 60 s using a Bruker portable X-ray fluorescence TRACER III–V+ system. The instrument was set at 45 kV and 25 μA with a combination Al (0.3048 mm), Ti (0.0254 mm), Cu (0.0254 mm) filter to suppress background noise in the region of interest. Raw detector counts were translated into quantified measures of near-total Pb elemental concentrations using a custom XRF calibration curve created from a subset of 48 LRM samples analyzed externally via ICP-AES following a nitric aqua regia digestion (3:1, v/v, HCl to HNO_3) in a graphite heating block by ALS Chemex in Elko, NV (method ME-ICP41). Aqua regia digestion has a Pb recovery rate of 70–95% in soil due to the retention of Pb at acid dissolution resistant aluminosilicate sites (Alloway, 1995; Chen and Ma, 2001, Sastre et al., 2002). Despite the potential underestimate of total Pb, aqua regia digestion provides the accuracy needed for environmental monitoring of Pb in soils (Kackstaetter and Heinrichs, 1997; Sastre et al., 2002). An additional ten samples, also sent to ALS Chemex for ICP-AES analysis but held out of the calibration procedure, were used for validation (Fig. 3).

2.2.3. X-ray analysis for Pb pellet counts

All undisturbed whole sediment cores were X-rayed to quantify Pb shot abundance and vertical distribution using a Varian medical systems A-192 X-ray tube (Salt Lake City, UT) at Gundersen Health System. Digital radiographs for a given core were stitched together in Adobe Photoshop and a moving window was used to manually count Pb shot at a 2 cm interval. Shot was clearly identifiable in the cores as bright white circles. Because radiographs provide only a two-dimensional perspective, a limited number of pellets may have been blocked from view by other shots. Therefore, X-rays were taken for 8 cores from dual perspectives to test for consistency of shot counts, and shot was separated from cores 7a and 7b and counted manually.

2.3. Two- and three-dimensional modeling

Results from the XRF Pb sediment analysis were assigned XYZ coordinates from the GPS and bathymetric datasets and brought into MATLAB for spatial interpolation using the natural neighbor method. Raw shot count data from the 3.175 cm radius sediment cores were scaled up to fit the modeled grid cell sizes. A map of total Pb shot was created by summing the scaled pellet data for each sediment core and interpolating the results across 2D space. A 'surface' 1 m^2 resolution 2D model of Pb concentrations was created using only samples from the upper 5 cm of LRM sediments. A 3D model (XYZ, 1 m × 1 m × 0.02 m) of Pb sediment concentrations was also created for the entire study area using data from both the upper 5 cm and the deeper sediment cores. Input data to the 3D model also included 'dummy' sediment cores with a uniform background Pb sediment level (50 mg/kg) and zero Pb pellets inserted along the four outside corners of the study area (well outside the expected area of Pb contamination) to create a more complete rectangular cuboid mesh.

Following the creation of the interpolated meshgrids, cells at elevations above the LRM bathymetric/topographic surface were set to NaN (Not a Number) to eliminate contributions from modeled values in non-sediment cells corresponding to air or water. Volumetric estimations of LRM sediments exceeding various regulatory threshold levels were calculated by summing the total number of cells above that value and then multiplying by grid cell dimensions.

3. Results

3.1. Marsh sediment properties

Sediment in the shot fall zone is typical of a floodplain marsh. Surface sediment is characterized by flocculent silt with high organic matter content and low bulk density, transitioning to high bulk density silt and clay with lower organic matter content (Fig. 4). Below this zone is a layer of sand, likely deposited during lateral migration of the La Crosse River. This general sequence is found throughout the study area, though intrusions showing abrupt changes in particle size and organic matter content were found in a number of the sediment cores. Sediment pH throughout the study area was generally acidic (mean = 5.6), ranging from 4.9 to 7.

3.2. Sediment Pb concentration results

A total of 1351 sediment samples (surface, sediment cores and footpath) were analyzed for Pb concentration. Sediment Pb concentrations in the cores sampled from the wetland ranged over nearly three orders of magnitude, from a mean background level of 51 mg/kg found in cores 28a and 28b located 150 m north of the potential shot fall zone to a maximum of 26,700 mg/kg found at a depth

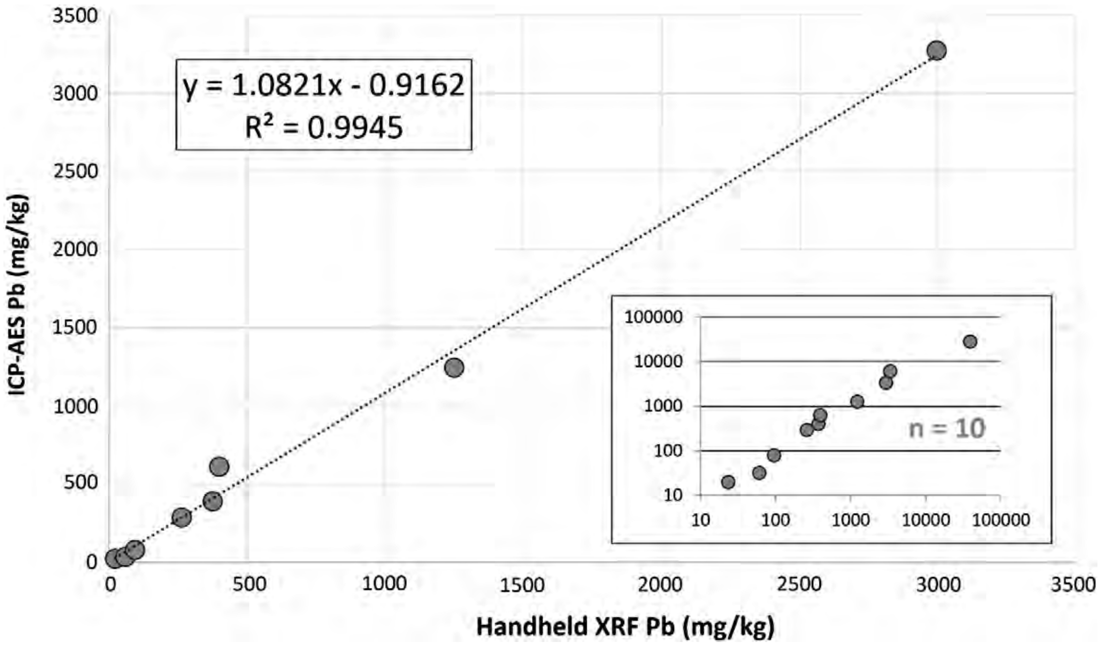

Fig. 3. Validation samples analyzed via ICP-AES and held out of custom calibration curve construction. Validation sample concentrations ranged from 19 to 26,700 mg/kg. Regression line shown for 8 samples <5000 mg/kg. Inset shows all 10 validation samples plotted on a log–log scale.

of 22 cm in Core 9 located 140 m north of the trap stations (Table 1, Fig. 1B). Sediment Pb concentrations in the core data generally show peak values in association with peak shot counts 10–30 cm below the sediment surface, typically followed by a decrease to background levels at depth.

Surface sediment concentrations in the aquatic portion of the shot fall zone were highly contaminated, with 21.3% of the samples exceeding the EPA's soil contamination threshold of 400 mg/kg. The highest surface sediment Pb concentrations corresponded with the region of highest shot counts and highest core Pb concentrations. All samples collected from the footpath that bisects the study area were below 400 mg/kg, with 84.7% below 130 mg/kg. Samples collected from the terrestrial surface adjacent to the former trap station sites all had Pb concentrations below 400 mg/kg.

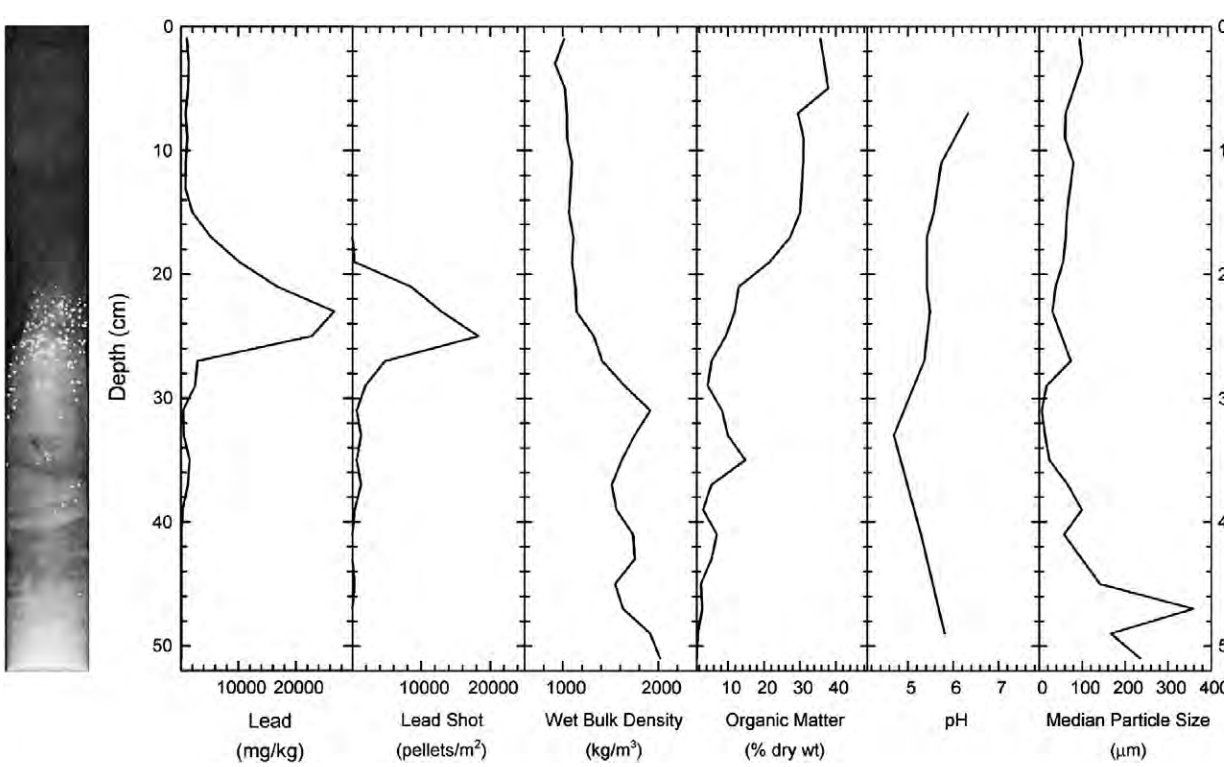

Fig. 4. Representative sediment core dataset for Core 9. X-ray image at left shows location and abundance of Pb shot within the core (white dots).

Table 1
Summary of Pb concentration from surface and core samples. The number of samples (n) and the percentage of the total (%) are given for each category.

Lead mg/kg	Shot fall zone cores (2 cm intervals)		Shot fall zone surface samples (0–5 cm)		Shot fall zone footpath samples		Background cores 28a and 28b (2 cm intervals)	
	n	%	n	%	n	%	n	%
0–36[a]	232	28.0	12	3.0	28	38.9	7	14
37–130[b]	304	36.7	174	43.4	33	45.8	43	86
131–400[c]	110	13.3	129	32.2	11	15.3	–	–
401–1200[d]	102	12.3	42	10.5	–	–	–	–
1201–5000	60	7.2	37	9.2	–	–	–	–
5001–10,000	13	1.6	3	0.7	–	–	–	–
10,001–20,000	5	0.6	1	0.2	–	–	–	–
>20,000	2	0.2	3	0.7	–	–	–	–
Mean (mg/kg)	602		715		71		51	
Median (mg/kg)	53		52		40		47	
Max (mg/kg)	26,709		42,854[e]		288		80	
Min (mg/kg)	14		26		26		15	

[a] Threshold effect concentration below which adverse biological effects in freshwater systems are expected to be rare.
[b] Probable effect concentration above which adverse biological effects in freshwater systems are expected to be frequent (MacDonald et al., 2000).
[c] EPA hazard criteria for bare soils in residential play areas.
[d] EPA hazard criteria for bare soils in residential non-play areas (US EPA, 2001).
[e] Outside of calibration curve maximum of 27,700 mg/kg.

3.3. Sediment Pb shot results

Lead shot was typically buried 10–30 cm below the LRM sediment–water interface. The greatest concentration of shot (51,154 pellets/m^2) was found in Core 9 in the center of the study area, 140 m north of the former trap shooting stations (Fig. 1B). Shot was easily identifiable in the radiographs as white dots (Fig. 4), and close agreement ($R^2 = 0.99$) in repeat shot counts made from radiographs of the same core taken from dual perspectives demonstrates the effectiveness of using X-ray imaging to estimate shot counts. Counts of Pb shot physically separated from cores 7a and 7b confirm the accuracy of the manual radiograph counts, though the radiograph counts for these cores were 4% to 9% higher. These values likely represent maximum potential error because of the high concentration of shot in these cores, and the error is expected to approach zero in cores with lower shot counts.

Lead shot sampled from the cores 7a and 7b had a mean diameter of 2.231 mm, and an average mass of 0.0485 g (Fig. 5). All shots examined under a stereomicroscope had a pitted, irregular surface coated with a corrosion crust (Fig. 5C), and little to no unaltered metallic Pb visible on the surface. X-ray diffraction analysis indicates that lead oxides (PbO) are the dominant decomposition products found in the shot crust, with lesser amounts of cerussite ($PbCO_3$) and shannonite ($Pb_2O(CO_3)$) present.

3.4. Interpolated two- and three-dimensional results

From the 2D and 3D interpolated models for Pb sediment concentrations in the LRM study area (Fig. 6, Table 2), it is estimated that 8.9 ha of surface sediment and 64,270 m^3 of total sediment exceeds the 130 mg/kg Pb probable effect concentration above which adverse biological effects in freshwater systems are expected to be frequent

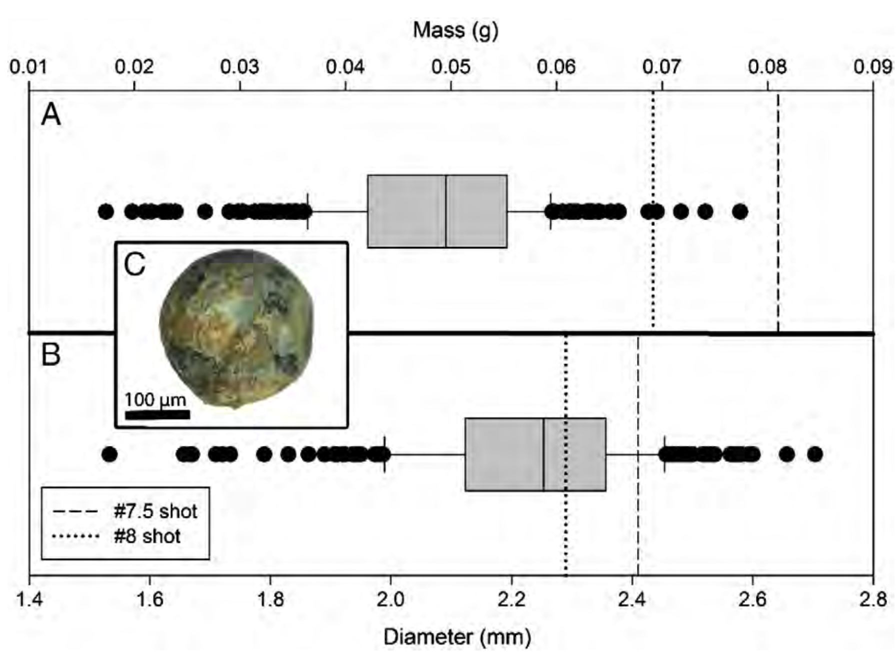

Fig. 5. (A) Mass and (B) diameter of lead shot taken from cores 7a and 7b relative to shot sizes #7.5 and #8 most commonly used during trap shooting (US EPA, 2003; MA DEP, 2009). (C) Lead shot with corrosion crust recovered from Core 7a at a depth of 27 cm below the sediment surface.

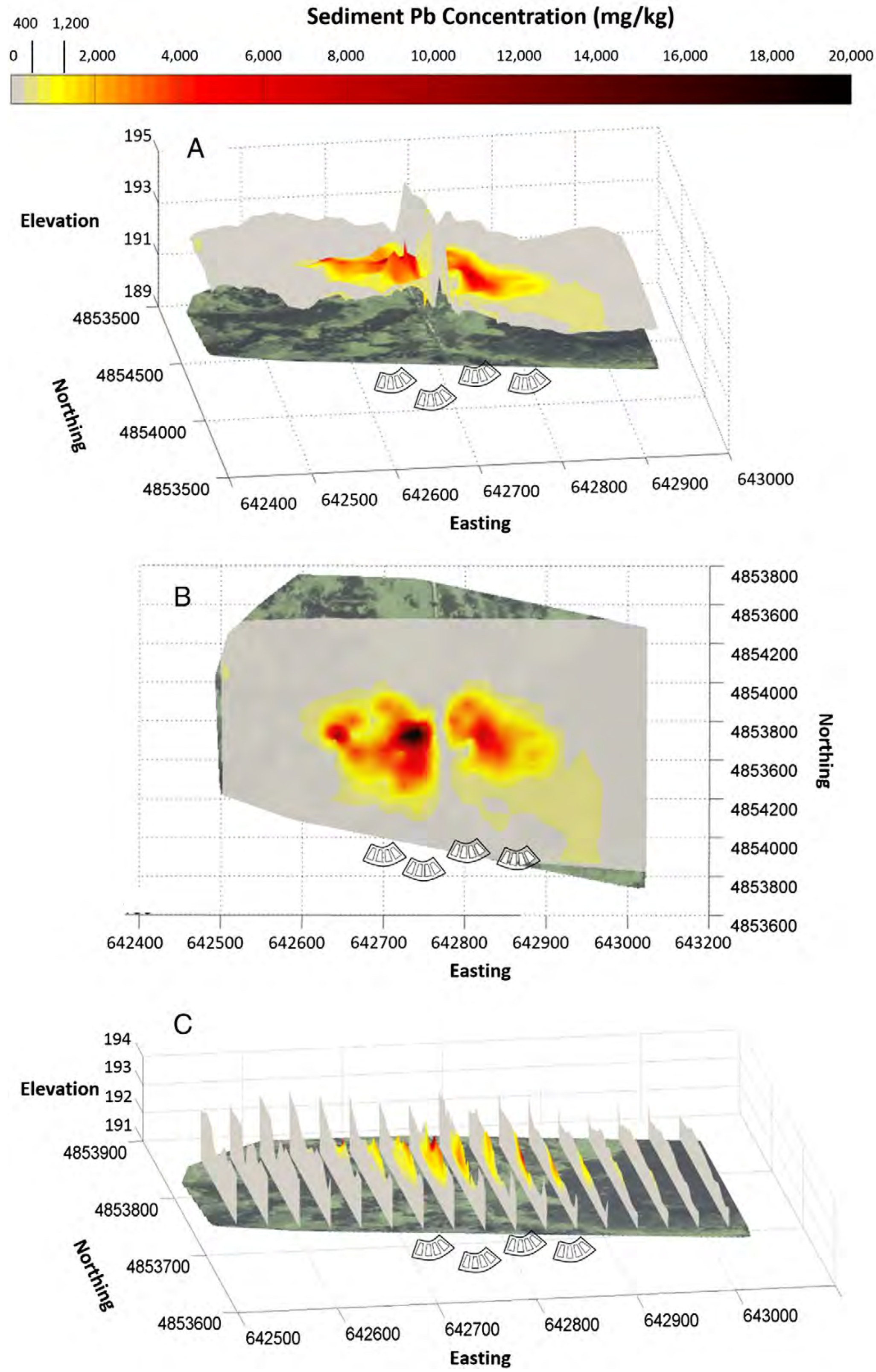

Fig. 6. Spatially interpolated Pb concentrations in LRM sediments. (A) Oblique view depicting surficial sediment concentrations of Pb, draped over a 10 m resolution DEM; (B) top–down view of the same data as shown in Panel A; and (C) 2D slices through volumetric model showing spatial distribution of Pb contamination with depth. 2010 aerial image and trap station locations provided for reference.

(MacDonald et al., 2000). The EPA's contaminated soil threshold of 400 mg/kg (US EPA, 2001) was exceeded across 3.8 ha of surface sediment and in 31,700 m^3 of total sediment. The 2 cm increment Pb shot count data was summed for each core and used to create an interpolated map of total buried Pb pellets (Fig. 7). It is estimated that 4.2×10^8 Pb pellets, or 2.0×10^4 kg based on the average mass of shot recovered

Table 2
Pb modeling results from surface and core sample data at three different threshold limits.

Threshold Pb concentration (mg/kg)	Surface sediment coverage (hectares)	Volumetric coverage (m^3)
1200	1.9	13,220
400	3.8	31,700
130	8.9	64,270

from cores 7a and 7b, remain in the LRM study area. No lead shot was found on the pedestrian path or on the dry upland terrace immediately adjacent to the former trap station sites.

4. Discussion

4.1. Spatial patterns of Pb contamination

The spatial pattern of surficial Pb contamination in the LRM, ranging between 60 and 220 m away from the former trap-shooting stations with a zone of maximum surface contamination ~160 m away, is similar to that observed in a previous work examining contamination patterns at an upland trap shooting range (Rooney et al., 1999). The magnitude of maximum contamination is also similar to that found in other wetland shooting range studies (Coffey, 1998; Hui, 2002).

In addition to the expected 'hot spot' contamination zones near the center of the study area, the southwestern quadrant contains slightly elevated surficial Pb concentrations (Fig. 6B). These elevated values may be due to new inputs of Pb-contaminated sediment from city storm sewers draining into this portion of the LRM, mobilization and redistribution of contaminated sediments due to wind and bioturbation, or legacy effects from the 1952 clean-up effort. Possible natural causes for lateral lead migration – wind and currents – seem unlikely in this shallow, relatively protected marsh, which contains dense aquatic vegetation during the growing season and thick ice cover during the winter. Furthermore, the sharply defined and confined contamination zone indicates minimal export of shot or Pb contaminated sediment to adjacent areas in the floodplain wetland complex or to the La Crosse River.

What sets our study apart is that we characterize how this Pb contamination varies with depth in wetland sediments, which can provide insight into the exposure risk for biota that uses former wetland shooting range sediments for habitat and forage, as well as baseline information for future ecological studies or remediation efforts. Although small numbers of Pb pellets were found at or near the sediment surface in some cores, most of the pellets responsible for contamination in the LRM are buried by 10–30 cm of organic rich silt. Pellet burial can be attributed to subsequent deposition of new organic-rich material and the progressive sinking of the heavy Pb pellets into the low density, bioturbated sediment. Elevated sediment Pb concentrations were found not only in close association with Pb pellets, but also in shot-free sections above, and often below, pellet locations. These elevated Pb concentrations indicate vertical mixing of sediment, likely by benthic invertebrates, fish, and carbon dioxide and methane degassing observed during field work. In some locations along the margins of the main shot fallout zone, elevated Pb concentration and shot counts are not reached until depths >20 cm, suggesting lateral differences in the amount of sediment mixing that is taking place.

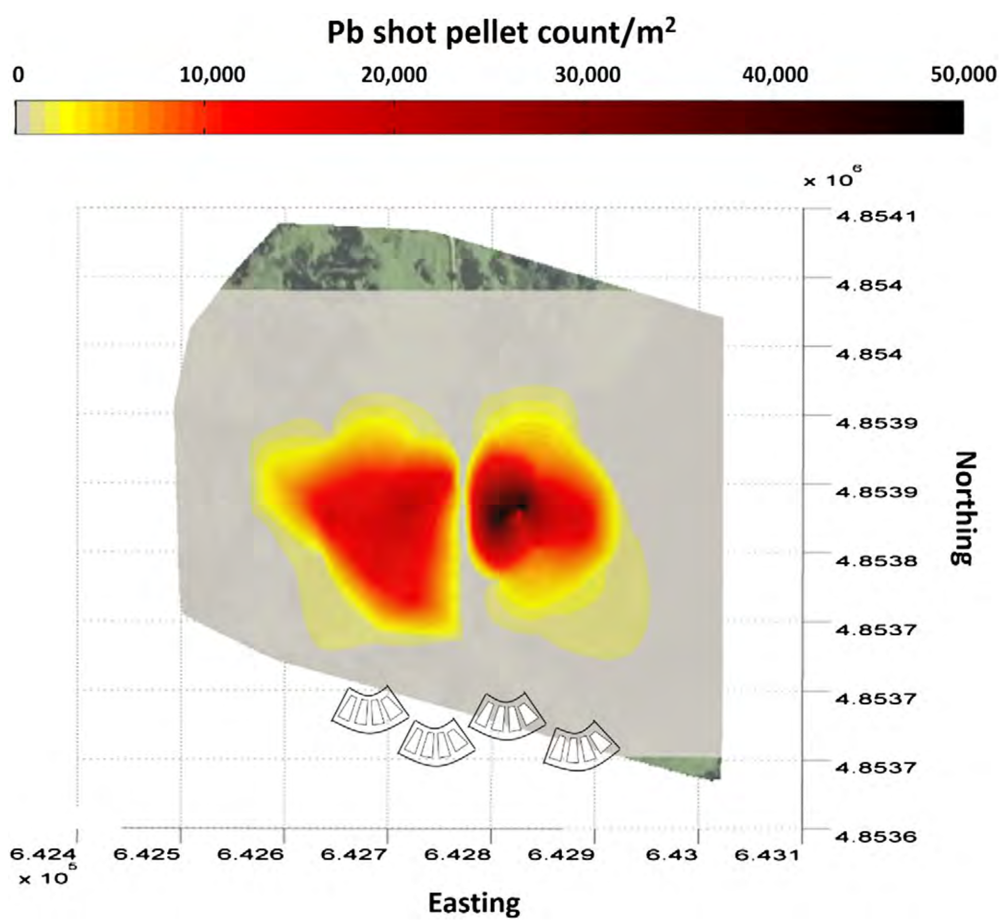

Fig. 7. Top–down view of the total number of Pb pellets in LRM study area sediments per square meter. 2010 aerial image and trap station locations provided for reference.

The average depth to reach 'clean' sediments below the 400 mg/kg threshold was 27 cm for all cores with Pb concentrations exceeding the EPA's contaminated soil threshold of >400 mg/kg. Major exceptions include cores 17 and 26b near the center of the study area, which have highly elevated Pb concentrations down their entire length. In fact, the highest Pb concentration in Core 17 occurred at the bottom of the core (0.76 m), suggesting that the contamination continues even deeper at this site. Given their central locations within the study area, these anomalous cores may be the result of mechanical disturbances and sediment mixing from the 1952 shot salvage operation. Other locations within the marsh may exhibit similar patterns, suggesting that our estimates of the total volume of affected sediments are likely conservative.

4.2. Potential sample processing artifacts

Although care was taken to identify and separate out Pb shot during sample preparation, some shot fragments inadvertently passed through the drying and grinding sample processing steps, thereby introducing small shot fragments to the bulk sediment samples that were subsequently analyzed via XRF. That said, we believe that the strong correlation between shot counts and sediment Pb concentration is not simply a result of sample preparation. The formation of the secondary minerals cerussite and shannonite, pitting on the shot surface, and the reduction in mass and diameter of shot in core sediment that was not ground during preparation provide strong evidence that the shot is corroding in the acidic wetland sediment. X-ray images of the prepared XRF cups also found very limited evidence of Pb shot fragments. The highest Pb concentrations in the sediment are therefore expected where shot concentration is greatest; had the samples not been ground prior to shot removal, the concentrations would still likely have exceeded the EPA's contamination criteria by a wide margin.

4.3. Ecological implications and conclusions

The biologically active zone in freshwater ecosystems typically extends 20–40 cm below the sediment surface, with some invertebrates and amphibians spending a portion of their life cycle at even greater depths (MacDonald et al., 2000; WDNR, 2003). Diving waterfowl observed in the study area can remove ~30 cm of fine sediment from wetland bottoms during intensive feeding activities (USGS, 2006). While the contaminated surface sediments pose the greatest risk for wildlife in the LRM study area, even the deeper areas of contamination reside within the LRM's biologically active zone and may therefore present a risk.

One measure for predicting lead toxicity to organisms living in contaminated sediment or sediment pore water is the use of consensus-based sediment quality guidelines (MacDonald et al., 2000). Adverse effects are rarely expected when sediment Pb is below the threshold effect concentration (TEC) of 36 mg/kg. Adverse effects are expected to occur frequently when Pb concentrations exceed the probable effect concentration (PEC) of 130 mg/kg. While the TEC and PEC are not meant to be used alone for making remediation decisions, they do provide guidance on whether monitoring and toxicity testing are necessary (Burton, 2002; Chapman and Smith, 2012; MacDonald et al., 2011). Because the TEC is exceeded in 72% of the core samples and 97% of the surface samples, and the PEC is exceeded in 36% of the core samples and 54% of the surface samples, further analysis of the site biogeochemistry and toxicity is warranted.

Initial results from surface and pore water, vegetation, benthic macroinvertebrates, and fish samples all show elevated Pb levels within the LRM study area, and concentration patterns generally mirror the spatial distribution of Pb in the sediments. Supernumerary antenna malformations were observed in Corduliidae (dragonfly) specimens collected within the LRM shot fallout zone (R. Haro, UWL Biology, pers. com.), and morphological deformities in benthic invertebrates have been connected to lead-contaminated sediments in other studies (De Bisthoven et al., 1998; Martinez et al., 2001). Ongoing toxicity assays and biological sampling, along with more detailed examinations of pore and surface water contamination levels and investigations into the geochemistry of the weathering processes affecting the Pb pellets, may explain how this contamination impacts the ecology of the LRM and similar settings.

Under normal water conditions contaminated sediments are generally below 0.5–2 m of water, and direct human exposure to Pb contamination in the LRM is limited. But under severe drought conditions, contaminated areas may become subaerially exposed. This was the case for the LRM in 2012, as experienced across the Midwestern United States (Hoerling et al., 2013; Mallya et al., 2013), and it is particularly worrisome due to the frequent use of the wetland complex by the public, including young children participating in educational programs at the adjacent EcoPark. Future prolonged or repeated droughts, as predicted under some climate change scenarios (Dai, 2012), could repeatedly drop water levels in this and similarly affected areas to the point of drying out contaminated sediment and increasing public exposure pathways.

The LRM presents a valuable case study for understanding the spatial distribution and long-term fate of Pb contamination in former wetland shooting ranges, and highlights the capacity of XRF and traditional X-ray technology to quickly and cost-effectively produce large datasets that can be used to generate fine-resolution 3D models of heavy metal contamination. If we had used only wet chemistry analytical techniques, we would have been able to analyze ~10% of the 1351 samples ultimately used in this study. This study provides an economical and proven methodology for predicting and evaluating the 3D distribution of shot and contaminated sediment at other shooting ranges and contaminated areas worldwide, where similar health risks and environmental hazards may require prompt monitoring and/or remediation efforts.

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Appendix B

WI DNR Report on Lead Contamination in LRM

Lead Contamination Investigations in the La Crosse River Marsh
Project Update – November 2012
John Sullivan and Kurt Rasmussen, WDNR- La Crosse

Background

The La Crosse Gun Club operated a large trap shooting range on the southern edge of the La Crosse Marsh for about 30 years (1932-1963). Cursory evaluations by the Department in 1989 and by an undergraduate student at the University of Wisconsin La Crosse (UW-La Crosse) in 1994 revealed moderate to high lead pellet densities in the upper foot of sediment in areas adjacent to the trap range. More detailed investigations by researchers at the UW-La Crosse in 2011 indicated maximum sediment lead concentrations of approximately 20,000 ug/g (ppm) with pellet densities exceeding 40,000 /m^2. UW-La Crosse was successful in obtaining an USEPA Urban Waters Small Grant to conduct additional research and public outreach to describe that fate of this legacy lead contamination and potential threats to aquatic resources, wildlife and the public. The Department is cooperating with the UW-La Crosse in this effort and has undertaken additional monitoring to evaluate this site. The primary goals of this investigation include:

- Determine the extent and level of lead contamination in the La Crosse Marsh and identify threats to aquatic life, wildlife the public and determine the need for sediment remediation.
- Cooperate and provide assistance to University-lead research and monitoring efforts
- Educate the public and strengthen partnerships of marsh stakeholders
- Provide assessment methods for evaluating similarly impacted wetland

This report summarizes the results of the Department's monitoring undertaken during April-September 2012.

Sediment Traps -

Cylindrical glass sediment traps (500ml tall –ICHEM jars) were deployed at three locations in the La Crosse Marsh during April 5– to July 3, 2012 to provide to provide a time-integrated sample for evaluating suspended sediment quality. Two sites (East and West) were in the areas where highest sediment lead concentrations were reported. A third site (North) was located in a portion of the marsh that was expected to have less direct influence from the former trap shooting range (Figure 1). The traps were deployed at the three depths within the water column (near surface, mid-depth and near the sediment-water interface). Traps were mounted to a 1 in. PVC tubing that was slid over a ¾ inch conduit that had been driven into the sediment. A vertical composite sample was obtained for each site by combining the accumulated sediment in each trap into a single sample then mixed prior to shipping to the State Laboratory of Hygiene for lead, total volatile solids (TVS) and total organic carbon (TOC) analyses. Final results from the lab were reported on October 17 (Table 1).

The sediment traps revealed very high lead concentrations (2,670 to 3,660 ug/g) at the East and West sites at locations where bed sediment lead contamination was expected. These concentrations were substantially greater than similar trap samples collected from the Mississippi River at Lock and Dam 3and 4 during the spring of 2012, which had concentrations of 12 ug/g at both sites. The trap samples deployed in the La Crosse Marsh contained sediment very high in organic matter as reflected in the TVS and TOC contents. Sediment traps in the marsh also accumulated more sediment at increasing water depths (Figure 2). It is suspected the bottom traps accumulated surficial bed sediment either due to sediment resuspension or entrainment of bed sediment as a result of the trap opening being below the sediment-water interface during the deployment period. The bed sediment at all sites was unconsolidated and flocculent in nature and resulted in some uncertainty in defining the depth of the sediment-water interface during trap deployment. The relatively shallow water depths (0.5 to 3 ft) suggests the trap samples were likely influenced by sediment mobilization due to wind-induced mixing or bioturbation of surficial sediment during the deployment period.

Table 1. Sediment trap results obtained for the La Crosse Marsh. Deployment period: April 5 to July 3, 2012.

Measurement	North Site	West Site	East Side
Total Lead ug/g	62	2,670	3,660
Total Volatile Solids %	27.3	41.8	32.3
Solids %	7.4	5.7	6.9
Total Organic Carbon %	8.59	14.2	8.8

Bed Sediments

Bed sediments were collected at the three La Crosse Marsh monitoring sites (North, East and West) on July 23 using a petite ponar. An additional sample was collected at Lizzy Pauls Pond (Pool 5) to serve as a reference. Several ponar grab samples were collected at each site and were placed into a large stainless steel bowl then mixed to obtain a composite sample. The sediment was then placed into lab-supplied sampling bottles for TVS, TOC, lead analysis. A small portion of this composite samples was placed into Ziploc bags for particle size analysis. The remainder of the sample (about 2 gallons) was placed into lab-supplied 5-gallon pails and secured with a cover. These latter samples were analyzed for sediment toxicity. All samples were placed on ice during transit to the laboratory. Chemical analysis and toxicity testing was performed by the Wisconsin State Laboratory of Hygiene. Sediment particle size and pH analysis was performed by the University of Wisconsin Soil and Plant Analysis Laboratory.

Sediment from the La Crosse Marsh was silty with very high organic matter content as indicated by high TOC and TVS. Sediment lead concentrations in the La Crosse Marsh indicated moderate to very high lead contamination (59 to 5,360 ug/g) with highest levels reported at the East and West sites, locations where maximum lead shot fallout from the former trap shooting range would be expected. Lead concentrations at the East and West sites greatly exceeded the probable effect concentration (PEC,130 ug/g) identified in the Department's Consensus-Based Sediment Quality Guidelines. The North site had substantially lower lead contamination with concentrations exceeding the threshold effect concentration

(TEC, 36 ug/g) indicated in these guidelines. In contrast, bed sediment lead concentrations from the reference site (Lizzy Pauls Pond) were low (11 ug/g).

Sediment from the East site contained the highest level of lead contamination (5,360 ug/g) and this material had leachable lead concentrations (TCLP analysis) slightly exceeding hazardous material classification (> 5 mg/L). The TCLP analysis is normally performed on contaminated material to help classify the material for disposal purposes and to provide an index to potential contaminant leaching. The testing was conducted here to provide a cursory evaluation of lead mobility and it should be recognized that this potential is strongly influenced by ambient conditions which may differ substantially from leaching conditions performed in the laboratory.

Although sediments from two sites in the La Crosse Marsh were found to have very high lead concentrations, sediment toxicity evaluations using the midge, Chironomus tentans, and the amphipod, Hyalella aztetca, were negative.

Table 2. Bed sediment results obtained for the La Crosse Marsh and Lizzy Pauls Pond. Samples collected in the La Crosse Marsh (N, W and E sties) on July 23 and Lizzy Pauls Pond on July 24, 2012.

Measurement	North Site	West Site	East Side	Lizzy Pauls Pond
Lead ug/g	59	3,820	5,360	11
Lead TCLP[1] mg/L	*	2.01	5.13	*
Total Volatile Solids %	28.1	37.5	24.4	16.1
Solids %	13.2	11.7	16.6	16.4
Total Organic Carbon %	10.4	11.1	9.1	5.9
Sediment Toxicity	negative	negative	negative	negative
Sand %	19	23	11	3
Silt %	60	60	61	80
Clay %	21	17	28	17
pH	6.7	6.5	6.3	6.8

*No test performed because of low sediment lead concentrations
[1]Toxicity Characteristic Leaching Procedure

Water

Surface water quality field measurements (DO, pH, conductivity, turbidity, temperature) were collected at biweekly to monthly intervals from April to September 2012. Water chemistry (nutrients, metals, chlorophyll a) samples were collected at the three La Crosse Marsh sites and Lizzy Pauls Pond in late July and early August and coincided with sediment sampling or nutrient evaluations. A continuous dissolved oxygen and temperature logger was installed in the La Crosse Marsh (North Site) during July to September and Lizzy Pauls Pond during early August to early September to document diurnal changes. A measurement of duckweed production was also made in the La Crosse Marsh during August as part of separate nutrient evaluation for this system. The discussion of water measurements in this report is focused on the lead study investigations.

Field water quality measurements indicated a substantial reduction in dissolved oxygen in the La Crosse Marsh in early July and extended into early September and coincided with warm water and moderate to heavy aquatic vegetation growth (Figure 3). Dead and stressed game fish were found in the study area on July 3 and was likely a result of warm water and hypoxic to anoxic conditions (Figure 4). These conditions are not unusual for the La Crosse Marsh and fish kills have been reported in previous summers.

Water chemistry sampling indicated the La Crosse Marsh and Lizzy Pauls Pond had moderately hard water as indicated by total hardness values of 137 to154 mg/L $CaCO_3$ (Table 3). Nutrient concentrations in the La Crosse Marsh on July 23 indicated high to very high concentrations of total phosphorus (0.4 to 1.8 mg/L) and total kjeldahl nitrogen (2.9 to 11.7 mg/L). These concentrations were likely strongly influenced by sestonic material as reflected by relatively high turbidity levels, especially at the East and West sites, which had turbidity levels of 35 to 93 NTU. Total ammonia nitrogen concentrations were detected at all sites and were highest at the East and West sites in the La Crosse Marsh, 0.29 to 2.3 mg/L, respectively. It is suspected that these nutrient levels were strongly influenced by sediment disturbance or efflux from the sediments. Nitrite+nitrate-nitrogen (NO_2+NO_3-N) were not detected (<0.019 mg/L) at any site. This is commonly observed mid-summer in wetlands and backwaters along the Mississippi River and is related to reduced inflows of waters containing NO_2+NO_3-N, nutrient assimilation by plants and dentrification. Mid-summer field pH measurements revealed relatively low values (~6.5 to 7) at the East and West sites in the La Crosse Marsh in comparison to the North site or the reference site at Lizzy Pauls Pond (Table 3 and Figure 5). The reason for this difference was not determined but may be an important factor influencing the lead fraction in the dissolved versus particulate phase.

Total lead analysis was initially performed using atomic absorption (AA Furnace), which had a lead detection level of about 1 ug/L (ppb). If lead concentrations in the water samples were below detection using this method, then the lab was instructed to re-run the analysis on separate samples that were collected flowing low-level techniques followed by low-level lead analysis (ICP-MS), which yield substantially lower detection levels (0.004 ug/L). This approach was followed to try to save on analytical costs. Total lead concentrations in samples from the La Crosse Marsh ranged from 12.6 to 68.4 ug/L. Highest concentrations were present at the East and West sites, locations were bed and suspended sediments (traps) also revealed high lead levels. The West site revealed an anomaly where the initial lead result reported using atomic absorption method was <1 ug/L but the low-level analysis indicated 31.4 ug/L. The reason for this discrepancy was not established but may have reflected greater sestonic material in the sample collected for low-level lead analysis. The highest total lead concentration (68 ug/L) reported at the East site exceeded chronic toxicity criteria when factoring in the total hardness of this sample (137 ug/L). Both the East and West sites had high to very high sestonic material in the sample as indicated by the high turbidity, 38 and 93 NTU, respectively. The high water column lead concentrations at these sites may have been strongly influenced by this particulate material, especially if this material reflected mobilized bed sediment particles or detritus of plant material containing lead.

Table 3. Field water quality and lab water chemistry results obtained for the La Crosse Marsh and Lizzy Pauls Pond. Samples collected in the La Crosse Marsh (N, W and E sties) on July 23 and Lizzy Pauls Pond on July 24, 2012.

Measurement	North Site	West Site	East Side	Lizzy Pauls Pond
Dissolved oxygen mg/L	2.1	4.0	0.3	4.5
Temperature C	23.6	25.7	26.5	25.8
pH	8.6	6.9	6.7	8.3
Conductance uS/cm @ 25C	409	480	423	281
Turbidity NTU	10.9	34.9	93.3	6.2
Total Lead (AA Furance) ug/L	12.6	< 1	68.4	< 1
Total Lead (ICP-MS) ug/L	na	31.4	na	0.0416
Total Calcium mg/L	26.9	26.7	27.6	20.5
Total Magnesium mg/L	19.5	21.4	16.7	21.5
Total Hardness mg/L	147	154	137	139
Total Kjeldahl-Nitrogen mg/L	2.94	4.15	11.7	0.90
NO3+NO2-N mg/L	< 0.019	< 0.019	< 0.019	< 0.019
NH3+NH4-N mg/L	0.079	0.292	2.33	0.060
Total Phosphorus mg/L	0.423	0.389	1.84	0.183
Dissolved Ortho-P mg/L	0.118	0.018	0.048	0.087
Chlorophyll a ug/L	ns	ns	ns	18.0

na – not analyzed
ns – no sample

Fish Tissue

Fish were collected in close proximity to the East and West monitoring sites on August 28, 2012 in the La Crosse marsh. The fish were collected for tissue analysis for lead. The fish species present in the La Crosse Marsh at the time of collection were limited due to a recent fish kill (dead and stressed fish were observed as early as July 3). The fish kill was likely due to low oxygen and very warm temperatures resulting in anoxic conditions throughout the marsh. After the fish kill, bullheads were observed at the surface of the water "gulping" air. Bullheads are extremely tolerant fish and have the ability to survive in very low oxygen and extremely warm temperature waters.

Fish were collected with the aid of a backpack electrofishing unit. The electrofishing unit delivers pulsed direct current electricity into the water through a handheld anode probe which causes electrotaxis in the fish. Electrotaxis causes the fish to swim towards the anode probe and allow the operator to collect the fish with a dip net.

Backpack electrofishing sampling in the La Crosse Marsh yielded a fish population that was largely dominated by black bullheads. The largest bullheads were collected to be used for tissue analysis. The bullheads were measured and placed in foil packages each containing at least five fish. The foil packages were then wrapped in freezer paper and placed in bags with collection cards containing all pertinent information. Three small bluegills were also collected and packaged using a similar process. The packages were then frozen and taken to Wisconsin State Lab of Hygiene for tissue analysis. Lead tissue results will be available later.

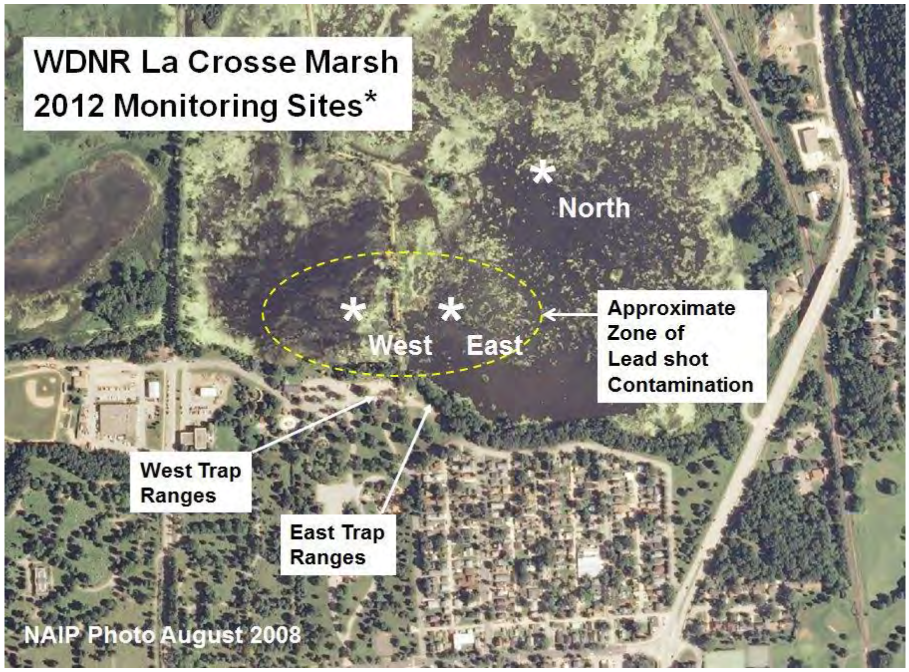


Figure 1. La Crosse Marsh aerial photo showing sampling locations used the Wisconsin DNR during investigations during the summer of 2012.

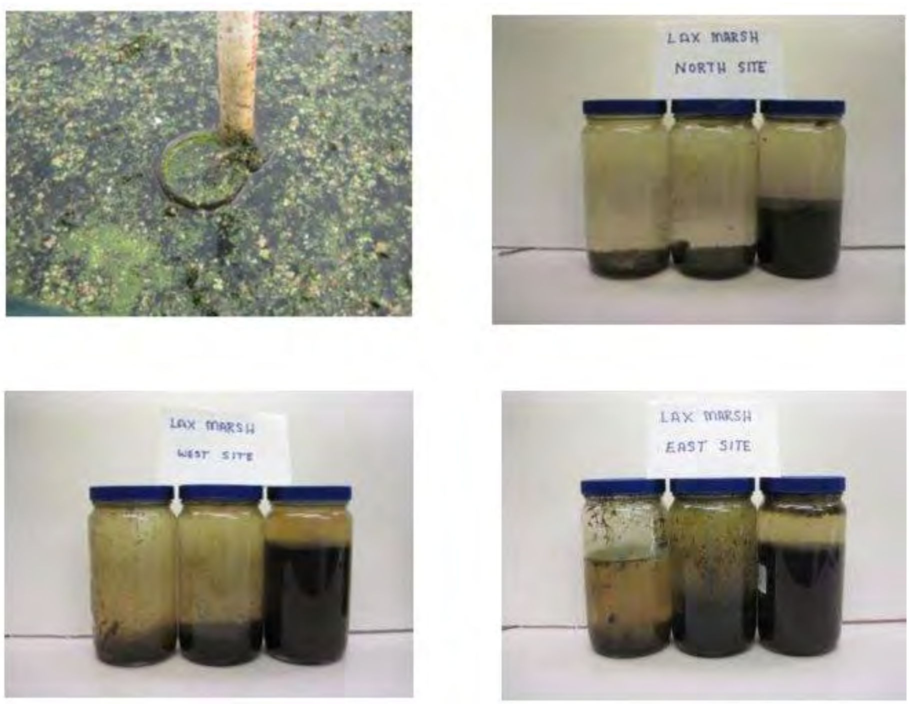
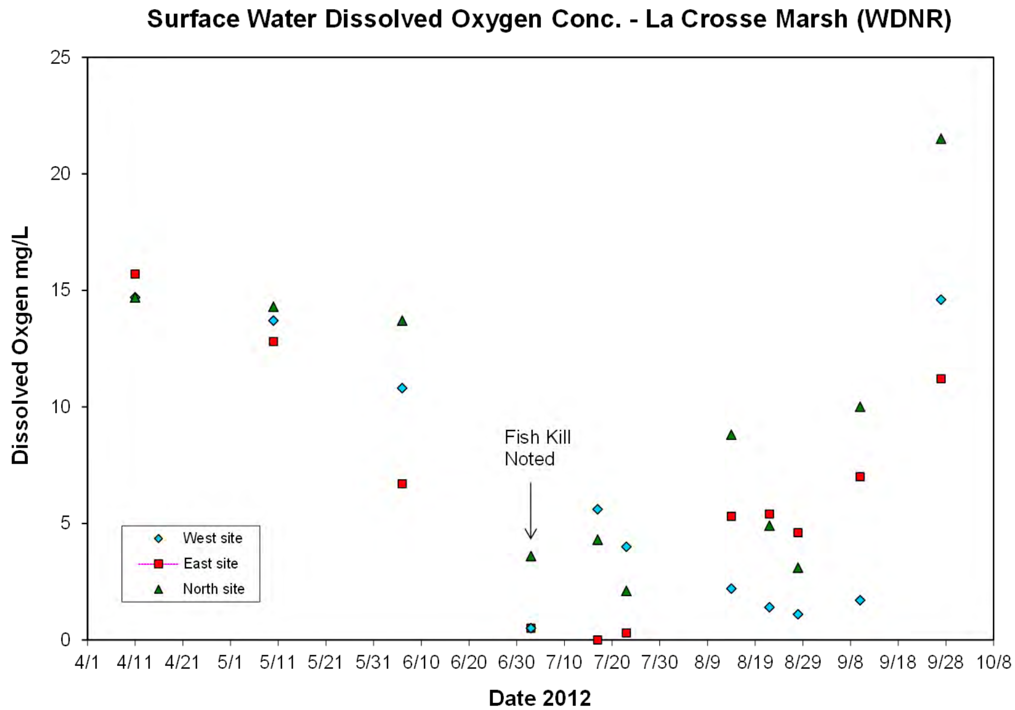


Figure 2. La Crosse Marsh sediment trap samples showing sediment material collected after the deployment period (April 5 to July 3, 2012).



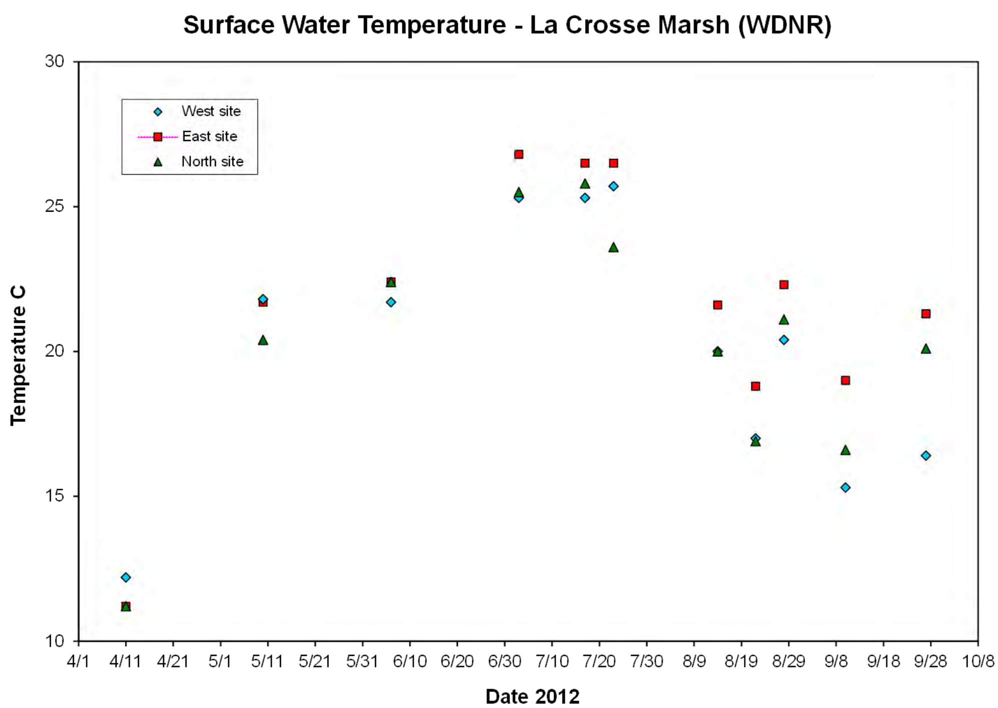


Figure 3. Field measurements of dissolved oxygen (top) and water temperature (bottom) measurements collected in the La Crosse Marsh during April to September 2012. Samples were collected about 0.5 ft below the water's surface.

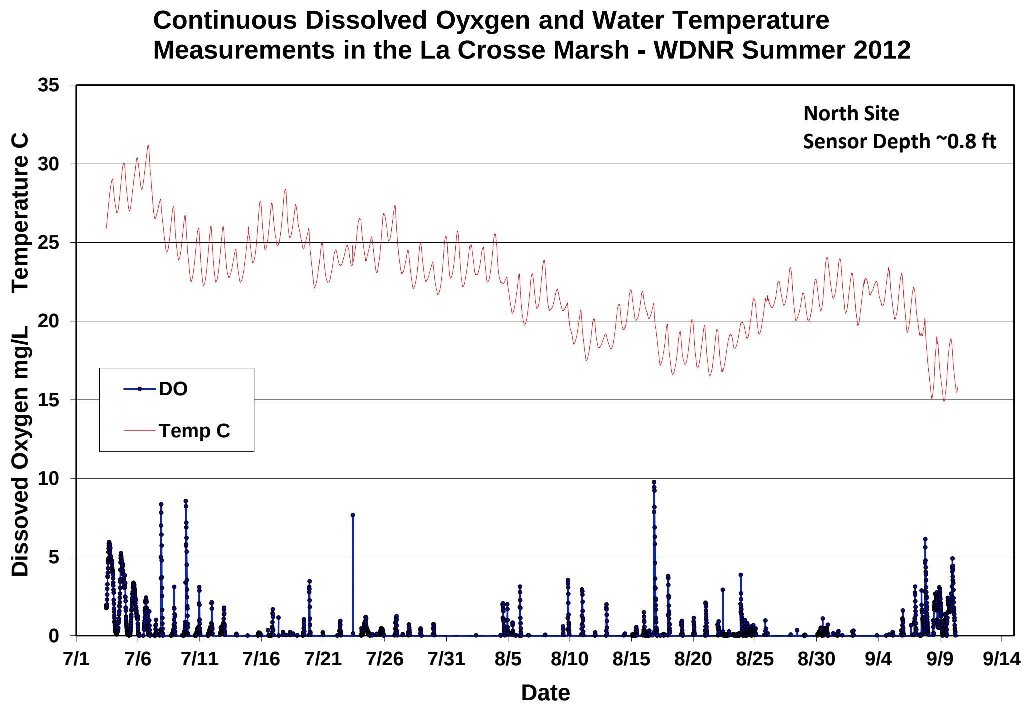


Figure 4. Continuous dissolved oxygen and water temperature monitoring results collected near the North site in the La Crosse Marsh in the summer of 2012.

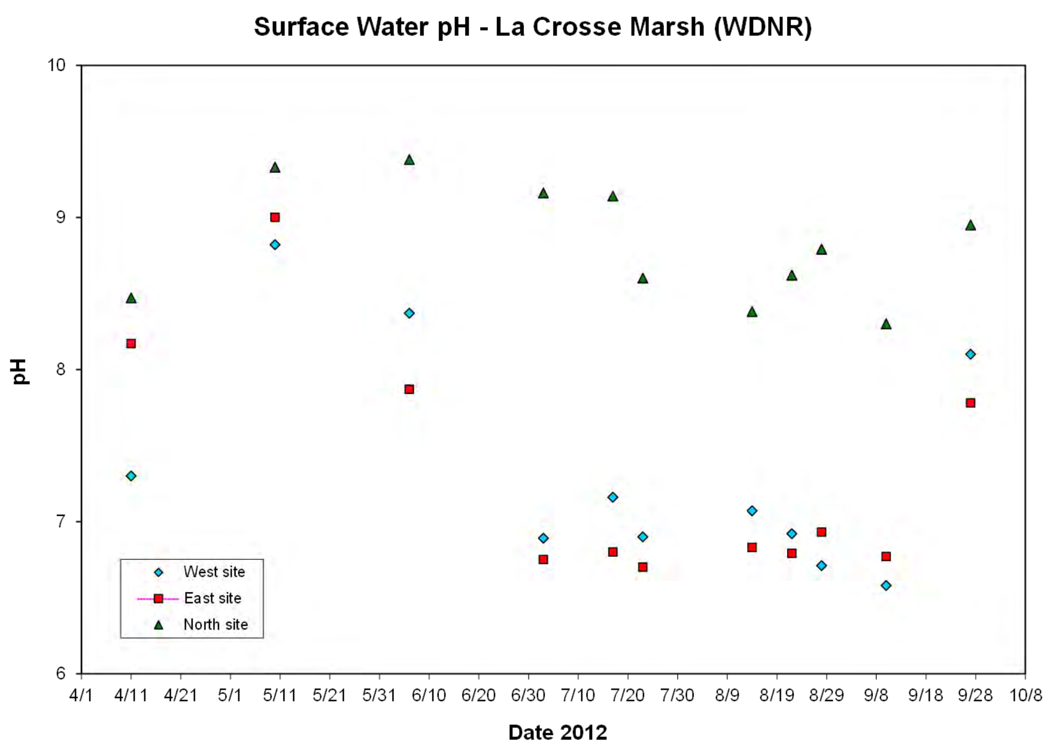


Figure 5. Field measurements of pH measurements collected in the La Crosse Marsh during April to September 2012. Samples were collected about 0.5 ft below the water's surface.

Appendix C

WI DNR Report on LRM Sediment Toxicity

SEDIMENT TOXICITY TESTS

La Crosse Marsh Lead Study

Tested July-August 2012

By the Wisconsin State Laboratory of Hygiene

Environmental Toxicology Section

Laboratory Report Number FX000096-099

Report Date: October 8, 2012

Reviewed by: Steve Geis   Date: 10/19/2012

INTRODUCTION

John Sullivan of the Wisconsin Department of Natural Resources collected four sediment samples for the La Crosse Marsh Lead Study July 23-24, 2012 and delivered them to the Wisconsin State Laboratory of Hygiene (WSLH). WSLH tested the sediments for toxicity along with formulated sediment as a laboratory control. Solid phase sediment toxicity tests were performed using the amphipod, *Hyalella azteca*, and the larval stage of the midge, *Chironomus tentans*. These two organisms, which burrow and come into direct contact with the sediments, are recommended for use in sediment toxicity testing (USEPA, 2000).

TEST METHODS

Sediments were received in 5 gallon high density polyethylene buckets on July 25, 2012 and stored in the dark at 4°C. On July 27, each sediment sample and the synthetic laboratory control sediment were thoroughly homogenized by mixing the sample in a five gallon bucket using a large stainless steel spoon. Homogenized sediment was placed in test beakers and stored at 4°C until July 29. On July 29, dechlorinated tap water was added to each test beaker at a ratio of 1:1.75, sediment to overlying water and the test beakers were randomly placed into a walk-in environmental chamber at 23 ± 1°C with a 16 hour: 8 hour light:dark cycle. After allowing the sediments to settle overnight, organisms were randomly added to the test beakers on July 30, 2012. Test conditions are summarized in Table 1 (USEPA, 2000).

Chironomus tentans

Chironomus tentans egg masses were purchased from Aquatic Biosystems, Fort Collins, CO and hatched in the Environmental Toxicology section of WSLH. Larval *C. tentans* were 10-11 days old on the day the test was initiated. Ten individuals were randomly placed in each test beaker with eight replicates per sediment site and lab control. Overlying water was replaced twice daily and organisms were fed 1.5 ml Tetramin® flake fish food mixture daily (1.5 ml contained 6.0 mg of dry solids). Dissolved oxygen, pH, and temperature of the overlying water were recorded daily. Hardness, alkalinity, ammonia and conductivity were measured at the beginning and at the end of the test (day 0 and day 10, respectively). On day 10, the organisms were recovered from the sediment to determine the number of survivors. Surviving organisms were subsequently dried overnight at 100°C and weighed to determine dry weight. The organisms were then ashed at 550°C for a minimum of 2 hours and weighed to determine ash-free dry weight (USEPA, 2000).

Hyalella azteca
Juvenile *H. azteca*, cultured in the Environmental Toxicology Section of WSLH, were 10-11 days old on the day of test initiation. Ten individuals were randomly placed in each test beaker with eight replicates per sediment site and lab control. Overlying water was replaced twice daily and organisms were fed 1.0 ml YFC (yeast/fish food/cereal leaves). Dissolved oxygen, pH, and temperature of the overlying water were recorded daily. Hardness, alkalinity, ammonia and conductivity were measured at the beginning and at the end of the test (day 0 and day 10, respectively). On day 10 the organisms were recovered from the sediment to determine the number of survivors in each replicate. Survivors were subsequently dried overnight at 100ºC and weighed to determine dry weight (USEPA, 2000).

Statistical analyses
Statistical analyses were conducted using a PC-version of SAS® (SAS Institute, Cary, NC). One-way analysis of variance (ANOVA) followed by a multiple comparison test (Student-Newman-Keuls) was used to identify differences among treatments in survival and weight of survivors of *Chironomus tentans* and *Hyalella azteca*. Results with $p < 0.05$ were considered significant.

SUMMARY OF RESULTS

The test for *H. azteca* met the minimum requirements for test acceptability, but the *C. tentans* test did not (see Table 1 and Figures 1, 2, 7 and 8). *C. tentans* survival was 52.5% in the control sediment which is below the requirement of 70%, but the average weight per individual was greater than requirement of 0.48 mg (at 2.18 mg). *H.azteca* survival in the control sediment was 87.5% and the average weight increased from 0.0264 mg/individual to 0.1305 mg/individual.

Overlying water chemical parameters
Dissolved oxygen (DO) and temperature values in overlying water were within acceptable limits for both tests according to USEPA, 2000 (see Table 1 and Figures 3, 5, 9, and 11). DO should remain above 2.5 mg/L, which was the case throughout the test as DO never dropped below 3.02 mg/L. There are no criteria set for pH values but results are summarized in Figures 4 and 10. Results of conductivity, hardness, alkalinity, and ammonia analyses from samples collected on the first and last days of the tests are summarized in Figures 6 and 12. According to USEPA (2000), values for hardness, alkalinity and ammonia should not vary by more than 50% during the test. This was the case for hardness and alkalinity in both tests. However, ammonia values did vary by greater than 50% in many of the sites for both species. Overall, the levels of

ammonia in overlying water were low (≤ 2.37 mg/L) and not at levels that have been associated with toxicity in sediment tests in the past (20 -310 mg/L, USEPA, 2000). There are no criteria set for conductivity measurements.

Chironomus tentans
Survival of *C. tentans* was only affected at the lab control with a survival of 52.5% (Figure 1). Survival was not significantly different among any of the other sites. *Chironomus tentans* ash-free dry weight (AFDW) was not significantly different in any of the sites and the lab control.

Hyalella azteca
Survival of *H.azteca* was not significantly different among any of the sites and the lab control. There were some significant differences in *H.azteca* dry weight between the lab control and the test sites; however, all differences were positive. Sites 001, 003 and 004 were not significantly different than the lab control, but 002 had a significantly higher dry weight (Figure 8).

CONCLUSIONS

C. tentans survival and ash-free dry weights did not indicate any evidence of toxicity from the sediment samples. It is unclear as to why the survival in the lab control was low as this has not happened in previous tests.

Toxicity from the sediment samples was not evident as indicated by *H.azteca* survival and dry weights. Site 002 had an average of 42% larger *H. azteca* than the lab control. It appeared that a few, very large *H. azteca* were present at that site. One explanation for the occasional, large *Hyalella azteca* could be that they were native to the sediment and were present when the tests were set. However, we cannot definitively conclude this because we did not see organisms while we were setting the sediments, and we did not find more than 10 individuals in any replicate.

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United States Environmental Protection Agency (USEPA). Methods for measuring the toxicity and bioaccumulation of sediment-associated contaminants with freshwater invertebrates. Second Edition. 2000. EPA/600/R-99/064. Office of Research and Development, U.S. Environmental Protection Agency, Washington, D.C.

Table 1. Summary of Test Conditions for Conducting Sediment Toxicity Tests

Parameter		Conditions
1.	Test Type	Whole sediment toxicity test with renewal of overlying water
2.	Temperature	23 ± 1ºC
3.	Light Quality	Wide-spectrum fluorescent lights
4.	Illuminance:	About 100 to 1000 lux
5.	Photoperiod	16L:8D
6.	Test Chamber	470 ml polypropylene Beaker (*C. tentans* and *H. azteca*)
7.	Sediment Volume	100 ml (*C. tentans* and *H. azteca)*
8.	Overlying Water Volume	175 ml (*C. tentans* and *H. azteca)*
9.	Renewal of Overlying Water	2 volume additions/d (*C. tentans* and *H. azteca*)
10.	Age of Organisms	Second to third instar larvae (*C. tentans*) 7- to 14-d old, within a 1 to 2 day range (*H. azteca)*
11.	Number of organisms/chamber	10 (*C. tentans* and *H. azteca)*
12.	Number of replicates/treatment	8 (*C. tentans* and *H. azteca)*
13.	Feeding	1.0 ml YFC (1800 mg/l stock) daily to each test chamber (*H. azteca*) 1.5 ml Tetramin flake fish food mixture (1.5ml contains 6.0 mg of dry solids) to each test chamber (*C. tentans*)
14.	Aeration	None, unless dissolved oxygen in overlying water drops below 2.5 mg/L
15.	Overlying water	dechlorinated tap water
16.	Test chamber cleaning	If screens become clogged during a test; gently brush the outside of the screen
17.	Overlying water quality	Hardness, alkalinity, ammonia, DO, pH, and conductivity at the beginning and end of a test. Temperature, pH and dissolved oxygen daily.
18.	Test duration	10 d (*H. azteca* and *C. tentans*)
19.	Endpoints	Survival and growth (dry weight) (*H. azteca*) Survival and growth (ash free dry weight) (*C. tentans*)
20.	Test acceptability	Minimum mean control survival of 70%, minimum mean weight per surviving control organism of 0.48 mg ash free dry weight (*C. tentans)* Minimum mean control survival of 80% and measurable growth of test organisms in the control sediment (*H. azteca*

Appendix D

UWL Summary of Pb Levels in LRM Fish

Concentration of Pb within all fish collected in the La Crosse River Marsh by UWL researchers.

Species	Site	Length (cm)	Wet Weight (g)	Unit Analyzed	Pb (µg/g, wet wt)
Northern Pike	19	46.2	NA	Fillet	0.102
Northern Pike	19	38.5	NA	Fillet	0.0838
Northern Pike	19	38.0	NA	Fillet	0.0523
Northern Pike	19	42.0	NA	Fillet	0.0540
Green Sunfish	19	19.4	NA	Fillet	0.127
Black Bullhead	20	12.3	25.8	Whole Body	6.3
Black Bullhead	13	13.1	25.7	Whole Body	3.0
Black Bullhead	20	7.8	6.1	Whole Body	0.96
Black Bullhead	13	19.0	60	Whole Body	0.70
Black Bullhead	13	8.1	6.1	Whole Body	0.65
Black Bullhead	20	19.1	110	Whole Body	0.34
Black Bullhead	13	7.0	308	Whole Body	0.242
Black Bullhead	7	7.4	4.6	Whole Body	0.24
Black Bullhead	3	11.5	13.7	Whole Body	0.238
Black Bullhead	3	7.6	6.3	Whole Body	0.21
Black Bullhead	3	12.5	22.8	Whole Body	0.179
Black Bullhead	20	18.5	90	Whole Body	0.098
Black Bullhead	3	17.8	140	Whole Body	0.075
Bluegill	13	7.6	7.5	Whole Body	2.45
Bluegill	20	8.5	12	Whole Body	0.478
Bluegill	13	7.4	7.4	Whole Body	0.448
Bluegill	3	6.6	4.9	Whole Body	0.411
Bluegill	3	10.0	19.8	Whole Body	0.370
Bluegill	13	7.0	6.1	Whole Body	0.320
Bluegill	13	8.6	13.6	Whole Body	0.266
Bluegill	20	10.2	20	Whole Body	0.260
Bluegill	20	9.5	17.4	Whole Body	0.211
Bluegill	7	9.1	17.3	Whole Body	0.142
Bluegill	3	11.0	23.7	Whole Body	0.128
Bluegill	3	9.0	14.8	Whole Body	0.0797
Bluegill	7	7.6	6.9	Whole Body	0.047
Bluegill	7	18.9	160	Whole Body	0.022
Bluegill	20	20.4	190	Whole Body	0.014
Bluegill	7	19.6	190	Whole Body	0.013
Golden Shiner	20	12.5	19.3	Whole Body	0.467
Golden Shiner	13	4.0	0.5	Whole Body	0.449
Golden Shiner	20	7.6	3.7	Whole Body	0.443
Golden Shiner	3	8.8	5.1	Whole Body	0.280
Golden Shiner	3	9.1	5.6	Whole Body	0.210
Golden Shiner	3	8.0	3.5	Whole Body	0.201
Golden Shiner	3	13.3	19.3	Whole Body	0.0644
Northern Pike	20	42.0	440	Whole Body	0.032
Northern Pike	20	53.6	1010	Whole Body	0.019
Northern Pike	20	41.5	470	Whole Body	0.018
Northern Pike	7	43.1	510	Whole Body	0.00948
Northern Pike	7	44.6	500	Whole Body	0.008
Northern Pike	7	44.0	520	Whole Body	0.00685
Northern Pike	20	39.9	410	Whole Body	0.006
Northern Pike	7	45.0	490	Whole Body	0.00457

Appendix E

UWL Research Presentations Connected to LRM Study

Research Presentations Connected to Lead Study (43 total).

*denotes undergraduate student author; **denotes graduate student (MS) author.
†denotes student award for best presentation or travel award through national or regional competition

<u>International and National Presentations (13)</u>

Platform

C Mertens*†, R Perroy, C Belby, S Erickson.* 2013. Three-dimensional modeling of lead contamination in an urban wetland. Association of American Geographers Annual Conference. Los Angeles, CA. †**Awarded competitive travel grant through UWL.**

Y Lor*, T Cyphers**, and TC King-Heiden. 2013. Developing a Gene Expression Biomarker for Pb-Toxicity in Zebrafish for Environmental Biomonitoring. 19th Annual McNair Research Conference. Niagara Falls, NY. July 11-13.

S Erickson*, C Belby, R Perroy. 2012. Measuring the spatial distribution of lead contaminants in the La Crosse River Marsh. 28th National Conference on Undergraduate Research. Oden, UT.

Poster

S Ryan**, G Gerrish, C Belby, R Haro, T King-Heiden. 2015. The mobilization of lead from lead shot to macroinvertebrates in a riparian wetland. International Society for River Systems. La Crosse, WI.

A Olson*†, Y Lor*, T Cyphers**, and TC King-Heiden. 2014. □-aminolevulinate dehydratase (ALAD): Gene Expression Biomarker for Pb-Toxicity in Zebrafish for Environmental Biomonitoring? 35th Annual meeting for the Society of Environmental Toxicology and Chemistry, North America. Nov 2014, Vancouver, British Columbia, Canada. †***Awarded competitive travel award through SETAC and UWL***

S Oxley*†, C Belby, K Rolfhus. 2014. The Dissolution of Lead Contaminants in the La Crosse River Marsh. Association of American Geographers Annual Conference. Tampa, FL. †**Awarded competitive travel grant through UWL.**

C Belby, G Gerrish, T King Heiden, R Perroy, S Ryan, T Cyphers. 2013. Lead bioavailability from contaminated wetland sediments at a former shooting range. Ecological Society of America. Minneapolis, MN.

T Cyphers**†, S Ryan**, R Perroy, C Belby, G Gerrish, and TC King-Heiden. 2013. Assessing legacy lead contamination in a unique urban watershed. 34th Annual meeting for the Society of Environmental Toxicology and Chemistry, North America. Nov 2013, Nashville, TN. †***Awarded competitive travel award through SETAC and UWL***

M Goldade*, C Mertens*, C Belby, R Perroy. 2013. pH analysis of lead contaminated sediment and water in the La Crosse River Marsh. 27th National Conference on Undergraduate Research. La Crosse, WI.

C Schneider*, T Cyphers**, R Perroy, C Belby, G Gerrish, and TC King-Heiden. 2013. Are La Crosse River Marsh sediments toxic to zebrafish larvae? National Conference for Undergraduate Research. La Crosse, WI.

C Belby, R Perroy, N Feldmeier. 2012. Mapping the spatial distribution of lead shot in the La Crosse River Marsh using X-ray image analysis. Association of American Geographers Annual Conference. New York, NY.

S Erickson*†, R Perroy, C Belby. 2012. Measuring the spatial distribution of lead contaminants in the La Crosse River Marsh. Association of American Geographers Annual Conference. New York, NY. †**Awarded competitive travel grant through UW-L.**

C Mertens*†, R Perroy, C Belby. 2012. Three Dimensional Modeling of Lead Contamination in an Urban Wetland. Applied Geography Conference. Minneapolis, MN. †**Awarded "Best Student Poster Presentation"**

Regional Presentations (20)

Platform

C Belby. 2016. Lead Contamination in the La Crosse River Marsh. University of Northern Iowa Geography Department Colloquium. Cedar Falls, IA.

C Belby. 2016. Lead Contamination in the La Crosse River Marsh. WisCorps EnviroWednesdays. La Crosse, WI.

C Belby. 2015. Lead Contamination in the La Crosse River Marsh. Earth Fair. La Crosse, WI.

C Belby, R Perroy, and TC King-Heiden. T. 2014. Lead Contamination in the La Crosse River Marsh: Spatial Distribution and Legacy Effects. Winona State University Earth Talks Series. Winona, MN.

T Cyphers**, C Schneider*, and TC King-Heiden. 2013. Bioavailability and toxicological assessment of lead-contaminated sediments from Myrick Marsh. Mississippi River Research Consortium. La Crosse, WI.

T Cyphers**†, S Ryan**, R Perroy, C Belby, G Gerrish, and TC King-Heiden. 2013. Bioavailability of lead from lead-contaminated sediments in an urban riverine marsh. Midwest Regional Chapter of the Society of Environmental Toxicology and Chemistry (MRC-SETAC) Annual Meeting. La Crosse, WI, March 19-20. †***Awarded Midwest SETAC student travel award***

C Schneider*†, T Cyphers**, R Perroy, C Belby, G Gerrish, and TC King-Heiden. 2013. Pb-Contaminated surface sediments from the La Crosse River Marsh cause developmental toxicity in zebrafish larvae. Midwest Regional Chapter of the Society of Environmental Toxicology and Chemistry (MRC-SETAC) Annual Meeting. La Crosse, WI, Mar 19-20. †***Awarded Midwest SETAC student travel award***

C Belby, R Perroy, N Feldmeier. 2012. Mapping the spatial distribution of lead shot in the La Crosse River Marsh. Annual Meeting of the Mississippi River Research Consortium. La Crosse, WI.

S Erickson*, C Belby, R Perroy. 2012. Lead Contamination in Water and Biota at the Site of a Former Trap Shooting Range. National Great Rivers Research and Education Center Intern Symposium, Alton, Illinois.

J Sullivan. K Rasmussen, C Belby, T King-Heiden, G Gerrish, R Perroy. 2012. Lead Contamination Investigations in the La Crosse River Marsh. Water Quality Technical Section Meeting. Upper Mississippi River Conservation Committee (DNR). Fairport, IA.

Poster

S Ryan**, C Rivera Perez**, S Erickson**, G Gerrish, C Belby, T King-Heiden, R Haro. 2015. Lead Shot in the La Crosse River Marsh: a UW-La Crosse, Wisconsin Department of Natural Resources and City of La Crosse Collaboration. Annual Earth Fair Event. La Crosse, WI.

Y Lor*†, T Cyphers**, and TC King-Heiden. 2014. Aminolevulinate dehydratase (ALAD): Gene expression biomarker for Pb-toxicity in zebrafish for environmental Biomonitor? Environmental Toxicology and Chemistry (MRC-SETAC) Annual Meeting. Chicago, IL. †***Awarded Midwest SETAC student travel award and "Outstanding Student Poster Presentation"***

S Erickson*, C Belby, R Perroy, C Mertens*, M Goldade.* 2013. Lead contamination in water and biota at the site of a former trap shooting range. Wisconsin Wetlands Association Conference. Sheboygan, WI.

M Goldade*, C Belby, R Perroy. 2013. Ph analysis of lead contaminated sediment and water in the La Crosse River Marsh. Mississippi River Research Consortium. La Crosse, WI.

M Goldade*, C Belby, R Perroy, S Erickson*, C Mertens.* 2013. Analysis of pH in lead contaminated sediment and water in the La Crosse River Marsh. Wisconsin Wetlands Association Conference. Sheboygan, WI.

C Mertens*, R Perroy, C Belby, S Erickson.* 2013. Three-dimensional modeling of lead contamination in an urban wetland. Mississippi River Research Consortium. La Crosse, WI.

S Ryan**, T Cyphers**, S Erickson*, C Mertens*, G Gerrish, C Belby, T King-Heiden, R. Perroy. 2013. Mobilization of lead shot in a wetland from sediment to plants and animals. Mississippi River Research Consortium Annual Meeting. La Crosse, WI April 23-25.

C Belby, R Perroy, N Feldmeier. 2012. Mapping the distribution of lead shot in the La Crosse River Marsh. Wisconsin Wetlands Association Conference. Lake Geneva, Wisconsin.

S Erickson*, C Belby, R Perroy. 2012. Measuring the spatial distribution of lead contaminants in the La Crosse River Marsh. Mississippi River Research Consortium. La Crosse, WI.

S Erickson*, C Belby, R Perroy. 2012. Measuring the spatial distribution of lead contaminants in the La Crosse River Marsh. Wisconsin Wetlands Association Conference. Lake Geneva, WI.

Local (UWL) Presentations (10)

Platform

C Belby. 2013. Spatial Distribution of Lead Contamination in the La Crosse River Marsh. 18th Annual UWL Faculty Research Day.

T Cyphers**, C Schneider*, and TC King-Heiden. 2013. Bioavailability and toxicological assessment of lead-contaminated sediments from Myrick Marsh. Annual UWL Graduate Student Research Celebration.

S Erickson*, C Belby, R Perroy. 2012. Measuring the spatial distribution of lead contaminants in the La Crosse River Marsh. UWL Celebration of Student Research & Creativity. La Crosse, WI.

Poster

C Cullimore*, C Belby. 2014. Using X-ray Fluorescence to Quantify Lead Content in Vegetation," UW-L Celebration of Student Research & Creativity. La Crosse, WI.

K Lee*†, A Olsen*, and TC King-Heiden. 2014. Is the lead within La Crosse River Marsh sediments bioavailable under extreme conditions? Can we shake it out? Annual UWL SAH Summer Undergraduate Research Symposium. †***WiscAMP Fellow***.

Y Lor*[†], T Cyphers**, and TC King-Heiden. 2014. Aminolevulinate dehydratase (ALAD): Gene expression biomarker for Pb-toxicity in zebrafish for environmental Biomonitor? UW-L Celebration of Student Research and Creativity. [†]***Dean's Distinguished Fellow.***

A Olson*[†], Y Lor*, and TC King-Heiden. 2014. Myrick Marsh lead contamination: development of a gene expression biomarker for understanding sediment toxicity. Annual UWL SAH Summer Undergraduate Research Symposium. [†]***Dean's Distinguished Fellow***

C Mertens*[†], R Perroy, C Belby. 2012. Three-Dimensional Modeling of Lead Contamination in the La Crosse River Marsh. 6th Annual UWL SAH Summer Undergraduate Research Symposium. La Crosse, WI. [†]***Dean's Distinguished Fellow***

C Schneider*[†], C Belby, R Perroy, G Gerrish, and TC King-Heiden. 2012. Toxicity of Pb-Contaminated Sediments from Myrick Marsh. 2012. 6th Annual UWL SAH Summer Undergraduate Research Symposium. [†]***Awarded Sigma Xi "Best Student Presentation"***

S Erickson*[†], C Belby, R Perroy. 2011. Spatial Distribution of Lead Contaminants in the La Crosse River Marsh. 5th Annual UWL SAH Summer Undergraduate Research Symposium. La Crosse, WI. [†]***Dean's Distinguished Fellow***

Thesis writings

T Cyphers** (Faculty Mentor: T King-Heiden). 2015. Bioavailability and toxicological assessment of lead-contaminated sediments in an urban riverine marsh. Submitted to University of Wisconsin La Crosse. La Crosse, WI.

S Ryan** (Faculty Mentor: G. Gerrish) 2015. Mobilization of lead (Pb) in the La Crosse River Marsh. Submitted to University of Wisconsin La Crosse. La Crosse, WI.

S Ryan** (Faculty Mentor: G. Gerrish) 2013. Mobilization of lead from the sediment of the La Crosse River marsh to the invertebrates *Leptocerus americanus* and the effect of lead toxicity on the population of *Daphnia pulex* over time.

Appendix F

UWL Research Funding Connected to LRM Study

UWL Research Funding Connected to Lead Study ($79,864 total)

Student Research Grants ($39,250) *denotes undergraduate student; **denotes graduate student

A Olson*. (Faculty Mentor: T King-Heiden). 2014. Refining our Understanding of the Toxicity of the Sediments from Myrick Marsh. UWL Undergraduate Research and Creativity Grant. $2,000.

K Lee* (Faculty Mentor: T King-Heiden). 2014. Exploring the bioavailability of lead from La Crosse River Marsh Sediments. WiscAMP Fellowship. $3,500

C Cullimore*. (Faculty Mentor: R Perroy). 2013. Using X-ray Fluorescence to Quantify Lead Content in Vegetation. UWL Undergraduate Research and Creativity Grant. $1,500.

Y Lor*. 2013. (Faculty Mentor: T King-Heiden). Assessing the La Crosse River Marsh lead contamination – is it just lead? UWL Dean's Distinguished Fellowship. $4,500.

S Oxley*. (Faculty Mentor: C Belby). 2013. Measuring the Dissolution Rate of Lead Contaminants in the La Crosse River Marsh. UWL Undergraduate Research and Creativity Grant. $1,500.

S Oxley*. (Faculty Mentor: C Belby). 2013. Dissolution of lead contaminants in the La Crosse River Marsh. UWL Dean's Distinguished Fellowship. $4,500.

S Ryan** (Faculty Mentor: G Gerrish) 2013. The evolution of tolerance to increased levels of lead by Daphnia in the La Crosse River Marsh. UWL Office of Graduate Studies $2,173.

M Goldade*. (Faculty Mentor: C Belby). 2012. pH Analysis of Lead Contaminated Sediment and Water in the La Crosse River Marsh. UWL Undergraduate Research and Creativity Grant. $1,500.

C Mertens*. (Faculty Mentor: R Perroy). 2012. Creating a 3-dimensional model of lead contamination in the La Crosse River Marsh. UWL Dean's Distinguished Fellowship. $4,250.

C Schneider*. (Faculty Mentor: T King-Heiden). 2012. Developmental toxicity of Pb-contaminated sediments from Myrick Marsh. UWL Dean's Distinguished Fellowship. $4,250.

S Erickson*. 2011. (Faculty Mentors: C Belby & R Perroy). Spatial distribution of lead contaminants in the La Crosse River Marsh. UWL Dean's Distinguished Fellowship. $4,250.

C Mertens*. (Faculty Mentor: R Perroy). 2011. Using X-Ray Flourescence and Statistical Analysis to Quantify the Spatial Distribution of Lead Contamination in La Crosse River Marsh Sediments (0-15cm). UWL Undergraduate Research and Creativity Grant. $1,500.

S Erickson*. (Faculty Mentors: C Belby & R Perroy). 2010. Measuring the Spatial Distribution of Lead Contaminants is La Crosse River Marsh. UWL Undergraduate Research and Creativity Grant. $1,500.

Faculty Research Grants ($40,614 total)

T King-Heiden. 2013. Toxicity of the La Crosse River Marsh Sediments. UWL College Grant (sponsored by the UWL River Studies Center). $2000.

C Belby, R Perroy. 2012. Lead transfer from shot contaminated soils in the La Crosse River Marsh, Upper Mississippi River. Sponsored by The National Great Rivers Research and Education Center. $5,997.

G Gerrish, C Belby, R Perroy, T King-Heiden. 2012. Mapping the distribution of lead contamination in the La Crosse River Marsh. Sponsored by UWL River Studies Center. $3,400.

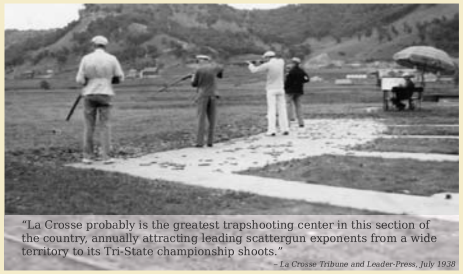
T King-Heiden. 2012. Assessing the bioavailability and toxicity of the lead-contaminated sediemnts of the La Crosse River Marsh, UWL. Faculty Research Grant, $15,888.

C Belby, R Perroy. 2011. Mapping the Vertical Distribution of Lead in the La Crosse River Marsh Sediment Using X-ray Fluorescence. UWL Faculty Research Grant. $13,329.

Appendix G

Pb-Focused Signage for Placement in LRM

AN UNINTENDED LEGACY:
Trapshooting and Lead Pollution in the La Crosse River Marsh



The Marsh and the La Crosse Gun Club

You are standing next to what was once a five-station trapshooting field built by the La Crosse Gun Club. Clay pigeon shooting was a popular community pastime at this location beginning in the 1920s, until the facility closed in 1963. Myrick Park was the site of four trap fields as well as a gun club shelter (now used as a picnic shelter). If you look around carefully near the marsh shoreline you can still find fragments of the clay pigeons used over 50 years ago!

What is Legacy Pollution?

In addition to clay pigeons, trapshooting over the marsh for nearly 40 years left millions of lead shot pellets buried in the marsh sediment. Most of the lead pellets remain in the shot fall zone. This shot has been breaking down over time, releasing lead into the sediment. Due to the potentially harmful environmental health effects of lead, scientists have studied its legacy in the marsh ecosystem.

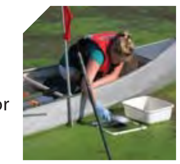
Studying the Marsh's Legacy Pollution

Is Lead from Old Shot Affecting Plants and Animals in the Marsh?

Funded by the U.S. Environmental Protection Agency's Urban Waters program, UW – La Crosse, and the UW – La Crosse River Studies Center, a research team from the River Studies Center and the Wisconsin Department of Natural Resources set out to answer that question. The team analyzed water samples, aquatic floating plants (duckweed), aquatic insects (long-horned caddis flies), and fish (bullhead, bluegill, northern pike) for lead content. Toxicity tests were also performed in the laboratory to determine whether lead in the sediments impacts the development and survival of fish and invertebrates.

Results indicate that as lead in the sediment increases, the concentration of lead in the water, duckweed and caddis flies also increases. Over time, lead from the shot can move from the marsh sediment and accumulate in plants and animals living in the shot fall zone. Although lead is transferring through the food web, minimal toxicity was detected in laboratory tests.

What Does this Mean for the Marsh and Public Health?



While lead has been found to escape the sediment, the amount of lead in the water, plants and animals, and the toxicity tests currently do not exceed the threshold for impairment.

Through the City's partnership with UW-La Crosse, the Wisconsin Department of Natural Resources and the U.S. Environmental Protection Agency, ongoing sampling will monitor legacy lead pollution to determine if there is a threat to public health.

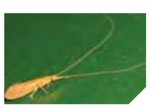
At this time, it is recommended that the public avoid contact with marsh sediment in the contaminated area.

How Does the Marsh Food Web Work?

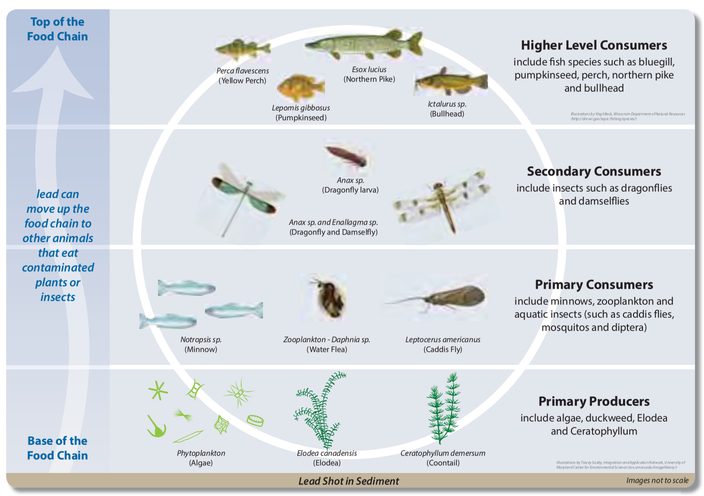
The La Crosse River Marsh is home to a remarkable variety of plants and animals. If lead is found in duckweed and caddis flies, it is potentially also making its way into other plants and insects in the marsh. Once lead is in plants and insects, it can be introduced into the marsh food web. The lead can then move up the food chain to other animals that eat contaminated plants or insects, including fish and waterfowl.

Common Marsh Species

Duckweed (*Lemna* sp.) are tiny plants that float on the surface of the water. They are an important food source for many animals in the La Crosse River Marsh.

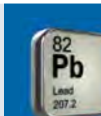


Long-horned caddis flies (*Leptocerus americanus*) are the most abundant insect living in the marsh. The larvae swim through the water and feed mostly on decaying plant matter. They live in a cone-shaped case that they spin from their own silk. The insects hatch in June and July.



The Marsh Food Web

Did You Know?



LEAD *(chemical symbol Pb)*
Lead is a naturally occurring element found in small amounts in the earth's crust. While it has some beneficial uses, it can be toxic to humans and animals if ingested.

For More Information

Project partners are working together to make sure the La Crosse River Marsh remains a healthy and vibrant ecosystem and a community treasure for generations to come. If you would like more information or have questions about legacy lead pollution, monitoring or other topics, please contact:

University of Wisconsin – La Crosse River Studies Center
608.785.8261 or http://www.uwlax.edu/river-studies-center/

Wisconsin Department of Natural Resources
1-888-936-7463 or http://dnr.wi.gov/

Appendix H

Wetland Value Signage for Placement in LRM

La Crosse River Marsh

Welcome

The La Crosse River Marsh is a defining feature of the community. The 1,000 acre wetland is located directly between north and south La Crosse, and is an extension of the La Crosse and Mississippi Rivers. The marsh is a critical link in the Coulee region's diverse natural landscape of rivers and bluffs, and it has a storied history of human uses and impacts.

History and Recreation

The wetland in front of you is a dynamic environment, shaped over thousands of years by natural events and human actions. It formed during the past 10,000 years by downcutting and migration of the La Crosse River as its waters flowed into the Mississippi and Black Rivers. Pre-historic artifacts recovered near the margins of the marsh indicate humans have occupied the area for over 8,000 years, likely utilizing the marsh's diverse resources for hunting, fishing, trapping, and gathering.

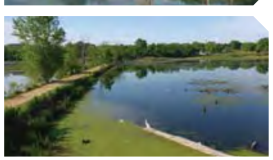
The rapid growth of La Crosse in the late 19th century increased human activities in and near the marsh. Early uses by residents included fairgrounds, a racetrack, a music pavilion, toboggan runs and even a golf course. As La Crosse expanded, an estimated 50% of the original wetland was filled to make space for roads, rail lines, businesses, industry, and sporting fields. Recreational trails first opened in the marsh in 1976. Thousands of visitors annually take advantage of the marsh's recreational opportunities, including hiking, jogging, biking, fishing, snowshoeing, canoeing, and wildlife watching. The marsh is an active learning environment, drawing in students from the local universities and schools to study the rich ecosystem in this outdoor classroom.

La Crosse, Wis., county seat of La Crosse County 1887. Beck & Pauli Lith. Co., Library of Congress.

As you enjoy the area's trails, you will come across another reminder of the past – remnants of a trapshooting target range built along the south shoreline by the La Crosse Gun Club in 1926. Although closed in 1963, fragments of clay pigeons are still found along the marsh's edge. The City of La Crosse has partnered with UW-La Crosse, the Wisconsin Department of Natural Resources and the U.S. Environmental Protection Agency to ensure lead shot from the trapshooting activities does not pose an environmental or public health risk. Signage adjacent to the remaining shooting station provides more information about these efforts.

La Crosse Tribune and Leader-Press, August 2, 1934

The Value of Wetlands



Wetlands are part of the foundation of our nation's water resources and are vital to the health of waterways and communities. The La Crosse River Marsh is a wonderful example of a functioning wetland located in the heart of an urban landscape. It helps reduce flood heights by storing water and slowing its movement downstream. Runoff that is delivered to the marsh from the surrounding urban areas is cleansed as excess nutrients, pollutants, and sediments are filtered out of the water.

During dry periods, the marsh supplies water to adjacent rivers. A large number of plants and animals are dependent on the marsh for the food, water, and shelter it provides. The area immediately north of Myrick Park has some of the highest biodiversity in the La Crosse River Marsh due to its habitat complexity. Wetlands like the La Crosse River Marsh are also economic drivers because of their key role in fishing, hunting, and recreation.

Biodiversity

Plants and Animals of the La Crosse River Marsh

Plants: >100 species of seed and non-seed plants, including northern hackberry, box elder, button bush, common burreed, river bank grape, Virginia creeper, duckweed, watermeal, coon's tail, and common waterweed.

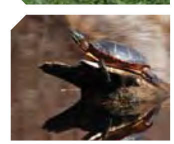
The invasive reed canary grass has also become prevalent throughout large portions of the marsh.

Mammals: >20 species, including beaver, muskrat, red fox, river otter, and deer.

Birds: >150 species, including geese, mallards, blue-winged teal, great egrets, yellow-headed blackbirds, red-tailed hawks, brown thrashers, great blue heron, bald eagles, and great horned owls.

Reptiles and Amphibians: >10 species, including snapping turtles, painted turtles, Blanding's turtles, western chorus frogs, eastern gray tree frogs, leopard frogs, green frogs, American toads, northern spring peepers, and eastern garter snakes.

Fish: northern pike, perch, sunfish, bass, and bullhead.



The Mississippi Flyway

The La Crosse River Marsh is located along the Mississippi Flyway, an important corridor for birds during their spring and fall migrations. Wetlands situated along the Mississippi Flyway provide a reliable source of food, water, and resting habitat to millions of birds traveling between the Arctic Circle and the Gulf of Mexico. Platforms placed throughout this portion of the marsh provide safe nesting sites for breeding birds, including Canada geese.

Looking Forward

The community continues to express strong support for the protection and enhancement of the marsh and our other natural resources. The City works closely with the community, La Crosse County, area cities and townships, UW-La Crosse, the Wisconsin Department of Natural Resources, and other partners to maintain these remarkable areas. Enjoy your visit to the La Crosse River Marsh!

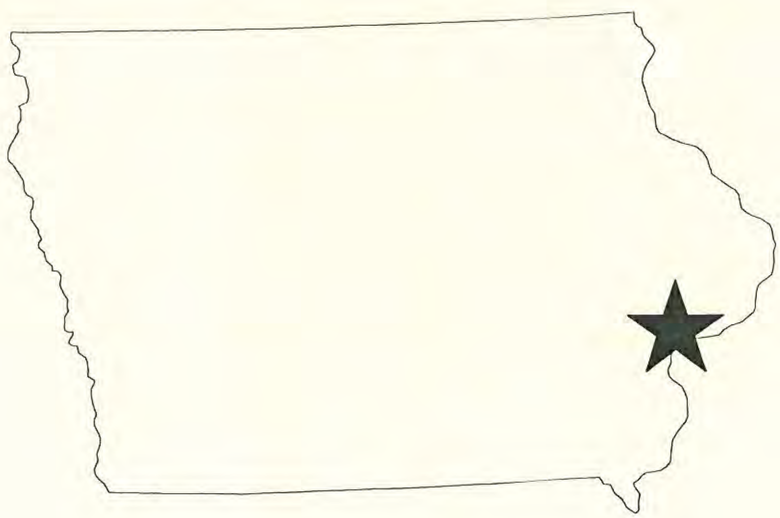
City of La Crosse · Wisconsin Dept. of Natural Resources · United States Environmental Protection Agency · UW-LA CROSSE · Technical Assistance Services for Communities (TASC)

Appendix I

Ecological Risk Assessment for Nahant Marsh Report

U.S. Fish and Wildlife Service
Region 3
Contaminants Program

Ecological Risk Assessment
for
Nahant Marsh, Davenport, Iowa



U.S. Fish and Wildlife Service
4469 - 48th Avenue Court
Rock Island, Illinois 61201

1998

Screening Level Ecological Risk Assessment

for

Nahant Marsh, Davenport, Iowa

by Mike Coffey

U.S. Fish and Wildlife Service
Rock Island Field Office
4469 48th Avenue Court
Rock Island, Illinois 61201

FINAL REPORT - June 9, 1998

prepared for
U.S. Environmental Protection Agency, Region VII
Under Interagency Agreement Number 92220-1910-37YC

Disclaimer

Announcement

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Washington, DC 20240

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Introduction

In 1994, natural resource personnel discovered lead poisoning problems from trap and skeet range operations at Nahant Marsh, Davenport, Iowa. Shortly thereafter, officials from Region VII of the U.S. Environmental Protection Agency (USEPA) and Region 3 of the U.S. Fish and Wildlife Service (USFWS) started to discuss the contaminant problems and solutions for Nahant Marsh.

The USEPA initiated site characterization work under their authorities in 1996. The USFWS was tasked to complete the first phase of the ecological risk assessment under an existing Interagency Cooperative Agreement (IAG) for Superfund technical assistance. The USEPA project manager under the IAG was Steve Wharton. The phase one work included a screening level assessment of lead shot contamination. The screening level assessment follows Steps One and Two of the eight steps for the Superfund ecological risk assessment process.

The eight steps in the ecological risk assessment process are outlined below (USEPA 1997).

Step One.	Screening level problem formulation, develop tentative assessment endpoints and toxicity affects evaluation.
Step Two.	Screening level exposure estimates and risk calculations.
Step Three.	Baseline problem formulation, in depth ecotoxicological literature review, develop conceptual model, evaluate exposure pathways, finalize assessment endpoints and risk questions.
Step Four.	Develop measurement endpoints and study design
Step Five.	Verification of study design.
Step Six.	Site investigation and data analysis
Step Seven.	Risk characterization.
Step Eight.	Risk management.

A site history and the results of the screening level ecological risk assessment are contained in this report. Screening level problem formulation, exposure estimates and risk calculations for this assessment were based on field information collected by USFWS and field data collected by a USEPA contractor (Ecology and Environment, Inc., Overland Park, Kansas - E & E) Preliminary Assessment and Site Investigation reports.

Site History

Between 1969 and 1995, a private gun club used an urban area known as Nahant Marsh for a trap and skeet range. Tons of lead shot were deposited in the marsh based on estimates by the gun club using shooting records. The lead shot fall zone contains mostly wetland habitats.

Nahant Marsh is located along the Mississippi River at the southwestern edge of the City of Davenport, Scott County, Iowa (Figure 1). Davenport is one of the municipalities that make up the Quad Cities. There are about 350,000 people in the Quad Cities.

The marsh is bordered by Interstate 280 to the south, agricultural fields to the west, an industrial park to the north, a railroad yard and municipal sewage treatment plant (STP) to the east. The marsh proper is owned by three parties including the gun club and two individuals that lease their land for corn and soybean production. The shot fall zone is believed to be entirely within the gun club property.

During the 1970's, one of the landowners adjacent to the gun club dredged recent sediments from a drainage ditch that the runs through the marsh and placed the spoil back into the water in violation of the Clean Water Act. The spoil was removed and placed in the woods next to the gun club shooting area as mitigation. The spoil may contain lead shot because it was originally located along the back extent of the shot fall zone. The density of shot in the spoil heap is expected to be very low because it was from 230 to 250 yards from the shooting platforms which is slightly greater than the traveling distance for small lead shot. Number 7 to 9 size lead shot travels up to 225 yards.

During the early 1980's, the U.S. Army Corps of Engineers - Rock Island District (USACOE) studied Nahant Marsh as part of an area flood protection project. A report was issued in 1982 by the USACOE that included information on local topography, hydrology and cultural resources for Nahant Marsh (USACOE 1982).

A citizen action group (River Action, Inc.) is in the process of developing a conservation plan for Nahant Marsh (see information in the newsletter in Appendix A). River Action, Inc. hopes to facilitate the purchase of the gun club property for use as an educational park. The gun club is interested in selling their property. The parties working with River Action, Inc. and interested in purchasing the Nahant Marsh property include the Iowa Natural Heritage Foundation, Augustana College (Rock Island, IL), Izaak Walton League, local and counties. The gun club now leases the property to a local motorcycle club.

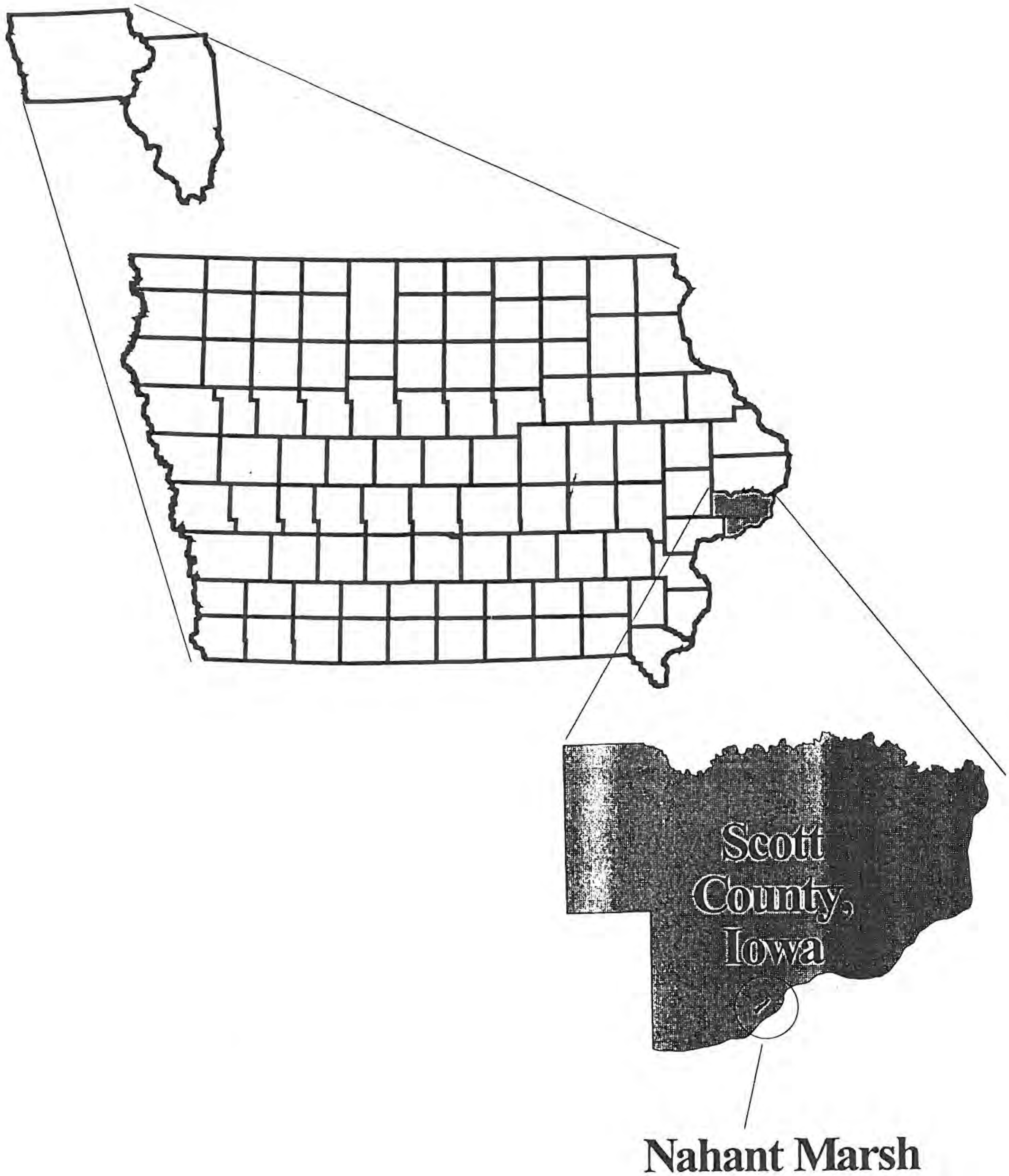

Figure 1. Location of Nahant Marsh, Scott County, Iowa.

In 1997, E & E conducted an integrated site assessment for Nahant Marsh under contract by the USEPA. E & E completed the following for the assessment: soil and sediment TCLP analysis, shot density estimates, chemical analysis of soils, wetland sediments and water. Nahant Marsh was listed in CERCLIS in 1997.

Site Visit

Natural resource personnel have monitored Nahant Marsh since 1994. In addition, local government officials, college researchers and field volunteers studied plant communities and wildlife use at the marsh for a local environmental education project. Lists of the plant, bird and small mammal species found at the site are in Appendix B. Scientific names for the plant and animal common names used in this report are in Appendix C.

Iowa Conservation Officer Ed Kocal, U.S. Fish and Wildlife Service (Service) Special Agent Walt Kocal, Service Contaminants Biologist Michael Coffey have periodically walked around the marsh with waterfowl hunting dogs to search for sick or dead birds. In addition, resource personnel have periodically canoed around the marsh to look for birds and collect field samples within the shot fall zone.

Search for Dead Birds

A total of five sick waterfowl and a grebe were recovered during the 1994 and 1997 site visits. Four of these birds were submitted to the National Wildlife Health Center[1] (NWHC) for examination by veterinary pathologists. One of the birds was submitted to the National Fish and Wildlife Forensics Laboratory[2] for examination by veterinary pathologists. The five waterfowl specimens were diagnosed with lead poisoning. The necropsy results are summarized in Table 1. The necropsy reports are in Appendix D.

At least fourteen scavenged waterfowl carcasses were seen along the marsh shoreline in 1994. These carcasses were believed to be sick birds taken by predators.

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[1] The National Wildlife Health Center was a USFWS research facility that was eventually transferred to the U.S. Geological Survey when the National Biological Survey was formed. The facility employs board certified veterinary pathologists and provides wildlife necropsy and epidemiology services for the U.S. Department of Interior.

[2] The National Fish and Wildlife Forensics Laboratory is an USFWS forensics facility that employs board certified veterinary pathologists and provides wildlife necropsy services for the USFWS Division of Law Enforcement.

Table 1. Summary of necropsy findings for moribund birds recovered from Nahant Marsh in 1994 and 1997. The source of these data is from necropsy and related laboratory reports. The National Wildlife Health Center uses 6.7 micrograms of lead per gram of tissue wet weight as an elevated liver lead concentration and 27 micrograms of lead per gram of tissue wet weight as diagnostic of lead toxicosis.

Species	Date Collected	Diagnosis	Number of Shot in Gizzard	Liver Lead Concentration[1]
Canada goose	April 1994	Lead Poisoning	37	35.86
Canada goose	November 1994	Lead Poisoning	50	14.00
Mallard	November 1994	Lead Poisoning	>20	35.55
Mallard	November 1994	Lead Poisoning	20	33.33
Mallard	November 1997	Lead Poisoning	30	58.92

[1] Micrograms per gram, wet weight

Marsh Substrate Quality

There were different types of wetland substrates in the shot fall zone. Wetland substrate types included silty/sand areas, clay-muck bottom and organic substrates.

Wetland substrate samples near the gun club contained high densities of lead shot per grab sample. The area between 109 and 177 yards from the shooting platforms contained the highest density of lead shot. Samples containing up to 470 shot per square foot were collected by the USFWS at this distance. Samples containing up to 533 shot per square foot in the shot fall zone were collected by the USEPA contractor working at the site (E & E 1997)

Marsh Ecology

Nahant Marsh is in the floodplain of the Mississippi River, but is isolated from the river by a railroad grade levee. Floodwater from the Mississippi River can flow into Nahant Marsh through a ditch and culvert system that runs under Interstate highway 280 and through a series of wetlands that are between the Mississippi River and Nahant Marsh (Figure 2). The agricultural lands and industrial park also drain surface water into the marsh through a ditch system at the north end. Beaver dams at the marsh's outlet help maintain deep water.

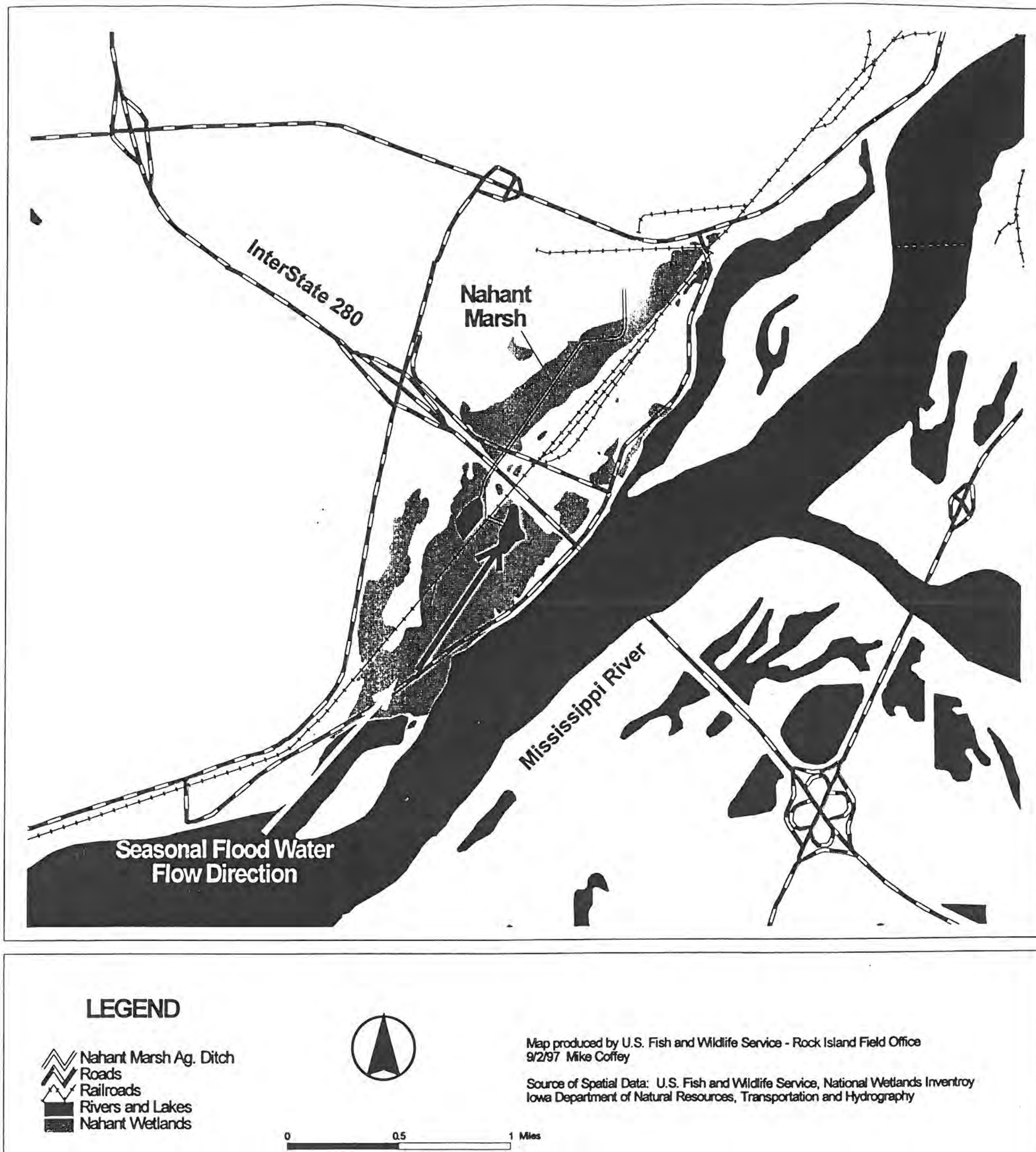

Figure 2. Hydrology of the Nahant Marsh area showing location and direction of Mississippi River floodwater flow.

The Nahant Marsh system included 92 acres of wetland habitats, 43 acres of bottomland forest habitat and less than 10 acres dry grassy cover (Figure 3). The wetland habitats included a mosaic of cattail, bulrush and open water patches. The dominant bottomland forest tree species include silver maple, willow species and cottonwood. There are also patches of catalpa trees around the marsh. The grassy openings supported mostly the exotic nuisance species, reed canary grass.

Historically, the open areas around Nahant Marsh contained vast sedge meadows (Guldner 1960). Relict plant populations from these communities are present in some grassy openings. Plant species believed to be extirpated from Scott County (*eg.* Turtle head) were discovered in the grassy areas by amateur botanists.

Canada goose, mallard, woodduck and killdeer are some of the wetland bird species that nest at the marsh. Great-blue herons from a nearby rookery along the river commonly use the marsh as a feeding site. Large numbers (500 to 1000 per day) of waterfowl and other wetland bird species use the marsh during migration periods (pers. obs.). The other wetland bird species include the great egret, American coot, pied-billed grebe, common snipe, woodcock, rails and shorebirds. Bald eagles regularly forage at the marsh during the late winter and early spring. This area of the Mississippi River supports a large number of wintering bald eagles because of ice free water below the dam in Davenport.

Common wetland fauna such as frogs, snakes, turtles, small mammals and furbearers were observed at the marsh. Mammal species included deer mouse, vole, mink, muskrat, beaver, river otter, fox, coyote and deer. Frog species included northern leopard frog, western chorus frog and bullfrog. Snake species included water snake and garter snake. The turtle species include Blanding's turtle, western painted turtle and common snapping turtle. The marsh fishery included the common carp, bowfin, green sunfish, bluegill and mudminnow.

Nahant Marsh is part of a larger wetland complex that extends to the south side of Interstate Highway 280. The wetlands on the south side of the interstate includes another estimated 400 acres of marsh and forested wetlands.

The Nahant Marsh complex may provide suitable habitat for size dependent wetland species such as rails and yellow-headed blackbirds (Weller and Gredrickson 1974). Habitat suitability may not be optimum for these sensitive marsh species because of limited open water with submergent plant beds and lack of extensive grassy perimeter (Schroeder 1982). Most of the marsh is surrounded by woody habitats or developed lands.

The lead shot fall zone contains about 5 percent surface area of the Nahant Marsh complex. A wetland functional assessment was completed for the shot fall zone.

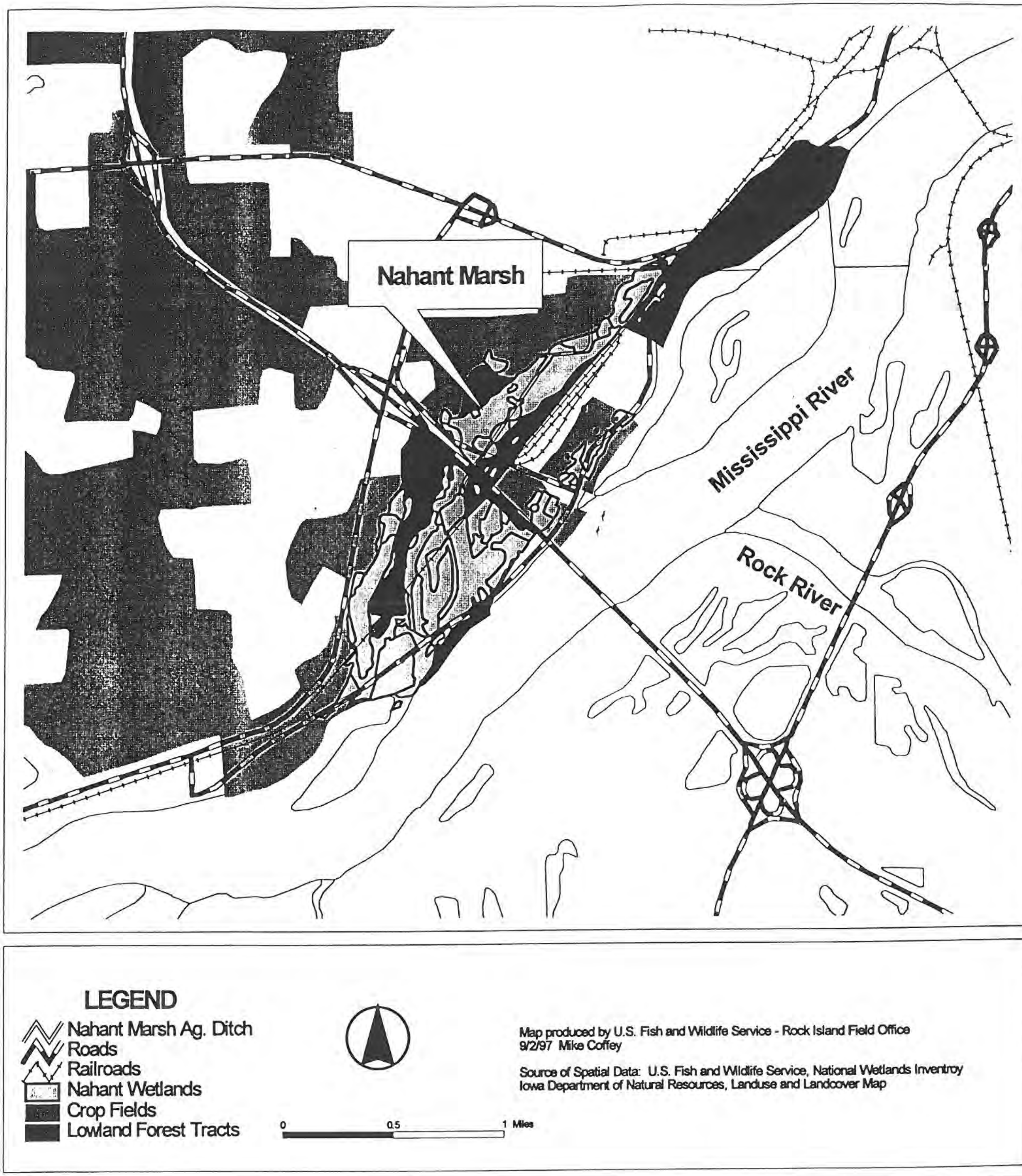

Figure 3. Habitat types and land cover around Nahant Marsh, Davenport, Iowa.

Wetland Functional Assessment Results

Wildlife Habitat The wetland portion of the lead shot fall zone is a characteristic hemimarsh habitat. Cattail and river bulrush are the dominant emergent plant species. The open water patches in the cattail usually contain small beds of coontail, pondweeds and duckweeds. There were no other obligate plant species observed in the wetland portion of shot fall zone.

The grassy portion of the shot fall area contains zones grading from the shoreline to wet meadow to dry weedy field habitats. The wetland plant species along the shoreline and in the wet meadow zone include arrowhead, sedges, rushes, horehound or bugleweed, wild iris, reed, reed canary grass and indigo bush.

The juxtaposition of the hemimarsh and this grassy area increases the suitability for wetland dependent species. Wetlands adjacent to grassy cover versus woods or cropfields are preferred by a variety of wetland species including ducks and rails.

Food chain production is likely high in the wetland portion of the shot fall zone. Aquatic submergent plants provide substrates for macroinvertebrates for birds and fishes. Aquatic submergent plant species and annual grasses produce seeds for a food source for migrating birds.

Fish Habitat The wetland portion of the shot fall zone does not have high fish habitat value. This area may support fish during wet years. The fish assemblage includes green sunfish, bluegill, bowfin and nuisance species such as common carp. During dry years the wetland portion has been a monotypic stand of cattail with little standing water.

Water Quality The wetland portion of the shot fall zone likely contributes to the overall function of improving water quality of agricultural run off and other upland surface run off. The water quality treatment function likely includes nutrient removal and sediment trapping. Denitrification and assimilation of nutrients can be high in a cattail habitat compared to other wetland types.

Natural Heritage Today, a small percent of Iowa's natural wetlands remain in the state and especially in urban areas. We believe that some the sedge wetlands and especially the wet meadow habitats at Nahant Marsh are relict components of the presettlement landscape. For this reason, we place high value on the wet grassy portion of the shot fall zone. The hydrology and soils may be ideal for restoration of high quality meadow communities even though the current plant community is not unique or rare.

Cultural There is good access to Nahant Marsh at the shot fall zone. This part of the marsh was developed for the gunclub and includes driveways, picnic spots and observational towers. However, recreational activities such as fishing and bird watching at the shot fall zone are limited at this time because the land is private.

Disturbances Noise pollution is high at Nahant Marsh. Interstate automobile traffic and railroad yard activities contribute to the noise pollution problem.

Disturbances Associated with Response Alternatives Removal of up to a foot of substrate from within the deep emergent plant zone as a risk management action may or may not alter that plant community. Cattail communities are believed to quickly recolonize disturbed areas. Deep water may drown cattail or removal of hydric soils may expose underlying sand layers which may be unsuitable for many species of aquatic plants.

Deepening the deep emergent zone to create a pond habitat may or may not be beneficial. Creation of additional submergent vegetation beds along emergent plant stands improves habitat suitability for some unique wetland birds such as the yellow-head blackbird. The diversity of wetland animals may change if the depth of the water column is permanently increased to allow fish to overwinter and affect the wetland community structure.

Removal actions in the grassy portion of the shot fall zone could permanently change the existing grassy community. The wet meadow habitat may change to a deep water emergent plant community. The terrestrial old field habitat may change to a wet meadow habitat. Pioneer nuisance plant species such as the reed canary grass, may spread if not controlled because of the disturbance.

Many plant species in a meadow habitat have specific life history requirements often related to the amount and timing of water saturation. It is believed that restoration success rates of meadow communities are low because it may be difficult or costly to reproduce life history requirements.

The plant community in the wet meadow zone contains relatively common species and few native wetland forbs. The grass community of the meadow includes reed canary grass or small sedges. This part of the site also contains the clay target debris zone.

In summary, the wet grassy portion of the shot fall zone may be important and contribute significantly to the overall value of the Nahant Marsh ecosystem. The importance of the wet grassy opening in the shot fall zone is primarily based on potential wildlife habitat and natural heritage functions described above and not the quality of the existing plant community.

Step One. Problem Formulation, Tentative Assessment Endpoints and Toxicity Evaluation

Problem Formulation

Lead Shot Risks

Lead shot from trap and skeet range operations were deposited and concentrated over time in an estimated 26 acre area of Nahant Marsh. The area estimate was determined using Geographical Information Systems (GIS) analysis (Figure 4). The size of the shot fall zone was based on trajectory information for historic shooting platforms and maximum traveling distance for trap shotgun loads. We calculated the size of the impacted area to be 18.5 acres mix of open water and cattail/river bulrush cover, 2.9 acres of terrestrial grassy cover and up to 4.2 acres of bottomland and upland woods.

Ingestion of spent lead shot by birds is believed to be the most significant ecological hazard at the site. Birds ingest the lead shot while they are foraging in the wetland substrate and on adjacent soils in search of food and grit. Grit refers to small stones or other hard material retained in the muscular stomach of some birds that is used to help grind up food items. A good summary of wildlife lead poisoning problems is contained in the Environmental Impact Statement for Use of Lead Shot for Hunting Migratory Birds (USFWS 1986). Highlights from this summary are discussed below.

The size of the lead shot used for trap and skeet is the preferred size of grit and plant seeds for ducks and geese. The lead shot is absorbed under the low pH conditions in the stomach. A progressive illness results in a few weeks and terminates in death with the ingestion of a single lead shot.

Clinical signs of lead poisoning include muscular weakness. The animal may lose its ability to escape predators. Heavy predation at wetlands helps prevent the accumulation of dead animals that might cause people to notice a die-off. Large die-offs from lead shot poisoning are the result of a special combination of environmental factors.

Lead poisoning has been commonly reported for many species of birds (Eisler 1988). More information is available for waterfowl (ducks, geese, swans), columbiforms (doves, pigeons) and galliforms (quail, grouse, pheasant) likely because these species use grit the size of lead shot as part of their diet or the shot resembles their food items (Kendall *et al* 1996).

Waterfowl are believed to be at the greatest risk from the deposited lead shot in the marsh because of their food habits, grit use and attraction to this wetland during migration times. The waterfowl - lead shot exposure pathway may be incomplete in deep water and dense emergent vegetation. Visiting ducks, geese and potentially swans and many of the mallards and Canada geese produced annually at the site may be affected by lead poisoning. An estimated 1.6 to 2.4 million waterfowl die annually across the nation from the problem of lead shot ingestion (USFWS 1986).

The bald eagle, red-tailed hawk and great horned owl may be at risk from eating the ill or dead birds found at the site. These birds-of-prey are at risk from secondary poisoning from ingesting any lead shot contained in the stomach tract of the avian food items.

The mourning dove may be the upland wildlife species at greatest risk from the ingestion of lead shot because of their food habits and grit use.

Direct Toxicity and Bioaccumulation

Lead has contaminated the marsh surface water, wetland sediments and shoreline soils (E & E 1997). It is not known how the lead is partitioned in the wetland sediments and soil. It is not known how the elemental lead shot and fragments have contaminated the surrounding aerobic and anaerobic media.

Available lead can cause toxic effects in plants and invertebrates living in contaminated media (Eisler 1988).

Wildlife may be exposed to harmful amounts of lead from ingesting highly contaminated water, sediment and soil particles (Beyer *et al* 1997).

Lead can bioaccumulate in plants and invertebrates living in contaminated media (Eisler 1988). Wildlife may be exposed to lead from ingesting the contaminated food items, although lead does not biomagnify in the food chain (Eisler 1988).

Food Chain Risks

A variety of other wildlife species may be at risk for the site that include fish, amphibians, reptiles, mammals and other bird species either because they forage on plants growing in contaminated media, they consume animals that have accumulated lead in their tissues or they incidently ingest the contaminated media.

The earthworm can bioaccumulate lead from contaminated soil with bioaccumulation factors greater than one in some instances (Beyer 1990). The earthworm is relatively tolerant of metal pollution and therefore can survive in contaminated soil (Neuhasuser *et al* 1986). This is an ecological problem because the organism is an important food source for many wildlife species. Vermivorous birds and small mammals are at risk because earthworms make up most of these animals' diet (Martin *et al* 1951). Two wetland vermivores, the woodcock and short-tailed shrew, and the terrestrial vermivore, the robin, occur at the site.

Muskrat may be at risk if the potato-like tubers that are part of the root system of cattail and bullrush have bioconcentrated lead. The marsh supports a population of muskrat.

Shoreline species such as frogs and small mammals bioaccumulated lead and were adversely affected by living around lead contaminated soil at a trap range site in Jew Jersey (see Stansley and Roscoe 1996).

Colonial birds (*eg.* great-blue heron) that use the marsh to forage for frogs and small fish may be at risk if these food resources are contaminated. There is a colonial bird rookery (300+ great-blue herons) near the city of Andalusia, Illinois which is about four miles from the site.

Birds-of-prey (*eg.* red-tailed hawk) that feed on small mammals such as voles and mice may be at risk if these food resources are contaminated.

All of the above mentioned birds are protected under the Migratory Bird Treaty Act. Bald eagles are listed as threatened under the Endangered Species Act and protected under the Migratory Bird Treaty Act, the Bald and Golden Eagle Protection Act. A waterfowl species, the trumpeter swan, is listed as endangered under the Endangered Species Act.

Other Risk Problems

A zone along the shoreline zone in front of the shooting platforms contains clay target debris. Clay targets may contain petroleum pitch (Remington 1990). The pitch contains polycyclic aromatic hydrocarbon (PAH) compounds (Remington 1990). PAH chemicals may accumulate in the soils and reach toxic concentrations. PAH products can weather and bioremediate. The clay target debris may form a physical barrier over the soil and limit plants.

Risk management and response actions at the site may cause adverse ecological consequences. For example, as parts of the marsh are deepened from excavation, then certain existing wetland community types may be permanently changed to new communities that are less desirable.

Tentative Receptors and Assessment Endpoints

The selection of the following receptors and assessment endpoints was based on information in the problem formulation, the fact that there are high densities of lead shot in the wetland part of the lead shot fall zone and that highly contaminated soils are found in front of the shooting platforms.

> **Assessment Endpoint 1:** Waterfowl mortality resulting from the ingestion of lead shot.

Large numbers of waterfowl presently use the marsh, either seasonally or year-round. In addition, trumpeter swans are being reintroduced in Iowa along the Mississippi River flyway, and they may stage at the marsh in the future. Exposure to lead shot creates a potential for direct toxicity to these waterfowl. An indirect effect resulting from lead poisoned waterfowl occurring at the site is the potential for toxicity to predators and scavengers, such as bald eagles, that feed on weakened and/or dying organisms and the carcasses. Risks to predators and scavengers will be evaluated qualitatively.

The mallard was selected as a receptor for the lead shot ingestion pathway in wetland habitats. The mallard is a common waterfowl species that use grit and is found at the marsh and will represent all of the waterfowl species that may nest or use the site during migration times.

The mourning dove was not selected as a receptor for lead shot ingestion in terrestrial habitats for the following reasons: The high density lead shot areas are believed to be in the wetland habitats and not in the terrestrial habitats. The terrestrial plant living biomass, the slow decaying litter horizon, and the clay target debris all may break this exposure pathway with a physical barrier.

> **Assessment Endpoint 2:** Mortality to vermivorous birds through lead exposure from contaminated food and incidental soil ingestion.

The woodcock was selected as a receptor for the food chain transfer pathway in wetland areas. The robin was selected as a receptor for the food chain transfer pathways in terrestrial areas.

> **Assessment Endpoint 3:** Mortality of wetland plants and invertebrates serving as food resources for the selected receptors resulting from exposure to lead contaminated wetland soils and sediments.

The survival of selected wetland plant communities plays a key role in wildlife nutrition and in the site's overall primary and secondary production.

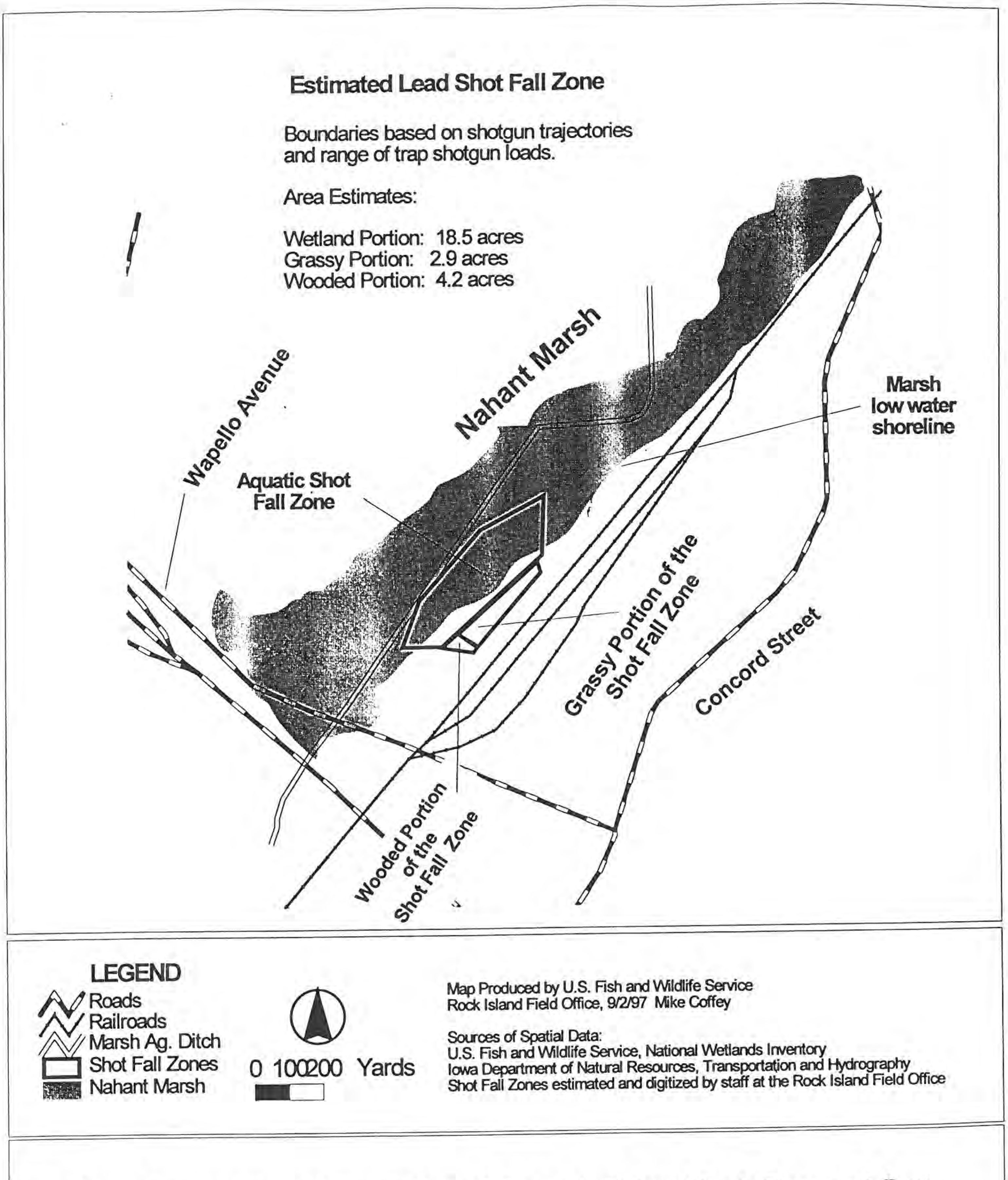

Figure 4. Approximate location of shot fall zones in Nahant Marsh, Davenport, Iowa.

Toxicity Evaluation

This section includes information on relevant toxicity studies available in the literature that contain preferred toxicological benchmark data. Exposure levels that represent conservative thresholds for adverse effects were selected from these study reports.

Lead Shot Ingestion

The range of lead shot densities in hunted marsh sites from across the country was between zero and 2.71 per square foot (USFWS 1986). An average of one shot per square foot has been suggested as a background density for North American marshes (Irwin and Karstad 1972). Toxicity testing has not confirmed the value of one shot per square foot or other background densities as a no-observed-adverse-effect-level (NOAEL).

Irwin and Karstad (1972) exposed mallards to a series of particulate lead (325 mesh - 0.044 millimeter) equivalent to shot densities of 10, 50 and 100 shot per square foot in artificial wetlands. Exposures of 10 shot per square foot value had very low toxicity for the birds. Exposures of 50 shot per square foot value resulted in chronic lead toxicosis. Exposures of 100 shot per square foot value resulted in subacute lead toxicosis. The ten shot per square foot value may be used as the lowest-observed-adverse-effect-level (LOAEL). The ten shot per square foot value was used to screen for waterfowl - lead shot ingestion risks.

Toxicity from Exposure to Contaminated Abiotic Media

Published ecotoxicological benchmark values for lead contaminated water, wetland sediments and upland soils will be used to screen for ecological risks.

The screening value selected for lead in water is the USEPA chronic ambient water quality criterion of 2.5 micrograms per liter (µg/L) at a water hardness of 100 milligrams per liter (mg/L) as calcium carbonate (USEPA 1986). Water quality data available from the USEPA contractor working at the site indicate specific water hardness values for the wetland between 149 and 320 mg/L as calcium carbonate (E & E 1997). These values correspond to site specific water quality criteria of 3.7 to 8.0 µg lead /L (dissolved).

The screening value selected for lead in sediments and wetland soil was the Ontario Ministry of the Environment lowest effect level of 31 milligrams per kilogram (mg/Kg) dry weight (Jaagumgi 1992). The screening values selected for the PAH compounds in sediments and wetland soil were the Ontario Ministry of the Environment lowest effect levels (see Table 5 on page 22). (Jaagumgi 1992).

The screening value selected for lead in soil was set at 45 mg/Kg dry weight. This value is based on the lowest available toxicity concentration value for terrestrial invertebrates and higher plants (EA Engineering 1991 and USEPA 1992).

Total leaf area of red oak was significantly reduced by 29 percent in sandy loam amended with a 50 mg lead (Dixon 1988).

Lead soil concentrations between 100 and 400 mg/Kg dry weight resulted in toxic responses to plants that include leaf necrosis, stunted growth, decreased photosynthesis and transpiration rates (Phalsson 1989, Davies 1990).

Total mortality within three weeks was observed for black-eyed Susan plants grown in urban soils with a bulk lead concentration of 900 mg/Kg dry weight (Miles and Parker 1979).

Test populations of springtail insects fed fungi grown in media amended with 45 mg/kg lead nitrate had decreased growth rate of second generation adults and reduced second generation adult survival (Bengtsson *et al* 1985).

Maximum allowable lead concentration for forest litter or soil that caused no adverse effects to invertebrates was between 100 and 200 mg/Kg (Bengtsson and Tranvik 1989).

The lethal concentration (LC_{50}) for an earthworm species was 5941 mg/Kg (Neuhasuser *et al* 1986). Survival and reproduction were reduced in woodlice fed soil litter treated with 12,800 mg lead/Kg (Beyer and Anderson 1985).

Toxicity from Exposure to Contaminated Food

The screening value selected for the soil food chain pathway for vermivorous birds was the estimated wildlife NOAEL value (metallic lead) of 3.85 mg/Kg per day (mg/kg-d) for the American robin and the common woodcock. (Sample 1996).

It should be noted that the availability of lead increases approximately three fold as the element is converted to the acetate form. The estimated wildlife NOAEL concentration for lead acetate for the robin and woodcock is 1.13 mg/kg-d.

Step Two. Screening Level Exposure Estimates and Risk Calculations

Exposure Estimates

Lead Shot Ingestion

Field sampling data from the USFWS indicated that wetland substrates in the shot fall zone contained an average of 236.7 (standard deviation = 225.3, n = 8) and a maximum of 470 lead shot per square foot. The USFWS sampling method used an Ekman dredge to collect substrate samples from the high lead shot density zone. Information provided in the Nahant Marsh integrated risk assessment indicated that an average of 26.8 (standard deviation = 87.3, n = 48) and a maximum of 533 lead shot were observed per square foot (E & E 1997). The E & E sampling method used a coring tool to collect substrate column samples along line transects throughout the lead shot fall zone. The different sampling methods and strategies used by the two organizations likely explain the disagreement in the results.

There are no shot density data available for the soil cover in the grassy portion of the shot fall zone.

Surface Water Toxicity

One surface water sample collected in the shot fall zone indicated a concentration of dissolved lead at 0.80 μg/L (E & E 1997).

Wetland Sediment/Soil Toxicity

The concentration of lead in two wetland sediment samples collected from within the shot fall zone were 9.4 and 27.3 mg/kg. The samples contained lead shot, but the shot was extracted by sieving prior to chemical analysis.

Ten different PAH compounds were detected in the two wetland substrate samples near the shoreline of the marsh in front of the club house (see Table 5 page 22).

Terrestrial Soil Toxicity

The concentration of lead in eighteen soil samples collected from between the club house/driveway and marsh shoreline ranged 15.1 to 35,900 mg/kg determined by chemical analysis (E & E 1997). The mean and 95% upper confidence limit for these data are 7525 and 4724, respectively. Many of the samples contained lead shot when collected in the field, but the shot was extracted by sieving prior to chemical analysis.

Contaminated Food Chain Pathway

The food chain exposure estimates for the woodcock and robin feeding entirely on earthworms that are living in the lead contaminated soil area are outlined in Table 2.

Table 2. Exposure estimates (mg/Kg-d) for selected soil lead concentrations for the woodcock and robin food chain pathways.

Species	Soil Lead[1] Maximum	Soil Lead Mean	Soil Lead 95% UCL[2]
Woodcock	2849	597	375
Robin	20,212	4237	2660

[1] Micrograms per gram, dry weight, n=18
[2] Upper Confidence Limit

The following formula was used to calculate the screening level exposure estimates:

Dose = soil lead concentration X average bioaccumulation factor X
average food ingestion rate X dry weight to wet weight conversion factor.

The maximum soil lead concentration at Nahant Marsh was 35,900 mg/Kg, mean was 7525 mg/kg and 95% upper confidence limit was 4724 mg/Kg (all in dry weight).

Bioaccumulation factors (BAF) are reported in the literature for earthworms (Beyer 1990, Morgan and Morgan 1991, Wei-chun Ma 1987). The literature provides a range of BAFs for lead in earthworms of 0.07 to 9.15 (average 1.24).

The average weight for woodcock is 0.196 kilograms (Joyce 1990). Woodcock species ingest an average of 0.042 kilograms of food daily (Joyce 1990). Normalized for body weight, this equals 0.21 grams food per gram body weight per day. We assume for this model that the woodcock's diet consisted of earthworms from the contaminated soil.

The average weight for the robin is 0.0773 kilograms (Dunning 1984). Robin species ingest an average of 0.1175 kilograms of food daily (Hazelton, *et al* 1984). Normalized for body weight, this equals 1.52 grams food per gram body weight per day. We assume for this model that the robin's diet consisted of earthworms from the contaminated soil.

The wet weight to dry weight conversion factor of 0.2987 was based on an average of two values for percent moisture reported in the literature of 70 and 84 percent (average 77) (USEPA 1994 and Tyler 1973).

Contaminated Soil Ingestion Pathway

The exposure estimates for the woodcock and robin incidental soil ingestion while foraging for earthworms that are living in the lead contaminated soil area are outlined in Table 3.

Table 3. Exposure estimates (mg/Kg-d) for selected soil lead concentrations for the woodcock and robin soil ingestion pathways.

Species	Soil Lead[1] Maximum	Soil Lead Mean	Soil Lead 95% UCL[2]
Woodcock	230	48	30
Robin	1532	321	202

[1] Micrograms per gram, dry weight, n=18
[2] Upper Confidence Limit

The following formula was used to calculate the screening level estimate for soil ingestion:

Dose = soil lead concentration X average food ingestion rate X
soil ingestion rate factor X dry weight to wet weight conversion factor.

The soil ingestion rate factor for woodcock is 0.1and 0.094 for the robin (Beyer *et al* 1994).

Risk Calculations

The screening level hazard quotients (HQ) were calculated by dividing the exposure estimate by the no effect or low effect benchmark ecotoxicity value.

The HQs exceeded one in the waterfowl lead shot ingestion pathway, terrestrial soil toxicity and avian food chain/soil ingestion exposure pathways (Table 4).

The HQ did not exceed one for surface water and for wetland sediment toxicity. These media are not predicted to be contaminated to the level to inhibit the production of waterfowl food (Table 4).

Table 4. Risk hazard quotients for the screening level contaminant exposure pathways at Nahant Marsh, Davenport, Iowa.

Exposure Pathway	Assessment Endpoint	Hazard Quotient
Lead Shot Ingestion	Waterfowl Mortality	24[a]
Surface Water Toxicity - Lead	Aquatic Life Health	<1
Wetland Sediment Toxicity - Lead	Aquatic Life Health	<1
Wetland Sediment/Soil Toxicity - PAHs	Aquatic Life Health	<1-21
Terrestrial Soil Toxicity - Lead	Wetland Plant Health	105[b]
Food Chain	Woodcock Mortality	97[b]
Soil Ingestion Pathway	Woodcock Mortality	8[b]
Food Chain	Robin Mortality	691[b]
Soil Ingestion Pathway	Robin Mortality	53[b]

[a]Based on mean shot density
[b]Based on 95% UCL soil concentration

Lead Shot Ingestion

The averages from two studies on lead shot distribution for the wetland portion of the shot fall zone (26.8 to 236.7) exceeded the LOAEL value of ten. The lead shot ingestion pathway HQ was much greater than one.

Surface Water Toxicity

The exposure estimate for surface water lead (0.80 μg/L) did not exceed the lowest site specific screening value (3.7 μg/L). The HQ for direct toxicity to aquatic life from exposure to lead contaminated surface water is less than one.

Wetland Sediment/Soil Toxicity

The maximum exposure estimate for lead in wetland sediments (27.3 mg/Kg) did not exceed the screening value (31 mg/Kg). The HQ for direct toxicity to benthic macroinvertebrates from exposure to lead in sediments is less than one.

The maximum concentrations for seven of the ten PAHs compounds detected at the marsh exceeded the respective chemical screening values (Table 5). The HQ for direct toxicity to benthic macroinvertebrates from exposure to PAH contaminated substrate is greater than one for the PAH compounds.

Table 5. Screening values (mg/Kg), exposure estimates (mg/Kg) and risk hazard quotients for the ten detected polycyclic hydrocarbon compounds that were detected in wetland soils and lowland fill sediment at Nahant Marsh, Davenport, Iowa.

Analyte	Screening Value[1]	Exposure Estimate[2]	Risk Hazard Quotient
Phenanthrene	0.56	11.930	21
Anthracene	0.22	0.086	0.4
Flouranthene	0.75	11.267	15
Pyrene	0.49	1.383	3
Benzo (a) anthracene	0.32	0.767	2
Chrysene	0.34	2.3	7
Benzo (b) flouranthene	-	1.173	-
Benzo (k) flouranthene	0.24	0.099	0.4
Benzo (a) pyrene	0.37	0.5	1.3
Benzo (ghi) perylene	0.17	0.3	2

[1] Lowest effect levels in Ontario Ministry of the Environment sediment quality criteria (Jaagumgi 1992).
[2] Maximum concentration detected for sampling station number 2 and 3. Sampling station two was in suspected terrestrial soil or upland fill material and next to a shooting platform.

Terrestrial Soil Toxicity

The maximum soil lead concentration of 35,900 mg/Kg exceeded the screening value for soils of 45 mg/Kg. Thirteen out of 18 (72 percent) of the soil test values exceeded this screening level value. The HQ for direct toxicity to terrestrial invertebrates and plants from exposure to lead contaminated soil exceeds one.

Contaminated Food and Soil Ingestion Pathway

The predicted dose of lead for the woodcock from feeding on contaminated food items (375 mg lead/Kg-d) and incidental soil ingestion (30 mg lead/Kg-d) were evaluated independently and compared with the NOAEL value of 3.85 mg lead/Kg-d.

The calculated HQs for the woodcock food chain and soil ingestion pathways each exceeded one. Adverse effects are predicted for the woodcock from feeding in the wet meadow and terrestrial portions of the lead shot fall zone. This calculation is based on the 95% upper confidence limit value for soil lead contamination.

The predicted dose of lead for the robin from feeding on contaminated food items (2660 mg lead/Kg-d) and incidental soil ingestion (202 mg lead/Kg-d) were evaluated independently and compared with the NOAEL value of 3.85 mg lead/Kg-d).

The calculated HQs for the robin food chain and soil ingestion pathways each exceeded one. Adverse effects are predicted for the robin from feeding in the terrestrial portion of the lead shot fall zone. This calculation is based on the 95% upper confidence limit value for soil lead contamination.

Uncertainty Analysis

Surface Water Toxicity

The single measurement exposure estimate for surface water lead may underestimate actual concentrations. Lower pH conditions related to high respiration rates of phytoplankton during blooms that occur later in the summer may increase the dissolved lead concentration. The water retention or flushing rates for the wetland during late summer may be longer and help maintain dissolved lead concentrations. These conditions could result in an HQ greater than one.

Lead concentrations in the surface water from within the shot fall zones at six former trap and skeet ranges from across the country were between 1.4 and 838 µg/L (Stansley *et al* 1992). Only one surface water sample was available from the site for evaluating this exposure pathway.

Wetland Sediment/Soil Toxicity

The exposure estimate for lead and PAH contamination to wetland sediments is based on only two samples. Additional samples are needed to adequately characterize the wetland substrate because of their potential heterogeneity.

Terrestrial Soil Toxicity

The HQ for soil toxicity is much greater than one. However, the leaves or flowers of plants growing in the terrestrial portion of lead shot fall zone do not appear to show symptoms of chemical stress. There does not appear to be any bare ground areas, even in the spots with a layer of clay target debris. However, the nearshore and shoreline zone adjacent to the shooting platforms contain cattail plants with deformed flowers. This screening level assessment has not fully characterized the bioavailability and ecotoxicity to cattail species from lead residues in the wetland soils.

Contaminated Food and Soil Ingestion Pathway

The food chain transfer models used to estimate the levels of lead in earthworms and exposure to the avian receptors are based on conservative desk top calculations and not site specific data from the marsh. There are uncertainties as to the potential of bioaccumulation of lead in earthworms living in the soil at the site.

Site specific soil parameters such as pH, grain size, organic carbon content may regulate the bioaccumulation of lead in soil dwelling invertebrates. The state in which the lead is partitioned in the soil column (fragments of elemental lead or sobbed and dissolved ions) may regulate the bioaccumulation of lead in soil dwelling invertebrates. These factors may result in a different estimate of exposure.

Conclusions

The screening level ecological risk assessment for Nahant Marsh predicted lead poisoning and potential mortality in waterfowl receptors from the ingestion of a spent lead shot in the marsh. The recovery of lead poisoned ducks and geese by natural resource personnel monitoring the site confirm the risks predicted for this exposure pathway.

The adversity of the predicted risks from the other exposure pathways evaluated in the screening level ecological risk assessment has not been confirmed. However, there may be adequate information in the screening level ecological risk assessment report to generally characterize ecological risks and help make risk management decisions for the site.

The uncertainties for the water toxicity and wetland sediment toxicity pathways may be resolved if necessary by collecting additional field data. The use of the additional field data will help increase the confidence and statistical power for the screening level risk calculations.

The remaining ecological risk pathways with uncertainties that were presented in the screening level ecological risk assessment include: 1) soil lead toxicity to plants and invertebrates, and 2) food chain lead hazards to avian receptors. The following risk questions were developed help resolve the uncertainties associated with the soil toxicity and food chain pathways. These risk questions may be used to help guide the development of measurement endpoints and future site investigations if deemed necessary.

Risk Questions:

1. What concentration of lead in the terrestrial soil represents a site specific threshold for adverse effects to plants and soil dwelling invertebrates? Could this concentration be used as a preliminary clean up goal?

2. What is the long term impact to the meadow habitat in the lead shot fall zone from implementing the various risk management scenarios?

3. What is the site specific earthworm bioaccumulation factor? Do the site specific risk calculations for the avian food chain transfer models show the potential for adverse effects?

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Appendix J

Removal Site Evaluation Report for Nahant Marsh

TETRA TECH, INC.

FILE COPY

January 23, 2006

Mr. Roy Crossland
START Project Officer
U.S. Environmental Protection Agency, Region 7
901 North 5th Street
Kansas City, Kansas 66101

Subject: **Removal Site Evaluation Report**
Nahant Marsh Site, Davenport, Iowa
U.S. EPA Region 7 START 2, Contract No. 68-S7-01-41, Task Order No. 0265
Task Monitor: Don Lininger, On-Scene Coordinator

Dear Mr. Crossland:

Tetra Tech EM Inc. is submitting the attached Removal Site Evaluation Report for the Nahant Marsh site in Davenport, Iowa. If you have any questions or comments, please contact the project manager at (913) 495-3930.

Sincerely,

for

Jeff Pritchard
START Project Manager

for Hieu Q. Vu, PE, CHMM
START Program Manager

Enclosure

G9011/0265

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REMOVAL SITE EVALUATION REPORT

NAHANT MARSH SITE – DAVENPORT, IOWA

Superfund Technical Assessment and Response Team (START)

Contract No. 68-S7-01-41, Task Order No. 0265

Prepared For:

U.S. Environmental Protection Agency
Region 7
901 North 5th Street
Kansas City, Kansas 66101

February 6, 2006

Prepared By:

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CONTENTS

TABLES

1.0 INTRODUCTION

The Tetra Tech EM Inc. (Tetra Tech) Region 7 Superfund Technical Assessment and Response Team (START) was tasked by the U.S. Environmental Protection Agency (EPA) Region 7 Superfund Division to conduct a removal site evaluation (RSE) at the Nahant Marsh site in Davenport, Iowa. The Quad City Skeet and Trap Club (QCSTC) operated a shooting range at the site from 1969 to 1995. During that time, an estimated 9 tons of lead shot was deposited on the site annually, for a total of 243 tons of lead shot. From 1994 to 1997, state and federal wildlife officials documented the presence of ailing or moribund waterfowl in Nahant Marsh. Veterinary pathologists at the National Wildlife Health Center in Madison, Wisconsin, diagnosed the birds with lead poisoning, based on lesions characteristic of lead poisoning and shot recovered from gizzards (United States Fish and Wildlife Service [USFWS] 1998).

Previous to this RSE, environmental investigations conducted at the site by the USFWS and EPA had determined that elevated levels of lead (and lead shot) were present in on-site soils and sediments. Because of the lead contamination, an EPA-funded removal action—including excavation of lead-contaminated soil and sediment—was conducted at the site in 1999. However, since the 1999 removal action, the USFWS has reported continued discoveries of ailing and moribund waterfowl at the site. The purpose of this RSE was to evaluate whether any lead-contaminated media remain at the site that present a threat to the environment, including waterfowl. RSE activities focused on an area of approximately 11.5 acres located south of the area excavated during the removal action, where shooting activities had occurred early in the site's history (Ecology and Environment [E&E] 1999). RSE activities included collection of soil samples from terrestrial areas and sediment samples from the marsh for field and laboratory analyses.

2.0 BACKGROUND INFORMATION

This section provides a brief overview of the site location and previous environmental investigations involving the site.

2.1 SITE LOCATION

The Nahant Marsh site is located at 4220 Wapello Avenue, just within the southwest city limits of Davenport, Iowa. The City of Davenport owns the site. A laboratory and research station for field biology and wetland education is located on the site. The site is within the northeast quarter of Section 8 of Township 77 North, Range 3 East, in Scott County, Iowa (see Appendix A, Figure 1). The geographic coordinates of the Nahant Marsh site are latitude 41° 29' 25.6" north and longitude 90° 38' 7.3" west. The site encompasses 115 acres and is bounded by agricultural fields to the northeast, a railroad line that parallels the Mississippi River to the southeast, and U.S. Interstate 280 to the west. The site includes 70 acres of emergent plant habitat containing a mosaic of cattail, rushes, and open water patches (USFWS 1998). The marsh is partially surrounded by 45 acres of bottomland forest habitat. A ditch (approximately 6 feet deep) runs through the center of the marsh. The remainder of the marsh is approximately 1 to 2 feet deep. Local topography on the site slopes gently into the marsh or to the south alongside the marsh. The marsh drains to the southeast into a second marsh located on the south side of I-280. Surface water from the site eventually empties into the Mississippi River approximately 3,000 feet south of where the marsh intersects I-280 (E&E 1999).

The area investigated for this RSE was a former shooting area (not addressed during past investigations and cleanup activities) covering approximately 11.5 acres, located in the south corner of the Nahant Marsh site property (see Appendix A, Figure 2). This rectangular area extends approximately 1,000 feet in a southwest-northeast direction, immediately west of (and parallel to) a set of railroad tracks. The area of interest is approximately 500 feet wide.

2.2 PREVIOUS INVESTIGATIONS

Previous investigations at the site had been conducted by the USFWS and EPA. In 1994, the USFWS collected sediment samples that contained elevated levels of lead shot (as high as 283 lead shot per sample). No report was prepared for the USFWS sampling activities. As previously mentioned, ailing waterfowl were recovered from the marsh during site visits conducted by state and federal wildlife management officials from 1994 to 1997. Following examination by veterinary pathologists, the birds were diagnosed with lead poisoning. Furthermore, the USFWS determined that the ingestion of lead shot was a significant risk associated with the site.

From 1996 to 1999, EPA-funded assessment and removal activities were conducted at the site to evaluate and reduce the amount of lead and (lead shot) in soil and sediment at the site. Previous EPA investigations have included an integrated site assessment (ISA), preliminary assessment/site inspection (PA/SI), expanded site inspection (ESI), removal assessment, and removal action. EPA assessments determined that soil and sediment located in the vicinity (within approximately 600 feet) of the five main QCSTC shooting platforms contained elevated concentrations of heavy metals, primarily lead. Lead concentrations were detected in on-site soil and sediment as high as 64,000 milligrams per kilogram (mg/kg) and 726,000 mg/kg, respectively. Lead shot counts as high as 2,687 per square foot were found in the sediment samples. Elevated levels of antimony and polycyclic aromatic hydrocarbons (PAH) were also detected in soil samples collected from the former shooting area. Both of these contaminants were found attributable to the site. Antimony is/was used as a hardener for lead shot, and the PAH contamination was associated with shooting targets (clay pigeons). Target fragments were concentrated mostly in areas directly in front of the target throwing stations (E&E 1999). Based on these findings, in 1999, EPA conducted a removal action involving excavation of lead-contaminated soil and sediment. Eleven acres of the marsh and terrestrial areas around the shooting platforms (north of the area being investigated for this RSE) were excavated. For the excavation activities, a removal action level (RAL) of 10 lead shot per square foot was established by the USFWS (USFWS 1998). Levels below 10 shot per square foot were determined to present a very limited threat to birds. Furthermore, a RAL of 1,000 mg/kg was established for lead-contaminated soil in the terrestrial areas. A total of 49,162 cubic yards (yd^3) of sediment was excavated from the marsh, and 10,416 yd^3 of soil was excavated from the surrounding terrestrial areas. In addition, the areas identified as containing elevated levels of PAHs (from target fragments) were excavated during the removal. Post-excavation sampling reflected an average of five shot per square foot in the marsh sediment. Post-excavation samples collected from the terrestrial areas did not contain contaminant levels above background concentrations.

3.0 SITE ACTIVITIES

Tetra Tech START conducted RSE activities at the Nahant Marsh site on November 28th through December 1st, 2005. RSE activities involved construction of a grid across the 11.5-acre investigation area and subsequent soil and sediment sampling to determine whether any lead-contaminated media remain at the site. The Tetra Tech START team members were Anthony Brewer, Jeff Pritchard, Keith Brown, Rob Monnig, and Jason Heflin. The EPA Region 7 On-Scene Coordinator (OSC) for the project was Susan Sweet. Photographic documentation of the site activities is in Appendix B.

3.1 SOIL AND SEDIMENT SAMPLING

The proposed sampling grid consisted of 231 grid points spaced 50 feet apart (see Appendix A, Figure 3). However, 24 of the grid points were not marked or sampled during RSE activities because of difficulties accessing those proposed locations (during the time of the RSE activities, approximately 2 inches of ice covered the marsh; the inaccessible grid points were located in the open water portion of the marsh).

Following construction of the grid, soil/sediment samples were collected from each of the marked grid points. At each grid point in the terrestrial area, the top inch of ground cover and soil was removed with a stainless steel trowel from a 1-foot by 1-foot area and placed into a 1-gallon Ziploc bag, which was labeled to identify the sample location. For the grid points located in the marsh, a wooden box (with open top and bottom) measuring 1 foot by 1 foot by 3 feet high was driven into the substrate. Next, water was decanted from the wooden box. Then the top inch of sediment was removed with a stainless steel trowel and placed into a labeled, 1-gallon Ziploc bag.

Each sample was placed into a 2-millimeter sieve (small enough to prevent the smallest sized lead shot [# 9 size] to pass through) and sprayed with running water to wash away soil and sediment, leaving the lead shot and detritus. The remaining material in the sieve was placed on white paper, and the lead shot was segregated and counted. The lead shot count for each grid point was recorded in the field notes.

In addition to the samples collected for counting lead shot, six samples (four soil and two sediment) were collected from selected grid points for laboratory analysis to determine concentrations of heavy metals in the investigation area. Figure 3 in Appendix A illustrates these sample locations. Four of the six samples were collected for analysis of total metals. Of the four samples submitted for total metals, three were collected from the terrestrial area, and the fourth was collected from the marsh. The other two samples (one from the terrestrial area and one from the marsh) were collected for analysis of leachable metals according to the Toxicity Characteristic Leaching Procedure (TCLP). Sample locations were selected to provide geographic coverage of the sampling area and to span the approximate range of lead concentrations over that area (based on lead shot counts in the samples). Samples were placed into labeled 8-ounce jars and stored on ice pending delivery to the EPA Region 7 laboratory in Kansas City, Kansas. Table 1 summarizes the sample locations and analyses performed.

TABLE 1
SAMPLE SUMMARY
NAHANT MARSH SITE, DAVENPORT, IOWA

EPA Sample Number	Sample Location	Laboratory Analysis
2851-2	Grid Point 16	Total Metals
2851-3	Grid Point 69	Total Metals
2851-4	Grid Point 161	Total Metals
2851-5	Grid Point 169	Total Metals
2851-101	Grid Point 16	TCLP Metals
2851-102	Grid Point 77	TCLP Metals

Notes:
EPA United States Environmental Protection Agency
TCLP Toxicity Characteristic Leaching Procedure

Notably, target fragments (clay pigeons) were observed on the ground surface across the site grid, particularly concentrated in the central portion of the grid (in the terrestrial area). Target fragments were not observed in any of the sediment samples collected from the marsh. Past investigations at the site have associated PAH-contaminated soil with the target fragments; however, samples collected during this RSE were not analyzed for PAHs.

4.0 LEAD SHOT COUNT AND ANALYTICAL RESULTS

Samples collected for quantifying lead shot were prepared and counted on site. The six samples collected for laboratory analysis were submitted to the EPA Region 7 laboratory in Kansas City, Kansas, on December 5, 2005. For interpreting lead shot counts, the results were compared to the action level of 10 lead shot per square foot, established by the USFWS. A Screening Level Ecological Risk Assessment completed for the Nahant Marsh site by the USFWS in 1998 concluded that a lead shot density of less than 10 per square foot in wetlands presented a very low threat for waterfowl and birds. Analytical results from the six samples submitted for laboratory analysis were compared to applicable health-based standards (EPA Region 9 preliminary remediation goals [PRG]) (EPA 2004) and regulatory TCLP limits. Appendix C contains the laboratory data package.

4.1 LEAD SHOT COUNT RESULTS

During the RSE activities, 207 samples were collected and processed on site for counting lead shot. Lead shot in the samples ranged from 0 (95 samples contained no lead shot) to 70 (grid point 161). Fifty-two of the 207 samples contained more than 10 lead shot. Only two grid points contained more than 50 lead shot (grid points 161 and 204). Figure 3 in Appendix A illustrates the site grid and corresponding lead shot results for each sampled grid point. Most grid points that contained more than 10 lead shot were located in the southern portion of the grid. Appendix D summarizes the lead shot results.

4.2 ANALYTICAL RESULTS

Four samples (three soil samples collected from the terrestrial area and one sediment sample collected from the marsh) were submitted for analysis of total metals. Numerous metals were detected in the samples; however, none was detected at concentrations that pose a threat to human health or the environment. Lead was detected in all four of the samples at concentrations that ranged from 18.2 mg/kg to 339 J mg/kg. A J-coded value indicates that the analyte has been positively identified, but the quantitation is an estimate. The reported lead concentrations were below EPA Region 9 PRGs established for residential and industrial soils, which are 400 mg/kg and 1,000 mg/kg, respectively. Antimony, a contaminant of concern during the 1999 removal action, was not detected above its laboratory reporting limit of 2 mg/kg. Table 2 shows the total lead results.

TABLE 2
TOTAL LEAD RESULTS
NAHANT MARSH SITE, DAVENPORT, IOWA

EPA Sample Number	Sample Location	Lead Shot Count	Total Lead (mg/kg)
2851-2	Grid Point 16	20	339 J
2851-3	Grid Point 69	0	18.2
2851-4	Grid Point 161	70	105
2851-5	Grid Point 169	0	51.2
EPA Region 9 PRG – Residential Soil			400
EPA Region 9 PRG – Industrial Soil			1,000

Notes:
1,000 mg/kg was the removal action level established for lead-contaminated soil during the 1999 EPA removal action.

EPA United States Environmental Protection Agency
J Analyte has been positively identified in the sample, but the quantitation is an estimate
mg/kg Milligrams per kilogram
PRG Preliminary remediation goal

Two samples (one soil and one sediment) were submitted for leachable metals analysis. Neither of the samples contained concentrations that exceeded TCLP regulatory limits. TCLP lead results were 0.160 milligrams per liter (mg/L) in sample 2851-101 and non-detect (less than 0.50 mg/L) in sample 2851-102. The TCLP lead results were well below the regulatory limit for leachable lead, which is 5.0 mg/L. Table 3 shows the TCLP lead results.

TABLE 3
TCLP LEAD RESULTS
NAHANT MARSH SITE, DAVENPORT, IOWA

EPA Sample Number	Sample Location	Lead Shot Count	TCLP Lead (mg/L)
2851-101	Grid Point 16	20	0.160
2851-102	Grid Point 77	0	0.05 U
TCLP Regulatory Limit			5.0

Notes:

EPA United States Environmental Protection Agency
mg/L Milligrams per liter
TCLP Toxicity Characteristic Leaching Procedure
U Compound not detected at or above the reporting limit

5.0 SUMMARY

Tetra Tech START was tasked to conduct a RSE at the Nahant Marsh site in Davenport, Iowa. The RSE was conducted from November 28 through December 1, 2005. RSE activities involved constructing a grid across the 11.5-acre investigation area, conducting soil and sediment sampling from grid points for counting lead shot, and collecting samples (soil and sediment) for laboratory analyses of total metals and TCLP metals. Samples were collected from 207 grid points to determine the number of lead shot. Fifty-two of the 207 samples were found to contain more than 10 lead shot (in a 1-square-foot area), which was the action level established by the USFWS. Six samples were submitted for laboratory analysis (four for total metals and two for TCLP metals). Metals were not detected in the samples at concentrations that pose a threat to human health or the environment. Specifically, total lead was detected at concentrations that ranged from 18.2 mg/kg to 339 J mg/kg, which were below EPA Region 9 PRGs for residential and industrial soil. TCLP sample results were well below established regulatory limits for leachable metals.

5.1 REMOVAL CONSIDERATIONS

During the RSE, samples from 52 grid points (from a grid consisting of sample points spaced 50 feet apart) contained more than 10 lead shot (samples were collected from 1-square-foot areas). Based on the USFWS action level of 10 lead shot per square foot, removal activities may be warranted for those areas, where a significant risk may be posed to waterfowl and birds. Most grid points that exceeded the action level were located in the southern portion of the grid (in the terrestrial area). None of the sediment samples collected from the marsh exceeded 10 lead shot. Samples collected during the RSE for laboratory analysis of total metals and TCLP metals indicated no significantly elevated levels of those contaminants in the investigation area. A Removal Site Evaluation form for the site is in Appendix E.

5.2 PRE-REMEDIAL CONSIDERATIONS

Pre-remedial issues have been evaluated in previous site assessment reports (PA/SI, ISA, and ESI) completed by the EPA. The ESI, which was finalized after the completion of the 1999 EPA removal action, concluded the exposure pathways (soil, groundwater, and surface water) posed minimal threat to human health and the environment. Consequently, no further pre-remedial response is required at the site.

6.0 REFERENCES

Ecology and Environment, Inc. (E&E). 1999. Expanded Site Inspection/Removal Assessment for the Nahant Marsh Site, Davenport, Iowa. December 27.

Environmental Protection Agency (EPA). 2004. Preliminary Remediation Goals. Region 9 Waste Programs Table. October 1. On-line address: http://www.epa.gov/region09/waste/sfund/prg/index.htm.

United States Fish and Wildlife Service (USFWS). 1998. Screening Level Ecological Risk Assessment for Nahant Marsh, Davenport, Iowa, Rock Island, Illinois. June 9.

Appendix K

Memorandum for Lake Geneva Threat Assessment

Exhibit 6 – US EPA Determination of imminent and substantial threat – Lake Geneva, Wisconsin

Exhibit 2

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 5
77 WEST JACKSON BOULEVARD
CHICAGO, IL 60604-3590

REPLY TO THE ATTENTION OF

MEMORANDUM **HSE-5J**

DATE: JUL 19 1994

SUBJECT: ACTION MEMORANDUM - Determination of Threat to Public Health or Welfare or the Environment at the Southern Lakes Trap and Skeet Site, Lake Geneva, Walworth County, Wisconsin (Site ID #TX)

FROM: Brad Benning, On-Scene Coordinator Donald J. Bruce for
Emergency Response Section II

TO: William E. Muno, Director
Waste Management Division

THRU: Jodi Traub, Acting Associate Division Director
Office of Superfund

I. PURPOSE

The purpose of this memorandum is to document the determination of an imminent and substantial threat to public health and the environment posed by the presence of hazardous substances at the Southern Lakes Trap and Skeet Club, located in Lake Geneva, Walworth County, Wisconsin. The hazardous substance is lead in the form of lead shot which has accumulated in a wetland over the course of the sites operation since 1968. In January of 1992, the United States Fish and Wildlife Service (USFWS) documented the die-off of 218 Canada geese that occurred on Lake Geneva. Necropsies performed on several of the geese revealed that the birds were in good health but had ingested large numbers of lead shot and had died of acute lead poisoning.

CERCLIS ID No. WID988637278

II. SITE CONDITIONS AND BACKGROUND

A. Site Description

1. Removal site evaluation

The investigation focused on the Southern Lakes Trap and Skeet club located 3-4 miles from where the geese were recovered on Lake Geneva. Examination of the ingested shot revealed the size shot utilized for skeet and showed deformations consistent with having been fired from a shotgun. Bottom samples were taken by USFWS and revealed in excess of 24 million shot pellets per acre in parts of the wetland. Additional evidence suggests that the geese ingested the lead shot during a very cold period in January. A spring fed stream that traverses the wetland provided some of the only open water in the area. The geese were attracted to the open water and fed on grasses there and at the same time ingested lead shot, taking it for grit.

2. Physical location

The Southern Lakes Trap and Skeet club is located on the grounds of the Americana Resort in Lake Geneva, Wisconsin approximately 3-4 miles northeast of Lake Geneva, (T2N-R18E-SWSW Sec. 20). The surrounding land use is agricultural and recreational with limited residential within 1/2 mile.

3. Site characteristics

Southern Lakes has operated the range since 1981, although it has been in operation under different ownership since 1968. The site consisted of a trap and skeet range with three skeet houses and three trap bunkers. The shooting stations were set so that the clay pigeons and shot fell into a large wetland located directly in front of the houses. Large piles of clay pigeons and numerous shotgun wads were evident in the wetland. The wetland is about 34 acres in size mostly covered with cattails and sedges and is listed on WDNR's wetland inventory as persistent and nonpersistent narrow leaved emergent vegetation in wet soils or open water (E2H, E2K, and E4/WOH). A channelized stream flows from east to west in front of the range, and ultimately joins the White River.

4. Release or threatened release into the environment of a hazardous substance, or pollutant or contaminant

As a result of the USFWS investigation, the release of lead into the environment has allegedly resulted in the death of a significant number of migratory water fowl. The lead shot continues to pose a threatened release into the environment via leaching into wetland sediments and surface waters.

5. NPL status

The Southern Lakes Trap and Skeet site is not on the National Priorities List (NPL), and is not likely to be proposed for the NPL.

6. Maps, pictures and other graphic representations

Attachment III

B. <u>Other Actions to Date</u>

1. Previous actions

As part of the Damage Assessment required by USFWS a plant inventory was conducted in August to characterize the plant community, especially in terms of rare, threatened, or endangered species. No previous removal actions have occurred at the site.

2. Current actions

The Assessment Plan for the Natural Resource Damage Assessment, received limited comments during the 30-day comment period, no significant changes were made to the "draft" Assessment Plan, which is now in "draft-final" version. USEPA is currently negotiating with the PRP's to perform a site assessment to determine the extent of lead contamination at the site.

C. <u>State and Local Authorities' Roles</u>

1. State and local actions to date

WDNR collected the initial samples at the Southern Lakes site on February 19, 1992, to determine the extent of lead shot at the site. WDNR was also involved in the recovery of dead geese and many of the necropsies that were conducted on the geese.

2. Potential for continued State/local response

On November 25, 1992, the USFWS notified the WDNR of potential co-trusteeship at the site. The WDNR has declined to participate as a trustee for this case. USEPA does not anticipate any significant involvement by the WDNR, but they will be kept informed as the removal progresses.

III. THREATS TO PUBLIC HEALTH OR WELFARE OR THE ENVIRONMENT, AND STATUTORY AND REGULATORY AUTHORITIES

A. <u>Threats to Public Health or Welfare</u>

The conditions at the Southern Lakes Site meet the criteria for a removal action as stated in the National Contingency Plan (NCP), Section 300.415(b)(2).

*Actual or potential exposure to hazardous substances or pollutants or contaminants by nearby populations, animals, or the food chain.

This factor is present at the site due to the existence of lead shot in a wetland utilized as a feeding area for migrating birds. In January 1992, the USFWS investigated the death of 218 Canada geese on Lake Geneva, Wisconsin. USFWS determined that the cause of death was acute lead poisoning after ingestion of lead shot from the site. The concentration of total lead in the sediments is high enough to warrant concern even without preferential ingestion for grit. Potential ingestion by any bottom feeding organisms able to engulf lead shot might be expected to suffer injury.

*Actual or potential contamination of drinking water supplies or sensitive ecosystems.

This factor is present at the site due to the existence of lead shot throughout a 36 acre wetland. Sediment samples at the site revealed up to 24 million pellets per acre. The geologic resource may potentially be impaired to the point of being unable to provide suitable habitat for waterfowl and other wetland species.

*High levels of hazardous substances or pollutants or contaminants in soils largely at or near the surface, that may migrate.

This factor is present at the site due to the existence of a large source of lead shot concentrated in a wetland area. The potential exists for the lead shot to slowly dissolve and migrate into the sediments and surrounding surface waters.

IV. ENDANGERMENT DETERMINATION

Due to the existence of lead shot in a wetland which is utilized as a feeding area for migrating birds, that the geologic resource may potentially be impaired as a suitable habitat, and that lead may potentially migrate into sediments and surface waters, actual or threatened releases of hazardous substances from the South Lakes Trap and Skeet Club, if not addressed by implementing the response actions selected in this Action Memorandum, may present an imminent and substantial endangerment to public health, or welfare, or the environment.

V. PROPOSED ACTIONS AND ESTIMATED COSTS

A. Proposed Actions

1. Proposed action description

Pursuant to the AOC, the PRPs intend to undertake the following actions to mitigate threats posed by the presence of hazardous substances at the Southern Lakes site:

a. Implement the Site Health and Safety Plan

b. Conduct an approved assessment plan pursuant to USEPA response authority and the USFWS Natural Resource Damage Assessment (NRDA) authority under CERCLA.

c. Conduct an appropriate removal action based on lead shot distribution, to mitigate the threat of lead exposure to migratory birds and the environment.

d. The removal action shall utilize the Best Demonstrated Available Technology (BDAT) for the removal of lead shot.

e. Conduct site restoration as deemed appropriate by the USEPA and USFWS.

f. If necessary, implement appropriate measures to restrict site access to migratory birds to prevent feeding in the wetland area.

g. Conduct adequate confirmation sampling to verify completion of the removal action.

2. Contribution to remedial performance

The proposed removal action will remove all hazardous substances from the site, eliminating future sources of contamination.

3. Description of alternative technologies

Reuse/recycling of hazardous substances at the site will be the preferred option prior to any off-site treatment and disposal.

4. Applicable or relevant and appropriate requirements (ARARs)

Federal ARARs determined to be applicable for the site are the Resource Conservation and Recovery Act, the Migratory Bird Treaty Act and the Clean Water Act. WDNR was contacted as co-trustee of the wetland but has declined to participate. Any State ARARs identified in a timely manner for this removal action will be complied with to the extent practicable.

5. Post Removal Site Control

The OSC has begun planning for provision of post-removal site control, consistent with the NCP. Elimination of all surface threats during this removal action is, however, expected to minimize the need for post-removal site control.

The response actions described in this memorandum directly address actual or threatened releases of hazardous substances, pollutants of contaminants at the facility which may pose an imminent and substantial endangerment to public health and safety, and to the environment. These response actions do not impose a burden on affected property disproportionate to the extent to which that property contributes to the conditions being addressed.

VI. EXPECTED CHANGE IN THE SITUATION SHOULD ACTION BE DELAYED OR NOT TAKEN

Delay or non-action may result in an increased chance of direct contact threat to wildlife populations accessing the site and the degradation of the wetland and surface water conditions.

VII. OUTSTANDING POLICY ISSUES

No significant policy issues are associated with the the Southern Lakes Site.

VIII. ENFORCEMENT

The PRP's have been identified and appropriate enforcement action has been initiated. For Administrative purposes, information concerning the enforcement strategy for this site is contained in the Enforcement Confidential addendum. (Attachment I)

IX. RECOMMENDATION

This decision document represents the selected removal action for the Southern Lakes Trap and Skeet site in Lake Geneva, Wisconsin, developed in accordance with CERCLA as amended, and not inconsistent with the NCP. This decision is based on the Administrative Record for the site. (Attachment III). Conditions at the site meet the NCP section 300.415(b)(2) criteria for a removal action.

APPROVED: Wm. E. Muno DATE: 7/19/94
DIRECTOR, WASTE MANAGEMENT DIVISION

DISAPPROVED: ______________________ DATE: __________
DIRECTOR, WASTE MANAGEMENT DIVISION

cc: T. Johnson, OS-210
Don Henne, U.S. Department of the Interior
Custom House, Room 217
200 Chestnut Street
Philadelphia, PA 19106
K. McKutcheon, WDNR Superfund Coordinator