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

Ryan L. Perroy a,⁎, Colin S. Belby b,1, Cody J. Mertens b,2

a Department of Geography and Environmental Science, University of Hawaii at Hilo, 200W. Kawili Street, Hilo, HI 96720-4091, United States
b Department of Geography and Earth Science, University of Wisconsin La Crosse, 1725 State Street, La Crosse, WI 54601, United States

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 superficial (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. Superficial 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 m³ 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/m² 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.

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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...
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/m² 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 fallout zone (Fig. 1B). We established a 20 × 20 m grid for superficial (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.

![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.](image-url)
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 with a Geotek Geoscans-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; Døl 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 HNO₃) 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 (Rackstaetter 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 m² 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 floculent 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 footprint) 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...
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.
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/m²) 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 (PbCO₃) and shannonite ($\text{Pb}_2\text{O}$(CO₃)) 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 m³ 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.
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 m³ 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 $4.2 \times 10^8$ Pb pellets, or $2.0 \times 10^4$ kg based on the average mass of shot recovered.

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).
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.
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 sediment prior to shot removal, the concentrations would still likely have exceeded the EPA’s contamination criteria by a wide margin. 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 Cordulidae (dragonfly) specimens collected within the LRM shot fallout zone (R. Haro, UW L, pers. com.), and morphological deformities in benthic invertebrates have been connected to lead-contaminated sediments in other studies (De Bishoven 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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References


Calvert JH. Pheasants poisoned by swallowing shots. Field 1876:47–189.


