Environmental impacts of lead shot at skeet shooting ranges and arsenic-based pesticides in golf courses in Florida

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Abstract
This is year two of a 3-year proposal addressing two of the 17 issues (#9-lead shot at skeet shooting ranges and #10-arsenic-based pesticides on golf courses) outlined in the 1998 RFP from the Center. Since Pb and As are both trace metals of environmental concern, they will be studied together in this proposal. Preliminary surveys are being conducted to obtain information on primary sources of these two metals in Florida. Based on the survey, 25-50 soil/sediment/water/plant samples will be collected and analyzed from 5 to 10 shooting ranges and golf courses (up to 500 samples) to determine metal contamination in soil/sediment/water/plant. Metal leachability (impacts on surface and groundwater) and bioavailability (impacts on human and wildlife) in these samples will be determined. In addition, these samples will be subjected to the EPA TCLP and SPLP tests to determine their toxicity and leachability, and to a chemical fractionation procedure to determine their chemical and mineralogical properties. Results from this study will be useful to both FDEP for environmental regulation and the respective industry for pollution control purposes.

Introduction
Lead and arsenic are all trace metals of environmental concern due to their adverse impacts on humans and animals. Many anthropogenic processes, such as use of lead shot at skeet shooting ranges and application of arsenic-based pesticides on golf courses, have significantly increased concentrations of these metals in the environment. Therefore, it is very important to evaluate their impacts on the environment.

Skeet shooting has become a popular recreational sport. It has been realized that large amounts of metallic lead (Pb) may be deposited on the shooting ranges. In lead shot, Pb comprises 95-97% of the weight, with Sb contributing 0.4-2.0 %, arsenic 0.2-0.8, and Sn, Se, Mn, Cd, Cr, Cu, and Ni having average concentrations > 30 μg/g (Fisher and Hall, 1986). Until recently it has been assumed that lead shot in soil is stable and therefore it has not been considered as a source of environmental lead contamination, except by direct ingestion of shot or sinkers by animals. However, ultimately all of the metallic lead in shot may be transformed into dissolved and particulate species and spread over the environment (Jorgensen and Willems, 1987). The weathered Pb shot are mostly composed of cerssite, hydrocerssite ($Pb(CO_3)_2(OH)_2$), and small amounts of anglesite (Sever, 1993; Shreir, 1976). In Florida, several natural factors, such as low soil pH, low clay and organic matter content (Chen et al., 1998), and high rainfall, can accelerate lead shot weathering and thus increase the risk of contamination of environment. However, little information is available as to the impacts of Pb shot on the environment in Florida.

In addition to Pb contamination from shooting ranges, arsenic contamination from golf courses is another concern. Modern golf courses are subject to intense management including frequent application of tricalcium arsenate ($Ca_3(AsO_4)_2$) to control grubs and bluegrass. Most golf courses are constructed using mixtures of sand, soil, and peat and have high infiltration rates with underdrains of 10 cm of gravel and drainage tiles. The combination of high rate of pesticide application, frequent irrigation and a good drainage may result in arsenic loss from the golf course or arsenic accumulation in the soil. Johnson and Hiltbold (1996) studied the fate of three arsenicals applied to golf courses and found that arsenic concentrations decreased with depth and greater arsenic application rates resulted in greater arsenic leaching. Duble et al (1978) found significant arsenic concentrations in both drainage and runoff from golf courses. Arsenic concentrations as high as 8 ppm were found in the drainage water from the golf course with average arsenic concentration of 1-3 ppm. However, little information is available on the possibility of arsenic accumulation in soils of golf courses in Florida.

Methodology/Scientific Approach

The primary objective of this study is to assess the environmental impacts of Pb from lead shot at skeet shooting ranges and arsenic from arsenic-based pesticides used on the golf courses. We have obtained a FEDP approved QA/QC plan for this project (Comprehensive QA Plan #990111). The research will be divided into three parts: preliminary survey to obtain critical information on these two metal sources in Florida (on-going), soil/sediment/water/plant sample collection and analysis to determine the extent of metal contamination from these two sources, and laboratory study to further understand the leachability and bioavailability of these two metals in soil/sediment/water.

<u>1. Preliminary survey (on-going)</u>

To better understand the potential impacts of Pb and arsenic on the environment, we are conducting a preliminary survey on the primary contributors of these two metals. This information will not only help us to select representative places for sampling, but also help the state to assess the extent of metal contamination from these two sources. The following information is being obtained from the surveys:

Skeet shooting range

i. Number of large skeet shooting ranges and their locations in Florida;
ii. The amounts of lead shot used on an annual basis;
iii. How many years they have been in operation;
iv. What steps they take to prevent environmental contamination of Pb.

Golf course

i. Number of large golf courses using arsenic-based pesticide and their locations in Florida;
ii. The amounts and types of arsenic-based pesticide used on an annual basis;
iii. How many years they have been using arsenic-based pesticide;
iv. What steps they take to prevent environmental contamination of arsenic.

<u>2. Soil/sediment/water/plant sample collection and analysis</u>

25-50 soil/sediment/water/plant samples will be collected from 5 to 10 representative skeet shooting ranges and golf courses based on the information obtained above and from FDEP at Tampa. This will result in a total of up to 500 samples. These samples will be digested, except water samples, using EPA method 3051a to determine total-recoverable metal concentrations (Chen and Ma, 1998). These results will then be used to determine the extent of metal contamination on the sites. In addition to potentially contaminated soil/sediment samples, nearby clean soil/sediment samples will also be collected for comparison. Metal concentrations in these samples will be compared to our database of background concentrations of trace metals in Florida surface soils (Chen et al, 1998). Metal concentrations and their locations will then be put on GIS on a statewide map whenever it is possible.

3. Laboratory study:

Leachability test
Fresh lead shot and arsenic pesticides will be mixed with 6 representative soils collected from shooting ranges (3) and golf courses (3) at different rates in a column to determine their leachability at different time intervals after incubation for different times. Soil/sediment samples collected will also be included in this study. In addition, the EPA TCLP and SPLP tests will be used to determine metal toxicity and leachability in samples. These results will determine potential surface and groundwater contamination from these two sources.

Fractionation test
Representative soil samples contaminated with Pb and arsenic will be fractionated using the Tessier & Campbell (1988) method to better understand the bioavailability and leachability of these two metals in soils/sediments.

Bioavailability test
An *in vitro* method of Ruby et al (1996) will be used to determine the bioavailability of these two metals to assess the impacts of these metals on human and wildlife.

Mineralogical analysis
Representative soil samples contaminated with Pb and arsenic will be analyzed using x-ray diffraction and scanning and transmission electronic microscopes to determine their mineralogical properties. This information will further help to understand the bioavailability and leachability of the two metals in soils/sediments.

Practical and Specific Benefits for End Users

This research will serve at least three groups of users, i.e. FDEP, skeet shooting range operators, and golf course owners in addition to the general public. Our preliminary survey will show the potential impacts of these two sources on metal contamination in Florida. Our soil/sediment sample collection and analysis will reveal further information as to the extent of metal contamination from these two sources. Our lab studies will determine the leachability and bioavailability of metal contaminated soil/sediment. The results from this study will help FDEP to establish proper regulation on these two activities and help the respective industry to establish proper procedures to minimize environmental contamination from these two metals.

Deliverables

A survey report on skeet shooting range and golf course;
A map showing Pb and arsenic concentrations in soil/sediment and their locations in Florida;
Leachability and bioavailability of Pb and arsenic in soils/sediments;
Publications in journals and magazines, and presentations in state and national meetings;
Monthly and annual reports.

Research schedule

	1st quarter	**2nd quarter**	**3rd quarter**	**4th quarter**
Year 1	QA/QC plan Survey-shooting ranges	Survey of shooting ranges and golf courses	Sample collection Sample analysis	Sample collection & analysis Annual report
Year 2	Sample collection Sample analysis	Sample collection Sample analysis	Leachability test Fractionation test	Leachability/fractionation test Annual report
Year 3	Fractionation test Mineralogical analysis	Mineralogical analysis Bioavailability test	Mineralogical analysis Bioavailability test	Bioavailability test Annual report

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Professional Interests

Land application of non-hazardous wastes.
Chemical remediation and phytoremediation of trace metal contaminated water, soils, and wastes;
Biogeochemistry and speciation of trace metals in water-soil-waste system;

Education

Ph.D./ M.S.	05-1991/12-1988.	Colorado State University. Soil/Environmental Chemistry.
B.S.	07-1985.	Shenyang Agricultural University, China. Soil Chemistry.

Professional Experience

Associate Professor, Soil and Water Science, University of Florida (7/99-present)
Assistant Professor, Soil and Water Science, University of Florida (1/94-6/99)
Senior Research Associate, School of Natural Resources, Ohio State University (1/91-12/93)
Graduate Research Assistant, Soil and Crop Science, Colorado State University, (8/86-12/90)

Grants (last five years)

Ma, **L.Q.,** W. Harris, A. Hornsby and K. Pothier Background concentrations of arsenic in Florida urban soils Florida Power & Light Company 1/2000-12/2002 $180,000

Ma, **L.Q.,** W. Harris, and P. Nkedi-Kizza. Field demonstration of metal immobilization in contaminated soils using P amendments. Florida Institute of Phosphate Research. $230,447. 4/1998-3/2001.

Rockwood, D. and **L.Q. Ma**. Phytoremediation of metal contaminated soils using woody biomass. Florida Department of Environmental Protection. $200,000 11/1997-10/2000.

Ma, **L.Q.** Sewage sludge compost as a soil amendment in tropic soils. USDA/CBAG. $91,238. 7/1/96-6/30/99.

Ma, **L.Q.,** W. Harris, and A. Hornsby. Background concentrations of trace metals in Florida surface soils. Florida Center Solid Hazardous Waste Management. $136,041. 3/96-2/99.

Ma, **L.Q.** Effects of soil amendments on leachate chemistry of forest soil. USDA. $108,583. 9/95-8/98.

Ma, **L.Q.** and N. Comerford. Changes in soil and water chemistry after high-volume wood ash application on a dry sandy soil. Georgia-Pacific Corporation. $93,000. 8/95-7/98.

Publications-Peer reviewed (last five years)

Chen, M., **L.Q. Ma**, and W.G. Harris. 1999. Baseline concentrations of 15 trace elements in Florida surface soils. J. Environ. Qual. 28:1173-1181.

Chirenje, T. and **L.Q. Ma**. 1999. Effects of acidification on metal mobility in a papermill-ash amended soil. J. Environ. Qual. 28:760-766.

Ma, L.Q. and G.N. Rao. 1999. Aqueous Pb reduction in Pb-contaminated soils by Florida phosphate rocks. Water Soil Air Pollution. 110:1-16.

Xiao, C., **L.Q. Ma**, and T. Sarigumba. 1999. Effects of soil on trace metal leachability from papermill ashes and sludge. J. Environ. Qual. 28:321-333.

Chen, M. and **L.Q. Ma**. 1998. Comparison of four EPA digestion methods for trace metals using certified and Florida soils. J. Environ. Qual. 27:1294-1300.

Ma, L.Q. and G.N. Rao. 1997. Chemical speciation of trace metals in contaminated soils. J. Environ. Qual. 26:259-264.

Ma, L.Q, F. Tan and W.G. Harris. 1997. Concentrations and distributions of 11 elements in Florida soils. J. Environ. Qual. 26:769-775.

Ma, L.Q. and G.N. Rao. 1997. The effect of phosphate rock on Pb distribution in contaminated soils. J. Environ. Qual. 26**:** 788-794.

Ma, L.Q., A.L.Choate, and G.N. Rao. 1997. Effects of incubation and phosphate rock on Pb extractability and speciation in contaminated soils. . J. Environ. Qual. 26: 801-807.

Ma, L.Q. 1996. Factors influencing the effectiveness and stability of aqueous Pb immobilization by hydroxyapatite. J. Environ. Qual. 25:1420-1429.

Ma, L.Q. and W.L. Lindsay. 1995. Estimation of Cd and Ni activities in contaminated and uncontaminated soils by chelation. Geoderma**.** 68:123-133.

Ma, L.Q., T.J. Logan, and S.J. Traina. 1995. Lead immobilization from aqueous solutions and contaminated soils using phosphate rocks. Environ. Sci. Technol . 29:1118-1126.