Distribution and availability of metal contaminants in shooting range soils around Australia

Peter Sanderson[A,B,D], Nanthi Bolan [A,B], Mark Bowman[C] and Ravi Naidu[A,B]

[A]Centre for Environmental Risk Assessment and Remediation and CRC CARE, University of South Australia, Mawson Lakes, SA.
[B]CRC CARE, University of South Australia, Mawson Lakes, SA.
[C]Directorate of Environmental Impact Management, Department of Defence, Canberra ACT 2600.
[D]Corresponding Author Email: peter.sanderson@postgrads.unisa.edu.au

Abstract
The Department of Defence operates shooting ranges across Australia to train soldiers in marksmanship and maintain their capabilities. It has been recognised that this practice can lead to significant contamination of the environment. Shooting ranges are characterised by high loading of bullets, which releases lead (Pb), antimony (Sb), and arsenic (As), copper (Cu), nickel (Ni) and zinc (Zn) and into the soil. Spent ammunition is subject to weathering in the soil; therefore intact bullets represent a significant source for Pb release. Lead concentrations exceeding 10,000 mg Pb/kg soil are commonly reported at shooting ranges around the world. The concentration of Pb including intact bullets may be upward of 500,000 mg/kg.
Soil samples collected from the surface and subsurface of Defence shooting ranges around Australia have been analysed to characterise the distribution and bioavailability of metal contaminants. The highest concentration of soil Pb found in sieved surface samples was up to 81,000 mg/kg in stop butt. The range floors contained as little as 22 mg/kg. Concentrations in the subsurface were up to 21,000 mg/kg. Comprehensive characterisation and analysis of shooting range soils will serve as a basis for the management and remediation of contamination.

Key Words
Shooting range, lead, antimony, bioavailability, risk assessment.

Introduction
To defend Australian national interests Defence requires shooting ranges to train and maintain the capabilities of soldiers in marksmanship. It has been recognised that this practice can result in significant contamination of the local environment. Therefore, to continue the necessary operation of these ranges and ongoing use of the land requires a response to the issue of contamination. Lead poses a serious threat to human and ecosystem health, due to potential exposure and uptake of Pb, which remains near the surface of the soil (Ryan *et al.* 2004). It is toxic to humans having deleterious effects on organ systems, particularly the central nervous system, the kidneys and the blood (Tong *et al.* 2000). It is readily absorbed by and accumulated by plant roots, though translocation to shoots is relatively poor. Pb contamination has been reported to decreases microbial biomass and respiration and the biomass of enchytraeid worms (Rantalainen *et al.* 2006). Secondary contamination of fauna may also occur by consumption of contaminated plant material, soil organisms and other contaminated prey.

Contamination of Shooting Range soils
Lead contamination at shooting ranges has been under increased scrutiny in recent years, due to concern over the high intensity of Pb loading, which may become mobile through the weathering of spent bullets. In many countries Pb-based ammunition is a significant source of Pb pollution. Annual deposition by hunting and shooting is around 500 tons in Switzerland (Scheinost *et al.* 2006), 800 tons annually in Denmark (Jorgensen and Willems 1987) and up to 60,000 tons per year in the United States (Craig *et al.* 1999).
Spent ammunition is subject to weathering when it comes into contact with the soil or water. Metals may be oxidized to a number of secondary forms such as oxides and carbonates, which are soluble and serve as a source that can release labile metals into the soil. Though much of the research on shooting range contamination has focused solely on Pb, the other components of bullets Sb (a hardening agent), As (an impurity in the Pb), Cu (casing of the bullet), Ni and Zn (alloys with copper) in addition to Pb have been identified as contaminants of concern at shooting ranges (Peddicord and LaKind 2000). Although these metals are only present in small amounts in Pb-based bullets they can also accumulate at elevated levels in the soils (Table 1).

Studies on the distribution of contaminants in shooting ranges have focused on the characterization of the contamination and the effect of weathering processes, primarily with respect to Pb (Cao *et al.* 2003, Hardison *et al.* 2004, Duggan and Dhawan 2007). More recently studies have examined the distribution and weathering of Sb (Johnson *et al.* 2005, Scheinost *et al.* 2006). Hydrocerussite [$(Pb(CO_3)_2(OH)_2$] is the predominant weathering product of Pb in many of the ranges examined (Cao *et al.* 2003 and Duggan and Dhawan 2007). Other common minerals include cerussite [$(PbCO_3)$], massicot [(PbO)], and litharge [(PbO)] (Cao *et al.* 2003; Dermatas *et al.* 2006). In the presence of high P, Pb solubility may be controlled by the less soluble Pb phosphate (Cao *et al.* 2003).

Table 1. The highest levels of metals reported in Shooting Range Studies.

Pb	Sb	As	Cu	Ni	Zn	
80935	4022		552	37.5	79.8	Knechtenhofer *et al.* 2003
515800	17500		4450	770		Johnson *et al.* 2005
397840	845	1057	318			Dermatas *et al.* 2006
167760	437		817			Spuller *et al.* 2007
156000	8230		6200	1490		Robinson *et al.* 2008

Risk based management and Remediation

The need to manage the environment in a sustainable way in order to carry out operations now and into the future has been recognised by the Department of Defence, which operates shooting ranges at army bases around the country to train soldiers in marksmanship. This study determined the distribution and bioavailability of contaminants at Defence shooting ranges across Australia as it relates to differing soil types and soil proprieties to aid the implementation of best management practices at these sites. Remediation by in situ chemical stabilisation of metal contaminants was to be examined at these sites.

Methods

Soil samples were collected from several defence shooting range sites around Australia. Samples were taken at a depth of 0-10 cm, along a transect from the firing line (1.5, 31.5, 61.5 and 91.5m). A soil profile sample was taken just before the backstop berm to 100 cm depth using a soil core. Samples were also collected from the top, middle and bottom of the berm at the 25 cm depth and combined into a composite sample. A final sample was collected from 5 m behind the backstop berm. Samples were weighed and dried for 24 hours, and re-weighed to determine moisture content. Soils were classified using the Australian Soil Classification key. The soil physical and chemical properties (pH, EC Eh (redox potential) CEC, OC, DOC, Total P, metal content) were determined by standard methods. Soil pH and EC were measured in a 5:1 deionised (DI) water suspension and a 5 mmol/L $CaCl_2$ suspension, using as Orion pH/EC meter. CEC was determined by the USEPA 9080 ammonium method. The Walkey Black (1934) procedure was used to measure organic carbon and DOC was measured using the Zhou (2001) method and a total organic carbon analyser. The metal content was examined by microwave assisted acid digestion using the USEPA SW-846 Method 3051A. The digests were analysed by ICPMS according to SW-846 Standard Method 6010. Sequential Extraction (SE) by Tessier (1979) was used to determine contaminant distribution among the soil fractions. XRD was used to examine contaminant mineralogy.

Results

The distribution of metal contaminants at shooting ranges is predominantly associated with spent bullets in the impact berm. Soil properties play a large role in determining distribution of metal contaminants in shooting range soils in Australia. Concentrations of Pb may be as low as 22 mg/kg on the range floor and up to 81,000 mg/kg in the impact berm. Significant contamination of subsurface soil may also be found in more acidic soils, with concentrations of up to 21,000 mg/kg reported. Concentrations of TCLP leachable Pb were found to be as high as 300 mg/l. The highest reported concentrations of the other metallic elements were Sb 600, As 50, Cu 350, Ni 260, and Zn 100 mg/kg, which were associated with the highest densities of bullets.

Conclusions

This study indicates that concentrations of Pb were elevated in surface soils at defence shooting ranges, particularly at the impact berm. The speciation and distribution of metal contaminants in range soils reflect the soil properties which influence the weathering of spent bullets.

References

Cao X, Ma LQ, Chen M, Hardison DW, Harris WG (2003) Lead transformation and distribution in the soils of shooting ranges in Florida, USA. *The Science of The Total Environment* **307**, 179-189.

Craig JR, Rimstidt JD, Bonnaffon CA, Collins TK, Scanlon PF (1999) Surface Water Transport of Lead at a Shooting Range. *Bulletin of Environmental Contamination and Toxicology* **63**, 312-319.

Duggan J, Dhawan A (2007) Speciation and Vertical Distribution of Lead and Lead Shot in Soil at a Recreational Firing Range. *Soil & Sediment Contamination* **16**, 351-369.

Dermatas D, Cao X, Tsaneva V, Shen G, Grubb D (2006) Fate and behavior of metal(loid) contaminants in an organic matter-rich shooting range soil: Implications for remediation. *Water, Air, & Soil Pollution: Focus* **6**, 143-155.

Hardison DW, Ma LQ, Luongo T, Harris WG (2004) Lead contamination in shooting range soils from abrasion of lead bullets and subsequent weathering. *Science of The Total Environment* **328**, 175-183.

Johnson CA, Moench H, Wersin P, Kugler P, Wenger C (2005) Solubility of Antimony and Other Elements in Samples Taken from Shooting Ranges. *J Environ Qual* **34**, 248-254.

Jorgensen SS, Willems. M (1987) The fate of lead in soils: The transformation of lead pellets in shooting range soils. *Ambio* **16**, 11-15.

Knechtenhofer LA, Xifra IO, Scheinost AC, Fluhler H, Kretzschmar R (2003) Fate of heavy metals in a strongly acidic shooting-range soil: Small-scale metal distribution and its relation to preferential water flow. *Journal of Plant Nutrition and Soil Science* **166**, 84-92.

Peddicord RK, LaKind JS (2000) Ecological and human health risks at an outdoor firing range. *Environmental Toxicology and Chemistry* **19**, 2602-2613.

Rantalainen M-L, Torkkeli M, Strömmer R, Setälä H (2006) Lead contamination of an old shooting range affecting the local ecosystem -- A case study with a holistic approach. *Science of The Total Environment* **369**, 99-108.

Robinson BH, Bischofberger S, Stoll A, Schroer D, Furrer G, Roulier S, Gruenwald A, Attinger W, Schulin R (2008) Plant uptake of trace elements on a Swiss military shooting range: Uptake pathways and land management implications. *Environmental Pollution* **153**, 668-676.

Ryan JA, Scheckel KG*, et al.* (2004) Peer Reviewed: Reducing Children's Risk from Lead in Soil. *Environmental Science & Technology* **38**, 18A-24A.

Scheinost AC, Rossberg A, Vantelon D, Xifra I, Kretzschmar R, Leuz A-K, Funke H, Johnson CA (2006) Quantitative antimony speciation in shooting-range soils by EXAFS spectroscopy. *Geochimica et Cosmochimica Acta* **70**, 3299-3312.

Spuller C, Weigand H, Marb C (2007) Trace metal stabilisation in a shooting range soil: Mobility and phytotoxicity. *Journal of Hazardous Materials Stabilisation/Solidification Treatment and Remediation: Advances in S/S for Waste and Contaminated Land* **141**, 378-387.

Tessier A, Campbell PGC, Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry* **51**, 844-851.

Tong S, Von Schirnding YE, Prapamontol T (2000) Environmental lead exposure: A public health problem of global dimensions. *Bulletin of the World Health Organization* **78**, 1068-1077.

Walkley A, black IA (1934) An Examination of the Degtjareff Method for Determining Soil Organic Matter, and A Proposed Modification of the Chromic Acid Titration Method. *Soil Science* **37**, 29-38.

Zhou LX, Wong JWC (2001) Effect of dissolved organic matter from sludge and sludge compost on soil copper sorption. *Journal of Environmental Quality* **30**, 878-883.