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# Ecotoxicity of chemically stabilised metal(loid)s in shooting range soils

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ABSTRACT

Five chemical amendments (soft rock phosphate, lime, commercial phosphate amendment, red mud and magnesium oxide) were applied across four different shooting range soils to chemically stabilise metal (loid)s in the soils. Soils were contaminated with Pb between 2330 and 12,167 mg/kg, Sb from 7.4 to 325 mg/kg and soil pH ranged from 5.43 to 9.29. Amendments were tested for their ability to reduce the bioavailability of Pb, Sb, Zn, Ni, Cu and As in the soils to soil organisms after one year of aging, by measuring a series of ecotoxicological endpoints for earthworms and plants and soil microbial activity.

Growth-based endpoints for earthworms and plants were not significantly affected by amendment addition, except in the most contaminated soil. Per cent survival and weight-loss reduction of earthworms was enhanced by amendment addition in only the most contaminated soil. Plant biomass and root elongation was not significantly affected by amendment addition ($p= < 0.05$). Red mud and magnesium oxide appeared toxic to plants and earthworms, probably due to highly alkaline pH (9–12).

Lead in soil organisms was relatively low despite the high concentrations of Pb in the soils, suggesting low bioavailability of Pb. Uptake of Pb by earthworms was reduced by between 40 and 96 per cent by amendments, but not across all soils. Amendments reduced Sb in earthworms in Townsville soil by up to 92 per cent.

For lettuce the average uptake of Pb was reduced by 40 to 70 per cent with amendment addition in Townsville, Darwin and Perth soil. The effect of amendments on the uptake of Sb, Zn, Ni, Cu and As was variable between soils and amendments. Microbial activity was increased by greater than 50 per cent with amendments addition, with soft rock phosphate and lime being the most effective in Murray Bridge and TV soils and commercial phosphate and MgO being the most effective in Darwin and Perth soils.



## 1. Introduction

Contamination of the environment by heavy metals has occurred over many years through anthropogenic activity including smelters, fuels, mining and various industrial processes (Barzi et al., 1996). Dispersion of toxic metal(loid)s in the environment increases the likelihood of human or animal exposure to contaminants and potential adverse health effects.

Shooting ranges represent a source of heavy metal(loid)s contamination. Shooting range activity deposits considerable amounts of Pb-based bullets into shooting range soils, with the deposited bullet subject to weathering over time (Hardison et al., 2004; Sanderson et al., 2012a), mobilisation of metal(loid)s from bullets in the soil profile (Duggan and Dhawan, 2007) transport of contaminants to receiving waters (Craig et al., 1999; Wersin et al., 2002). Shooting ranges may also contain elevated concentrations of other metal(loid)s such as Sb, Cu, Zn, Ni and As, which are minor components of bullets (Sanderson et al., 2012b).

Soil organisms are directly exposed to soil and heavy metal pollution can detrimentally affect plant growth and the diversity and activity of soil organisms (Vig et al., 2003; Naidu et al., 2001), some of which are key to soil fertility (Giller et al., 1998). Other soil processes such as carbon sequestration by stabilization of soil organic carbon may also be affected (Jastrow et al., 2007), which has implications for climate change. Elevated Pb concentration in shooting range soils and bioconcentration by the surrounding biota has been reported (Hui, 2002; Labare et al., 2004; Lewis et al., 2001; Migliorini et al., 2004).

Ecological impacts of the contamination will vary from site to site due to abiotic factors such as soil characteristics, contaminant speciation and biotic uptake factors (Labare et al., 2004). This necessitates risk assessment and management of these sites to ensure contamination is not adversely affecting the environment. Risk assessment of shooting ranges has been undertaken in a number of studies (Bennett et al., 2007; Peddicord and LaKind, 2000) using selected representative species to examine the effects of Pb and co-contaminants such as Sb. Considerable work has

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focused on the ecotoxicological effects of heavy metal pollution by examination of quantifiable biophysical characteristics, which are sensitive to disturbance due to toxicity and related to health of the organism. More recent studies have examined the effect of remediation on these ecological endpoints (Ahmad et al., 2012; Chang et al., 1997). Ecotoxicological endpoint measurements are a more relevant indicator of treatment success than the commonly used chemical methods, which are difficult to relate to effect on biological systems (McGrath, 1999).

There has been a move toward risk based management of contaminated sites in place of total contaminant level as a decision criterion (Khadam and Kaluarachchi, 2003; Naidu et al., 2008; NEPM, 2013). Risk is not directly related to total metal concentrations, but the fraction of the metal that may be available for uptake by a receptor organism, i.e. the bioavailable fraction (Naidu et al., 2008). Risk may be managed by reducing the contaminant bioavailable fraction of the soil (Harmsen and Naidu, 2013).

Chemical stabilisation is one such method of reducing the bioavailable fraction of contaminants in the soil through immobilisation by the addition of amendments to promote reactions such as sorption and precipitation within the soil matrix. Chemical stabilisation of Pb, predominantly by phosphorus has been widely investigated (Berti and Cunningham, 1997; Ma et al., 1993; Park et al., 2012; Ruby et al., 2002) including implementation as a best management practice (BMP) (US Environmental Protection Agency (USEPA), 2001). Amending shooting range soils with phosphorus may not achieve the desired result due to a number of factors. The reaction of phosphate with Pb to form pyromorphite may be kinetically inhibited due to pH (Laperche et al., 1996), the presence of organic matter (Lang and Kaupenjohann, 2003), competing ions (Ma et al., 1994a, 1994b) and solubility of the P source (Chrysochoou et al., 2007). Alternative treatments may be more suitable where soil properties are unfavourable to pyromorphite formation or where phosphate (Dermatas et al., 2008) or Sb leaching (Kilgour et al., 2008) may be of concern. Other potential soil amendments for stabilisation of Pb and other metal (loid)s identified in the literature include: Lime (Cao et al., 2008), Red Mud (Lombi et al., 2002; Liu et al., 2011), and MgO (Illera et al., 2004). Sanderson et al. (2012a) reviews chemical stabilisation applied to shooting range soil comprehensively.

In a previous study the change in metal concentrations in porewater, under the toxicity characteristic leaching procedure (TCLP) and under the physiologically based extraction test (PBET) for chemically stabilised shooting range was monitored over a 12 month period (Sanderson et al., 2013). The amendments varied in their effectiveness, but demonstrated the ability to reduce leaching and/or bioaccessible Pb and Sb in shooting range soils by amendment addition. Critical parameters used to assess the effectiveness of soil amendments also include reduction of ecotoxicological effects of contaminants and reduction of risks to human health. Therefore, in this study we investigate the effectiveness of a series of commonly used amendments for reducing the ecotoxicity of contaminants. To this end ecotoxicological end points were selected to represent a range of ecological receptors including plants, earthworms and microbial organisms.

## 2. Methods

### 2.1. Soil physicochemistry

Soil samples were collected from the surface (0–10 cm) of the stop butt of four shooting ranges around Australia. The shooting ranges were located in Murray Bridge (MB), Townsville (TV), Darwin (DA) and Perth (PE). Soils were sieved to $<2$ mm to remove large bullet fragments, but smaller bullet fragments clearing the sieve comprise part of each soil sample. Soil properties were determined by standard methods presented in Sanderson et al. (2012b). In brief, the analyses included soil pH (1:5 water suspension), cation exchange capacity (CEC) (USEPA 1986; method 9081), organic matter (wet oxidation), dissolved organic carbon (DOC) (extraction), free iron oxide content (oxalate extraction), soil texture (hydrometer method) and total metals (aqua regia digest following USEPA 3051a).

The four shooting ranges are predominantly sandy soils. They differ in soil physicochemistry and extent of contamination. Key differences are pH, DOC, CEC, FeOx content, texture and degree of contamination (Sanderson et al., 2013). The MB soil is an alkaline, highly contaminated soil; TV soil is circum-neutral with moderate contamination; DA and PE soils are both acidic with lower levels of contamination. The range of soil pH was Metal(loid) content ranged from 233 mg/kg Pb in PE soil to 12,000 mg/kg for Pb and between 7 and 325 mg/kg for Sb. Copper and Zinc, were also present at elevated concentrations, upto 3555 and 735 mg/kg, respectively. The concentrations of Ni and As were relatively low. Soil organic matter was highest in TV soil, but less than 1 per cent in all four soils. Detailed soil physicochemical analysis is in Sanderson et al. (2012b, 2013).

The regional climate of the sites also plays an important role differentiating the sites, with MB and PE from temperate/semi arid climate and TV and DA from tropical climates. This has implications for weathering rates of Pb, Pb secondary minerals present in the soils and the potential for transport of Pb in the soil profile (Sanderson et al., 2012b).

A series of amendments were selected to represent different immobilisation mechanisms (pH-induced adsorption, P-induced precipitation, sorption to oxides): soft rock phosphate (SRP), lime, commercial phosphate amendment (CP), red mud (RM) and magnesium Oxide (MgO). Amendments were applied to 300 g of soil in ziplock bags and mixed thoroughly. The soil was then brought up to 60 per cent moisture holding capacity by the addition of Milli-Q water and incubated in a glass house for 12 months, where soils were routinely mixed and moisture level maintained. The amendment rates were five times stoichiometric P:Pb ratio for SRP, 5 per cent soil weight for lime, 10 per cent CP, 2 per cent RM and 2 per cent MgO. Each treatment had three replicates.

During the incubation period 6 g sub samples were collected (at 1, 3, 6, 9 and 12 months) from each replicate for analysis by TCLP and PBET and pore-water metals were monitored using rhizon samplers. This data is presented in Sanderson et al. (2013). It was noted that metal content rebounded after around 3 months in the treated soils and so amendments were reapplied to the soil after 6 months at the same as the initial rate. The total amendment rate was ten times stoichiometric P:Pb ratio for SRP, 10 per cent for lime, 10 per cent CP, 4 per cent RM and 4 per cent MgO. Monitoring of the soil continued through to 12 months.

At this time the soils were transferred to plastic polypropylene pots for ecotoxicity testing. Each pot contained approximately 270 g of soil. Each replicate was transferred to a separate pot.

Exchangeable metal(loid)s were also determined by $MgCl_2$ extraction using 1 g soil and 8 ml of 1 M $MgCl_2$ solution, placed in an end over end shaker for 1 h.

### 2.2. Ecotoxicological study

#### 2.2.1. Earthworms

An earthworm survival assay based on US Environmental Protection Agency (USEPA) (1989) was conducted to examine the toxicity of the soils to earthworms (*Eisenia fetida*). Earthworms with clitellum were depurated on moist filter paper overnight and weighed before being added to each pot for a period of 14 days. Ten earthworms were added to each pot. The soils were moist and incubated at 20 degrees under light so the earthworms remain in the soil. Lids were used to cover the soils to prevent escape, with small pinholes placed in the lid to allow air in. Mortality and avoidance behaviour was monitored over this period and soil moisture maintained. After 14 days the surviving worms were removed and rinsed with Milli-Q water before being depurated overnight on moist filter paper, after which the worms were rinsed again and change in weight was recorded. The worms were then euthanized by placing them in the freezer and accumulation of metal(loid)s was determined by digestion of worms on a block digest with nitric acid.

#### 2.2.2. Plant growth

Lettuce (*Latuca sativa*) was sown into the same pots subsequent to earthworm testing. A seaweed based (N and P free) fertilizer was applied to the soil every 2 weeks of the growing period. Plants were grown in a glass house for 8 weeks and were watered every few days to maintain moisture in the pots. Plants were removed from the soil after 8 weeks and root elongation was measured, then the shoots were separated from the roots. Both shoots and roots were rinsed with Milli-Q water and then dried at 60 °C in an oven. Shoot biomass was measured after drying in the oven. Accumulation of metal(loid)s in plants was determined by digestion of dry plant material with nitric acid on a block digest.

Metal content of the digestion and extraction solutions was measured by ICP OES (Perkin-Elmer Optima 5300 DV). Quality control samples including blanks, spikes and duplicates were included in the analysis.

#### 2.2.3. Microbes

The microbial endpoint selected for measurement was $CO_2$ respiration, an indicator of microbial activity (Carballas et al., 1979). Respiration was measured by taking moist soil (at least 50 g dry weight) and placing in 500 ml airtight jars with a