Current Pollution Reports (2018) 4:175–187
https://doi.org/10.1007/s40726-018-0089-5

LAND POLLUTION (GM HETTIARACHCHI, SECTION EDITOR)

Contamination, Fate and Management of Metals in Shooting Range Soils—a Review

Peter Sanderson[1] · **Fangjie Qi**[1] · **Balaji Seshadri**[1] · **Ayanka Wijayawardena**[1] · **Ravi Naidu**[1]

Abstract

Pollution of shooting range soils by lead from bullets represents a widespread and potentially significant concern for impact on the environment. High concentrations of lead in particular are reported in bullet impact berms and shot fall zones. The other components of bullets used in shooting including antimony, copper and zinc may also be present at elevated concentrations. Antimony is a concern due to its mobility in the environment. It has been recognised that the status of contamination is important for the risk presented by shooting ranges. Lead bullets are subject to weathering in the soil, forming secondary minerals, which may be solubilised and may release lead and co-contaminants into the soil. The mobility and availability of contaminants in the soil affect their potential for spreading in the environment and for uptake and toxicity in organisms. Soil physicochemical properties affect bullet weathering and availability of contaminants in the soil. A number of strategies have been researched for management of shooting range pollution such as chemical stabilisation, phytoremediation and soil washing. This review considers the current state of knowledge and research of contamination and management of shooting ranges from recent literature (2014–2017) reflecting on new knowledge and novel management strategies for shooting range soil management. Ultimately, management of pollution in shooting range soils should seek to remove bullets from soil, reduce the weathering of bullets and reduce the mobility and bioavailability of contaminants. Adopted management practices should be based an understanding of site-specific condition, to achieve the most optimal outcome.

Keywords Lead · Antimony · Shooting ranges · Chemical stabilisation

Introduction

Shooting ranges have long been recognised as a potential source for environmental contamination due to the large accumulation of lead (Pb) in soil as a result of shooting activities. There are many thousands of shooting ranges operated around the world for recreational activity and military training. Concentrations of Pb in shooting range soil have been reported ranging from 10,000 to 70,000 mg/kg, with 10 to 80% of Pb extractable by toxicity characteristic leaching procedure (TCLP) [18]. Numerous research investigations have been undertaken in recognition of the potential significance of the impact on the surrounding environment. The focus of these investigations has been on Pb, which is the primary contaminant, and characterisation of the extent of contamination (distribution and mobility) [14, 68, 69, 75]. Lead in shooting ranges may be phytotoxic and may pose risk to soil and terrestrial biota and human health [18, 59, 79, 80].

More recently, co-contaminants of Pb in shooting ranges, including antimony (Sb), copper (Cu), zinc (Zn) and nickel (Ni), have also been investigated [26, 34, 64]. Antimony is a hardening agent comprising 1–2% of a bullet core. This element is of particular interest due to its anionic nature and relative mobility in the environment compared to Pb. The extent of contamination varies with shooting range type and use and soil properties are an important factor for the fate of Pb and co-contaminants in the soil [44, 49, 68, 69].

Current Management Practice

Management of shooting ranges continues to draw on guidance documents, particularly 'Best management practices for lead outdoor shooting ranges' [87]. This framework covers an

This article is part of the Topical Collection on *Land Pollution*

✉ Peter Sanderson
peter.sanderson@newcastle.edu.au

[1] Global Centre for Environmental Remediation, University of Newcastle and CRC for Contamination Assessment and Remediation of the Environment (CRCCARE), Newcastle, Australia

integrated approach of four management areas: control and containment of bullets, prevention of migration of contaminants, removal and recycling of bullets, and documentation and evaluation of environmental management plans. Control and containment methods are based on range operation and configuration and include bullet curtains and traps which aim to contain bullets and reduce loading in the soil.

Research has examined a number of the suggested management approaches including bullet removal and methods for prevention of migration including change soil for sand berm, addition of lime or phosphate and vegetation to reduce erosion. A recent review by Fayiga and Saha [18] provides an overview of contamination of shooting range soils and reviews best management practices.

Bullet fragmentation has been demonstrated from bullet on bullet impact with a significant shift in size fraction of Pb, Sb and Cu, with greater portion in < 1-mm and < 250-μm size fractions [47]. Yin et al. [95] investigated the effect of a sand berm, liming and bullet removal. Sand berm and liming reduced Pb concentrations significantly due to lower moisture levels, organic content and higher pH. However, bullet removal transferred significant Pb to the soil by abrasive action. Liu et al. [39] confirmed the effectiveness of a sand berm due to reduced moisture and organic matter, but noted bullet removal was effective in trap/skeet ranges as pellets may be less subjected to fragmentation. According to [19], bullet removal and vegetation may be effective for reducing bioavailable and leachate Pb. It has been noted that consideration should also be given to Sb if elevated levels are present, which may be mobilised by the addition of lime [15].

Reviews with a particular focus on chemical stabilisation for managing shooting range soils have been previously published [5, 68, 69]. Chemical stabilisation is discussed in detail under the section on management of shooting range contamination.

Shooting ranges remain a significant environmental issue and continue to be investigated to better understand the following: the extent and severity of contamination, contaminant mobility and fate under a wide range of environmental conditions and means of effectively managing contamination. This review examines the current research on shooting range contamination and management and reflects on the expansion of knowledge in the area. Journal articles considered for the review were published between 2014 and 2017 and based on database searches (Google Scholar, Scopus) of search terms: Pb shooting range, antimony shooting range, shooting range contamination, shooting range management and shooting range immobilisation. Articles that were focused on outdoor shooting range pollution and management were selected for inclusion in this review.

The review covers contamination and fate, bioavailability and mobility, ecotoxicity and management practices with a focus on novel aspects of shooting range contamination characterisation and management. Management practices including chemical stabilisation, soil washing, phytoremediation and other utilised strategies are considered. The contribution of recent studies will be reflected on in light of current guidance and best practice and recommendations made for shooting range management.

Contamination and Fate

The extent of contamination and fate of contaminants continues to be investigated at shooting ranges. Co-contaminants of Pb have been a greater focus of recent research. A summary of shooting range characterisation is given in Table 1. For pistol and rifle ranges, the highest contaminant concentrations are reported in the berm or stop butt. However, Pb may also be elevated at the firing and target lines as a result of shooting activities [76]. For target ranges, the fallout zone contains the highest concentrations of Pb [60]. The total concentrations of co-contaminants such as Sb, Cu, Zn and Ni are typically orders of magnitude lower, but may be higher in soluble concentration than Pb [55]. Elevated levels of mercury (above the 500 μg kg^{-1} guideline value) have been reported in some samples collected from shooting ranges in Switzerland, attributed to past use as primers [81].

A recent study by Sehube et al. [76] investigated Pb contamination at eight military shooting ranges in South Africa, which had been in operation for more than 20 years. These ranges were characterised by high contaminant loads in the berm soil (2000–38,386 mg/kg Pb). The pistol range contained the lowest concentration of total Pb. The synthetic precipitation leaching procedure leachable Pb was high in six out of eight ranges, with the highest reported 798 mg/kg.

Shooting range contamination represents potentially high contaminant loads, but it is increasingly understood that the nature/status of the contamination is an important factor. Lead in the soil of shooting ranges is deposited as bullets or pellets that also fragment on impact producing small metallic fragments. These fragments are subject to weathering and oxidation to produce secondary minerals, which may be subject to dissolution in the soil depending on soil physicochemistry.

A three-step weathering mechanism of metallic Pb including oxidation, carbonation and dissolution was proposed by Ma et al. [42]. Weathering is driven by soil moisture, temperature, pH and organic content [37, 67, 76]. Low soil pH, organic matter and soil moisture promote weathering in the soil [42, 49].

Li et al. [37] investigated bullet corrosion in three different shooting ranges in different climatic zones in China reporting different secondary minerals present due to climate conditions and pH. Cerussite ($PbCO_3$) was the predominant mineral on the weathering crust on bullets. In humid and semi-arid

Table 1 Recent research characterising contamination of shooting range soils

Investigation	Methods	Result	Reference
Assessment of Cu, Cr, Ni, Pb and Zn	Total metals, available metals, pollution index	Pb 6309, Zn 264, Cu 98, Cr 79 and Ni 33 mg/kg CaCl2 extractable: 57.4% Pb, 32.8% Cu, 26.3% Zn, 4.5% Ni and 0.12% Cr.	[64]
Assessment of Pb, Cu, Zn and Sb in small arms located on mires	Total metals and SE	Acidic mire: Pb 13 g/kg, Cu 5.2 g/kg, Zn 1.1 g/kg and Sb 0.83 g/kg Discharge water: Pb 0.18, Cu 0.42, Zn 0.63 and Sb 65 μg/L	[44]
Small arm range on peatland	Total metals, extractable metals, DGT	Soil: Pb 1400 mg/kg, Cu 843 mg/kg and Sb 110 mg/kg Stream water: Pb 6.9 μg/L, Cu 24.0 μg/L and Sb 7.4 μg/L	[55]
Assessment of Pb, Cu, Sb and Cd in two military shooting ranges	Total metals, SE, TCLP	Pb 3900–18,600 mg/kg, Cu 318–562 mg/kg, Zn 104–123 mg/kg, Sb 26–108 mg/kg and Cd 7.45–8.11 mg/kg	[26]
Contamination assessment of Pb and Cu	Total metals, SE and pollution index	Pb 414–2763 mg/kg and Cu 104–307 mg/kg 27 to 72% residual Pb	[38]
Military shooting ranges	Total Pb, SPLP, SE, XRD	2000–38,386 mg/kg Pb in berms Pb carbonate: 46–68% OM: 2–47% fractions	[76]
Mapping Pb at wetland trap shooting range	Total metals, XRF	26,700 mg/kg Pb and shot densities of > 50,000 pellets/m^2 in shot fallout zone	[60]
Soil acidification at a biodegradable trap and skeet range	Chemical analysis, XRD	Positive correlation between target cover and SO_4^{2-} and negative correlation of pH with SO_4^{2-}	[50]
Bullet fragmentation in different soil types	Total metals, particle size fractionation, XRD	Significant change in lead bullet fragmentation from firing in for loess, sandy clay and sandy soils	[47]
Bullet weathering	EMPA, SEM, XRD	Soil conditions affected mineralogy: cerussite, hydrocerussite, shannonite	[37]
Weathering of metallic Pb bullets used in dove hunting area	Concentrations, XRD	Average Pb: 80 ppm. Minerals: hydrocerussite, litharge and hydroxypyromorphite	[67]

environments, hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) was reported as the primary secondary mineral. In acidic soils, no secondary minerals were reported. In arid environments, thermal decomposition caused shannonite ($Pb_2O(CO_3)$) to form. Rubio et al. [67] reported the presence of hydrocerussite, litharge (PbO-tetragonal) and hydroxypyromorphite ($Pb_5(PO_4)_3(OH)$) on weathered bullets. These findings are in line with previous research on weathering of Pb bullets in the soil [14, 89].

The state of mineralisation of Pb in the soil is an important factor and the physicochemical conditions of shooting range sites play an important role in the weathering and mobility of contaminants. Lead minerals in the soil may be converted to more stable forms (sulphates; phosphates) or sorbed to soil (clay, iron oxides) or in solution [68, 69]. Investigation of runoff in shooting range soil using simulated rainfall reported 40.4–65.6 μg/mL Pb and sediment enrichment ratios up to 2.5 [16].

Several recent studies have examined shooting range contaminants under different environmental conditions (Table 1). Mariussen et al. [44] investigated the contamination status of small arms shooting ranges located on minerotrophic mires. The highest mean total concentrations (Pb 13 g/kg, Cu 5.2 g/kg, Zn 1.1 g/kg and Sb 0.83 g/kg) and soluble concentrations in discharge water (0.18 mg/L Pb, 0.42 mg/L Cu, 0.63 mg/L Zn and 65 μg/L Sb) were reported for a range located on an acidic mire (Table 1). Although, in surface waters with high pH (pH ~ 7), there was a trend of high concentrations of Sb and lower relative concentrations of Cu and Pb. Johnson et al. [28] have previously reported release of Sb from shooting range soils to be higher than for other co-contaminants.

Okkenhaug et al. [55] examined Pb, Cu and Sb in a small arm range on peatland. Peatland areas are characterised by high dissolved organic carbon (DOC) and high groundwater table. The contaminant transport in the upper peat layer due to hydraulic conductivity close to the surface and the high groundwater table were the source of downstream contamination by Pb, Cu and Sb (Table 1). Pb and Cu were found to be associated with DOC, but there was no association for Sb.

Hockmann et al. [24] investigated Sb released from a shooting range soil under waterlogged and drained conditions in field lysimeters. Under drained conditions, there was a seasonal fluctuation in Sb concentrations between summer and winter (110 and 40 μg L^{-1} Sb) which correlated with fluctuations in DOC. Under anaerobic conditions from waterlogging, Sb in leachate decreased to 2–5 μg L^{-1} Sb and remained stable at this level due to reduction of Sb(III) to Sb(V).

In a trap and skeet shooting range, the use of biodegradable targets was implicated in acidification of soil [50]. Soil pH was reduced to < 3 in some locations, which was attributed to the oxidation of S in the targets to H_2SO_4. This has implications for Pb in pellets in the soil of these ranges as secondary minerals of Pb typically reported in shooting range soils are soluble at this pH range, posing risk to the surrounding environment.

These studies demonstrate that shooting range siting is an important determinant of contaminant fate. Shooting ranges subject to different environmental conditions such as those found in mires, peat and environments subject to water logging may be subject to greater contaminant mobility due to groundwater and DOC. The chemistry of redox sensitive elements such as Sb, which differs substantially in mobility in waterlogged and drained conditions, needs to be understood for effective management.

Runoff from shooting ranges is a concern, particularly where surface water may be impacted. Greater consideration should be given to potential aquatic toxicity from shooting range contamination, including for co-contaminants such as Sb and Cu.

Bioavailability and Ecotoxicity of Pb

The soluble and available fractions indicate potential for environmental risk by movement through the soil profile, surface water runoff and also bioavailability to human or ecological receptors.

Previous investigations of bioavailability and extractability of Pb in shooting ranges using chemical methods have reported Pb to be highly bioavailable, relative to other contamination sources. Smith et al. [78] reported the gastrointestinal bioaccessibility (the quantity or fraction available for adsorption in the GI tract) of 31 peri-urban soils in a simulated human gastrointestinal tract. Shooting range soil Pb had the highest bioaccessibility (> 75% in eight of nine soils) and soils contaminated by mining and smelting were on average 55% bioaccessible. Bannon et al. [11] found mean bioaccessibility using acid-extractable lead as a percent of total lead in the soil to be approaching 100%. This was suggested to be due to high concentration of Pb in the soil present as oxides and carbonates from bullet weathering.

Sequential extraction and other single extractions have been utilised in recent research of shooting range contamination to indicate the associations of metals in the soil (Table 1). Islam et al. [26] investigated associations of Pb, Sb and Cu with soil fractions by sequential extraction to indicate their potential bioavailability, reporting 42% of Pb in bioavailable (exchangeable and carbonate) and 55% potentially bioavailable fractions (Fe and Mn oxide and organic/sulphide). A majority of Cu was in potentially bioavailable fractions (up to 69%), whilst 32 and 48% were bioavailable and potentially bioavailable for Sb, respectively. A high proportion of Pb has been reported (~ 50%) in the carbonate fraction of shooting range soils [30, 76], but significant Pb has also been reported in the residual fraction [38]. Rodríguez-Seijo et al. [64] reported 57.4% Pb, 32.8% Cu, 26.3% Zn and 4.5% Ni extractable by $CaCl_2$, indicating that Pb in particular was in an available form.

Studies have also examined organism uptake (plants, earthworms, humans, birds, mammals) particularly of Pb from shooting range contaminated soils. In humans, bioavailability can be defined as the fraction of an ingested chemical dose that reaches systematic circulation [52]. For plants, it is the fraction that may be taken up from the soil (phytoavailability). Bioavailability can also refer to the fraction available to soil organisms such as earthworms.

Bannon et al. [11] found the mean relative bioavailability using swine studies to be (108 ± 18% and 95 ± 6%, respectively). The bioavailability of Pb in soil to different receptors can be influenced by the soil physiochemical properties [93]. In a swine study on Pb contaminated soils, the soil properties, pH, CEC and clay content are the most important predictors of in vivo relative bioavailability of Pb [9]. Soil pH and clay content accounted for 85% of the partition coefficient's variability. High bioavailability of shooting range soils indicate increased health risks and therefore need of strict cleanup measures to prevent human health and ecological risk from contamination [18].

The effect of shooting range contamination to ecological receptors is also dependent on bioavailability. In a study exposing *Eisenia andrei* to shooting range soils, Luo et al. [41] found high mortality and weight loss of earthworms in the two most polluted soils. Available Pb was negatively correlated with earthworm survival and reproduction and positively correlated with weight loss [41]. Similarly, Sanderson et al. [70] reported significant weight loss and mortality in earthworms exposed to the most highly contaminated shooting range soil (10,000 mg/kg Pb). Earthworm uptake in all four soils was correlated with $MgCl_2$ exchangeable metals. The bioaccumulation of Sb in plants and earthworms was relatively small compared to Pb, though in one soil, Sb accumulated in plants was around 50% of the accumulated Pb, perhaps due to the low iron oxide concentration in the soil compared to the other soils examined.

Rodríguez-Seijo et al. [66] reported relatively low bioaccumulation factors (0.06–0.26) for earthworms exposed to a moderately contaminated, slightly acidic shooting range soil. Bioaccumulation was slightly positively correlated to available Pb ($r = 0.45$; $p < 0.05$). The toxicity to three aquatic organisms (*Raphidocelis subcapitata*, *Daphnia magna*, *Vibrio fischeri*) from shooting range soil elutriates was also examined and found to be low to moderate. The percentage growth rate of inhibition of *R. subcapitata* was 0.7 to 42. The EC_{50} for *V. fischeri* bioluminescence inhibition was 7000–9990 mg/kg and *D. magna* immobilisation was 0%.

Soil microbes are also known to be affected by shooting range contamination. Fayiga et al. [19] noted increased microbial activity with bullet removal and reduced Pb burden in the soil. Sanderson et al. [70] reported relatively low microbial activity in untreated shooting range soils; however, chemical amendments such as phosphate and lime greatly increased microbial activity.

Birds and mammals are exposed to Pb by ingesting lead shot and associated bullet fragments or through indirect modes. Scavenging birds are vulnerable to exposure to Pb bullets used in hunting due to their foraging strategies and physiological processes that facilitate the absorption of lead [21]. Ingestion of spent shot in waterfowl from wetland shooting is well documented [56]. The review by Golden et al. [21] provides detailed discussion of the effect of ingestion of spent shot. This topic is not considered further in this review.

The downstream impact of contamination from an abandoned shooting range has been examined by Mariussen et al. [46]. Elevated concentrations of Pb, Cu and Sb (14, 6.1 and 1.3 μg/L, respectively) were reported in a downstream lake. Bioaccumulation and toxicity were reported in the brown trout and brown trout eggs for Pb.

The assessment of availability of contaminants in shooting range soil and through chemical extractions and in vitro bioaccessibility tests has been a staple of the recent research. These tests are insightful from both the characterisation and management perspective as it is increasingly recognised that the available and leachable fractions are the risk drivers for these sites. The research on availability and leachability of Pb from contaminated sites is quite well developed. The availability and leachability of Sb in shooting range soils have been illuminated in recent research and further research will continue to increase the understanding of Sb as a contaminant in shooting ranges.

Ecotoxicity is also an important consideration for assessing and managing the impacts of shooting range contamination, which compliments chemical assessment. Ecotoxicity of Pb is relatively well understood having previously been widely investigated. Recent studies have continued to use ecotoxicity endpoints examining bioaccumulation and toxicity to soil biota and aquatic organisms of Pb from shooting range soils. Greater understanding of the contribution of Sb to shooting range ecotoxicity would be beneficial.

Management of Shooting Range Contamination

The management of shooting range soils may take a number of approaches and may include implementation of multiple strategies to reduce contaminant burden and stabilise contaminants in the soil. These strategies may broadly be categorised as mobilisation, stabilisation and removal (Fig. 1). Mobilisation strategies involve the addition of a chemical agent to mobilise contaminants for removal from the soil such as soil washing and enhanced phytoremediation. Stabilisation refers to a method which seeks to enhance the association of the contaminant with the soil and may include chemical stabilisation and phytostabilisation. Removal refers to physical removal of the bullets and fragments from the soil and includes separation techniques and excavation. The trend in shooting range research since 1990 is demonstrated in Fig. 2. Lead contamination and management were the focus of initial research. The research has expanded to examine Sb and management techniques beyond phosphate for Pb stabilisation including the use of biochars and iron oxide amendments.

Chemical Stabilisation

The mechanisms of achieving Pb immobilisation include adsorption, precipitation, complexation and liming effect (Fig. 1). A number of amendments may be applied to the soil to stabilise contaminants. Lead bioavailability can be reduced when it is bound to Fe and Al oxides, adsorbed to organic and inorganic components or precipitated as Pb-phosphates or other Pb minerals ([9, 14]). Consideration of Pb chemistry in soil can be utilised to manage and reduce risk from Pb contamination of shooting ranges. Chemical stabilisation by addition of soil amendments has been researched for management of Pb in shooting range soil [5, 68, 69]. Ahmad et al. [5] reviewed different sources of lime-based waste materials, noting the main mechanism of Pb immobilisation by these amendments was closely associated with sorption and precipitation at high soil pH. Sanderson et al. [68, 69] noted a range of amendments had been utilised for treating shooting range soils. Varying degrees of immobilisation based on amendment type, soil properties and soil moisture influence on reaction kinetics.

An overview of recent studies of chemical stabilisation of shooting range soils is given in Table 2. These recent studies have examined varied application of phosphate-based amendments, such as phosphate-containing wastes, phosphate-based nanoparticles and phosphate coatings of bullets. Other amendments that have seen increased research for application to shooting ranges include iron oxide-based amendments and biochar. The use of these amendments is discussed below.

Phosphate

Phosphate has been a particular focus of research of stabilisation of Pb in shooting ranges due to the precipitation of Pb with phosphate to form pyromorphite which is stable over a wide soil pH range [2, 12, 57, 71, 77]. Several kinds of P compounds have been used for Pb immobilisation including hydroxyapatites, rock phosphate, phosphate-based salts, diammonium phosphate, phosphoric acid and their combinations [32].

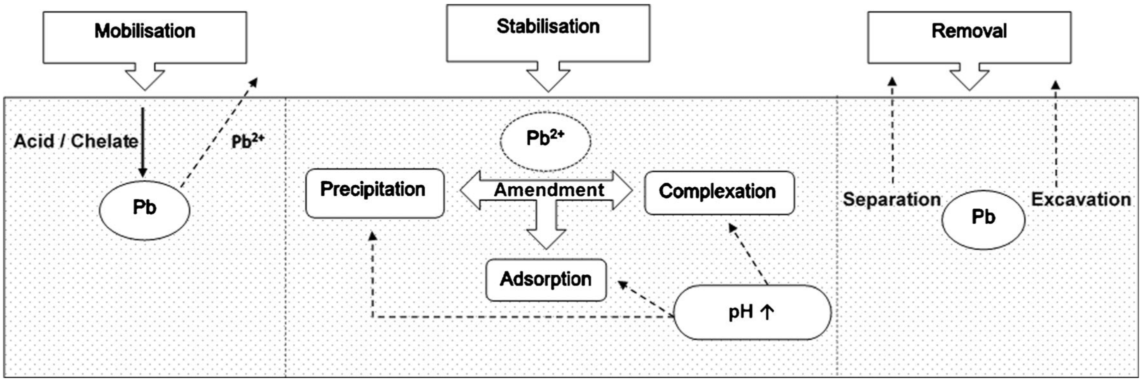

Fig. 1 Schematic diagram illustrating the management approaches to Pb in shooting range soils

Seshadri et al. [77] showed that both soluble and insoluble P compounds are effective in achieving long-term stabilisation of Pb. The P-induced immobilisation of Pb varied between the P treatments based on their solubility. The use of phosphate compounds like diammonium phosphate (DAP) and triple super phosphate (TSP) has shown ability to significantly decrease the availability of Pb by immobilisation [48, 88]. The increase in pH and the rise in surface charge were found to enable immobilisation via adsorption of Pb in the presence of phosphate compounds [12].

However, not all phosphate compounds are necessarily effective in the immobilisation of Pb, which requires the phosphate ions to be in soil aqueous phase and the solubilisation of existing Pb species for transformation [92]. This may be inhibited in the soil. The immobilisation of metals was found to be relatively ineffective when phosphate rock was applied to calcareous soils, which can be attributed to the poor reactivity of apatite [88]. A previous study by Moseley et al. [51] examined three phosphate fertilisers and reported large amendment masses were required to achieve relatively modest reductions in bioaccessibility.

Whilst soluble P compounds which drive down soil pH are effective in immobilising Pb, they may cause the leaching of P, which is harmful to the environment. It is therefore preferable to use insoluble P compounds to limit P leaching. Phosphate solubilising bacteria (PSB) can be used to facilitate P solubilisation from insoluble P compounds such as rock phosphate, thereby promoting Pb immobilisation [57].

Sanderson et al. [72] used phosphate and magnesium oxide to chemically stabilise Pb in three shooting range soils. The speciation results using X-ray absorption spectroscopy combined with linear combination fitting showed up to 17% of Pb present as pyromorphite from phosphate treatment. They observed further increase in Pb as pyromorphite (38%) when treated with the combination of phosphate and magnesium oxide. Substantial Pb in the soil remained associated with iron oxide.

Other approaches utilising phosphate include a hydroxyapatite, derived from flue gas and desulphurisation gypsum, which

Fig. 2 Number of papers published on different aspects of shooting ranges since 1990. Scopus was utilised as the database and search terms were a combination of shooting range and the following: lead, antimony, phosphate, iron oxide, biochar and soil washing + phytoremediation (other)

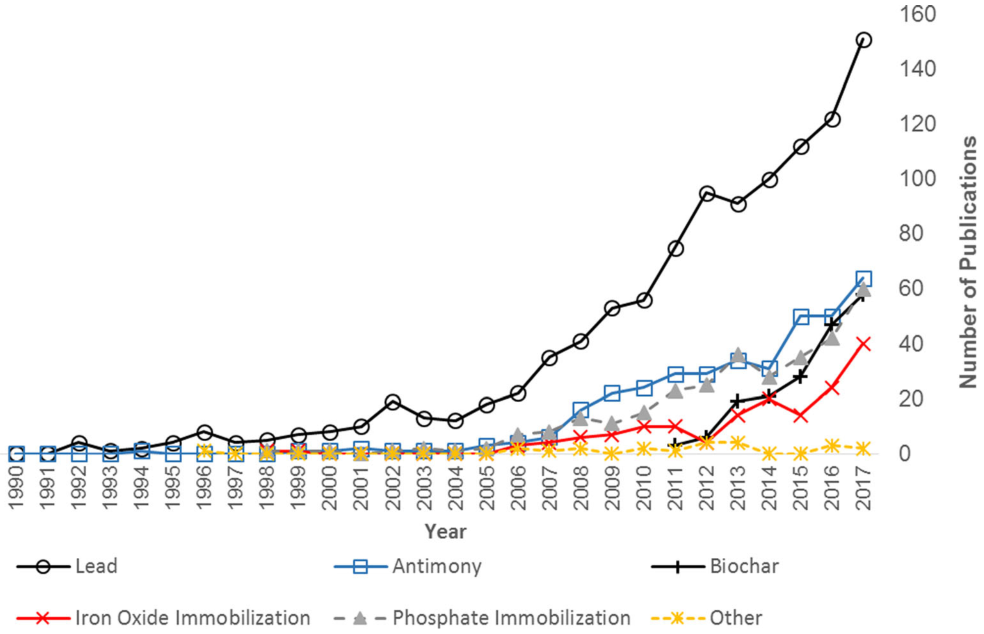

Table 2 Overview of recent research on chemical stabilisation of shooting range soils

Amendment	Metals examined	Amendment applicate rate	Result	Reference
Phosphate rock, phosphoric acid	Pb	4:1 P:Pb	TCLP Pb reduced from up to 800 mg/L to <1 mg/L	[20]
Phosphate alkaline residue	Pb	0–20%	TCLP Pb reduced from > 100 mg/L to < 5 Bioaccessible Pb reduced 20–70%	[94]
Phosphate, lime, MgO, red mud	Pb, Sb	2:1 P:Pb, Lime, red mud and MgO 2%	Pb bioaccessibility reduced by 20–55% Sb bioaccessibility by 10–20%	[71]
Phosphoric acid, MgO	Pb	1% P, 10% MgO	XAS-pyromorphite formation up to 38%. P + MgO reduced bioaccessibility by up to 25%	[72]
Phosphate coating	Pb	Bullet surface coating	Leachable Pb was reduced by 77–98% by FePO4 or AlPO4 surface coating	[22]
Ca3(PO4)2 nanoparticles	Pb, Cu, Zn	5%	CaCl2-extractable Pb and Cu reduced by > 90% and Zn 50%.	[8]
Mussel shell, cow bone and biochar	Pb, Sb	5%	Maize uptake reduced by up to 71% Pb and 53.44% for Sb	[4]
Hydroxyapatite and ferrihydrite	Pb, Sb	5%	Water-soluble lead and antimony by 99.9 and 95.5%, respectively	[53]
Ferric oxyhydroxide with limestone	Pb, Sb	1–4%	Water- and 1 M NH4NO3-extractable l Pb reduced by 89–99%, Sb 89–90%	[54]
Red mud, zero valent iron, iron sulphate	Pb, Sb	1:19 Fe:Soil, 1:4 red mud:soil, 2% goethite	Pb leaching reduced from > 700 to < 10 μg/kg and Sb 450 to < 10 μg/kg	[82]
Biochar, iron oxide, gibbsite, silver nanoparticles	Pb, Sb, Cu	5% biochar, 0.1% iron oxides and nanomaterials	Pb extractability reduced by 13–94% Sb by up to 20%	[62]
Biochar	Pb, Sb, Cu	10%	Exchangeable Pb reduced by 88.08%, Cu by 86.73%, Sb by up to 50%	[6]
Cow bone powder, biochar, egg shell powder	Pb	5%	Water-soluble Pb in amended soil significantly decreased with saline water irrigation.	[7]
Biochar, carbon nanotubes	Pb, Sb, Cu	0–2.5%	BC reduced the concentrations of Pb and Cu in the soil by 17.6 and 16.2%	[90]

was able to immobilise Pb by precipitation and Cu by ion exchange, demonstrating potential of modified waste materials for remediation of shooting range soils [40]. Another novel approach used a phosphate-based surface coating (FePO4 or AlPO4) of bullets to reduce leaching of metals from bullets [22]. Arenas-Lago et al. [8] used $Ca_3(PO)_42$ nanoparticles, demonstrating reduced extractable Pb and Cu by more than 90%.

Sanderson et al. [73] examined the effect of environmental conditions and soil physicochemistry on stabilisation of Pb by phosphate. Wet-dry cycles and organic matter were found to inhibit the effectiveness of monocalcium phosphate, whilst application of ammonium nitrate or chloride with the phosphate increased the effectiveness of the treatment. The reduction in bioaccessible Pb obtained was only between 20 and 40% with the most optimal treatment conditions, and the transformation of Pb to pyromorphite was indicated to be relatively limited.

Additionally, treatment of shooting ranges with phosphate should consider co-contaminants, particularly Sb, which may be mobilised by phosphate [31]. Sanderson et al. [71] Sb was generally reduced in porewater by addition of rock phosphate in four shooting range soils.

Other Amendments

Other amendments have been examined and applied to shooting range soils recently including lime, MgO, red mud, iron oxyhydroxides and biochar (Table 2). These amendments represent a range of stabilisation mechanisms (Fig. 1) and demonstrate ability to stabilise contaminants in shooting range soils, depending on site-specific conditions. Amendments which increase the soil pH (liming effect) such as lime and MgO are effective in reducing leachable Pb (water extractable and TCLP) and have varying effectiveness for bioaccessibility reduction [71]. However, the effect of these amendments was generally to mobilise Sb in porewater.

Iron-based amendments have been found to be effective both for the stabilisation of Pb and Sb [44, 54, 82]. Iron oxyhydroxide amendments reduced $NH_4NO_3^-$-extractable levels of Pb by up to 99 and 90% for Sb by adsorption to the iron oxide surface [54]. Concentrations in soil leachates were 55–94% less for Sb and reduced by 79–99% Pb, Cu and Zn using iron-based amendments [44, 45].

Combined application of amendments may be necessary for effective stabilisation of both Pb and Sb [53, 54, 82].

Tandy et al. [82] reported $FeSO_4$ reduced Sb(V) to Sb(III) and decreased Sb leaching; however, a great increase in Pb leaching required the combined application with a red mud amendment. A combined application of charcoal and iron hydroxide in successive filters was found to reduce Cu, Sb and Pb in shooting range runoff water by 89, 90 and 93%, respectively [43].

Biochar

Biochars, carbon-rich products from thermochemical conversion of biomass under oxygen-deficit environment [35], have been widely reported to be effective in heavy metal stabilisation in soils [61], Inyang et al. 2015. Several studies have examined biochars for metal stabilisation in shooting range soils [3, 6, 13, 58, 62, 85]. In most cases, various types of biochars were found to effectively immobilise Pb and Cu [3, 62, 85], whilst Sb has been found to be unfavourably mobilised ([3, 85, 90] or unaltered [62] by biochars in shooting range soils. Vithanage et al. [90] examined effects of carbon nanotube and biochar on bioavailability of Pb, Cu and Sb in shooting range soil. Biochar reduced the concentrations of Pb and Cu in the soil by 17.6 and 16.2%, respectively. However, both carbon nanotubes and biochar increased Sb bioavailability by 1.4- and 1.6-fold, respectively, in DTPA extraction.

Biochar can increase cation exchange capacity, releasing large amount of cations (K^+, Na^+, Ca^{2+} and Mg^{2+}) and anions (Cl^-, CO_3^{2-}, PO_4^{3-}, SO_4^{2-}), increasing soil organic carbon and increase soil pH [25, 61, 62]. Correspondingly, the stability of Pb by biochars can be through electrostatic attraction (ion exchange) [3], Pb-phosphate precipitation [13, 25] and surface complexation [63, 91] and by increase of pH [4, 25]. Higher pH favours precipitation of Pb as metal hydroxide [5], Pb bound to organic matter [25] and formation of other Pb sorptive components including carbonates, iron and manganese oxides [25].

The formation of Pb precipitates with various cations and anions in soil systems has been reported to be the dominant Pb stabilisation mechanisms [25]. For example, phosphorous content in biochars was found to convert less stable $PbCO_3$ to more stable hydroxypyromorphite [$Pb_5(PO_4)_3OH$] [13], forming stable chloropyromorphite [$Pb_5(PO_4)_3Cl$] [6, 62] or lead phosphate ($Pb_3(PO_4)_2$ [25] in shooting range soils. Association of Pb with other minerals like Al and Si content in biochars can also aid Pb stabilisation in soils [4]. The reported stabilisation mechanism for Cu in shooting range soils was complexation with surface functional groups [62, 84]. However, similar to Cu stabilisation in non-shooting range soils, Cu can also be stabilised by other mechanisms such as electrostatic attraction, association with biochar mineral phases, precipitation as carbonate or Cu oxide phase in biochar-amended shooting range soils [61]. In contrast, the increase of soil pH and the release of phosphorous by biochar amendment can induce Sb mobilisation through enhanced electrostatic repulsion and sorption competition from phosphate [3, 4].

Metal stabilisation in shooting range soils by biochars is strongly relevant to biochar properties that are mainly determined by biochar feedstocks and production temperature [61]. Among all biochar feedstocks, phosphorus-rich manure-based biochars are favourable for Pb stabilisation through precipitation [13]. Low-temperature biochars have been reported to favour stabilisation of Pb by releasing more P, Ca, etc. (350 than 650 °C) [85], more abundant surface functional groups (300 than 700 °C) [3, 62] and more surface-negative charge (temperature increase at < 500 °C) [25]. Uchimiya et al. [84] also suggested biochars richer in carboxyl functional groups exhibited greater Pb and Cu stabilisation capacities in shooting range soil. Hence, phosphate functional group rich biochars are recommended for shooting range soil management whilst mobilisation of Sb should be carefully monitored and avoided. Meanwhile, proper application ratio should be tried before large-scale application of biochars into shooting range soils in order to achieve optimal immobilisation effects at the lowest cost.

Most research on chemical stabilisation of shooting ranges has utilised lab-based approaches to study amendment application. Preliminary studies may focus on testing a range of amendment application rates in a batch study before examining optimal rates in at a larger bench scale, with more detailed analysis. Other studies will use a set amendment rate guided by previous literature and explore application of the amendment to a particular site and conditions. It is important in these studies to consider the effect of the amendment not just on the primary contaminant Pb, but also on co-contaminants such as Sb, which is sorbed and mobilised by different mechanisms than Pb.

Laboratory trials enable testing of important parameters, such as amendment rates and other conditions like the effect of soil moisture level. Site-specific conditions such as contamination status, soil pH and organic content influence the successful application of chemical stabilisation at any given site. Research studies provide important insight to the applicability of different amendments for site risk management or remediation. Indeed, treatability studies to examine optimal application for site-specific conditions are important and chemical stabilisation vendors often use these to determine the most appropriate amendment formulation for a given site. It must also be noted that lab studies often utilise the < 2-mm fraction of soil, which excludes intact bullets and larger fragments, which are present in the field. Therefore, consideration must be given to potential ongoing release of metals from bullets and fragments remaining in the soil. The removal of bullets in addition to the use of amendments may be required.

Field-based trials provide valuable information for observing treatment at scale under real-world conditions overtime. In a field-based study by Okkenhaug et al. [54], the remediation was reported to be stable over the 4 years of the experimental period. Such a demonstration is important for the implementation of approaches researched in the lab to the field.

Field-based application should consider application which is effective for the incorporation of the amendment into the top soil layer (~ 0–20 cm), where the contamination is concentrated, with caution to mechanical disturbance of the soil, which may cause abrasion of intact bullets and fragments. A slurry injection of the amendment may be preferable to rototilling for applying amendments to shooting ranges.

Phytoremediation and Other Management Practices

Phytoremediation may be in the form of phytoextraction (mobilisation) or phytostabilisation (Fig. 1). Phytoremediation of shooting range soil was recently reviewed by Bandara and Vithanage [10], who recommended more studies be conducted on a wider variety of plants and plants suited for practical application in the field, including ability to remove metals and metalloids and symbiotic relationships of plants with microbes to enhance the efficiency of phytoremediation. A study by Adler et al. [1] demonstrated the isolation of lead-resistant bacteria that could be utilised to assist phytoremediation. Tariq and Ashraf [83] examined phytoextraction potential of four species for metal removal in shooting range soil and reported *Pisum sativum* to be a hyperaccumulator of Pb, with removal efficiency of 96.23%, whilst *Zea mays* removed 74% assisted by EDTA application. The other two examined species (*Helianthus annuus* and *Brassica campestris*) extracted relatively little Pb.

The use of plants in phytostabilisation applications has also been investigated for shooting range soils. The grass *Agrostis capillaris* was recently investigated for managing contamination of trap shooting range soils [65]. The average soil concentration of Pb ranged from 29 to 724 mg/kg. High accumulation of Pb in the roots (up to 1107 mg/kg) was reported, but there was relatively low translocation to shoots (135 mg/kg). This indicates potential for management of the relatively disperse contamination at trap shooting ranges by phytostabilisation. However, weathering of bullets may be favoured by acidity, organic matter, available P and microbial activity as well as by dissolved $CaCO_3$ coming from the clay target residues [65], so caution needs to be applied and soluble concentrations of metals should be monitored.

The effects of two best management practices for shooting ranges (bullet removal and vegetation) on bioavailability and leachability of Pb were recently examined [19]. Bullet removal and/or vegetation reduced bioavailable and leachate Pb across the three shooting ranges. High uptake in the root indicated St. Augustine grass could be used for phytostabilisation.

A combined approach utilising a phytoremediation and chemical stabilisation technique was employed by Katoh et al. [29]. Heavy metals in the contaminated soil were transported toward the plants via water suction from the roots and were immobilised by soil amendment. The concentrations of Pb and Sb stabilised were 8–25 and 69–533 times higher, respectively, than that removed by phytoextraction.

Other means have been examined for the management of shooting range contamination. Islam and Park [27] used a novel hydrothermal treatment (HT) to immobilise Pb and found a drastic reduction in bioavailable fraction from 41.33 to 14.66% and increase of non-bioavailable fraction from 2.9 to 15.76%, by repartitioning of Pb to more stable fractions in the soil. Novel management and remediation approaches for shooting range contamination should continue to be investigated with an emphasis on cost-effective and sustainable approaches.

Soil Washing

Soil washing is a well-known technique for remediation of metal contamination, which continues to be investigated for application to shooting ranges [17, 23, 33, 36, 96]. Researchers have investigated a range of approaches using this technique.

Guemiza et al. [23] and Lafond et al. [33] investigated countercurrent leaching methods, which achieved metal removal yields of 80–90% for Pb and Cu, 50–80% of Sb and 30–44% of Zn. Countercurrent leaching utilises a process where treated waters are reused in a flow opposite to the flow of solid, allowing the leachate to be reused for multiple leaching steps and reused in multiple cycles. Both authors noted significant reduction in water and chemical consumption, which is important for cost-effectiveness and sustainability of soil washing. However, disturbance of the soil structure is a drawback of using acid washing to remove metals.

Alternative extractants such as ferric chloride have been investigated to remove lead from shooting range soil [96]. Whilst ferric chloride was effective in removing Pb, it caused similar acidification of the soil. Etim [17] utilised an acetic acid/potassium chloride washing solutions combined with electrochemical reduction, achieving up to 87% removal of Pb. Sanderson et al. [74] used a biodegradable mobilising agent in combination with phosphate amendment to determine whether more Pb could be immobilised through combined technique. In two of the four soils, a greater reduction in bioaccessible Pb was achieved by the use of a mobilising agent prior to application of phosphate.

Considerations for Managing Shooting Range Contamination

Environmental regulations and contaminant threshold limits are likely to inform management goals for shooting range operators. Environmental management plans for shooting ranges should give consideration to these as well as the site-specific properties, which affect management of contamination.

Regional scale assessments of shooting ranges have been undertaken in order to inform management of shooting ranges, using a risk-based screening approach to identify shooting ranges which are driving risk (Darling and Thomas 2003; [79]). The EPA in Victoria, Australia, is currently undertaking a desktop human health and environmental risk assessment of about 150 shooting ranges across Victoria. These studies have utilised available data (land use, groundwater, soil properties, distance to sensitive receptors) to identify sites posing potential risk from contamination for further study. Such approach represents a means of targeting resources where they are most needed. This is particularly beneficial for gun clubs which have limited operational budget.

Characterisation of shooting ranges should identify contaminant hotspots on sites (particularly for trap/skeet ranges). The use of portable X-ray fluorescence (XRF) allows for collection of a relatively large number of data points and spatial interpolation of the dataset [60, 86]. This information allows for a targeted approach to the highest contaminant burden or risk areas that would be beneficial where finances constrain management options.

Application of best management practices to shooting range soils, such as liming and replacement of soil berm with sand, could serve to reduce the risk from Pb in shooting range soils. Such a management technique is particularly applicable for shooting ranges with acidic clayey soils. Other amendments, such as phosphates and biochar, may be able to achieve a higher level of stability of contaminants than lime addition, which may be desirable for protection of the environment or human health. Such management approaches should consider site-specific conditions, including understanding the potential effects on the mobility of co-contaminants of Pb. It should also be appreciated that for some sites, Sb may be more of a concern for mobility in the environment than Pb and the application of iron hydroxide-based amendments may be beneficial for stabilisation of Sb.

The removal and recycling of bullets from shooting range soils has the potential to substantially reduce contaminant burden and environmental and human health risk. However, caution should be exercised as mechanical removal of Pb may result in abrasion of Pb fragments and enrichment of Pb in soil. Density-based separation may be a better means of bullet removal from the soil and reduce abrasion. Soil washing methods may be applicable to remove contamination where there is a high proportion of contaminants sorbed to the soil. Alternative extractants and methods, such as countercurrent leaching (with recycling of washing solution), may provide a more sustainable and cost-effective approach.

Conclusions

Shooting ranges remain an ongoing environmental concern. Researchers continue to investigate and characterise the fate of contaminants, bioavailability and toxicity, and management practices for these sites. The fate of co-contaminants, such as Sb in particular, continues to be investigated in shooting range soils, with the appreciation that Sb behaves quite differently to Pb in the soil.

Site-specific physicochemical conditions are important for the weathering and mobility of contaminants and these need to be understood by range operators to apply the most appropriate management practice. Consideration should also be given to the forms of Pb and other metals in the soil, which play an important role in the environmental and human health risk of shooting range contamination. Shooting range sites with different conditions from the norm, such as those sited on mires or peat or those in acidic environments, may have greater mobility of contaminants and need more careful management.

Management strategies should seek to reduce the weathering of bullets in the soil and limit the mobility and bioavailability of contaminants. Techniques such as chemical stabilisation and phytoremediation have demonstrated potential, but need to take into consideration site-specific conditions, and utilise trials to optimise their application at a given site. Ongoing research into novel amendments such as biochar and iron oxides and combined applications of amendments for stabilisation of Pb and Sb in shooting range soils will assist in providing additional approaches for application of chemical stabilisation, in addition to the well-researched application of lime or phosphate. Research should continue into identifying novel, cost-effective approaches for management of contamination of shooting range soils that may be applied where funds for management and remediation are limited.

Compliance with Ethical Standards

Conflict of Interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

1. Adler A, Devarajan N, Wildi W, Poté J. Metal distribution and characterization of cultivable lead-resistant bacteria in shooting range soils. Soil Sed Contam. 2016; 18;25(4):378–94.
2. Adriano DC, Wenzel WW, Vangronsveld J, Bolan NS. Role of assisted natural remediation in environmental cleanup. Geoderma. 2004;122(2–4):121–42. https://doi.org/10.1016/j.geoderma.2004.01.003.
3. Ahmad M, Lee SS, Lee SE, Al-Wabel MI, Tsang DCW, Ok YS. Biochar-induced changes in soil properties affected immobilization/mobilization of metals/metalloids in contaminated soils. J Soils Sed. 2017;17(3):717–30. https://doi.org/10.1007/s11368-015-1339-4.

4. Ahmad M, Lee SS, Lim JE, Lee S-E, Cho JS, Moon DH, et al. Speciation and phytoavailability of lead and antimony in a small arms range soil amended with mussel shell, cow bone and biochar: EXAFS spectroscopy and chemical extractions. Chemosphere. 2014;95:433–41. https://doi.org/10.1016/j.chemosphere.2013.09.077.
5. Ahmad M, Lee SS, Moon DH, Yang JE, Ok YS. A review of environmental contamination and remediation strategies for heavy metals at shooting range soils. In: Malik A, Grohmann E, editors. Environmental protection strategies for sustainable development. Dordrecht: Springer Netherlands; 2012. p. 437–51.
6. Ahmad M, Ok YS, Rajapaksha AU, Lim JE, Kim B-Y, Ahn J-H, et al. Lead and copper immobilization in a shooting range soil using soybean stover- and pine needle-derived biochars: chemical, microbial and spectroscopic assessments. J Hazard Mater. 2016;301:179–86. https://doi.org/10.1016/j.jhazmat.2015.08.029.
7. Almaroai YA, Usman AR, Ahmad M, Moon DH, Cho JS, Joo YK, Jeon C, Lee SS and Ok YS. Effects of biochar, cow bone, and eggshell on Pb availability to maize in contaminated soil irrigated with saline water. Environmental Earth Sciences. 2014;71(3), pp. 1289–1296
8. Arenas-Lago D, Rodríguez-Seijo A, Lago-Vila M, Couce LA, Vega FA. Using Ca 3 (PO4)2 nanoparticles to reduce metal mobility in shooting range soils. Sci Total Environ 2016;571:1136–1146. doi: https://doi.org/10.1016/j.scitotenv.2016.07.108, Using Ca 3 (PO 4) 2 nanoparticles to reduce metal mobility in shooting range soils
9. Ayanka Wijayawardena MA, Naidu R, Megharaj M, Lamb D, Thavamani P, Kuchel T. Using soil properties to predict in vivo bioavailability of lead in soils. Chemosphere. 2015;138:422–8.
10. Bandara T, Vithanage M. Phytoremediation of shooting range soils. In: Ansari AA, Gill SS, Gill R, Lanza GR, Newman L, editors. Phytoremediation. Cham: Springer International Publishing; 2016. p. 469–488.
11. Bannon DI, Drexler JW, Fent GM, Casteel SW, Hunter PJ, Brattin WJ, et al. Evaluation of small arms range soils for metal contamination and lead bioavailability. Environ Sci Technol. 2009;43(24): 9071–6. https://doi.org/10.1021/es901834h.
12. Bolan NS, Adriano DC, Naidu R. Role of phosphorus in (im)mobilization and bioavailability of heavy metals in the soil-plant system. Rev Environ Contam Toxicol. New York, NY: Springer New York; 2003. p. 1–44.
13. Cao X, Ma L, Liang Y, Gao B, Harris W. Simultaneous immobilization of lead and atrazine in contaminated soils using dairy-manure biochar. Environ Sci Technol. 2011;45(11):4884–9. https://doi.org/10.1021/es103752u.
14. Cao X, Ma LQ, Chen M, Hardison DW, Harris WG. Weathering of lead bullets and their environmental effects at outdoor shooting ranges. J Environ Qual. 2003;32(2):526. https://doi.org/10.2134/jeq2003.5260.
15. Conesa HM, Wieser M, Studer B, González-Alcaraz MN, Schulin R. A critical assessment of soil amendments (slaked lime/acidic fertilizer) for the phytomanagement of moderately contaminated shooting range soils. J Soils Sed. 2012;12(4):565–75. https://doi.org/10.1007/s11368-012-0478-0.
16. Etim EU. Distribution of soil-bound lead arising from rainfall-runoff events at impact berm of a military shooting range. J Environ Prot. 2016;7(05):623–34.
17. Etim EU. Lead removal from contaminated shooting range soil using acetic acid potassium chloride washing solutions and electrochemical reduction. J Health Pollut. 2017;7(13):22–31. https://doi.org/10.5696/2156-9614-7-13.22.
18. Fayiga AO, Saha U. The effect of bullet removal and vegetation on mobility of Pb in shooting range soils. Chemosphere. 2016a;160: 252–7. https://doi.org/10.1016/j.chemosphere.2016.06.098.
19. Fayiga AO, Saha UK. Soil pollution at outdoor shooting ranges: health effects, bioavailability and best management practices. Environ Pollut. 2016b;216:135–45. https://doi.org/10.1016/j.envpol.2016.05.062.
20. Fayiga AO, Saha UK. Effect of phosphate treatment on Pb leachability in contaminated shooting range soils. Soil Sed Contam. 2017;26(1):115–26. https://doi.org/10.1080/15320383.2017.1245712.
21. Golden NH, Warner SE, Coffey MJ. A review and assessment of spent lead ammunition and its exposure and effects to scavenging birds in the United States. In: de Voogt WP, editor Rev Environ Contam 2016. Volume 237. Cham: Springer International Publishing; p. 123–191.
22. Guo J, Hua B, Li N, Yang J. Stabilizing lead bullets in shooting range soil by phosphate-based surface coating. AIMS Environ Sci. 2016;3(3):474–87.
23. Guemiza K, Mercier G, Blais JF. Pilot-scale counter-current acid leaching process for Cu, Pb, Sb, and Zn from small-arms shooting range soil. J Soils Sed. 2014;14(8):1359–69. https://doi.org/10.1007/s11368-014-0880-x.
24. Hockmann K, Tandy S, Lenz M, Reiser R, Conesa HM, Keller M, et al. Antimony retention and release from drained and waterlogged shooting range soil under field conditions. Chemosphere. 2015;134:536–43. https://doi.org/10.1016/j.chemosphere.2014.12.020.
25. Igalavithana AD, Lee S-E, Lee YH, Tsang DCW, Rinklebe J, Kwon EE, et al. Heavy metal immobilization and microbial community abundance by vegetable waste and pine cone biochar of agricultural soils. Chemosphere. 2017;174:593–603. https://doi.org/10.1016/j.chemosphere.2017.01.148.
26. Islam MN, Nguyen XP, Jung HY, Park JH. Chemical speciation and quantitative evaluation of heavy metal pollution hazards in two army shooting range backstop soils. Bull Environ Contam Toxicol. 2016;96(2):179–85.
27. Islam MN, Park J-H. Immobilization and reduction of bioavailability of lead in shooting range soil through hydrothermal treatment. J Environ Manag. 2017;191:172–8. https://doi.org/10.1016/j.jenvman.2017.01.017.
28. Johnson CA, Moench H, Wersin P, Kugler P, Wenger C. Solubility of antimony and other elements in samples taken from shooting ranges. J Environ Qual. 2005 Jan 1;34(1):248–54.
29. Katoh M, Hashimoto K, Sato T. Lead and antimony removal from contaminated soil by phytoremediation combined with an immobilization material. CLEAN–Soil, Air, Water. 2016 Dec 1;44(12): 1717–24.
30. Kelebemang R, Dinake P, Sehube N, Daniel B, Totolo O, Laetsang M. Speciation and mobility of lead in shooting range soils. Chem Speciat Bioavailab. 2017;29(1):143–52.
31. Kilgour DW, Moseley RB, Barnett MO, Savage KS, Jardine PM. Potential negative consequences of adding phosphorus-based fertilizers to immobilize lead in soil. J Environ Qual. 2008;37(5):1733. https://doi.org/10.2134/jeq2007.0409.
32. Kumpiene J, Lagerkvist A, Maurice C. Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments—a review. Waste Manag. 2008;28(1):215–25. https://doi.org/10.1016/j.wasman.2006.12.012.
33. Lafond S, Blais J-F, Mercier G, Martel R. A counter-current acid leaching process for the remediation of contaminated soils from a small-arms shooting range. Soil Sed Contam. 2014;23(2):194–210. https://doi.org/10.1080/15320383.2014.808171.
34. Lewis J, Sjöström J, Skyllberg U, Hägglund L. Distribution, chemical speciation, and mobility of lead and antimony originating from small arms ammunition in a coarse-grained unsaturated surface sand. J Environ Qual. 2010;39(3):863. https://doi.org/10.2134/jeq2009.0211.
35. Lehmann J, Joseph S, editors. Biochar for environmental management: science, technology and implementation. Routledge; 2015 Feb 20.

36. Lewińska K, Karczewska A, Siepak M, Gałka B, Stysz M, Kaźmierowski C. Recovery and leachability of antimony from mine-and shooting range soils. Journal of Elementology. 2017 Mar 1;22(1):79–90.
37. Li Y, Zhu Y, Zhao S, Liu X. The weathering and transformation process of lead in China's shooting ranges. Environ Sci: Process Impacts. 2015;17(9):1620–33. https://doi.org/10.1039/C5EM00022J.
38. Liu Y, Fang Z, Xie C, Li J. Analysis of Existing Speciation and Evaluation of Heavy Metals Pollution of Soil in a Shooting Range. Nature Environment and Pollution Technology. 2014 Sep 1;13(3): 449.
39. Liu R, Gress J, Gao J, Ma LQ. Impacts of two best management practices on Pb weathering and leachability in shooting range soils. Environ Monit Assess. 2013;185(8):6477–84. https://doi.org/10.1007/s10661-012-3039-5.
40. Liu Y, Yan Y, Seshadri B, Qi F, Xu Y, Bolan N, et al. Immobilization of lead and copper in aqueous solution and soil using hydroxyapatite derived from flue gas desulphurization gypsum. J Geochem Explor. 2016;184:239–46.
41. Luo W, Verweij RA, van Gestel CAM. Determining the bioavailability and toxicity of lead contamination to earthworms requires using a combination of physicochemical and biological methods. Environ Pollut 2014;185:1–9. doi:https://doi.org/10.1016/j.envpol.2013.10.017.
42. Ma LQ, Hardison DW, Harris WG, Cao X, Zhou Q. Effects of soil property and soil amendment on weathering of abraded metallic Pb in shooting ranges. Water Air Soil Pollut. 2007;178(1–4):297–307. https://doi.org/10.1007/s11270-006-9198-7.
43. Mariussen E, Johnsen IV, Strømseng AE. Selective adsorption of lead, copper and antimony in runoff water from a small arms shooting range with a combination of charcoal and iron hydroxide. Journal of Environmental Management. 2015;150:281–7.
44. Mariussen E, Johnsen IV, Strømseng AE. Distribution and mobility of lead (Pb), copper (Cu), zinc (Zn), and antimony (Sb) from ammunition residues on shooting ranges for small arms located on mires. Environ Sci Pollut Res. 2017a;24(11):10182–96. https://doi.org/10.1007/s11356-017-8647-8.
45. Mariussen E, Heier LS, Teien HC, Pettersen MN, Holth TF, Salbu B et al. Accumulation of lead (Pb) in brown trout (Salmo trutta) from a lake downstream a former shooting range. Ecotoxicol Environ Saf 2017c;135:327–36.
46. Mariussen E, Johnsen IV, Strømseng AE. Application of sorbents in different soil types from small arms shooting ranges for immobilization of lead (Pb), copper (Cu), zinc (Zn), and antimony (Sb). J Soil Sed. 2017b:1–1.
47. Martin WA, Nestler CC, Wynter M, Larson SL. Bullet on bullet fragmentation profile in soils. J Environ Manag. 2014;15(146): 369–72.
48. McGowen SL, Basta NT, Brown GO. Use of diammonium phosphate to reduce heavy metal solubility and transport in smelter-contaminated soil. J Environ Qual. 2001;30(2):493. https://doi.org/10.2134/jeq2001.302493x.
49. McLaren RG, Rooney CP, Condron LM. Control of lead solubility in soil contaminated with lead shot: effect of soil moisture and temperature. Aust J Soil Res. 2009;47(3):296. https://doi.org/10.1071/SR08195.
50. McTee MR, Mummey DL, Ramsey PW, Hinman NW. Extreme soil acidity from biodegradable trap and skeet targets increases severity of pollution at shooting ranges. Sci Total Environ. 2016;539:546–50. https://doi.org/10.1016/j.scitotenv.2015.08.121.
51. Moseley RA, Barnett MO, Stewart MA, Mehlhorn TL, Jardine PM, Ginder-Vogel M, et al. Decreasing lead bioaccessibility in industrial and firing range soils with phosphate-based amendments. J Environ Qual. 2008;37(6):2116. https://doi.org/10.2134/jeq2007.0426.
52. Naidu, R. "Bioavailability: Definition, assessment and implications for risk assessment." Chapter 3, Developments in soil science, Elsevier, Amsterdam, Netherlands, 39–51, 2008.
53. Ogawa S, Katoh M, Sato T. Simultaneous lead and antimony immobilization in shooting range soil by a combined application of hydroxyapatite and ferrihydrite. Environ Technol. 2015;36(20): 2647–56. https://doi.org/10.1080/09593330.2015.1042071.
54. Okkenhaug G, Grasshorn Gebhardt K-A, Amstaetter K, Lassen Bue H, Herzel H, Mariussen E, et al. Antimony (Sb) and lead (Pb) in contaminated shooting range soils: Sb and Pb mobility and immobilization by iron based sorbents, a field study. J Hazard Mater. 2016;307:336–43. https://doi.org/10.1016/j.jhazmat.2016.01.005.
55. Okkenhaug G, Smebye AB, Pabst T, Amundsen CE, Sævarsson H, Breedveld GD. Shooting range contamination: mobility and transport of lead (Pb), copper (Cu) and antimony (Sb) in contaminated peatland. J Soils Sed. 2017; https://doi.org/10.1007/s11368-017-1739-8.
56. Pain DJ, Cromie R, Green RE. Poisoning of birds and other wildlife from ammunition-derived lead in the UK. In Oxford Lead Symposium 2014 Dec 10 (p. 58).
57. Park JH, Bolan NS, Chung JW, Naidu R, Megharaj M. Environmental monitoring of the role of phosphate compounds in enhancing immobilization and reducing bioavailability of lead in contaminated soils. J Environ Monit. 2011a;13(8):2234–42. https://doi.org/10.1039/c1em10275c.
58. Park JH, Choppala GK, Bolan NS, Chung JW, Chuasavathi T. Biochar reduces the bioavailability and phytotoxicity of heavy metals. Plant Soil. 2011b;348(1–2):439–51. https://doi.org/10.1007/s11104-011-0948-y.
59. Peddicord RK, LaKind JS. Ecological and human health risks at an outdoor firing range. Environ Toxicol Chem. 2000;19(10):2602–13. https://doi.org/10.1002/etc.5620191029.
60. Perroy RL, Belby CS, Mertens CJ. Mapping and modeling three dimensional lead contamination in the wetland sediments of a former trap-shooting range. Sci Total Environ. 2014;487:72–81. https://doi.org/10.1016/j.scitotenv.2014.03.102.
61. Qi F, Dong Z, Lamb D, Naidu R, Bolan NS, Ok YS, et al. Effects of acidic and neutral biochars on properties and cadmium retention of soils. Chemosphere. 2017;180:564–73. https://doi.org/10.1016/j.chemosphere.2017.04.014.
62. Rajapaksha AU, Ahmad M, Vithanage M, Kim K-R, Chang JY, Lee SS, et al. The role of biochar, natural iron oxides, and nanomaterials as soil amendments for immobilizing metals in shooting range soil. Environ Geochem Health. 2015;37(6):931–42. https://doi.org/10.1007/s10653-015-9694-z.
63. Rinklebe J, Shaheen SM, Frohne T. Amendment of biochar reduces the release of toxic elements under dynamic redox conditions in a contaminated floodplain soil. Chemosphere. 2016;142:41–7. https://doi.org/10.1016/j.chemosphere.2015.03.067.
64. Rodríguez-Seijo A, Alfaya MC, Andrade ML, Vega FA. Copper, chromium, nickel, lead and zinc levels and pollution degree in firing range soils. Land Degrad Dev. 2016a;27(7):1721–30.
65. Rodríguez-Seijo A, Lago-Vila M, Andrade ML, Vega FA. Pb pollution in soils from a trap shooting range and the phytoremediation ability of Agrostis capillaris L. Environ Sci Pollut Res. 2016b;23(2):1312–23. https://doi.org/10.1007/s11356-015-5340-7.
66. Rodríguez-Seijo A, Cachada A, Gavina A, Duarte AC, Vega FA, Andrade ML, et al. Lead and PAHs contamination of an old shooting range: a case study with a holistic approach. Sci Total Environ. 2017;575:367–77. https://doi.org/10.1016/j.scitotenv.2016.10.018.
67. Rubio M, Germanier A, Mera MF, Faudone SN, Sbarato RD, Campos JM, et al. Study of lead levels in soils by weathering of metallic Pb bullets used in dove hunting in CÃ³rdoba, Argentina. X-Ray Spectrometry. 2014;43(3):186–92.

68. Sanderson P, Naidu R, Bolan N, Bowman M. Critical review on chemical stabilization of metal contaminants in shooting range soils. J Hazard Toxic Radioact Waste. 2012a;16(3):258–72. https://doi.org/10.1061/(ASCE)HZ.2153-5515.0000113.
69. Sanderson P, Naidu R, Bolan N, Bowman M, McLure S. Effect of soil type on distribution and bioaccessibility of metal contaminants in shooting range soils. Sci Total Environ. 2012b;438:452–62. https://doi.org/10.1016/j.scitotenv.2012.08.014.
70. Sanderson P, Naidu R, Bolan N. Ecotoxicity of chemically stabilised metal(loid)s in shooting range soils. Ecotoxicol Environ Saf. 2014;100:201–8. https://doi.org/10.1016/j.ecoenv.2013.11.003.
71. Sanderson P, Naidu R, Bolan N. Effectiveness of chemical amendments for stabilisation of lead and antimony in risk-based land management of soils of shooting ranges. Environ Sci Pollut Res. 2015a;22(12):8942–56.
72. Sanderson P, Naidu R, Bolan N, Lim JE, Ok YS. Chemical stabilisation of lead in shooting range soils with phosphate and magnesium oxide: synchrotron investigation. J Hazard Mater. 2015b;299:395–403. https://doi.org/10.1016/j.jhazmat.2015.06.056.
73. Sanderson P, Naidu R, Bolan N. The effect of environmental conditions and soil physicochemistry on phosphate stabilisation of Pb in shooting range soils. J Environ Manag. 2016;170:123–30. https://doi.org/10.1016/j.jenvman.2016.01.017.
74. Sanderson P, Naidu R, Bolan N. Application of a biodegradable chelate to enhance subsequent chemical stabilisation of Pb in shooting range soils. J Soils Sed. 2017;17(6):1696–705. https://doi.org/10.1007/s11368-016-1608-x.
75. Scheetz CD, Donald Rimstidt J. Dissolution, transport, and fate of lead on a shooting range in the Jefferson National Forest near Blacksburg, VA, USA. Environ Geol. 2009;58(3):655–65. https://doi.org/10.1007/s00254-008-1540-5.
76. Sehube N, Kelebemang R, Totolo O, Laetsang M, Kamwi O, Dinake P. Lead pollution of shooting range soils. S Afr J Chem. 2017;70 https://doi.org/10.17159/0379-4350/2017/v70a4.
77. Seshadri B, Bolan NS, Choppala G, Kunhikrishnan A, Sanderson P, Wang H, et al. Potential value of phosphate compounds in enhancing immobilization and reducing bioavailability of mixed heavy metal contaminants in shooting range soil. Chemosphere. 2017;184:197–206. https://doi.org/10.1016/j.chemosphere.2017.05.172.
78. Smith E, Weber J, Naidu R, McLaren RG, Juhasz AL. Assessment of lead bioaccessibility in peri-urban contaminated soils. J Hazard Mater. 2011;186(1):300–5. https://doi.org/10.1016/j.jhazmat.2010.10.111.
79. Sorvari J, Antikainen R, Pyy O. Environmental contamination at Finnish shooting ranges—the scope of the problem and management options. Sci Total Environ. 2006;366(1):21–31. https://doi.org/10.1016/j.scitotenv.2005.12.019.
80. Spuller C, Weigand H, Marb C. Trace metal stabilisation in a shooting range soil: mobility and phytotoxicity. J Hazard Mater. 2007;141(2):378–87. https://doi.org/10.1016/j.jhazmat.2006.05.082.
81. Stauffer M, Pignolet A, Alvarado JC. Persistent mercury contamination in shooting range soils: the legacy from former primers. Bull Environ Contam Toxicol 2017; 1;98(1):14–21.
82. Tandy S, Meier N, Schulin R. Use of soil amendments to immobilize antimony and lead in moderately contaminated shooting range soils. J Hazard Mater. 2017;324:617–25. https://doi.org/10.1016/j.jhazmat.2016.11.034.
83. Tariq SR, Ashraf A. Comparative evaluation of phytoremediation of metal contaminated soil of firing range by four different plant species. Arab J Chem. 2016. 1;9(6):806–14.
84. Uchimiya M, Bannon DI, Wartelle LH. Retention of heavy metals by carboxyl functional groups of Biochars in small arms range soil. J Agric Food Chem. 2012a;60(7):1798–809. https://doi.org/10.1021/jf2047898.
85. Uchimiya M, Bannon DI, Wartelle LH, Lima IM, Klasson KT. Lead retention by broiler litter biochars in small arms range soil: impact of pyrolysis temperature. J Agric Food Chem. 2012b;60(20):5035–44. https://doi.org/10.1021/jf300825n.
86. Urrutia-Goyes R, Mahlknecht J, Argyraki A, Ornelas-Soto N. Trace element soil contamination at a former shooting range in Athens, Greece. Geoderma Regional. 2017;10:191–9.
87. USEPA (2005): Best Management Practices for Lead at Outdoor Shooting Ranges. Division of Enforcement and Compliance Assistance, New York, NY, EPA 902/B-01-001
88. Valipour M, Shahbazi K, Khanmirzaei A. Chemical immobilization of lead, cadmium, copper, and nickel in contaminated soils by phosphate amendments: soil. CLEAN—Soil, Air, Water. 2016;44(5):572–8. https://doi.org/10.1002/clen.201300827.
89. Vantelon D, Lanzirotti A, Scheinost AC, Kretzschmar R. Spatial distribution and speciation of lead around corroding bullets in a shooting range soil studied by micro-X-ray fluorescence and absorption spectroscopy. Environ Sci Technol. 2005;39(13):4808–15. https://doi.org/10.1021/es0482740.
90. Vithanage M, Herath I, Almaroai YA, Rajapaksha AU, Huang L, Sung J-K, et al. Effects of carbon nanotube and biochar on bioavailability of Pb, Cu and Sb in multi-metal contaminated soil. Environmental Geochemistry and Health. 2017;39(6):1409–20.
91. Wang Z, Liu G, Zheng H, Li F, Ngo HH, Guo W, et al. Investigating the mechanisms of biochar's removal of lead from solution. Bioresour Technol. 2015;177:308–17. https://doi.org/10.1016/j.biortech.2014.11.077.
92. Xie ZM, Chen J, Naidu R. Not all phosphate fertilizers immobilize lead in soils. Water Air Soil Pollut. 2013;224(12) https://doi.org/10.1007/s11270-013-1712-0.
93. Yan K, Dong Z, Wijayawardena MAA, Liu Y, Naidu R, Semple K. Measurement of soil lead bioavailability and influence of soil types and properties: a review. Chemosphere. 2017;184:27–42. https://doi.org/10.1016/j.chemosphere.2017.05.143.
94. Yan Y, Qi F, Seshadri B, Xu Y, Hou J, Ok YS, et al. Utilization of phosphorus loaded alkaline residue to immobilize lead in a shooting range soil. Chemosphere. 2016;162:315–23. https://doi.org/10.1016/j.chemosphere.2016.07.068.
95. Yin X, Saha UK, Ma LQ. Effectiveness of best management practices in reducing Pb-bullet weathering in a shooting range in Florida. J Hazard Mater. 2010;179(1–3):895–900. https://doi.org/10.1016/j.jhazmat.2010.03.089.
96. Yoo J-C, Shin Y-J, Kim E-J, Yang J-S, Baek K. Extraction mechanism of lead from shooting range soil by ferric salts. Process Saf Environ Prot. 2016;103:174–82. https://doi.org/10.1016/j.psep.2016.07.002.