Lead in Soil

August 2020 www.epa.gov/lead

Lead naturally occurs in soil at low levels. Hundreds of years of human activities have contributed to increased levels of lead in soil, especially in and around urban areas and near older homes. Lead does not breakdown over time, so lead deposited in the past can still be a problem today. Lead in soil can contribute to overall environmental lead exposure. Other sources of environmental lead exposure include chipping lead-based paint, lead contaminated dust, and lead in drinking water.

Exposure to lead is a health concern[1], especially for young children and pregnant women. Lead can affect almost every organ and system in your body. The nervous system is the main target for lead poisoning in children and adults. Exposure to lead can cause developmental effects in children, including but not limited to reduced IQ and attention span, hyperactivity, impaired growth, and learning disability.

Sources of Lead in Soil

Higher levels of lead are found in soil:

- Near roadways as a result of air emissions from vehicles that used leaded gasoline
- Near the perimeter of buildings that used lead paint that deteriorated as chips and dusts, or from past renovation activities

Lead may also be found at high levels in soil near toxic waste sites and other areas close to industrial sites that release lead into the environment.

Exposure to Lead in Soil

Children and adults can be exposed to lead in soil through:

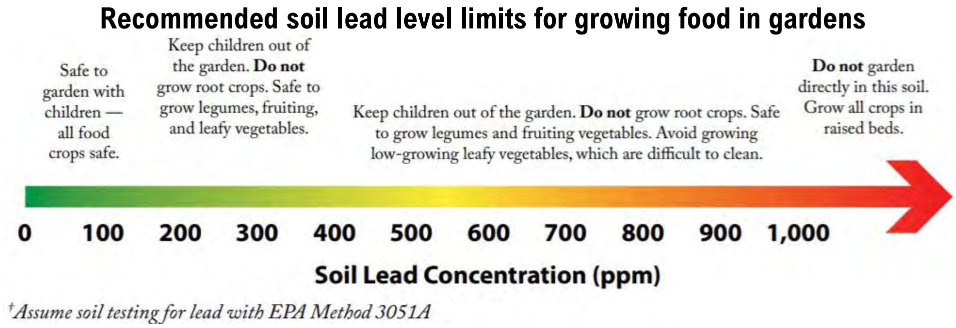
- Playing in bare soil
- Gardening
- Eating fruits and vegetables grown in contaminated soil
- Ingesting soil
- Touching hands to mouths (typical in young children)

Testing Soil

Soil can be tested for lead in several ways. The primary approach is to send samples to a laboratory that can identify the concentration of lead in the soil. Most laboratories associated with State university agricultural departments and agricultural extension offices offer soil testing for lead at cost. You may choose to contact a laboratory recognized under EPA's National Lead Laboratory Accreditation Program[2] (NLLAP) for lead paint chip, dust or soil sample analysis. You may also hear of an opportunity to have your soil screened for lead at "soilSHOP"[3] events where organizers use an instrument called an x-ray fluorescence (XRF) meter to quickly estimate the concentration of lead in the soil sample. A certified lead risk assessor can also identify lead hazards in soil. For help finding a lead risk assessor, call the National Lead Information Center at 1-800-424-LEAD (5323).

Interpreting soil lead results can be challenging. There is no single threshold that defines acceptable levels of lead in soil. State and federal regulatory and guidance values may only address specific situations and are mostly focused on cleaning up industrial properties.

[1] www.atsdr.cdc.gov/toxfaqs/TF.asp?id=93&tid=22
[2] www.epa.gov/lead/national-lead-laboratory-accreditation-program-list
[3] www.atsdr.cdc.gov/soilshop/index.html



From Kansas State University Agricultural Experiment Station and Cooperative Extension Service, and adopted by the Penn State Cooperative Extension Service

Depending on where you live, it is common to find lead levels in your yard or garden at or above guidance values. This is generally not cause for alarm as there are ways to reduce exposure to lead in soil. EPA defines a soil lead hazard as bare soil on residential real property or on the property of a child-occupied facility that contains total lead equal to or exceeding 400 parts per million (ppm) in a play area, or an average of 1,200 parts per million of bare soil in the rest of the yard based on soil samples. States may have their own values. You may decide to take a cautious approach if children routinely come in contact with soils that contain (or are suspected of containing) elevated levels of lead.

It is important to keep in mind that the results for one or two samples collected from your yard do not necessarily represent soil levels throughout the yard. Soil is highly variable and lead concentrations can be quite different even in samples collected from one or two feet of each other. If you are concerned about your soil lead results, consider contacting your cooperative extension service, public health department, or gardening organization to discuss the issue and next steps. Note that testing results identifying a soil-lead hazard at pre-1978 properties are records that must be retained and disclosed to future tenants/buyers in accordance with the Lead Disclosure Rule[4].

Recommendations to Reduce Contamination and Exposure to Lead in Soil

It is important to research the prior usage of your property and the surrounding area[5], especially before planning a community garden or recreational area. There are numerous options to reduce exposure to lead in soil, including:

- Cover contaminated soil with a thick layer of clean soil, vegetation, mulch or other materials.
- Limit access to more contaminated areas.
- Keep soil outdoors by using doormats, taking off shoes, and other lead-safe cleaning practices.
- Reduce exposure from pets that go outside by maintaining proper pet hygiene.
- Wash produce well, peel root crops, and discard outer leaves of leafy vegetables. Consider growing ornamental plants instead of food crops.
- Wear gloves or wash hands and other exposed skin areas after coming into contact with soil.
- Wash clothes after coming in contact with soil/dust separately from other clothes.
- Prevent children from playing in bare soil and watch children carefully to prevent them from eating soil.
- Wash toys and pacifiers frequently.
- Avoid growing produce directly adjacent to buildings, where lead levels are likely highest.
- Build raised beds with clean soil to grow food crops in more contaminated areas.
- Hire lead abatement contractors to remove or permanently cover the soil.

[4] www.epa.gov/lead/real-estate-disclosures-about-potential-lead-hazards
[5] www.epa.gov/sites/production/files/2015-09/documents/bf_urban_ag.pdf

Lead Toxicity

Cover Page

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Key Concepts

- Lead poisoning is a completely preventable disease.
- No safe blood lead level (BLL) threshold for children has been identified.
- Blood lead levels once considered safe are now demonstrated to be hazardous.
- Children of all races and ethnic origins are at risk of lead toxicity throughout the United States.
- Lead may cause irreversible neurological damage as well as renal disease, cardiovascular effects, and reproductive toxicity.
- Lead is one of the most commonly found hazards at Superfund sites.
- This case study is focused on lead exposure in the United States; exposures globally may vary.
- Primary prevention of lead exposure is the most important and significant strategy to protect children and adults from lead exposures.
- Families, service providers, advocates, and public officials need to be educated on primary prevention of lead exposure in homes and other facilities occupied by children so that lead hazards are eliminated before exposure occurs.

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This educational case study document is one in a series Other ATSDR of self-instructional modules designed to increase the Case Studies primary health care provider's knowledge of hazardous in substances in the environment and to promote medical Environmental practices that aid in the prevention, evaluation and care Medicine of potentially exposed patients. The complete series of ATSDR Case Studies in Environmental Medicine is located on the ATSDR Web site at URL: https://www.atsdr.cdc.gov/csem/csem.html. In addition, the downloadable PDF version of this educational series and other environmental medicine materials provides content in an electronic, printable format, especially for those who may lack adequate Internet service.

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Lead and lead toxicity in domestic and free living birds

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REVIEW

Lead and lead toxicity in domestic and free living birds

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At present, domestic and wild fauna are being exposed to aspects and factors which are foreign to the habitat in which they live. One that stands out is the enormous amount and variety of chemical compounds which, in many cases, are highly complex and which are constantly being released into the atmosphere, mainly from agricultural and industrial activity. All these substances affect some species more than others, whether they be plants or animals, from the most insignificant micro-organism to the most evolved species, among them birds. Finally, another cause of mortality in many birds is plumbism, namely death caused by the ingestion of lead. Lead has been one of the main causes of poisoning in man since ancient times due to its use in many activities although it is only recently that this toxicity has been recognized. Moreover, the use of lead pellets for shooting has resulted in the release into the environment of millions of these over many years, with serious repercussions for many bird species populations, which have ingested them either directly or indirectly. Added to this use of lead in cynegetic activities is the fate of the lead weights (sinkers or ballast) used by rod fishers, which sink to the bottom or accumulate on the banks of rivers, lakes, lagoons or reservoirs. The problem arises when these pellets or weights are ingested by birds, mainly *Anatidae*, which mistake them for the small stones or grit they use to triturate food in their gizzards. Small particles of lead enter the digestive tract, start dissolving in the form of lead salts, are incorporated into the bloodstream and the rest of the body, accumulate in organs like the liver or kidneys, and cause physiological or behavioural changes. When certain concentrations of lead are reached, the birds then die. If lead-poisoned birds are consumed by carrions or predators, the latter also ingest the lead so that they may also be affected or die from plumbism since, being a heavy metal, its degradation and/or elimination is very difficult. There is, therefore, no doubt that millions of birds die annually worldwide from lead poisoning (in the U.S.A., around 3 000 000), this problem being most acute in marshland. The solutions could include the introduction of legislation regulating or banning shooting, in the use of non-toxic ammunition in marshes and protected areas, the substitution of lead pellets for other non-toxic ones, such as steel, bismuth, tungsten or other suitable metals, and to go on studying other possible alternatives to end such a dramatic situation for birds all over the world.

Introduction

Lead poisoning is one of the intoxications most frequently found in the environment, mainly as a result of many years of man's cynegetic activity and ever since lead cartridges have been used for ammunition, this being a heavy metal with an evident toxicity.

Lead is one of the most toxic metals known and its negative effects range from slight biochemical or physiological disorders to serious pathological conditions, in which some organs and systems can be damaged or have their functions altered, according to the degree of exposure. Death from plumbism or saturnism is at present an unusual phenomenon in humans, although not so in domestic and free-living animals for which plumbism remains one of the major causes of death. This is especially significant in the case of birds, with

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several million deaths from lead poisoning estimated annually (in the U.S.A. alone, 1.5–3 million waterfowl) (U.S. Fish & Wildlife Service, 1990).

Although it is possible to resolve this problem, only some countries have taken corrective measures in this direction.

General characteristics of lead

Lead is highly resistant to corrosion and easily forms alloys and both organic and inorganic salts, the majority of which have a very low solubility. Except for nitrates and chlorides, which are much more soluble, lead has a great tendency to bind with organic ligands (Whitten *et al*., 1987).

The best known compound formed by lead is lead tetraethyl, an organic compound used in leaded petrol for cars, although this petrol type is now being eliminated because of its great toxicity.

Lead, for its special characteristics, has been used since ancient times, either pure or in alloys with other metals for many applications: in the manufacture of water pipes, coins, weights, printing typeface, and for the manufacture of armour and ammunition or in the extraction of silver (argentiferous lead). It has also been used in glazing for windows and roofs (leaded glazing), in toy manufacturing, in chemical industry material manufacturing (storage tanks or sulphuric acid transportation), in electricity material (fuses, wire coating, accumulators), in radiation protection (mainly X-rays), for noise and vibration insulation, or for welding, in paint manufacture, and it has an important use in the car industry, both in batteries and in petrol additives to prevent uncontrolled explosions generated by CH_2^- radicals as lead prevents their formation (Whitten *et al*., 1987).

Another application of lead has been in cynegetic activities, in which for many years lead cartridges have been used and left scattered about the countryside and wetlands (International Waterfowl and Wetlands Research Bureau, 1990; Pain, 1992; Guitart *et al*., 1994).

The toxic characteristics of lead and its compounds have been well known for years so that works have appeared describing the symptomatology resulting from exposure to lead or some of its by-products. In general, the toxicity of heavy elements is generated by their great tendency to bind to the phosphorus atoms present in the organism's molecules (Whitten *et al*., 1987; Body *et al*., 1991).

How lead affects birds

Birds have always been exposed to all types of toxic substances from the atmosphere in which they live so that they have had to adapt to the changes produced by those substances, which is part of the evolutionary process. However, harmful human activities have significantly increased the risk of intoxications from different products which, added to the destruction and fragmentation of their habitats, have taken many species to the brink of extinction. However, the case of plumbism in free-living birds is a fairly usual phenomenon, especially affecting marshes and, in particular, waterfowl (Bellrose, 1959). This type of mortality does not manifest itself very conspicuously and is highly difficult to detect, so that it has become known as the "invisible" bird disease, causing millions of bird deaths every year (U.S. Fish & Wildlife Service, 1990). Most hunters have no evidence that lead has caused the birds' death, a fact that has triggered much controversy. However, others, more sensitive to the cause, and groups of bird lovers, have proposed the exclusive use of non-toxic ammunition with steel pellets (U.S. Fish & Wildlife Service, 1990).

Lead in the environment

The main lead source for birds is the oral ingestion of lead from shotgun pellets. However, the hydrosphere, the natural environment of most free-living waterfowl, may also be contaminated by this metal from marine aerosols, wind-carried dust, or from an anthropogenic source such as mining, or the extraction of lead from lead sulphide ($PbS + 2O_2 \rightarrow Pb^{2+} + SO_4^{2-}$) in which not all the lead is extracted so that it can accumulate in the tips and reach the fluvial systems dragged along by the runoff. However, amounts of lead which are sufficient to present a risk can also remain accumulated in the soil, as in areas where, year after year, clay pigeon shooting competitions are held (Jorgensen & Willems, 1987).

Lead particles become more rapidly degraded when the soil or water are acidic or have a greater concentration of dissolved oxygen. Lead particles can dissolve in soil water and be assimilated by plants, generating alterations when the concentration exceeds certain limits, or can affect the herbivorous animals that consume them (Pain, 1992; Manninen & Tansakanen, 1993). Also, the lead particles can reach other areas due to erosion or to runoff. Furthermore, lead concentration in rivers is greater than in the sea. Lead in water is found in partially soluble ($PbCl_2$) or insoluble ($PbCO_3$) species.

The solubility of lead aerosols is around 90%, of which the majority are soluble and that solubility increases as the size of the particle is reduced. At the same time, lead is a common heavy element in the atmosphere's sediments, normally in an insoluble form such as carbonate ($PbCO_3$), sulphate ($PbSO_4$) and sulphur (PbS) (Whitten, 1987; Manninen & Tansakanen, 1993).

In the wetlands of many countries, hunting has been carried on for many years. The beginning of the use of lead ammunition led to the accumulation of lead pellets, together with the lead weights lost or thrown away by rod and line fishermen, in the depths and around the watery areas (Pain, 1992; Scheuhammer, 1991). Moreover, this metal takes between 100 and 300 years to become degraded and disappear completely from the ecosystems (depending on the climatic and environmental conditions). Taking into account that one cartridge holds about 280 pellets and that each cartridge weighs approximately 35 g, that more than one shot is necessary to shoot a waterfowl and that only a few pellets actually hit the animal, it can be estimated that over 1,000 pellets go astray into the water or onto the banks per shot (U.S. Fish & Wildlife Service, 1990). Added to that, every season more or less fixed target points are used, so that it is possible to approximately calculate the millions of pellets that may have accumulated in these areas. Thus, in Canada, it is estimated that hunters leave around 2,000 tons of lead pellets annually in the environment (Scheuhammer, 1991), with several hundred thousand per hectare in the first 20 cm of the soil, to which some long-billed birds can have access, reaching figures of between 40,000 and 180,000 lead pellets per hectare or even some wetlands with over 300,000 pellets per hectare (Mateo *et al*., 1994a). At present, the figure stands at about 2 billion pellets every year between hunting and recreational shooting, worldwide.

Birds use tiny stones, called gastrolites or grit, to help them to triturate food in their gizzards. At the same time, they may swallow the pellets (especially if the habitat has a deficit of these stones, as is often the case) accumulated in the substrate, as their diameter is very similar (Friend, 1987). Also, the different waterfowl species living in this type of ecosystem have different feeding and behavioural habits. The diving species which search for food by plunging their bills into the mud, together with the granivorous birds, are more likely to ingest pellets and suffer lead poisoning than those feeding on plants on the banks (Bellrose, 1959).

It can be affirmed that, within the waterfowl groups, those most affected on a world scale by this type of intoxication are the *Anseriformes* (ducks, geese and swans) (Pain, 1992; Blus *et al*., 1989), although waterfowl are not the only ones. Another important group often implicated, although considerably less so, are the predators, both captive and wild. In this case, the cause of poisoning is different and comes from the ingestion of lead in the animals (ducks, rabbits, hares, partridges, etc.) shot by hunters and left behind so that, badly injured, they are easy targets for birds of prey. The lead ingested is easily soluble because the pH in the predators' ventricle reaches around 1.0 and 2.0 (Benson *et al*., 1974).

In some cases, domestic species with clear symptoms of lead poisoning have also been recorded, such as pigeons (*Columba livia*) found in most cities and towns everywhere. This has been explained by the likelihood of their having inhaled fumes from car exhaust pipes, which contain lead particles coming from petrol (González & Tejedor, 1991).

Lead is circulated round the body by blood and accumulates in bones and vital organs (liver, kidneys, etc.), which can therefore be greatly harmed. However, lead may be mobilized later during times of bone demineralization (egg laying or in certain metabolic states) and lead to a toxic episode (Hartup, 1996). Moreover, there are two types of lead poisoning: acute, when it appears in birds ingesting a large amount (over 6 pellets) in a short time, causing their death in a few days; and chronic, when the birds consume only a small number of pellets or a relatively longer period of time elapses, and the birds gradually become weak and usually die of starvation (this occurs because the digestive system becomes paralysed) (Pain, 1992; Scheuhammer, 1991).

The toxic effects produced by the presence of lead pellets in the gizzard are similar, regardless of the intoxication route. However, when they are embedded subcutaneously or intramuscularly, no plumbism occurs since the pH conditions do not permit the dissolution of the lead.

Symptomatology of plumbism in birds

Plumbism is not contagious and the birds contract it individually taking about 3 weeks to die. The lead pellets accumulate in the gizzard, where they are slowly worn down (the metal is fairly soft) as they collide against the gastrolites present. At the same time, different acids facilitating the digestion of the food are released (among them, hydrochloric acid, HCl) causing a slow dissolution of the lead. The lead salts formed enter the stomach, then the intestine, where they are absorbed by the bloodstream, thereafter reaching the bird's tissues and organs. Within a few days, the poisoning symptoms start to appear (Lumeij, 1985; Friend, 1987). Externally, the birds show signs of abnormal behaviour, such as landing accidents. They also have anatomical malformations like unusual positions of the head and/or neck or vocal changes (high-pitched honk). The cloacal feathers turn green as a result of intense green-coloured diarrhoea (a very characteristic symptom) (Friend, 1985; Sowden, 1988). After 2 weeks, there is a paralysis of the digestive tract preventing the digestion of any food ingested. This makes the birds become very weak, with the consequent difficulty in flying, or even walking (they often appear to stagger). Their wing (primary) tips also usually trail on the ground or float in the water. As the days go by there is a progressive paralysis of the wing and claw muscles so that they can no longer walk (Jordan & Bellrose, 1951). Under these circumstances, the birds become very easy targets for the predators, which frequently swoop down on the weakest individuals.

Many individuals with poisoning symptoms remain isolated out of the water, or hide in the thick vegetation or between the rocks until their reserves are exhausted and they die. In the case of migratory species, the poisoned individuals remain behind or stay in the wetlands when their congeners have already migrated (Friend, 1985; Sowden, 1988). Other symptoms are loss of weight and of appetite (Jordan & Bellrose, 1951), although some authors do not see any direct relation between weight loss and lead poisoning (Anderson, 1975), but report that some birds with clear signs of plumbism have ingested food a short time before dying (Beer & Stanley, 1965). A prominent sternum is also a symptom (U.S. Fish & Wildlife Service, 1990), as is vomiting, and, occasionally, a yellowish dribble from the beak. Sometimes the bird's beak may remain half-open for a long time or even a slight rattle can be heard coming from its throat. In advanced phases there may be convulsions, and even blindness (Labonde, 1991). In some cases, the ingestion of lead pellets does not cause death and the birds manage to survive although, generally, with some type of sequela. In fact, the lead-poisoned birds' inability to find a mate, to build a nest at mating time, to lay eggs or to care for their young, has been reported (Pain, 1992). However, in spite of the different clinical symptoms of plumbism, researchers cannot always be absolutely certain that a bird has died from this cause. Many of them can only be observed with a necropsy.

Diagnosis and treatment of plumbism

Before diagnosing the disease in the birds, a careful examination of the external symptomatology should be carried out, with subsequently more exhaustive analyses, using different techniques, some of which can even be used on live birds. These tests range from the simple observation of the presence of pellets in the gizzard to those based on the analysis of haematological (anaemia, basophilic speckling in erythrocytes and diverse forms of poikilocytes), gastrointestinal and neurological symptoms. Thus, an analysis of the gizzard of apparently affected birds will reveal how its inside coating is black, soft to the touch, with signs of putrefaction and how it easily comes away and is inflamed, corroded and, very often, incomplete. The proventricle is usually also dilated and thin (Sanderson & Bellrose, 1986).

Another type of complementary test is the detection of lead particles in the digestive tract by radiological examinations or biochemical blood tests (there is an increase in the activity of diffeent enzymes). Indeed, some studies have concluded that of 35,000 birds shot by US hunters studied, 6.6% contained pellets in the gizzard (Bellrose, 1959; U.S. Fish & Wildlife Service, 1990). This figure is exceeded in European and Mediterranean wetlands, which implies that here the problem may get worse (Pain, 1992).

However, it is not always easy to detect plumbism at first sight or with radiological analyses since, in many cases, the pellets embedded in the gizzard are very worn and it is difficult to discern if the particles are lead or some other metal, and they may often even be regurgitated by the birds (Hovette, 1972; Pattee *et al*., 1981) or expelled anally (Hovette, 1972). Moreover, this is a costly test with a limited availability because of the need to transport them to where there are X-ray facilities (Furness & Robel, 1989).

Blood sample analysis is a determining factor when evaluating any increase in lead toxicity in waterfowl. At present, assays of diagnosis methods applied to other animal species, and even in humans, are being carried out. These methods are based on the influence of the lead on the biological synthesis of the haemo group, which may affect one of its stages. The technique most used is the valuation of the activity in the blood (this can also be observed in the brain or in the liver) of the enzyme d-ALA-d (d-aminolevulinate dehydratase or porphobilinogen synthetase) (Friend, 1985). This fairly simple and highly sensitive technique consists of directly measuring the enzymatic activity and comparing it with that obtained after reactivation (Pain, 1989a; Scheuhammer, 1989). Lead inhibits the activity of the d-ALA-d (alosteric enzyme with 28 thiol groups in its molecule) (Pain, 1989b), producing the accumulation of the enzyme's substrate (d-aminolevulinic acid, d-ALA), which is used as a form of a diagnosis in other animals and in humans based on the accumulation of this substance in urine. However, because of its difficulty, it is not applied in birds (Lumeij, 1985; Humphreys, 1990).

The level in blood of lead considered as being toxic (but sublethal) is 0.5 ppm, although from 0.2 on the toxicity symptoms begin to appear (U.S. Fish & Wildlife Service, 1990). Some researchers have determined that a considerable number of birds with lead concentrations of ≥ 0.5 ppm show a significant decline in the enzyme d-ALA-d, which may result in brain damage, so that the damage to the biochemical processes produced in the brain are previous to some external symptoms of the poisoned birds, such as collapsed wings. This can be reversed by using other metals, like zinc. Also, lead can also inhibit the function of the enzyme ferrochelatase (or haemosynthetase), which consists of binding the iron to the substrate of that enzyme (protoporphyrin), thus producing the accumulation of the free substrate or its binding with other metals like zinc (Lumeij, 1985; Pain, 1989a). An increase in levels of protoporphyrin in the blood in lead-poisoned birds has been recorded, so that their determination could be an indirect indicator of the amount of lead in the blood (Roscoe *et al*., 1975). If they are over 40 ppm, this is a clear proof of lead poisoning, and if over 500 ppm, the nervous system controlling the muscular activity may be affected with a consequent alteration in the motor functions (Roscoe *et al*., 1975).

Subsequent comparisons can be made using analytical techniques such as haematofluorimetry. This is a simple, inexpensive technique although it is not excessively precise or sensitive (Pain, 1989b; Scheuhammer, 1989).

However, the technique most used by workers, for its reliability, has been a diagnosis based on the measurement of the lead in tissues and organs. It is a relatively costly method and is based on the analysis of the blood of samples of live birds and, basically, on hepatic analyses (or secondly of the kidneys or the spleen), or bone analysis in the case of dead individuals (White & Stendell, 1977; Anderson, 1975). A short while after ingesting the pellets, the presence of the lead in the birds' wing bones can be found. Indeed, some ducks which had ejected some pellet remains from the digestive tract did not have any lead in the gizzard, but some lead residues were retained in the wing bones (Anderson, 1975). Thus, in a 1972–73 study, wing bones were collected from thousands of ducks with the result that those from the adults contained 2 times more lead than the wing bones of young ducks (Stendell *et al*., 1979), so that it is possible to be prove signs of plumbism in *Anatidae* when the lead concentration is over 1.5 mg/g lead on fresh weight (5.5 mg/g dry weight). However, although the lead content value in bones is of special overall importance, the determination of lead levels in bones is not really recommendable, since these are mainly due to a chronic type of poisoning (Friend, 1985; Pain, 1989a). If the measurement is taken from a blood analysis, plumbism can be confirmed at concentrations of over 0.2 mg/ml, although at an exposure of over 0.05 mg/ml, the abnormal effects caused by the lead begin to be noticed.

Methods frequently used to determine poisoning in birds have been the analysis of the liver, and, secondly, of other organs like the kidneys or the spleen. In some analyses of lead-poisoned birds (geese), average levels of lead of 102 ppm in the liver, 125 ppm in the kidney and 41 ppm in the wing bones (dry weight) were obtained, with a high correlation between the liver and kidney values (Szymczak & Adrian, 1978). The top values of lead in the liver are highly variable, although 8 ppm onwards (fresh weight) can be taken as being a clear diagnosis value of lead poisoning (Friend, 1985). With regard to limit values in other organs such as the kidney, values of between 6–20 ppm (fresh weight) have been given (Longcore *et al*., 1974; Humphreys, 1990; Scheuhammer, 1991).

Another common symptom in birds with plumbism is anaemia. Mainly responsible for this is the production of damaged and defective red corpuscles, producing a *haemosiderosis*, which normally appears in the liver, kidneys and spleen of the poisoned birds (Beer & Stanley, 1965).

The effect of plumbism on certain organs differs depending on the species, the degree of poisoning and its nature (acute or chronic). Likewise, it has also been seen how lead has an effect on the size of certain organs (liver, kidneys, heart, spleen), which are sometimes smaller than normal in poisoned birds (Jordan & Bellrose, 1951), although this is not a determining factor since some studies contradict this finding.

Treatment of affected birds

The simplest method for treating lead poisoning consists of extracting the lead pellets from the gizzard, although this is not an easy process and has to be done quickly to prevent the lead from entering the organism (Degernes *et al*., 1990).

Treatment should follow the following guidelines: decrease absorption, eliminate absorbed toxin, and support the patient. Conservative approaches to aid elimination of lead pellets include oral administration of mineral oil, corn oil, sodium sulfate (Glauber's salts) or 1% psyllium mixture. Use of activated charcoal (2–8 g/Kg) prior to administration of cathartics may help bind small particles of heavy metal. More intensive techniques such as gastric lavage, endoscopic retrieval and ventriculotomy should be reserved for those birds able to withstand surgical anesthesia or for which conservative approaches were unsuccessful (Hartup, 1996).

The extraction of pellets from the stomach muscle generally requires an expert and suitable facilities. Stomach pumping is probably the method most used and requires suction intubation, or the withdrawal of the pellet by regurgitation, for which is used a solution of 5% hydrosoluble vegetable fibre (Metamucil) with anaesthetic (generally isoflurane) and assisted respiration. As an alternative, in some cases a fibroendoscopy, and in other very difficult ones gastric surgery, have been performed (Degernes *et al*., 1990).

When the lead has entered the bloodstream and reached the different tissues and organs, its detection and elimination is more difficult. For that reason, the most suitable treatment is the use of chelating compounds which adsorb the lead particles by excreting them, mainly in the urine. The one most used is EDTA (tetraacetic ethylendiamin acid) although others sometimes used are DTPA (pentaacetic diethylentryiamin), DMSA (2,3-dimercaptosuccinic acid), BAL (dimercaprol) or D-penicillamin. The chelating agents have a variable stability depending on the atom, which acts as a coordination centre, and the nature of the chelating agent itself. EDTA is administered in the form of calcic diasodic salt (EDTA $CaNa_2$) intravenously using a dose of between 20 and 70 mg/Kg diluted at 1:4 in physiological serum (Redig, 1987; Degernes *et al*., 1990). The Ca-EDTA administered intravenously is used to diagnose the presence of heavy metals. If any lead-poisoned bird is injected with Ca-EDTA, the symptoms do not reappear for 48 hours. Several intraperitoneal injections of Ca-EDTA in a 6.6% solution enable the ducks to recover their appetites and be revitalized. However, D-penicillamine (PA) is an alternative chelator that can be used orally (55 mg/kg twice daily). Combined therapy with both PA and Ca-EDTA for several days followed by the use of PA for 3 to 6 weeks may be superior to Ca-EDTA alone.

A solution of 5% dextrose or a solution of ringer lactate during 3 to 7 days, two or three times a day, is also used, continuing the treatment until the lead levels in the blood drop to normal levels (< 0.04 ppm), probably lasting for several weeks (Redig, 1987; Sowden, 1988; Degernes *et al*., 1990). X-rays are usually taken to verify the elimination of the pellets. However, although intravenous injections are the most effective, veterinarians recommend intramuscular ones. The EDTA-Pb complex is mainly excreted through the kidneys so that it is recommendable to discontinue the injections for a few days because of the nephrotoxicity of EDTA, otherwise the lead salts are again dispersed throughout the tissues and organs from the kidneys.

A treatment therapy can also be used encouraging rehydration of the bird by administering fluids orally, such as glucose solutions, or intravenously or instraossicularly, using solutions like 5% glucose or ringer lactate (Degernes *et al*., 1990). If signs of anorexia are observed, the bird should be obliged to consume triturated food (Degernes *et al*., 1990). Nevertheless, it must be realized that liquids should be administered with care because the birds' renal system is unable to process large quantities of them at a fast rate.

In order to control possible convulsions diazepam can be given, as well as steroids like dexametazone to prevent cerebral oedemas and anabolic steroids like estanozol (Sowden, 1988; Labonde, 1988).

As a prophylactic measure to prevent aspergillosis, could supply 5-fluorocitosin PO (Degernes *et al*., 1990). In certain cases, it is recommendable to administer an antibiotic such as chloranphenicol or ampicillin. Intramuscular injections of multivitaminic complexes B may stimulate the birds' appetite and it appears that vitamin B1 (thiamin) prevents the accumulation of lead in the soft tissues. Selenium can also protect the thyroid gland from the effects of the lead.

An intramuscular injection of iron-dextrane is also indicated in birds with low haematocrit values (Labonde, 1988; Degernes *et al*., 1990).

Plumbism in marshes

In some parts of Europe and North America, the problem caused by the ingestion of lead pellets by birds is of a considerable magnitude, taking into account that hunting is a great tradition and seeing that every year millions of hunting licences are issued. Moreover, it is very important to consider the singularity and vulnerability of wetlands since, apart from having a multitude of advantages and functions (flood control, coast stabilization, water purification, etc.), they signify an incredible reservoir of biodiversity, as well as being real "oases" for many migratory birds.

Studies on plumbism in waterfowl are not new, as the first cases were recorded at the end of the nineteenth century (Calvert, 1876; Grinnell, 1894). In some wetlands the data obtained have been conclusive, with a range of lead pellet concentration in the 20 first cms of soil of between 6 and 54 pellets/m^2 in the different areas sampled. Indeed, a good plumbism indicator species because of being spread world-wide is the mallard (*Anas platyrhynchos*), 27% of whose population was found to be affected by it. If these data are extrapolated on a world scale the figure becomes extremely high (Guitart *et al*., 1994). In other later studies, equally alarming results were obtained (Mateo *et al*., 1994b).

In the present study, and with regard to the prevalence of the intoxication, it is worth highlighting the very high values detected for the pintail (*Anas acuta*) and the pochard (*Aythya ferina*), with values nearing or over 70% and, also, the notably high values of the teal (*Anas crecca*), mallard (*Anas platyrhynchos*), the shoveler (*Anas clypeata*) and the red-crested pochard (*Netta rufina*) (Table 1).

The presence of pellets in the habitats of birds being the source of poisoning, it is not surprising that the high lead concentrations in our wetlands consequently results in high poisoning rates in the birds captured.

It seems to be confirmed at any rate that the Mediterranean area is, on the whole, the one most affected by the problem of plumbism, and it is suggestive that attributed to this is the notable reduction in the populations of certain species detected in the past few years, during which the bird plumbism figures have significantly increased. This has been demonstrated in France and in other countries (Pain *et al*., 1992).

Table 1. *Average frequency of appearance of pellets in gizzards of waterfowl shot*[a]

Species	Number of samples examined	Pellets in gizzard (%)
Greylag goose (*Anser anser*)	20	10.0
Wigeon (*Anas penelope*)	28	3.6
Gadwell (*Anas strepera*)	27	11.1
Teal (*Anal crecca*)	58	17.2
Mallard (*Anas platyrhynchos*)	192	25.0
Pintail (*Anas acuta*)	89	73.0
Garganey (*Anas querquedula*)	2	0.0
Shoveler (*Anas clypeata*)	103	28.2
Red crested-pochard (*Netta rufina*)	78	12.8
Pochard (*Aythya ferina*)	42	76.2
Tufted duck (*Aythya fuligula*)	5	80.0
Coot (*Fulica atra*)	34	2.9
Snipe (*Gallinago gallinago*)	32	0.0

[a] Study realized between 1977 and 1995 in five important wetlands by Raimon Guitart and Rafael Mateo (Theoretical-Medical Course in Medicine and Surgery of wild birds, Faculty of Veterinary Medicine. UCM Madrid, October 1997).

On some occasions there have been cases of the poisoning of other bird types such as the flamingo (*Phoenicopterus sp.*), doubtless for their eating habits, as they constantly stir up the sediments of the water near the banks and filter the mud in search of food (invertebrates, seaweed, seeds, etc.), so they often ingest the pellets which have accumulated there. However, it is not frequent to find cases of massive mortality due to plumbism, as this pathology usually acts slowly and, even more so in species as singular and large as flamingos, although it does occasionally happen (Mateo *et al.*, 1994a; García *et al.*, 1998).

In some cases, to study those cases of mass mortality, it has been necessary to travel around on foot or by boat along the canals, reservoirs, pools or other watery areas in the vicinity of the marshes frequently used by the flamingos to pick up those dead or dying individuals (rejecting those that had been half devoured mostly by dogs or predators). Some fixed observations points were also set up. All the data obtained clearly points to the ingestion of lead pellets as the origin of the flamingo mortality (Mateo *et al.*, 1994b). Both the clinical symptomatology observed, coinciding with that previously described in this species, and the significant percentages of animals with pellets in the gizzard and high levels of lead in the liver does not leave room for any doubt (Ramo *et al.*, 1992). Cases of mass mortality in flamingos have been reported in all parts of the world (Schmitz *et al.*, 1990; Aguirre-Álvarez, 1989; Bayle *et al.*, 1986).

High mortality rates have been recorded in other bird groups such as the Canadian goose, poisoned by lead pellets ingested in cropping fields near the area they lived in (Szymczak & Adrian, 1978).

Another group that has suffered from poisoning from lead ingestion is that of birds of prey, many of which have their habitats in the marshes (lagoon eagles, bald eagles) although others only proceed there to find food. The species poisoned are those which prefer to base their food on prey wounded or killed by pellets and not recovered by hunters. On consuming these shot individuals, they inadvertently ingest the pellets. Currently, several cases of death from plumbism are known about in predators, including species like the golden eagle (*Aquila chrysaetos*), the Iberian imperial eagle (*Aquila adalberti*), the bald eagle (*Heliaaetus leucocephalus*) or the griffon vulture (*Gyps fulvus*) (Benson *et al.*, 1974; Pattee *et al.*, 1981).

In any event, with regard to the manner of poisoning, certain differences have been noted between the waterfowl and the birds of prey. While the former ingest the pellets mainly in their watery habitats, the latter cover a much wider territory so that their pellet ingestion cannot be circumscribed to specific areas and can occur as much in marshes by consuming a shot duck as in a game shooting estate by eating some animal that has been shot and left behind there (rabbits, partridges, pigeons, thrushes, etc.). Furthermore, although some countries have banned the use of lead pellets in their wetlands (Pain, 1989b; U.S. Fish & Wildlife Service, 1990; Canadian Wildlife Service, 1990) the millions of pellets lying around there from the many years of shooting enable the waterfowl to go on being poisoned. The poisoning in birds of prey, however, has sharply declined (Table 2).

Solutions to plumbism

The problem of plumbism is rife in most countries, although any reliable epidemiological data have only been obtained in about twenty of them, all of them industrialized ones (indicating a lack of the necessary facilities in other countries). In 1991, some decided to ban the use of lead pellets and substitute them for non toxic ones (steel, bismuth, etc.) in wetlands. Some northern and central European countries have already taken this step or are about to do so, as is the case of Norway, Finland, Holland, Denmark, Belgium, the United Kingdom, Germany or Sweden. The U.S.A., Canada, Mexico and Australia have taken measures in this regard (Vernon, 2001).

Table 2. *Relative frequency of intoxication from pellet ingestion in birds in the U.S.A.*[a]

Type of bird	Relative frequency
DUCKS	
Ducks in marshy area	very frequent
Esturary ducks	very frequent
Teal, Shoveler, tree ducks	rare
Wigeon	rare
Marine ducks	rare
Mergansers	rare
GEESE	
Canadian barnacle goose	rare
Nival goose and Ross goose	very frequent
Other geese	rare
SWANS	
Small swan	very frequent
Vulgar swan	frequent
Other swans	occasional
OTHER WATERFOWL	
Scolopacidae, Charadriidae	occasional
Coots and other rallidae	frequent
Gruidae	occasional
Gulls	occasional
Other species	rare
CYNEGETIC BIRDS	
Pheasants & quails	occasional
Turkey and tetraonides	rare
Pigeons	occasional
Woodcock	rare
PREDATORS	
Bald eagle	very frequent
Golden eagle	frequent
Other daytime predators	occasional
Night prey birds	rare

[a] M. Friend (1987).

For some time now, however, different types of steps have been taken to remedy the poisoning from lead pellets of waterfowl in marshes, in such a way that in some areas a relatively successful attempt has been made to prevent their ingestion by driving the birds away from those marshes contaminated with lead after the shooting season, or delimiting certain areas for shooting and periodically rotating them to ensure a lesser accumulation of pellets (Jordan & Bellrose, 1951). Another measure has been the scattering of gravel over the areas with a shortage of gastrolites (Osmer, 1940), so that the waterfowl have no alternative but to swallow the pellets. Currently, the most effective alternative is the use of steel pellets, although different assays have been performed with other materials.

Steel pellets obviously present different problems but this metal is considerably less harmful from an environmental and ecological viewpoint, although the hunting community have shown themselves to be reluctant to change, alleging problems like: that not all guns can be adapted to shooting them, that they ruin their guns, that the trajectory of the pellet with one metal or the other differs, that the steel pellet ricochets more easily than the lead one, many more birds are only injured and not killed outright or are not recoverable. Some experiments with lead and steel pellets demonstrated that the steel ones had a deficient killing ability at distances of over about 46 m (Bellrose, 1959). Later studies showed that improved steel pellets were more effective than lead ones at distances of over 46 m, although nowadays there are scarcely any significant differences between the two types of ammunition. As for the damage done to the guns by steel pellets, nowadays this concern is unfounded (U.S. Fish & Wildlife Service, 1990), so that this reason is not valid for rejecting the use of steel pellets.

Another argument against the use of steel pellets is the higher cost of cartridges for this type of ammunition. The difference, more than in the actual manufacture of these, is that the public is being overcharged for them. However, the more steel pellets are used by hunters, the more their price will tend to go down. At any rate, the slightly higher cost of the cartridges should not be a deterrent to their use, especially when considering that the decrease in waterfowl populations due to plumbism, as well as doing great harm to world biodiversity, could put an end to shooting activities. Two criteria should be taken into account in the hunters' decisions: that currently in some areas more individuals are dying from plumbism than from the direct effect of shooting, and that the benefits from the change will not have an immediate repercussion as the lead pellets used previously will remain in sediments as fatal traps for birds for many years.

Apart from steel, some countries such as the U.S.A. have experimented with other materials like bullets made with bismuth–tin and tungsten–plastic polymers, with very satisfactory results. Scientific tests have demonstrated that this type of pellet is not toxic for any component of the environment (Vernon, 2001).

Rod and line fishers also represent a certain hazard group as they use lead weights which are left around, thrown away, sink, and are mislaid on the banks of rivers, lakes and dams, with the resulting harm to waterfowl, and even to the ichtyofauna. Nowadays, weights made of other materials are available and, if acquired, can be of a great ecotoxological value.

The same independent legislative measures are being taken in many countries to attempt to partly resolve the problem of plumbism, the European Commission, aware of the increase in waterfowl and predator mortality due to poisoning, mainly from lead pellets, has issued some instructions to E.U. member countries recommending: the withdrawal of the use of lead pellets in marshland and waterfowl shooting areas; the promotion of a general change to the use of alternative ammunition; to establish a calendar for the substitution of lead pellets for alternative non toxic ones, so that manufacturers and distributors can co-ordinate their programming; to set up effective information sources, awareness and educational programmes before and after the establishment of lead pellet substitution programmes. Finally, it recommends the incoporation of the use of non-toxic ammunition by means of training programmes and examinations for hunters.

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RÉSUMÉ

Plomb et toxicité au plomb chez les oiseaux domestiques et en liberté

Actuellement, la faune sauvage et domestique est exposée à des aspects et facteurs qui sont étrangers à l'habitat dans lequel elle vit. Ce qui ressort, c'est la quantité énorme et la variété des produits chimiques qui, dans de nombreux cas, sont des complexes et sont issus des progrès scientifiques et technologiques constamment largués dans l'atmosphère, principalement dues à l'activité agricole et industrielle. Toutes ces substances affectent certaines espèces plus que d'autres, qu'elles soient animales ou végétales, des microorganismes aux espèces les plus évoluées et parmi elles les oiseaux. Finalement, une cause de mortalité chez de nombreux oiseaux est le saturnisme dû à une ingestion de plomb. Le plomb est l'une des causes principales d'intoxication chez l'homme depuis les temps anciens, de par son utilisation dans de nombreuses activités bien que cela fasse peu de temps que cette toxicité ait été reconnue. De plus, l'utilisation du plomb dans les cartouches pour la chasse en a libéré des millions dans l'atmosphère depuis des années et a eu des répercussions chez de nombreuses espèces d'oiseaux qui l'ont ingéré directement ou indirectement. En plus de l'utilisation du plomb dans les activités cynégétiques, ce sont les poids en plomb (hameçon ou lest) utilisés par les pêcheurs à la ligne, qui tombent dans le fond des rivières, lacs, lagons ou réservoirs ou sont accumulés sur les berges. Les problèmes arrivent quand ces plombs sont ingérés par les oiseaux, principalement les *Anatidae*, qu'ils prennent pour des petits cailloux ou du grit et qui leur servent à triturer la nourriture au niveau du gésier. De petites particules de plomb entrent dans le tractus digestif, commencent à se dissoudre sous forme de sels de plomb, sont incorporées dans le sang et le reste du corps, s'accumulent dans les organes tels le foie et les reins et causent des troubles physiologiques et du comportement. Quand certaines concentrations de plomb sont atteintes, les oiseaux meurent. Si les oiseaux empoisonnés au plomb sont consommés par des charognards ou des prédateurs, ces derniers ingèrent du plomb, ainsi ils peuvent également être affectés ou mourir de saturnisme puisque le plomb est un métal lourd, son élimination ou sa dégradation est très difficile. Il n'y a pas de doute que des millions d'oiseaux, par le monde, meurent annuellement d'intoxication par le plomb (environ 3 000 000 aux USA) ; ce problème étant plus grave dans les terrains marécageux. Les solutions peuvent être l'introduction d'une réglementation limitant ou interdisant la chasse en utilisant des munitions non toxiques dans les marais et aires protégées, la substitution des plombs de chasse par d'autres non toxiques comme l'acier, le bismuth, le tungstène ou autres métaux est d'étudier d'autres méthodes alternatives pour arrêter une telle situation dramatique pour tous les oiseaux du monde.

ZUSAMMENFASSUNG

Blei und seine Toxizität für domestizierte und freilebende Vögel

In der heutigen Zeit sind die domestizierte und die Wildfauna Fakoren ausgesetzt, die ursprünglich fremd sind für das Habitat, in dem sie leben. Vorrangig zu nennen ist die enorme Menge und Vielzahl chemischer Komponenten, die häufig hochgradig komplex sind. Sie stammen aus technologischen und Forschungseinrichtungen, von denen sie aufgrund landwirtschaftlicher und industrieller Aktivitäten konstant in die Atmosphäre abgegeben werden. Alle diese Substanzen beeinträchtigen einige Spezies mehr als andere, egal ob es Pflanzen oder Tiere sind; betroffen sein können alle vom unbedeutendsten Mikroorganismus bis zu den höchst entwickelten Arten, darunter auch die Vögel. So ist eine häufige Todesursache bei Vögeln eine chronische Bleivergiftung; die zu Todesfällen insbesondere nach Ingestion von Blei führen kann. Blei ist seit dem Altertum wegen seiner vielfältigen Verwendung eine der Hauptursachen für Vergiftungen des Menschen gewesen, obwohl diese Toxizität erst seit kurzem bekannt ist. Überdies hat die Verwendung von bleihaltigem Schrot für die Jagd zu ihrer millionenfachen Einbringung in die Umwelt geführt verbunden mit ernsthaften Auswirkungen auf viele Vogelarten, die diese direkt oder indirekt mit der Nahrung aufgenommen haben. Zusätzlich zu diesem Gebrauch von Blei bei agdlichen Aktivitäten kommt die Verwendung von Bleigewichten (Senker oder Ballst) durch Angler, die auf den Gewässerboden sinken oder an Ufern von Flüssen, Seen Lagunen oder Wasserreservaten angereichert werden. Daraus wird dann ein Problem, wenn diese Schrotkörner oder Gewichte von Vögeln, hauptsächlich *Anatidae,* aufgenommen werden, weil sie sie für kleine Steine oder Grit halten, die sie für die Futterzerreibung in ihren Muskelmägen benötigen. Kleine Bleipartikel gelangen in den Digestionstrakt, werden dort in Form von Bleisalzen gelöst, gelangen so in den Blutstrom und den Rest des Körpers, akkumulieren in Organen wie Leber und Niere und

verursachen Veränderungen in Physiologie und Verhalten. Bei Erreichen bestimmter Bleikonzentrationen sterben die Vögel. Wenn durch Blei vergiftete Vögel von Aasfressern oder Raubtieren gefressen werden, nehmen die Letzteren ebenfalls das Blei auf, so dass auch sie betroffen sein oder sogar an einer Bleivergiftung sterben können, da die Degradierung und/oder Eliminierung von Blei, weil es ein Schwermetall ist, sehr schwierig ist. Aus diesem Grund besteht kein Zweifel, dass weltweit jährlich Millionen von Vögeln an einer Bleivergiftung sterben (ca. 3 Millionen i den U.S.A.), wobei das Problem im Marschland am größten ist. Mögliche Lösungen für dieses Problem könnten sein die Einführung gesetzlicher Regulierungen oder ein Verbot für das Schießen, die Verwendung nicht toxischer Munition in Marschen und geschützten Arealen, der Austausch von Schrot aus Blei gegen ungiftigen Schrot aus Stahl, Bismuth, Wolfram oder anderen geeigneten Metallen und die Weiterführung von Studien über weitere mögliche Alternativen, um diese dramatische Situation für die Vögel auf der ganzen Welt zu beenden.

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Lead contamination in shooting range soils from abrasion of lead bullets and subsequent weathering

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Abstract

Contamination of shooting range soils from the use of Pb bullets is under increasing scrutiny. Past research on Pb contamination of shooting ranges has focused on weathering reactions of Pb bullets in soil. The objective of this study was to determine the significance of abrasion of Pb bullets in contributing to soil Pb contamination. This was accomplished by firing a known mass of bullets into sand and analyzing for total Pb after removing bullets, through field sampling of a newly opened shooting range, and a laboratory weathering study. Forty-one mg of Pb were abraded per bullet as it passed through the sand, which accounted for 1.5% of the bullet mass being physically removed. At a shooting range that had been open for 3 months, the highest Pb concentration from the pistol range berm soil was 193 mg/kg at 0.5 m height, and from the rifle range berm soil was 1142 mg/kg at 1.0 m height. Most soils from the field abrasion experiment as well as soil collected from the rifle range had SPLP-Pb >15 μg/l (Synthetic Precipitation Leaching Procedure). Typically, Pb concentration in the rifle range was greater than that of the pistol range. Based on a laboratory weathering study, virtually all metallic Pb was converted to hydrocerussite ($Pb_3(CO_3)_2(OH)_2$), as well as to a lesser extent cerussite ($PbCO_3$) and massicot (PbO) within one week. Our study demonstrated that abrasion of lead bullets and their subsequent weathering can be a significant source of lead contamination in soils of a newly opened shooting range.

Keywords: Metal contamination; Weathering; Shooting range; Lead; Hydrocerussite; Abrasion

1. Introduction

Approximately 80 000 tons/year of Pb was used in the production of bullets and shot in the United States in the late 1990s (USEPA, 2001). It can be hypothesized that the vast majority of this Pb finds its way into the soils of the many civilian and military shooting ranges across the country.

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Lead contamination in the environment is of concern as it is a known toxin, which has deleterious effects on the human neurological system. Lead present in soil and dust has been directly related to the Pb levels in blood (Davies, 1995). In the past, the federal government has not regulated shooting ranges. However, on March 29, 1993 the United States Court of Appeals for the Second Circuit ruled that Pb shot in shooting ranges met the statutory definition of solid waste,

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and if the Pb were not reclaimed it could be labeled hazardous waste subject to the Resource Conservation and Recovery Act (USEPA, 2001).

Many recent studies have quantified the amount of Pb contamination in the soils of shooting ranges. Total Pb concentration levels up to 54 000 mg/kg excluding pellets have been reported in shooting range soils (Manninen and Tanskanen, 1993).

Lead contamination in the state of Florida is of particular concern due to the soil and weather conditions that typify the state. The conditions that contribute to the risk of Pb migration in Florida soils include: low soil pH, low clay and organic matter content, and high amounts of rainfall (Chen and Ma, 1998). Another concern is that Florida groundwater is usually very shallow. This means that once Pb is in solution it has a short distance to travel before encountering the groundwater.

Past research on soil Pb contamination has focused on the contamination and geochemical weathering reactions of Pb bullets in the soil of shooting ranges that have operated for many years (Jorgensen and Willems, 1987; Lin, 1996; Lin et al., 1995). Contamination of soils due to the abrasion of Pb bullets passing through soil would result in a contamination of the soil with smaller metallic Pb particles. It was hypothesized that this material would contribute more to immediate contamination of these soils as well as environmental risk due to its quick buildup as fine particles and rapid transformation to more reactive compounds. Rooney et al. (1999) reported that residual Pb particles (<2 mm) in soil were completely dissolved by EDTA. Astrup et al. (1999) reported that small Pb bullet fragments in the soil (<2 mm) may have contributed to the total content of Pb in the soils they examined. This type of contamination has implications regarding the age of a shooting range for which best management practices must be implemented.

The objectives of this study were: (1) to quantify the amount of Pb that is physically abraded as a bullet passes through a berm soil; (2) to corroborate these results through field sampling in a newly opened shooting range; and (3) to determine the weathering rate of this abraded Pb through a laboratory experiment.

2. Materials and methods

2.1. Field abrasion experiment

This experiment was performed to quantify the amount of Pb contamination in a shooting range berm that results from physical abrasion of the bullet as it passes through the berm soil. A 0.6 m^3 wood box was constructed with an opening at one end. The box was transported to a shooting range located in Ocala, Florida (OSR) (Fig. 1), where the experiment was performed. At the shooting range, the box was half filled with play sand. The sand was slightly compacted within the box to simulate a shooting range berm. The box was then set up, with the opening toward the shooter.

Two hundred rounds of 0.22-caliber non-jacketed bullets were fired into the sand within the box from a revolver at a distance of approximately 7 m. The bullets were immediately removed from the sand on site at the completion of the experiment with a 2 mm sieve. This was done immediately at the shooting range to impede any weathering of the bullets that would result in further contamination of the sand beyond physical abrasion of the bullets as they passed through the sand. The sand was then transferred to five buckets that had been previously rinsed with nitric acid and deionized water to prepare for transport. The bullets were kept in plastic sample bags.

The bullets were weighed upon returning to the laboratory, and their mass was recorded. The sand was oven dried at 105 °C for 1 day, weighed, and homogenized per bucket. Four sub-samples were taken from each bucket. Sand samples were digested using the hot-block digestion procedure (USEPA Method 3050a: Acid Digestion of Sediments, Sludges, and Soils).

2.2. Field sampling

To corroborate the above experimental results, soil samples were collected at a newly opened shooting range (GSR) in Gainesville, Florida (see Fig. 1). Fig. 1 also shows a rough schematic of the shooting range, which had been in operation for 3 months prior to the first sampling. The pistol

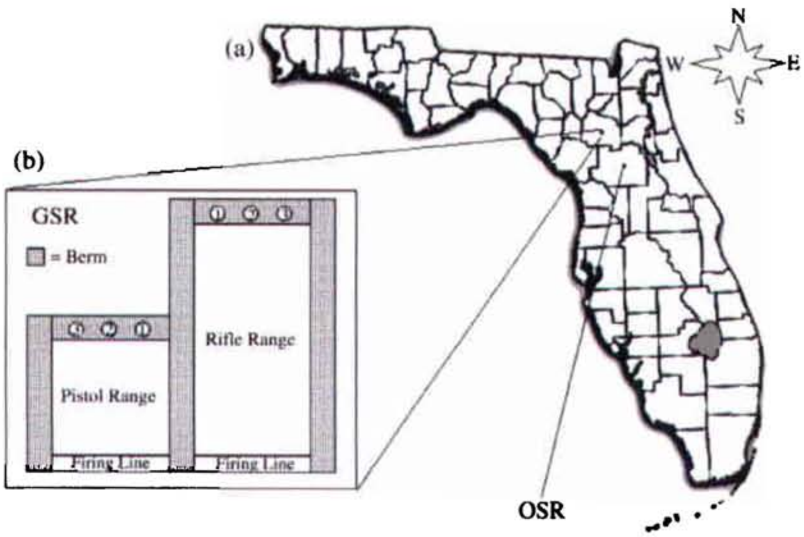

Fig. 1. The position of the study sites in Gainesville (GSR) and Ocala (OSR), Florida (a) and schematic of GSR pistol and rifle range. (b) Sampling locations on berms are numbered.

and rifle ranges are approximately 30 and 100 m from the firing line to the berm. There are also berms that line both sides of the ranges, separating the pistol from the rifle range. The soil on both ranges is very sandy, and vegetation is sparse on the range in the form of patches of grass. There is also very little vegetation on the berms at the end of the shooting range from which the samples were taken. Shrubs have been planted on the berms separating the two shooting ranges.

Soil samples were collected from three locations on the berm in both the pistol and rifle ranges (Fig. 1). Position numbers were located in the front of benches that were positioned along the firing line. At each location, samples were taken at 0.5, 1, 1.5 and 2.0 m from the bottom of the berm. Soil samples were not taken from the same exact location, but from the same general area.

Four soil samples from each location height were collected using a soil probe, and then composited. Only the surface 15-cm of the berm soil was sampled to minimize the effect of whole bullets. It was hypothesized that the majority of bullets would go deeper into the berm soil than the surface 15 cm. Occasional bullets were found in the samples that were collected, but they were few, and visible weathering appeared to be at a minimum in most situations.

Samples were collected at positions 1–3 on the pistol range, and position 1 on the rifle range (Fig. 1). Field soil samples were transported back to the laboratory where they were air dried, sieved to 2-mm and digested using the hot-block digestion procedure (USEPA Method 3050a: Acid Digestion of Sediments, Sludges, and Soils). Bullets and bullet fragments that were larger than 2 mm were manually removed and excluded from the digestion.

2.3. Laboratory studies

2.3.1. Leaching test

Synthetic precipitation leaching procedure (SPLP) was used to determine leachable Pb concentrations in the soils collected from the field abrasion experiment as well as field sampling. The SPLP method is believed to be an appropriate test for determining the mobility of Pb in the soils of shooting ranges (Cao et al., 2003; Peddicord, 1998; Reid and Cohen, 2000). It was done using extraction fluid No. 1 (pH 4.20 ± 0.05), which simulates unbuffered acid rain for sites east of the Mississippi. The SPLP Pb concentration was determined following the procedure of USEPA Method 1311 at a solid to liquid ratio of 1:20 (USEPA, 1994). This procedure is used to determine the mobility of inorganic elements present in soils according to the USEPA.

2.3.2. Abraded Pb weathering study

A study was performed to determine the weathering rate of abraded Pb, and the resulting weathering products. A Florida surface soil was collected, air dried, and sieved to 2-mm. The soil was elevated to 5% Pb by using a 200-mesh Pb powder to simulate abraded Pb. Final treatments consisted of 150 g of soil within 100 ml glass beakers. Triplicates of the soil were incubated at 25 ± 2 °C for 7 days at field moisture capacity. Deionized water was added daily to maintain the soil at field moisture capacity. At the end of 7 days, samples were taken via straws that removed cores from the beakers. Samples were then allowed to air dry in weighing boats. Soil samples were sieved using a 270-mesh sieve to filter Pb particles from soil.

The mineral components that passed through the 270-mesh sieve were characterized by X-ray diffraction (XRD) using a computer-controlled X-ray diffractometer equipped with stepping motor and graphite crystal monochromator. Samples were scanned from 2 to 50° 2θ using Cu Kα radiation at 35 kV and 20 mA. XRD has been previously used to determine Pb-minerals in the crust of pellets and bullets in shooting ranges (Cao et al., 2003; Jorgensen and Willems, 1987; Lin, 1996; Lin et al., 1995).

2.4. Chemical analysis

Lead concentrations were determined by flame atomic absorption spectrometry (Varian 220 FS with SIPS, Varian, Walnut Creek, CA). Lead concentrations < 1.0 mg l^{-1} were reanalyzed by graphite furnace atomic absorption spectrometry (Perkin–Elmer SIMMA 6000, Perkin–Elmer Corp, Norwalk, CT). Quality control samples including a standard reference material for soil (2709 San Joaquin Soil) were used with sample digestion (US Department of Commerce National Institute of Standards and Technology, Gaithersburg, MD 20899).

Table 1
Total and SPLP PB from field abrasion experiment

Sample	Total Pb (mg kg^{-1})	SPLP Pb (μg l^{-1})
Bucket 1	118.1 ± 32.7	71.7 ± 6.3
Bucket 2	126.4 ± 28.2	97.2 ± 4.6
Bucket 3	166.5 ± 30.3	109.1 ± 36.6
Bucket 4	14.9 ± 5.3	11.7 ± 0.6
Bucket 5	31.6 ± 5.3	15.9 ± 1.6

3. Results and discussions

3.1. Field abrasion experiment at ocala shooting range (OSR)

Total and SPLP Pb concentrations from the five buckets of sand that were collected from the field abrasion experiment are presented in Table 1. The average Pb concentration on a mass basis for the five buckets was 91 mg/kg, which translated to 8 g of abraded Pb for all 200 0.22-caliber bullets (data not shown). This represented 1.5% of the bullet mass being physically removed by abrasion. Total and SPLP Pb concentrations of samples removed from buckets four and five were significantly less than those of the other buckets (Table 1). These buckets represent the sand that was removed last from the wood box. Typically, the 0.22-caliber bullets did not penetrate past the surface 15 cm of sand. Therefore, the sand that was removed from the box last should have the least exposure to abraded metallic Pb.

It should be noted that a gray powder was clearly visible in the white sand as it was being removed from the box at the range. This possibly consisted of a fine Pb powder that results from friction that occured on the surface of the bullet as it passed through the sand. Also, the SPLP Pb concentration was considerably higher in these samples, with concentrations as high as 109 μg l^{-1} (Table 1). All but one sample exceeded the

15 $\mu g\ l^{-1}$ critical level of a hazardous waste (USEPA, 1995). This suggests that the material that is removed from the bullet is immediately bioavailable, as well as being susceptible to leaching. It has previously been reported that the mineralized forms of Pb commonly found in shooting ranges are predominantly Pb carbonates [$PbCO_3$ and $Pb_3(CO_3)_2(OH)_2$] (Jorgensen and Willems, 1987; Lin, 1996; Lin et al., 1995). These minerals are prone to leaching and are easily extracted by the SPLP method (Cao et al., 2003), in contrast to metallic Pb.

The high SPLP concentrations seen in these samples (Table 1) suggest that Pb minerals were present in the samples. This implies that the metallic Pb that had been physically removed from the bullet may have weathered and mineralized from the time of the experiment to the time at which the tests were performed. This may result from high weathering rate of this material due to the small size and increase in surface area compared to an intact bullet. Therefore, weathering studies were initiated to determine the weathering rate and products from abraded Pb. Based on the data it can be concluded that physical abrasion of Pb is a significant contributor to soil Pb contamination in shooting ranges, and may pose a more immediate concern for shooting range owners.

3.2. Field sampling at Gainesville shooting range (GSR)

Total and SPLP Pb concentrations at 0.5, 1.0, 1.5 and 2.0 m from the bottom of the berm at two positions of the pistol range are presented in Fig. 2a and Fig. 3a. Total and SPLP Pb concentration at the first position on the rifle range are presented in Fig. 2b and Fig. 3b.

The highest total Pb concentration from the pistol range berm soil was 193 mg/kg at 0.5 m (Fig. 2a). The highest total Pb concentration from the rifle range berm soil was 1142 mg/kg at 1.0 m (Fig. 2b). At each position, the lowest total (Fig. 2) and SPLP Pb (Fig. 3) concentrations were found at the 2-m height on the berm. It should be noted that Pb bullets and fragments above 2 mm were removed by sieving prior to digestion. Therefore, only abraded Pb and Pb solubilized or mineralized from bullets are included in total Pb data. The latter is hypothesized to be a smaller fraction of the total Pb due to previously reported rates of chemical weathering of Pb pellets. Jorgensen and Willems (1987) reported that within 6–13 years, only 5–17% of metallic Pb was transformed in Pb shotgun pellets. Lin et al. (1995) reported that in a period of 20–25 years, an average of only 4.8–16% of metallic Pb in these pellets had been transformed to lead carbonates [$PbCO_3$ and $Pb_3(CO_3)_2(OH)_2$] and $PbSO_4$. These data would suggest that after only 3 months of operation, little transformation of Pb would have occurred in the bullets within the range. However, it should be pointed out that accelerated weathering of Pb pellets could occur in Florida shooting ranges due to its tropical/subtropical climate. Sampling of the newly opened shooting facility corroborated the results from the field abrasion experiment, confirming that physically abraded Pb was a significant contributor to Pb contamination in the soils of shooting ranges.

The SPLP Pb concentrations in the shooting range samples were lower in proportion to total Pb concentrations than what was seen in the abrasion experiment (Table 1 and Fig. 3). Three of the four samples (Fig. 3b) taken from the rifle range exceeded the 15 $\mu g\ l^{-1}$ critical level of a hazardous waste (USEPA, 1995). However, only two samples (Fig. 3a) from the pistol range exceeded this level. The ratio of SPLP Pb to total Pb in the abrasion experiment was on average 0.066%, while those in shooting range samples was on average 0.014% (data not shown). This can be significant and suggest that some of the Pb is being leached out from the soil in the shooting range. It has been suggested that the SPLP test is a more appropriate test than the Toxicity Characteristic Leaching Procedure (TCLP) when assessing Pb mobility in shooting range soils (Reid and Cohen, 2000). The difference between these two procedures involves the extraction fluid used. The SPLP solution simulates unbuffered acid rain water, whereas the TCLP solution simulates buffered landfill leachate. The latter would be less

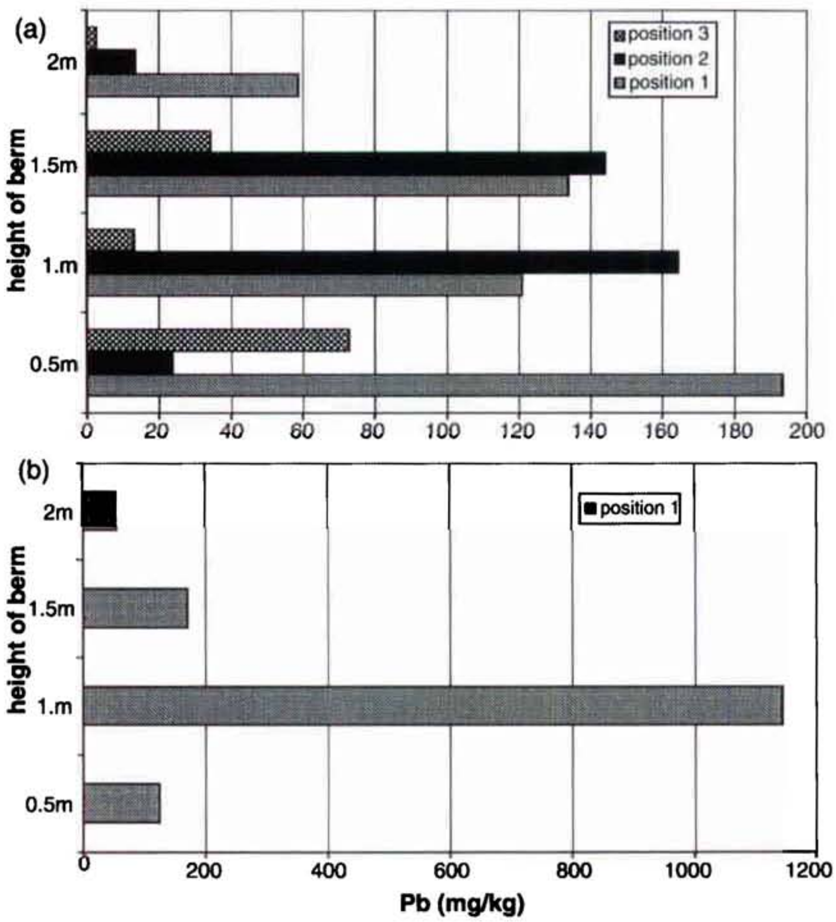

Fig. 2. Total Pb concentration in GSR Pistol (a) and Rifle (b) Range berm soils after 3 months of operation.

representative of the shooting range soil environment.

3.3. Abraded Pb weathering study

Based on the field abrasion experiment, it was concluded that abraded Pb consists of a fine Pb powder that is removed from the bullet as it passes through berm soil. It was hypothesized that this material would weather at an accelerated rate based on its small particles size and high SPLP Pb. A weathering study was thus performed using 200-mesh metallic Pb powder to simulate abraded Pb. Fig. 4a shows the XRD pattern for the metallic Pb used in this experiment, as well as standard hydrocerussite. The predominate metallic Pb peak from the powder was at a d-spacing of 2.84, as well as a secondary peak at $d=2.47$. The predominate peak for hydrocerrusite is at $d=2.62$, with secondary peaks at $d=3.27$ and $d=3.60$.

Fig. 4b shows an XRD pattern for the Pb in soil at field moisture capacity after one week. It is evident that while there are no apparent peaks for metallic Pb, hydrocerussite peaks are visible, as well as to a lesser extent cerussite ($PbCO_3$) and massicot (PbO). This suggests that abraded Pb in shooting range is weathered at an accelerated rate and rapidly converted to Pb-minerals. Virtually all metallic Pb was transformed to hydrocerussite as well as other Pb minerals within 7 days. Previous

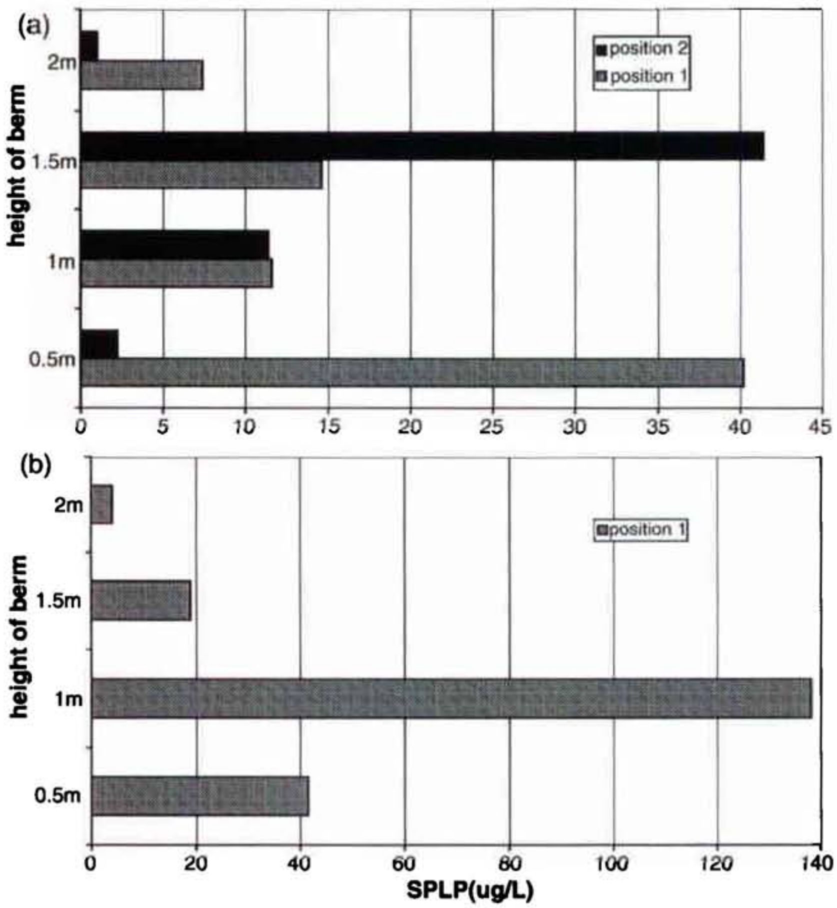

Fig. 3. SPLP Pb concentration in GSR Pistol (a) and Rifle (b) Range berm soils after 3 months of operation.

weathering rates of Pb shotgun pellets reported were 5–17% within 6–13 years (Jorgensen and Willems, 1987), and 4.8–15.6% within 20–25 years (Lin et al., 1995). The dramatic increase in weathering rate is most likely a result in the decrease in size of the material. When a Pb pellet weathers, the pellet is covered by a crust of the resulting weathered minerals (Jorgensen and Willems, 1987), resulting in a protective coat that inhibits further weathering of the inner metallic Pb. In contrast, the Pb powder is too small for a coat to form, and it is completely converted to Pb minerals.

This has implications when considering time periods and techniques for remedial action in shooting ranges. Typical techniques for the remediation of shooting range soils include mechanical sieving (USEPA, 2001), washing soils with EDTA (Samani et al., 1998), and soil amendments (USEPA, 2001). Mechanical sieving is not applicable in remediating abraded Pb, because this material would easily pass through a sieve due to its size. Washing soils with EDTA would remove abraded Pb from soil; however, time would be an important issue when using this remediation technique. Due to the rapid weathering rate of this material, washing the soil with EDTA on a regular basis would not be economically feasible. Ma et al. (1995) demonstrated that the use of phosphate rock is a cost effective way to remediate Pb-contaminated soils. Lead phosphates are extremely insoluble compared to other Pb compounds (Lind-

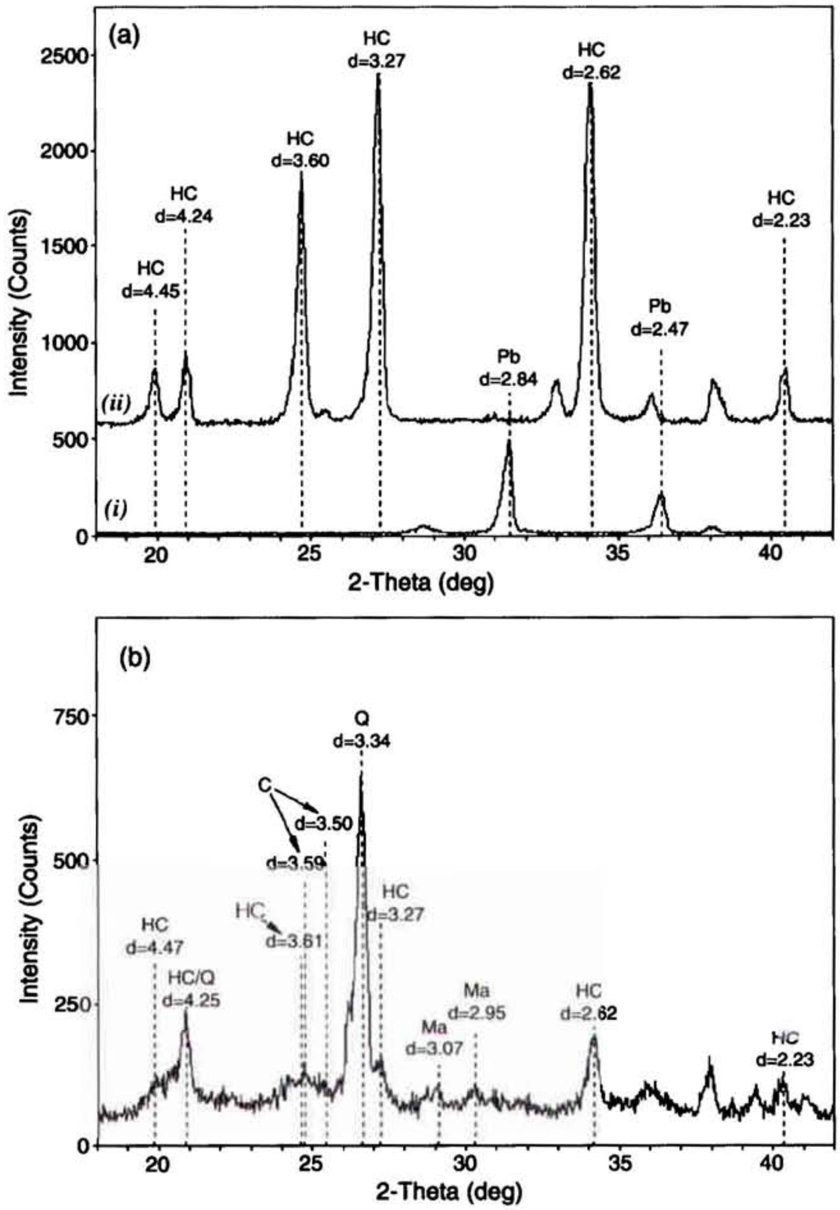

Fig. 4. X-Ray diffraction patterns for Pb powder (i) used in the incubation experiment, and standard hydrocerussite (ii) (a) and for Pb powder after 7 days of incubation in soil (b) at field moisture capacity: Q – quartz, HC – hydrocerussite, C – cerussite, Ma – massicot (PbO) Pb – metallic Pb.

say, 1979; Rickard and Nriagu, 1978), thus reducing the leachability of Pb in soils.

4. Conclusions

This study demonstrated that physical abrasion of Pb bullets passing through soil contributes substantially to soil Pb contamination in shooting ranges. The 0.22-caliber bullet used in the field abrasion experiment is the smallest caliber that is typically used in shooting ranges. An increase in Pb contamination in the form of physical abrasion would probably result from an increase in the size of caliber. This would be due to an increase in surface area of the bullet that is susceptible to physical abrasion as it passes through soil, as well as the fact that higher caliber rounds travel at higher velocities resulting in an increase in friction.

This fine form of metallic Pb is rapidly converted to Pb-minerals, and may pose a risk to groundwater contamination in shooting range soils. Our research has demonstrated that Pb contamination (elevation of Pb concentrations in soils) as well as Pb transformation (from inert metallic Pb to more reactive Pb compounds) in shooting range soils occurs rapidly in newly opened ranges. Therefore, it is important to develop best management practice to minimize the adverse impacts of Pb in all shooting ranges regardless of their ages.

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TECHNICAL GUIDANCE DOCUMENT

INDIANA DEPARTMENT OF ENVIRONMENTAL MANAGEMENT

Lead Issues at Small Arms Firing Ranges

www.idem.IN.gov

Mitchell E. Daniels, Jr. — **Governor**

Thomas W. Easterly — **Commissioner**

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Guidance Created: September 9, 2000
Revised: December 6, 2006 and March 10, 2010
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Notice

The Technology Evaluation Group (TEG) completed this evaluation of *Lead Issues at Small Arms Firing Ranges* based on professional expertise and review of items listed in the "References" section of this document. The criteria for performing the evaluation are generally described in the IDEM OLQ technical memorandum, *Submittal Guidance for Evaluation of Remediation Technologies*.

This evaluation does not approve this technology nor does it verify its effectiveness in conditions not identified here. Mention of trade names or commercial products does not constitute endorsement or recommendation by the IDEM for use.

Background

Lead is a bluish-gray metal which has been mined and utilized for thousands of years. Its use in batteries, plumbing, gasoline and paint; and the adverse environmental and health effects associated with those uses, are well known and much publicized. The Indiana Department of Environmental Management (IDEM) has several programs in place to protect human health and the environment from the adverse effects of lead from these sources. In response to questions received about the potential adverse environmental impacts of lead deposited at outdoor shooting ranges, IDEM has prepared this guidance to address the environmental and legal issues involved. These ranges may be public or private and operated by individuals, gun clubs, the military, state and local police departments, Olympic and Pan Am Games shooting committees, or the Indiana Department of Natural Resources. Due to the low mobility of metallic lead from spent ammunition, adverse effects are rare and site specific, however, re-use of rangeland is a concern of IDEM.

Lead is the primary projectile component of ammunition used in handguns, rifles and shotguns. Lead bullets and shot may be pure lead or may consist of lead alloys containing very small amounts of tin and antimony. In many cases the lead bullet is covered with a copper or steel jacket or covering. Shot used in shotguns may be made of non-toxic steel or bismuth. Clay targets and plastic shotgun wads are also among the materials found at shooting ranges.

Rifle and pistol ranges are generally designed so all shooting is done in one direction and usually into an earthen berm or hillside for safety sake. In such cases, spent bullets are usually limited to a relatively small area. Lead shot, clay targets and wads are generally much more widely dispersed at trap, skeet, and sporting clays ranges since these games require shooting shotguns in many directions at moving targets.

Legal and Regulatory Issues

At present there are no environmental regulations or statutes which specifically address outdoor shooting ranges. Because of the increased public awareness of adverse health and environmental effects of lead, there have been several lawsuits filed against range operators in state or federal courts, alleging violation of various statutes, regulations or environmental harm. In 1988, a lawsuit was filed in Indiana alleging that a shooting range violated hazardous waste rules, developed from the Resource Conservation and Recovery Act (RCRA). In response, the Indiana Department of Environmental Management sought the opinion of the United States Environmental Protection Agency on the matter. Their opinion was expressed in a September 6, 1988 letter to IDEM. This position was recently reiterated in the federal register on February 12, 1997 on page 6630 and remains from the 1988 letter. The position expressed in the EPA letter and preamble is the position IDEM has maintained in all matters relating to shooting ranges, as follows:

> Our office interprets the hazardous waste regulations as not extending to products whose use involves application to the land, or where use necessarily entails land application, when those products are used in a normal manner. The use of munitions (lead bullets, lead shot) does not constitute a waste management activity because the munitions are not "discarded." Rather the firing of munitions is within the normal and expected use of the product. Lead bullet and lead shot impact areas at small arms firing ranges are likewise not regulated by the hazardous waste regulations since hitting and remaining on the ground is a normal expectation of their use.

The practical application of this interpretation is that operators of shooting ranges would only be potentially subject to hazardous waste regulations if they generate a hazardous waste, in which case they would be regulated no differently than any other type of generator. There are no hazardous waste rules under RCRA Subtitle C or in state rules, which require the clean-up of lead bullets, shot, or other debris (e.g.,clay targets) from firing range impact areas. If a shooting facility does clean up spent munitions, debris, or soils for disposal; they would be subject to any applicable solid or hazardous waste rules for disposal of that material. Small arms firing range debris destined for disposal would only be considered hazardous if it exhibited any characteristic of hazardous waste. A representative sample of the waste would have to be evaluated to determine if it met characteristics. Our experience is that the materials will often exhibit the toxicity characteristic for lead, when tested using the toxicity characteristic leaching procedure (TCLP) (see Appendix A). If sufficient lead is present to make reclamation feasible, lead bullets and shot would be considered scrap metal, and would be exempt from the hazardous waste rules if destined for reclamation.

Regardless of the lack of specific regulations, lead is a hazardous substance. If a given range is having adverse effects on the environment, lawsuits may be filed to seek remedies under broader " imminent hazard" provisions of RCRA Sections 7002 and 7003; the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA); or state laws. These lawsuits may be initiated by private citizens or government agencies. This environmental threat (or perceived threat), and the resultant liability or fear of liability is a factor which drives some clean-ups of shooting ranges. Property transfers of rangeland can also be hindered by this liability, which may include future owners. Clean ups are sometimes performed to facilitate the sale of property. Remediation requirements should be determined on a case-by-case basis, taking into account site-specific risks and the planned reuse of the property.

Re-use of property is the primary reason IDEM has recommended remedial actions at closing ranges. In one case, a housing development was planned in the lead contaminated area. IDEM intervened. Any situation where children are directly exposed to contaminated soil from shooting ranges merits special concern and remedial action. In other situations, a site-specific evaluation to determine the risk posed (if any) is necessary to determine recommendations. Factors to consider in this evaluation, and general recommendations, are discussed in the remainder of this guidance.

Indiana Site Conditions

Although many factors affect the mobility of lead (see Appendix B), it has not been a problem in site conditions normal to Indiana. Lead bullets and shot will oxidize at a very slow rate to produce soluble compounds which can be somewhat mobile, but these forms will readily absorb to the clays, iron and manganese-rich sediments, carbonates, sulfur compounds and organic matter common to Indiana soils.

Rainwater in the Midwest is slightly acidic. This will solubilize lead and increase mobility. However, the buffering action of soils and groundwater will quickly neutralize acid rain. In Indiana, the only place where persistent acidic conditions are found is in coal mine drainage, marshes or swamps. A firing range in such an area might produce localized high dissolved lead levels, but this would be balanced by the low water flow conditions, high sediment levels, and high organic contents.

Surface or ground water pollution from firing ranges has not been a problem. Firing range lead does not migrate far from the source. Case studies have found that even in areas of extremely high shot density, most of the soluble lead absorbed to sediments or settled out within a short distance. No normal off-site transportation of lead via neutral to alkaline surface water has been observed (EA Engineering, Science, and Technology, 1996).

Health and Toxicity

For lead to be toxic to animals or humans, it must enter the body. The exposure pathways of concern for lead are inhalation and ingestion. Inhalation can be a factor when significant amount of airborne lead dusts and fumes are present, such as around lead smelters and recycling centers. Small, poorly ventilated indoor ranges firing large volumes of non-jacketed lead bullets into steel backstops have occasionally presented risks from inhalation for range employees upon long-term exposure. Excavation of the impact areas of a range could possibly generate lead dusts, so dust control measures should be used. Normally, lead inhalation at outdoor ranges has not been found to present a problem, because the amount of lead dust produced by outdoor firing ranges is very limited.

This leaves ingestion as the major pathway for toxic lead effects from a firing range. Drinking water is seldom affected by firing ranges because of the low solubility and restricted migration of metallic lead. Therefore, eating of lead or lead contaminated soils is the health risk normally encountered.

Pre-school children are the most vulnerable to lead toxicity because lead absorption in the gastrointestinal tract is greater for children than adults, children's nervous systems are more susceptible to neurotoxic effects, and children are much more likely to be in contact with, and eat, soil. If there is no contact, then there is no possibility of ingestion. A good vegetative cover helps prevent contact, but children should not be allowed to play in range impact areas.

Forms of Lead

Most of the cases of severe lead poisoning in children are due to exposure to lead-based paints or leaded gasoline residues, and this is the focus of much of the research and articles on lead toxicity (Xintaras, 1992; Mielke, 1999). These reports cannot be related to firing ranges. Lead from a firing range is much less toxic because there are direct relationships between toxicity and lead particle size, plus chemical form. Firing range lead is in metallic form, mostly as whole or fragmented bullets, with only a small amount of dust-sized particles. The larger particles are not as readily absorbed (Colorado Dept of Health, 1990). Leaded paints normally form dusts from the paints' flaking, weathering, and chalking, which are readily absorbed into the body. Also, the lead in paints exists in the form of oxides or salts, which can be over ten times more absorbable than metallic lead (Xintaras, 1992). Lastly, lead from paint concentrates in and around the house, where contact is unavoidable, and ingestion common.

Ecological Risks

Smaller lead particles (shot or fragments) can be ingested by wildlife, usually when mistaken for seeds or consumed by fowl looking for gizzard grit. Even one pellet may prove toxic to some birds, so precautions should be taken to make range impact areas uninviting to wildlife. This is a particular problem for waterfowl feeding in ponds, which is why there is a ban on lead shot for waterfowl hunting, and why firing ranges should not have open water in or near impact areas.

Fruit trees, grains, and other vegetation providing wildlife foods should not be located on firing ranges. Even grasses may prove a problem as ducks and geese prefer to graze in close-cropped grasses and may dig several inches into the soil. Range impact areas should not be closely mowed. Denser, low shrubs and bushes should be encouraged. If grasses are planted, they should be allowed to grow knee to waist high to discourage rooting wildlife.

Land Reuse

Future land use is the most important factor in determining if remediation is necessary. Is the range to be used for farmland, residences, industries, or a park? The type of re-use will determine if cleanup is needed to mitigate future lead exposure.

The goal of remediation is to prevent lead from harming humans or the ecology. Since ingestion is the exposure pathway of concern, the remediation method must prevent contact and possible ingestion of the lead. Obviously, a parking lot or industrial use will not present many opportunities for contact and ingestion; while residential use, with children playing and digging in the dirt, could pose a definite problem.

Reclamation

The most final and complete remediation is to remove the contamination and leave the site clean. If the lead fragments are distributed so that they can be gathered up, this option should be considered. This is most feasible if the lead is concentrated in small areas. In the case of a rifle or pistol range, most of the lead will be in the backstop behind the targets. Simple, limited excavation and sieving of the backstop impact area will remove most of the lead.

Shotgun ranges (trap and skeet) present a more difficult problem because the lead pellets are more widespread, but do not penetrate far beneath the surface. There are machines that remove the top few inches of soil, extract the lead, and replace the soil. These are often used at large ranges to recover and recycle lead shot.

There are firms which specialize in lead cleaning at firing ranges. Some of these are listed in “Environmental Aspects of Construction and Management of Outdoor Shooting Ranges.” If a large range is being closed, it may be worth calling a specialist. A small range may be cleaned by just a few people with shovels and sieves.

Another option is to chemically bind the lead with an on-site treatment. Several firms sell proprietary chemical mixes that will bind up the lead into insoluble forms such as lead phosphates. Some of these treatment chemicals come in solid form which can be simply tilled in. These can be used by a farmer to remediate his small range, or be used to remediate a very large facility. Some mixes have not performed as well as others, so a pilot study should be conducted to see if the proposed mix works at specific sites.

Waste Handling

Once the lead is separated from the soil, it can be taken to a metal recycler. This is not hazardous waste disposal, as metal recycling is exempt from the hazardous waste rules (Bruce Palin letter, Appendix C.) The only regulatory problem would be in the excavation and removal of contaminated soil and/or debris as waste material.

If debris or soil is removed from the site, the Federal Hazardous Waste Rules will apply. The waste sent off-site for disposal would be considered hazardous if the required toxicity characteristic leaching procedure (TCLP) test determined it above regulatory limits for lead, in which case the waste must be handled and disposed of under the hazardous waste rules. This can be extremely expensive, so it is usually more feasible to extract the lead and send it to a recycler, or to manage it on site.

Site Management

If it is impractical to remove the lead, it may be successfully managed on-site. The key idea is to prevent migration and contact, to prevent possible ingestion. All operating ranges should have a copy of “Environmental Management at Operating Outdoor Small Arms Firing Ranges,” and “Best Management Practices for Lead at Outdoor Shooting Ranges.” These documents detail the best environmental operating practices for the management of an open range to follow.

As noted in Appendix B, Lead Mobility, clay will bind to lead, so covering with clay soil is quite beneficial. A sufficiently thick soil cover, if seeded and maintained so there are no erosion problems, will also help prevent contact with lead.

Examples

The amount and type of remediation needed depends on specific site conditions - how much lead, how it is distributed, drainage, soil types, and what the future land use will be. The following are just general suggestions for hypothetical sites, as to what may be appropriate in some cases; not absolute guidelines, which are impossible to set without knowing site-specific information.

Example 1: A small, neighborhood rifle and shotgun slug range on a farm: It is an informal range, just a dirt bank on a section of hillside. Almost all of the bullets are concentrated in a small area, and a few are exposed on the surface due to erosion. The range is to be closed and the land is to continue as farmland and pasture. This site could be adequately controlled by hand excavation and sieving of bullet fragments, cleaning up the impact area, covering it with additional soil, reshaping the bank into a stable slope, and seeding it with grass.

Example 2: A large club area with multiple rifle and pistol ranges, plus several trap and skeet ranges: It has been re-zoned for industry, and the new owner plans to build a shopping center and office park. Most of the area is to be covered by buildings or pavement. The cover will prevent contact and exposure pathways, so the main concerns are to see that the lead impact areas are indeed covered by the paved or building areas, and that any building excavation or grading plan takes lead contamination into account. If soil is excavated from contaminated areas, it will need to be tested if it is taken off-site. Grading will need to be performed so lead areas are covered and contained, and not spread further across the site.

Example 3: A large trap and skeet club, with a small lake in the lead impact area: The property is to be made into a park. Since children will be playing in the dirt, more care is needed to prevent exposure. The impact areas need to be defined and the lead removed as much as possible. Some of the lead sifting machines should be considered for this. After reclamation, the area should be covered with a six inch layer of clean fill, and reseeded. To protect wildlife and children, the small lake should be dredged and cleaned, or filled in-place.

Example 4: A small to medium size rifle and pistol range, which the new owner wishes to turn into residential property: For residential re-use, property must be as close to risk free as possible. Children can be expected to spend great amounts of time around their homes, and the opportunities for digging and ingesting contaminated soils are much higher. Depending on site conditions and contaminant distribution, this re-use may not be recommended. Extensive cleaning and lead reclamation would be needed, plus a thick cap on the impact areas. It may not be economically feasible to do all this necessary work.

Example 5: A medium-sized trap and skeet club, which intends to stay open, but wants to prevent negative environmental impacts: The club should set up an environmental management program; with a plan for lead recovery and recycling, range management, erosion prevention, etc. The "Environmental Aspects of Construction and Management of Outdoor Shooting Ranges" outlines the steps needed for such a program.

Conclusion

Small arms firing ranges do not present extreme environmental hazards, nor are extensive remediation efforts usually required. Depending upon the site conditions; localized, small-scale cleanups or cover may be adequate. It is recommended that active ranges have an environmental management program to control lead contamination, and recycle spent materials.

Further Information

If you have any additional information regarding this technology or any questions about the evaluation, please contact Bob Sonnefield, Senior Geologist, at (317) 234-4688 or by E-mail at rsonnefi@ idem.IN.gov. This technical guidance document will be updated periodically or if new information is acquired.

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APPENDIX A

CHEMICAL TESTS

Chemical Tests

In order to establish a valid method for determining the possible extent of lead impacts on areas surrounding shooting ranges, it is necessary to use appropriate analytical models. Although lead is basically immobile in the environment, there are certain forms which can be mobilized, and therefore, have the potential to impact areas other than the immediate vicinity of the shooting range. A commonality of these forms of lead is their solubility in water or acids.

Leach modeling is the most appropriate method to assess the mobility of lead. Leach models act as a gauge of the totality of mobile lead. For the purposes of truly assessing mobility and contaminant risk in a site specific area, several other factors must be identified and accounted for. Average rainfall amounts, infiltration rates, soil cation exchange capacities, existence of lead-reactive ionic species, total volume of the area of interest, etc., must be considered in order to determine the level of risk associated with a shooting range site.

The model most commonly considered for use is the toxicity characteristic leaching procedure (TCLP), EPA SW-846 method 1311. This model is used to determine whether leachable lead levels exceed regulatory thresholds, and are considered hazardous for the purposes of disposal.

This model was designed to mimic leachate generated in a solid waste landfill, which accepts organic and inorganic wastes. These organic wastes may decompose, with attendant acid formation, which increases the likelihood of metal ion solubility. The premise behind the model makes it a poor candidate for assessing the level of leachable lead at a firing range, because the amount and type of acids the model uses typically would significantly exceed those types and amounts found naturally.

Water leach models, similar to the Indiana Neutral Leaching Method or the ASTM Water Leach Method, are more appropriate than TCLP, as they tend to reflect a more real estimate of the acidity encountered in the environment. The main shortcoming of these models is their use of distilled, deionized water, which does not exactly mimic the buffered water systems found in the environment. For shooting ranges over a standing body of water, such as some shotgun ranges, this would be the most appropriate leach model to assess the amounts of lead which may become mobile. Although rain would feed the standing water body, directly or indirectly, the size and buffering capacity of the standing water body and its matrix would cause the pH of the influx water to rapidly approach neutral.

Given the acidic nature of rainfall in Indiana, the leach model which could be considered appropriate for most shooting ranges would be the Synthetic Precipitation Leaching Procedure (SPLP), SW-846 method 1312. The vast majority of water that would be in contact with lead from the majority of shooting ranges would be encountered as rainfall. The pH of rainfall in Indiana ranges from around 4.5 to 5 standard units. The leach fluids stipulated for this model simulate the acidity and types of acids noted in rain. The leach fluid appropriate for determining lead mobility in Indiana has a pH of 4.2 ± 0.05

standard units, and would effectively model a worst-case scenario of lead mobilized by the effects of acid rain.

APPENDIX B

LEAD MOBILITY

Lead Mobility

A number of factors affect the mobility of lead in the environment. A partial list of the factors which affect lead in the environment follows.

- Lead oxidation is very slow (100 to over 300 years) for bullets, depending on site conditions.

- Cation exchange capacity: In soils, the ability to exchange cations binds lead into the soil matrix, but the process is reversible when new cations are introduced into the system.

- Sulfides: Sulfur has a high affinity for lead, which, after reacting to form lead sulfide, precipitates out, moving contamination from water into the sediments. In sediments, sulfides cause free lead to become effectively insoluble, preventing transfer into water resources by dissolution.

- Sulfites and Sulfates: In the presence of water-soluble sulfites/sulfates, lead tends to precipitate out of solution. Soils high in sulfites/sulfates will cause lead to become effectively insoluble, preventing transfer into water resources by dissolution. Depending on the amount of free oxygen present, sulfites tend to slowly oxidize to the sulfate species.

- Phosphates: Phosphate ion sources tend to be quite effective in immobilizing lead. Lead phosphate is insoluble, and is quite stable. Phosphate fertilizers can help immobilize lead.

- Hydroxides: Free lead, in the presence of hydroxide ions, forms lead hydroxide, which is insoluble.

- Humic substances: Lead forms complexes with these high molecular weight compounds, reducing their mobility and solubility.

- Carbonates: Lead/carbonate interactions decrease the solubility of lead.

- Acids: Lead is soluble in dilute acids.

- Clays, and iron or manganese oxides (all very common in southern and central Indiana), are highly lead absorbent, which restricts mobility.

APPENDIX C

PALIN LETTER

State Form 4336

DEPARTMENT OF ENVIRONMENTAL MANAGEMENT

INDIANAPOLIS

OFFICE MEMORANDUM

Date: July 3, 1997

To: John Rose
Assistant Commissioner
Office of Environmental Response

From: Bruce Palin BHP
Acting Assistant Commissioner
Office of Solid and Hazardous Waste

Subject: Small Arms Firing Range Accessment Workgroup,
RCRA Applicability to Fired Munitions

Our OSHWM representative on the Small Arms Firing Range Accessment Workgroup (FRW) has asked that I communicate OSHWM's policy with respect to the applicability of Indiana's Hazardous Waste Rules and Laws to small arms firing ranges. It is my understanding that your office is developing a guidance document to deal with the issue of lead deposition and clean up recommendations at shooting ranges.

Coincidentally, the U S. EPA has recently published a final rule regarding military munitions on February 12, 1997. Although this rule is applicable only to military ranges the preamble to this final rule on page 6630 (copy attached) discusses the EPA's position on Resource Conservation and Recovery Act (RCRA) applicability to non-military ranges. Their position was actually first expressed in a 1988 letter to this office from EPA in response to our inquiry The position expressed in the letter and preamble is the position this office has maintained in all matters relating to shooting ranges. The discharge of bullets and shot at shooting ranges does not constitute solid waste or hazardous waste disposal. To be regulated by our office under the solid or hazardous waste rules a material has to be a solid waste. Nothing in our Indiana statutes or rules suggest that our jurisdiction over shooting ranges is any different than under RCRA. Indiana's statutory definition of solid waste at IC 13-11-2-205 mirrors the federal definition under RCRA at 42 USCA 6903 Sec.1004(27). Federal regulations implementing this definition at 40CFR 261.2 have been adopted by reference in Indiana's hazardous waste rules at 329 IAC 3.1-6.

Our office interprets the hazardous waste regulations as not extending to products whose use involves application to the land, or where use necessarily entails land application, when those products are used in a normal manner. The use of munitions (lead bullets, lead shot) does not constitute a waste management activity because the munitions are not "discarded." Rather the firing of munitions is within the normal and expected use of the product. Lead bullet and lead shot impact areas at small arms firing ranges are likewise not regulated by the hazardous waste regulations since hitting and remaining on the ground is a normal expectation of their use.

The practical application of this interpretation is that operators of shooting ranges would only be potentially subject to hazardous waste regulations if they generate a hazardous waste, in which case they would be regulated no differently than any other type of generator.. There are no hazardous waste rules under RCRA Subtitle C or in our rules, which require the clean-up of lead bullets or shot or other debris (e.g.,clay targets) from firing range impact areas. If a shooting facility does clean up spent munitions, debris or soils for disposal they would be subject to any applicable solid or hazardous waste rules for disposal of that material. Small arms firing range debris destined for disposal would only be considered hazardous if it exhibited any characteristic of hazardous waste. A representative sample of the waste would have to be evaluated to determine if it met characteristics. Our experience is that the materials will often exhibit the toxicity characteristic for lead when tested using the toxicity characteristic leaching procedure (TCLP). If sufficient lead is present to make reclamation feasible, lead bullets and shot would be considered scrap metal and would be exempt from the hazardous waste rules if destined for reclamation.

The military munitions rule finalized by the US EPA on February 12, 1997 addresses all military munitions, not just small arms ranges which is the focus of the FRW. Our office is proceeding to adopt this rule with no changes at present. I trust that the above shall be sufficient information for the purposes of the FRW and will be reflected in the guidance being developed. If I or my staff may be of further assistance please let me know.

DWB
attachment

cc: Tom Linson
Jim Hunt
Mike Dalton
Richard Milton
Tom Neltner
Firing Range Workgroup

Lead distribution on a public shotgun range

James R. Craig · David Edwards · J. Donald Rimstidt · Patrick F. Scanlon
Thomas K. Collins · Oliver Schabenberger · Jeffrey B. Birch

Abstract A detailed study has been made of the distribution of lead on a public shotgun range in the George Washington – Jefferson National Forests in southwestern Virginia. Sampling of more than 100 sites has yielded data on the distribution pattern of the lead shot. Since opening in 1993 through 2000, 11.1 metric tons (t) of lead have been accumulated over an area 220×300 m (66,000 m^2) with an average rate of accumulation of 1.4 t/year. More than 85% of the total dispersed lead lies scattered in the forest that surrounds the approximately 60×60-m cleared shooting surface. Lead is irregularly distributed because of the use of stationary targets and the general trajectory of launched clay targets. Maximum concentrations occur at distances of ~28, ~80, and ~180 m, and reach a maximum value of more than 5,000 g/m^2. Significant amounts of fine particulate lead, generated during shooting and as a result of impact occur close to the shooting box, but are absent at distances beyond 50 m.

Keywords Lead · Shooting range · Shot · Shotgun

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Introduction

Recreational shooting is becoming increasingly popular with the American public and there is a growing need for facilities to accommodate this activity. Local, state, and federal organizations and agencies continue to develop shooting facilities, sometimes in isolated forest areas so that the discharge of weapons can be carried out safely. Shooting ranges vary from sites that are rigidly structured with high backstops to simple open clearings with or without a constructed backstop. Some are completely supervised whereas others are unsupervised and self-policed. In most cases, the sites are chosen and oriented such that they offer little or no direct threat to human habitation or normal activities. In large forested areas open to the public, such as the National Forests in Virginia, the establishment of formal shooting ranges has greatly decreased the incidence of random shooting in the forest and along roads. As a result, the safety of all of the recreating public on the forest is improved, and the potential for shot impacting on neighboring lands is reduced.

At the same time that formal ranges provide a clear benefit to the public, there is a growing concern among the public about the dispersal and fate of heavy metals such as lead in the environment. It is clear that the establishment of formal shooting ranges results in the accumulation of significant amounts of lead and other metals used in the manufacture of bullets and shot. The effects of lead on waterfowl in fluvial, lacustrine, and marine environments are well documented (Feierabend 1983; Sanderson and Bellrose 1986; Pain 1990), but much less attention has been given to the ecological and environmental effects of lead on birds and other organisms in upland environments (Kendall and others 1996).

This study was initiated as part of Forest Service monitoring of an active shooting range that is operated in the George Washington and Jefferson National Forests of the USDA Forest Service. It is about 5 km west of Blacksburg, Montgomery County, in southwestern Virginia (37°18′N; 80°26′30″W; Fig. 1). The range contains two shooting areas (Fig. 2), a rifle range and a shotgun range, and lies on the southeast flank of Sinking Creek Mountain approximately 0.4 km north of Route 460. The shooting range lies at an elevation of about 685 m in a second growth mixed hardwood forest on the Devonian Brallier Formation, which is composed primarily of a deeply weathered black shale. The ridge top is composed of Silurian sandstone, the

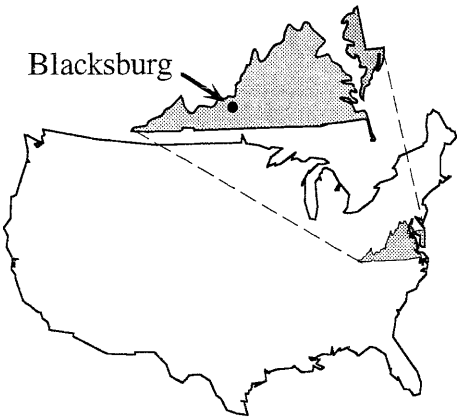

Fig. 1
General location map of the shooting range, which is located in the George Washington and Jefferson National Forests in Montgomery County in southwestern Virginia, approximately 5 km west of Blacksburg

Fig. 3
Recreational shooters are shooting out across the shotgun range from the shooting box. The closest trees at the back margin of the cleared area are 60–65 m from the shooting box and the width of the cleared area is approximately 60 m

Fig. 2
Oblique aerial photograph of the Blacksburg shooting range showing the rifle range (*elongate area in the foreground*) and shotgun range (*more equant area behind the rifle range*). The photograph was taken in January 2001, and the small white zones are residual snow accumulations. Photograph by J.R. Craig

float from which is scattered across the forested mountainside. The rifle range was cut into the slope such that there is a 4–5-m-high backstop behind the 100-m-long shooting lanes. The shotgun range occupies a cleared 60 m long by 60 m wide slightly sloping surface now covered with grass (Fig. 3). The shooting ranges are completely surrounded by second growth forest, last cut over in the 1930s, dominated by red and white oaks that are up to 31 cm in diameter and contain as many as 60 growth rings; some pine up to 33 cm in diameter contain up to 90 growth rings. The shooting range was established in 1993, has been in continuous use since that time, and appears to be receiving increasing amounts of use. Actual attendance data and the numbers of rounds fired are not known with accuracy, but the US Department of Agriculture (USDA) Forest Service made a rough estimate of 1 million rounds per year for both the rifle and shotgun areas (W. Compton 1993, personal communication). Limited range attendance data taken from a vehicle counter on the entrance road are: 1998 – 17,620; 1999 – 13,071; 2000 – 18,258; 2001 through 5 March – 7,052 vehicles. The counter has not been operative at all times, so these are conservative figures. Assuming estimates of 1.3 occupants per vehicle and the discharge of 50 rounds by each occupant on each visit, the numbers of rounds fired per year would be 1997 – 1.15 million rounds; 1999 – 0.85 million rounds; 2000 – 1.19 million rounds. These data all support the estimate of at least 1 million rounds being fired per year. Observations by the authors suggest that 90% of the total range usage is on the rifle range.

The Blacksburg range offers an excellent site for the study of metal distribution and accumulation because it is well defined geographically, has no encroachment by other metal-distributing activities, has remained in continuous operation, and is expected to remain open for the foreseeable future. The range appears to be typical in terms of simple construction and typical in terms of clientele served (target shooters, sports shooters, and hunters). The attendance is probably somewhat higher than that of many of the more remote shooting ranges in the National Forest, but is probably less than on ranges near greater population centers. It is important to note that this is an unsupervised range, so there are a wide variety of shooting activities and a very wide variety of firearms used at the site. Hence, samples from nearly any part of the range areas can contain bullets and shot of many types because shooters use munitions designed for target shooting as well as those designed for hunting. The discussions in this paper will refer to lead because it is the overwhelmingly dominant (probably 97% or more) metal present on the range. Other metals present are as jackets and firing caps (copper), pellets (steel), hardening agents (arsenic and antimony), casings (brass, aluminum, steel), and targets (all types of metals), but all of these together are estimated to total no more than 2 or 3% of the total metal present. The USDA does carry out periodic range cleaning, which clears the heaviest of the target debris on the shotgun range and many of the casings from the shooting box areas; little or none of the bullets and shot have been removed by cleaning. The authors believe that this range has similar characteristics with many outside ranges in the United States and, therefore, can serve as a representative model from which many useful conclusions may be drawn.

Shotgun range usage

The Blacksburg shooting range is generally open for public usage from dawn to dusk more than 350 days each year; it is closed periodically for maintenance and general cleaning. Although the two shooting areas are designated as a rifle range and a shotgun range, the ranges are not continuously supervised and there is some cross over of range usage as evidenced by the presence of bullets on shotgun range and shotgun casings on the rifle range. Most shooting on the shotgun range is conducted with 12-gauge shotguns using number 6 to 8 shot as evidenced by the discarded shells, boxes, and recovered pellets. There is also limited usage of 10-, 20-, and 410-gauge shotguns. The shotgun range has a centrally located shooting box that apparently is used by most shooters. A clay target launching site is located approximately 7 m to the right of the shooting box. Shooters may use mechanical launching devices or may have colleagues hand-throw the clay targets. No firm data exist on the numbers of shells discharged by individual shooters, but random observations of, and discussions with, typical shooters indicate that trips to the shooting range usually result in the discharge of a minimum of 30 shells and probably an average of 50 shells. Assuming that the average 12-gauge shotgun shells contains 30–45 g of lead, the typical shooter would discharge 1,500–2,250 g of lead shot per trip to the range. In general, bullets constitute only a few percent of the total lead recovered from any sampling site on the shotgun range. However, along the center line where targets are placed, bullets are more abundant. The greatest concentration of bullets was observed at a distance of 28 m on the center line where they constituted 874 g (or 17%) of the total 5,048 g Pb/m^2.

Scope of the present study

This paper presents data and discusses the lead distribution and loading on the area impacted by shooting activities on the shotgun range. This range (Fig. 3) consists of an open gently sloping surface, approximately 62 m in length by about 65 m in width, which was cleared in the forest. It is bounded on all sides by mixed hardwood second growth forest dominated by oak trees. The surface slopes slightly from left to right (from the shooters perspective) and rises away from the shooter at about a 5–6% slope. The ultimate area of study for which data are reported is approximately 220 m across by approximately 300 m in length. The study area as shown on the diagrams in this article is bounded by the shooting box (set as the 0 coordinate) and extends 100 m to the left of the shooter and 120 m to the right of the shooter. This slight asymmetry results from the positioning of the rifle range, which lies at about 100 m to the left of the shooting box. Hence, any measurements farther to the left than 100 m would be influenced more by the rifle range than by the shotgun range. The right side limit of 120 m and the maximum range limit were determined by the concentrations of shot recovered.

This study is part of a larger project examining the entire shooting range (rifle range and shotgun range) to determine (1) the area of impact of the shot, (2) the nature and uniformity (or lack thereof) of the lead distribution, (3) the loading (concentration) of the lead on the range, (4) the impacts of shooting on the vegetation immediately adjacent to the range surface, (5) any evidence of lead transport from the range or surrounding surfaces, (6) the nature of the corrosion phases on the lead, and (7) whether lead is present in ground and surface waters. A study of lead in surface water has been published (Craig and others 1999) and preliminary results on the corrosion of the lead shot have been presented (Rimstidt and Craig 2000).

Approach and methods

Sampling methods and patterns

Two of the major objectives of this study of the shotgun range were to determine (1) the area impacted by lead shot, and (2) the uniformity (or lack of uniformity) of lead distribution. The first estimate at the Blacksburg shotgun range was that much of the shot would occur on the approximately 60×60-m surface that had been cleared in front of the shooting box. Accordingly, the initial sampling was carried out at 5-m intervals along a line extending directly outward from the center of the shooting box towards the center of the far edge of the cleared area. Progression of sampling to the outer limit of the cleared area indicated that much shot must have carried beyond that area; hence, sampling was carried out at 10- or 20-m intervals to a distance of 320 m from the shooting box. It was apparent from the outset that shooting distributes shot in arc-like patterns because much of the shooting is at targets that have been launched or thrown (generally right to left) at varying heights. Observation of shooters revealed that shots ranged over a wide angle and at highly variable trajectories that would carry shot from far to the right of the open area, across the center, and far to the left of the open area. Accordingly, sampling was also carried out on a series of traverses at right angles to the center line. Most intensively, samples were taken along traverses at 50, 100, 150, and 200 m out from the shooting box. The full sampling included more than 100 sites as indicated on Fig. 4 and are given in Table 1.

Sampling was conducted as much as 100 m to the left of the center line and as much as 120 m to the right. Beyond 100 m to the left lies the rifle shooting area of the Blacksburg shooting range and this area contains considerable amounts of lead from the rifle shooting activities. The lead concentrations from the shotgun range activities have dropped to 20–25 g/m^2 at 100 m to the left; thus the impact of the shotgun range activity becomes small

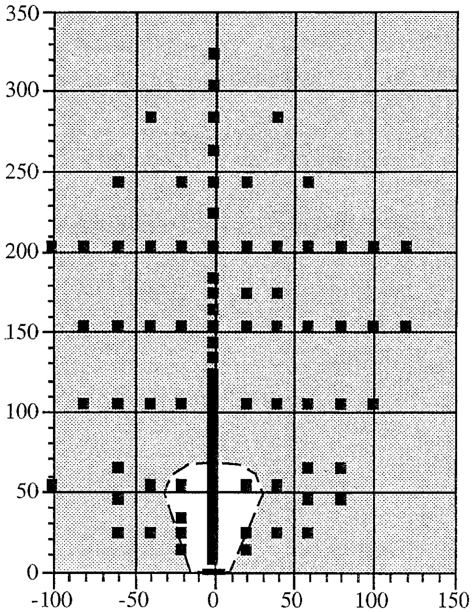

Fig. 4
Distribution of sample sites (marked by *squares*) used in the present study. The location of the shooting box is marked by the *heavy line at the bottom* and the margin of the cleared area is marked by the *dashed line*. A total of more than 100 sample sites were used in the model calculations presented in this paper

beyond that distance. Sampling was conducted farther to the right side of the range because there was no influence from a rifle shooting area that would contaminate the data and because there appears to be a slight right-hand bias to the shot distribution. That is, there are higher lead values at 80 and 100 m to the right than to the left; this probably results from some bias to shoot at aerial targets, launched from the right-hand side, before they reach the center of the range.

Initially the authors did not know the depth to which shot might have penetrated or been worked by subsequent activity. After testing several areas of various dimensions, it was found that sampling of areas 50×50 cm provided a significant areal coverage and when sampled to depths of 3 to 10 cm, provided 1–8 kg of total sample (soil, spent shot, pieces of clay targets, shot cups, various target materials, and wood or grass fragments). Thus, 50×50-cm^2 areas (Fig. 5) were located and sampled to a depth where it became apparent that there had not been deeper penetration by the shot and that there had not been reworking of material on the surface. Usually this occurred at the base of the A-soil zone, which was relatively darker and organic-rich; the underlying lead-free soil was a yellow-orange clay-rich zone. All material within the 50×50 cm^2 was extracted and sieved through a 6-mm metal sieve. Clods of soil and masses of root or organic material were disaggregated and worked until it was clear that there could not be shot left adhering to them. The coarser material primarily included shards of clay targets, pebbles, leaves, roots, shotgun shells and cups, and miscellaneous target materials (boxes, milk jugs, glass bottles, electronic devices, etc.; Fig. 6).

The progression of sampling revealed that most of the lead shot are dispersed in the surrounding forest; hence, most samples were taken from that area where the soil is cov-

Table 1
Lead concentration data from Blacksburg shotgun range. Samples were taken on 0.25-m^2 areas and then multiplied by four to give the data here, which represent concentrations per square meter. The data cover an area as shown in Fig. 3 and are assigned the same *x* and *y* coordinates as are shown on that figure. Data are rounded to the nearest full gram

x	*y*	Pb, g	*x*	*y*	Pb, g	*x*	*y*	Pb, g	*x*	*y*	Pb, g
–100	50	20	0	4	191	0	95	861	20	240	60
–100	200	35	0	5	216	0	100	778	40	20	18
–80	100	14	0	8	195	0	105	616	40	50	298
–80	150	50	0	10	552	0	110	585	40	100	113
–80	200	64	0	12	852	0	115	674	40	150	290
–60	20	4	0	15	1,973	0	120	527	40	170	428
–60	40	19	0	16	1,122	0	130	371	40	200	153
–60	60	29	0	20	1,425	0	140	413	40	280	4
–60	100	74	0	25	2,642	0	150	337	60	20	9
–60	150	72	0	28	5,048	0	160	243	60	40	42
–60	200	103	0	30	2,600	0	170	390	60	60	96
–60	240	25	0	32	2,072	0	180	766	60	100	66
–40	20	16	0	35	1,669	0	200	624	60	150	109
–40	50	124	0	36	2,416	0	220	223	60	200	208
–40	100	313	0	40	1,047	0	240	89	60	240	57
–40	150	206	0	44	629	0	260	30	80	40	12
–40	200	248	0	45	824	0	280	12	80	60	38
–40	280	1	0	50	1,526	0	300	1	80	100	32
–20	10	17	0	55	1,336	0	320	1	80	150	172
–20	20	75	0	60	1,752	20	10	18	80	200	236
–20	30	392	0	65	1,188	20	20	62	100	100	5
–20	50	517	0	70	1,478	20	50	952	100	150	164
–20	100	660	0	75	1,650	20	100	886	100	200	101
–20	150	292	0	80	3,065	20	150	361	120	150	70
–20	200	236	0	85	1,673	20	170	525	120	200	78
–20	240	49	0	90	2,618	20	200	283			

Fig. 5
Typical 50×50-cm sampling sites on the cleared range. The surface materials were removed and all shot and/or bullets recovered. Sampling was carried out to a depth to where no additional shot was found and to where there was no evidence of disturbance. The sampling depth thus varied from as little as 3 cm on parts of the cleared area to as much as 10 cm in portions of the forest where shot and leaves continually accumulate

Fig. 6
An example of the variety and density of debris that accumulates on the range as a result of normal recreational shooting. Sampling of areas at approximately 35 m out from the shooting box have yielded as much as 25 kg of debris per m^2 (not including lead shot). The most abundant materials are broken clay targets, shotgun shells, packing for pellets, and miscellaneous target materials (glass, plastics, wood, etc.)

ered by 5- to 10-cm-thick mass of flattened, overlapping, and decomposing leaves with penetrating roots (commonly referred to as "duff"). Recently fired shotgun shot pellets could be seen lying on or between the most recently fallen leaves whereas older shot were found dispersed throughout the mulch- to peat-like mass. These samples were carefully extracted so that pellets did not drop out before being collected and were then thoroughly disaggregated to release the shot. The investigators attempted to take samples that were unbiased, but did recognize that large trees clearly act as backstops and it is common to observe high concentrations of lead shot directly in front of the large tree trunks; many shot bounce off or just drop and accumulate in front of the trees. Conversely, behind the large trees, there were shadow zones where there were few or no shot because they were shielded by the tree trunk. Accordingly, samples were not taken directly in front of, or directly behind large trees because of the bias resulting from the backstop or shielding effects. Where such sites fell in the sampling patterns, the sample site was adjusted approximately one-quarter of a meter, left or right or front or back. This avoided the bias, but kept the sample in the same square meter area being represented. During sample processing, all material retained on the top of the sieve was examined before being discarded and all bullets and casings were extracted and retained to be added to the shot. Numerous samples also contained bullets of a variety of caliber; these were added to the recovered shot as they represent metals contributed to the range by the recreational shooting activities. The material that passed through the 0.25-inch sieve were collected in plastic bags, labeled, and returned to the laboratory for processing.

The disaggregated samples were dumped into 20-l plastic buckets. The buckets were filled with tap water and the mass of the material was stirred and agitated until the heavier fractions (the lead and related metals) had settled to the bottom. The floating organic material and much suspended fine clay and target waste were decanted off several times. Samples were then transferred to a 36-cm Garrett Gravity Trap gold pan, which was used to separate the lead and related metals from the much lower-density soil, sand, target fragments, and glass particles. When properly used, the gold pan is extremely efficient in separating the heavier from the lighter materials and it is relatively easy to monitor the presence and movement of lead shot or fragments in the pan. The lead shot, bullets, and shot and bullet fragments were separated and dried (Fig. 7). Once dried, the recovered metal materials were examined under a binocular microscope and all remaining extraneous materials were removed; the samples were then weighed on a top-loading balance with an accuracy of $\sim$0.1 g. The separation procedure was tested for reliability by adding 100 g of typical lead shot to a lead-free mass of soil and organic matter, which weighed several kilograms and was typical of the organic debris in the forest. This test sample was processed in the same manner as the regular samples; the result was recovery of 99.5 g of lead shot. It is recognized that some material could be lost during the recovery efforts at any site; however, the test indicated a very high rate of recovery – one that the principal investigators believe is typical. Nevertheless, it is proper to note that the potential for small losses means that the results given below are conservative; there was no opportunity for the introduction of lead into samples, but there was the possibility of small losses. Shot samples recovered from most of the range surface and the surrounding forest area consisted of intact shotgun pellets that appear to have fallen undamaged to the ground after travelling on a normal arc from the shooting box outward. However,

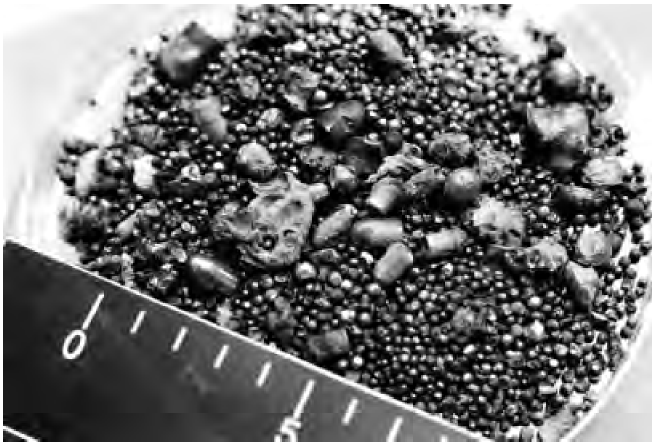

Fig. 7
An example of the typical materials recovered during the processing of samples in the present study. The majority of the lead and related metals occurs as lead shot of many different sizes, but significant amounts of metal may also occur as bullets and buckshot at some areas on the range surface. This sample was taken at 28 m out from the shooting box along the center line and contains several bullets apparently used for target practice

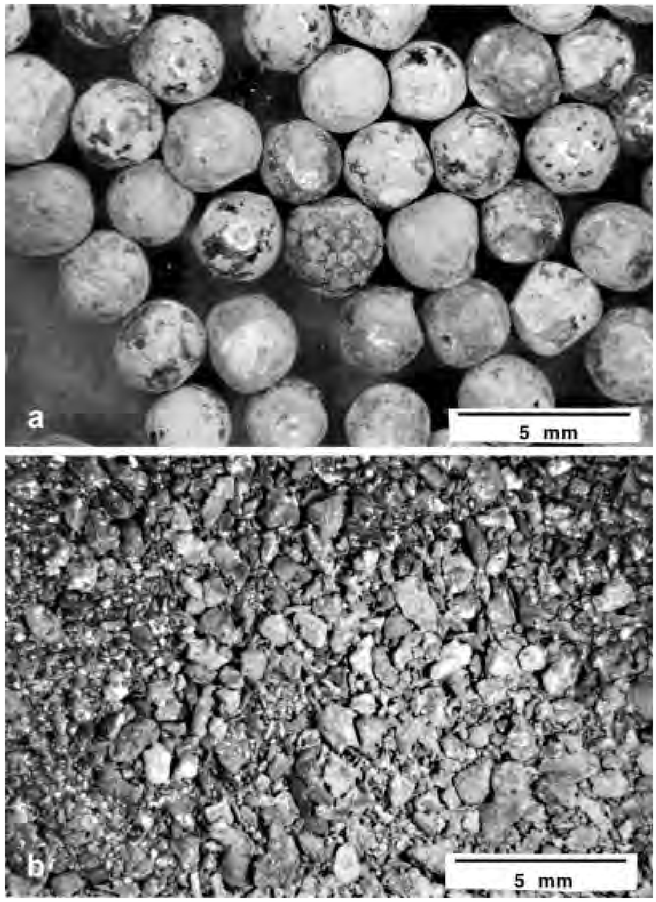

Fig. 8
a Shot recovered from a sample site at 180 m are typical of samples found on most of the impacted area. **b** Much finer material (photographed at the same scale) occurs near the shooting box along with typical shot (sample from 8 m). The finer irregular fragments are released upon firing, but do not travel very far because of their smaller mass and irregular shapes and hence accumulate close to the shooting box. All these materials passed through a 1-mm sieve, but particles range downward in size to 0.01 mm or smaller. The photographs were shot at the same camera settings and the *scale bar* is 5 mm in length

careful examination of samples taken close to the shooting box revealed that they contained significant amounts of finer and very irregular fragments of lead (and minor amounts of brass or other metals) as shown in Fig. 8. These fragments are apparently generated by the abrasion of the shot against one another, or against the choke at the mouth of the gun barrel as they exit the shotgun barrel. Because they do not possess so much mass as the larger pellets and are not very aerodynamic, they do not travel very far before falling to the ground. The particles range in size from 1 mm downwards to 0.01 mm or less. This fine size makes their recovery more difficult and required very careful panning (and in some cases, re-panning of the finest debris) to effect their recovery. No doubt, some of the finest material was lost, but the high specific gravity of the lead and other metals still allows for very high recovery rates. The presence of these particles is potentially very important as discussed below.

Statistical methods

The evolving sampling procedure resulted in non-uniform sampling of the shotgun range. In particular, it resulted in much more intense sampling along the center axis of the range (x=100 in Table 1) than on other parts of the affected area. Consequently, it was not appropriate to weight all samples equally and simply average the data from all sites. The higher lead concentrations along the center axis would have biased the total and would have given a gross over estimate of the lead. For example, the average lead concentration of all samples was 572 g/m^2; extrapolation onto the entire 220 by 300 m area would have yielded an estimate of 37.7 metric tons (t). Any similar statistical analysis based on simple summary statistics such as sample means will fail to produce a good match between the predicted lead profile (Fig. 9) and actual measurements because it does not take into account the spatial autocorrelation in lead distribution. In other words, having found high (or low) amounts of lead at a given site, it is reasonable to expect high (or low) concentrations in nearby sites.

To obtain a profile of the actual (not average) amount of lead on the range that allows unbiased estimation in the presence of a systematic and non-representative sampling design, geostatistical principles were applied. In this case, universal kriging (Cressie 1993; Chilès and Delfiner 1999; Schabenberger and Pierce 2001) was used. This best linear unbiased prediction method combines information about the spatial autocorrelation with a mean trend across the shooting range to reconstruct the profile of lead shot concentrations. This analysis was performed on the log-transformed data for four reasons. The spatial autocorrelation structure for these data is more easily discernible on the logarithmic scale, back-transformed predictions of lead are guaranteed to be non-negative, the back-transformed values will not overestimate the actual amount,

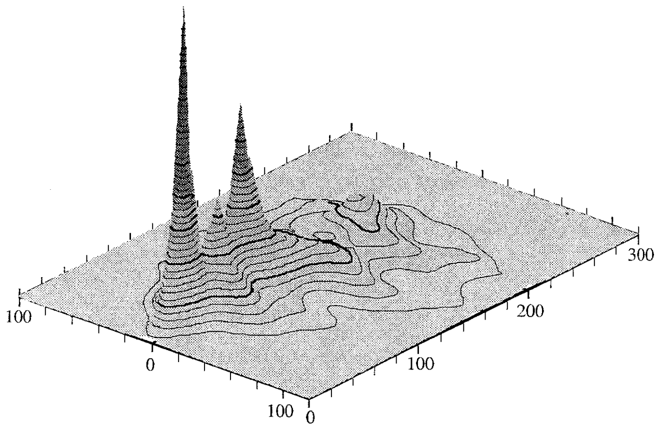

Fig. 9
Three-dimensional surface prepared by using kriging to analyze the data set given in Table 1. The contours on the surface are at 100-g intervals. This clearly shows the presence of the two major anomalies at approximately 30 and 80 m and the minor anomaly at about 180 m. It also shows a slight right-hand bias to the lead distribution; that is, there is a slightly higher concentration of lead to the right of the center line than to the left. This bias probably results from the release of flying targets from the right-hand-side of the shooting box and a slight tendency to shoot before they have reached the center axis of the range

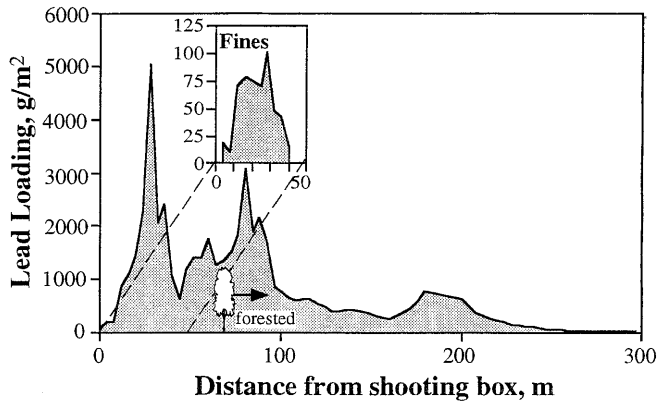

Fig. 10
A profile of the distribution of lead, in grams per square meter, along the center axis of the shotgun range from the shooting box to a distance of 320 m. This is a profile along the x=0 line in Fig. 9. It is apparent that there are two major maxima at ~30 and at ~80 m, and a smaller maximum at ~180 m. See discussion in text. The *insert* shows the concentration of fine lead particles (<0.1 mm and ash shown in Fig. 8b) along the center axis of the shotgun range. These particles have much larger surface areas per gram of lead and thus have much greater potential for surface reaction or dissolution than do the normal shotgun pellets

and the average lead amount can be modeled as a standard response surface on that scale. The result of the universal kriging takes into account the higher concentration along the center axis (Fig. 10) and permits development of a three-dimensional surface as shown in Fig. 9. This accurately shows the areas of maximum concentration and the much lower concentrations over most of the area and yields an estimate of 11.1 t of lead for the entire area affected.

Results and discussion

Lead densities

In more than 100 samples taken on and around the shotgun shooting range, the amounts of dispersed shotgun pellets and bullets ranged from zero to more than 5,000 g/m^2. Lead shot constituted more than 95% of all of the metal recovered in most samples except those taken at the sites where ad hoc stationary targets were set. Actually, the only sample ever taken that had no pellets was a sample taken 20 m behind and 20 m to the right of the shooting box. Every other sample (including one 20 m behind and 20 m to the left of the shooting box) had at least one pellet present. The greatest densities of lead shot lay along the center axis (the profile shown in Fig. 10 and the line where x=0 in Fig. 9), where the lead loading rises to more than 5,000 g/m^2 at a distance of 28 m. The lead concentration then drops to about 1,100 g/m^2 at a distance of 40–65 m and then rises to more than 3,000 g/m^2 at a distance of ~80 m. Beyond that maximum, the concentration of lead drops to a value of less than 400 g/m^2 at 130 m before rising to a third maximum of more than 750 g/m^2 at about 180 m.

To relate the lead concentrations to the numbers of shotgun pellets that occur in various areas, representative samples of the lead shot were examined and it was found that there were approximately 12.5 shot pellets per g. Thus, concentrations of 100 g/m^2 are equivalent to approximately 1,250 shotgun pellets per m^2. Given that typical 12 gauge shotgun shells contain 30–45 g of shot, the 100 g/m^2 areas are equivalent to about three shotgun shell loads per square meter. The most lead-rich sample (at 28 m along the center line) contained 4174 g of shot per m^2 (and 874 g of bullets). The 4,174 g of shot per m^2 are equivalent to approximately 115 shotgun shell loads per m^2. Assuming that 95% of the 11.1 t of total lead on the shotgun range is present as shot, there are approximately 132,000,000 individual pellets dispersed over the affected area. This is roughly equivalent to approximately 285,000 shotgun shells discharged there since the range opened in 1993.

Shot distribution

The primary objective of the study was to determine the distribution of the lead and related metals that have accumulated on the shooting range since it was opened in 1993. This information would provide a real measure of the total area of impact from activities on the shooting range, provide an estimate of the total amount of lead dispersed at the range, reveal areas of anomalous accumulation of lead, and provide background information that might prove valuable in the planning of other similar shooting ranges. The recovery and analysis of lead and related metals from more than 100 samples distributed across the shotgun shooting area of the Blacksburg shooting range revealed that the lead is not distributed in a regular pattern, but rather that there are distinct areas of high concentration. The scope of these anomalies is evident in a perusal of the data set in Table 1; Fig. 10 shows a profile outward along the center axis of the range, and Fig. 9 shows a three-dimensional model of the lead distribution.

Universal kriging predictions of the shot distribution profile based on a second-order response model for the average lead amount and a spherical autocorrelation model without nugget effect are shown in Fig. 9 after back-transformation onto the original scale. The total amount of lead under this profile gives an estimate of the total lead amount on the range, which equals 11.1 t or an average of 168 g of lead per square meter.

At the outset of the study, the investigators did not know the distance to which shot would be distributed into the forest beyond or beside the approximately 60×60-m cleared area. No data existed on the types of shot being used, the trajectories of the shooting, or the degree to which the forest trees (up to 12–15 m in height) might effectively reduce the travel distance of the shot. During the study, it was found that the National Shooting Sports Foundation (1997) had presented some diagrams of idealized shot distribution for skeet ranges where shooting was carried out under supervised conditions using approved shot and targets. Their diagrams indicated flight trajectories of up to ~225 m. Hence, the investigators anticipated that some samples of lead shot might be found 150 m or so beyond the cleared area. The Blacksburg shot gun range is, of course, significantly different than the NSSF ranges because of unsupervised general use of many types of weapons and detailed study revealed that more than 100 g Pb/m^2 existed in samples at distances of 260 and 280 m out from the shooting box. The farthest sample taken, 320 m from the shooting box along the center line, still contained two lead pellets (0.8 g/m^2). Thus, it was apparent that the area affected by the shotgun pellets extended outward as much as 300 m and laterally from –100 m on the left to +120 m on the right side. This is equivalent to 66,000 m^2.

The distribution of the lead shot on the shotgun range reflects the patterns of firearm use on the range. Hence, it is clear that the two principal anomalies result from two different shooting modes. The close anomaly at 25 to 30 m results from users mounting targets at this distance as shown in Fig. 11. The investigators have observed numerous range users firing at targets that have been set in the center of the cleared area at 25–30 m. Figure 11 shows targets set against a small log and the pattern of cleared vegetation resulting from shooting along the center line is clearly evident. Common targets include clay targets, golf balls, plastic milk jugs, glass bottles, small cardboard boxes, fruits, and vegetables. The investigators have also observed shooting at sofas. Numerous small pieces of wire and resisters, and even a small piece of a gold contact, apparently derived from electronic devices such as digital phones have been recovered (Fig. 12a). The investigators have been told of shooters using computers as targets; although the reports are anecdotal, confirmation appears to exist in the discovery of numerous damaged computer keyboard keys (Fig. 12b). The placement of the targets at

Fig. 11
Targets are commonly placed at 25–30 m, especially in the center of the cleared surface area, as shown in this photograph. The targets are most commonly clay pigeons, golf balls, bottles, boxes, and assorted fruit, but may range widely as shown in Fig. 12

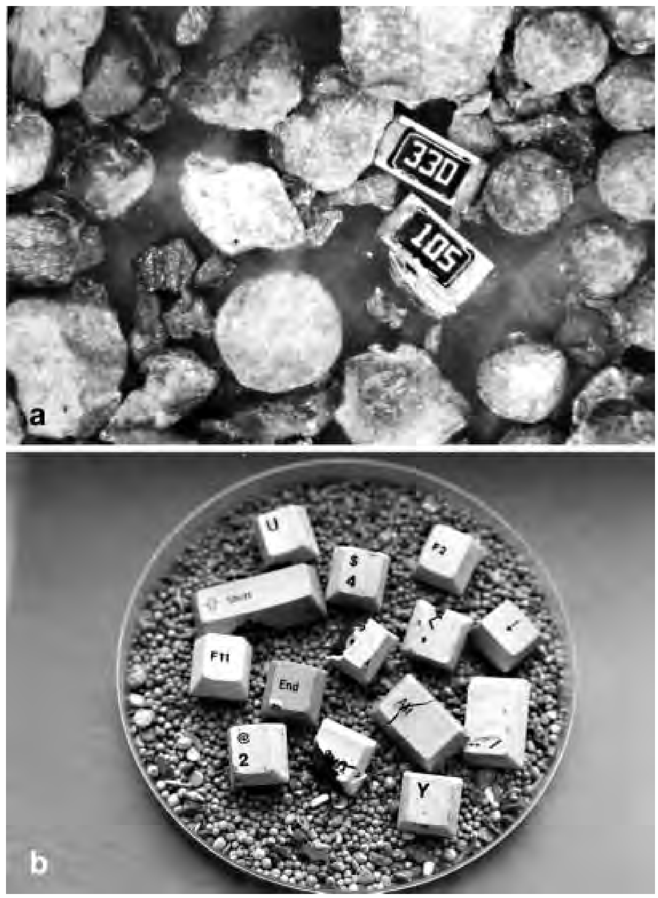

Fig. 12a,b
At approximately 30 m, the targets used vary widely in nature and the firearms employed range from shotguns to pistols and rifles. **a** Parts of small electronic devices intermixed with the shot evidence that shooters employ a wide variety of targets including cellular phones and computers. **b** The presence of numerous damaged computer keyboard keys appears to verify reports of computers being used as targets

25–30 m results in the accumulation of large amounts of lead at this distance, especially because there is a slight rise in the range surface at this distance that would tend to retain much of the shot. Samples taken from 20 to 40 m, and especially at 25–30 m, commonly contain rifle and pistol bullets as well as shot (Fig. 12c); this indicates that some shooters use the shotgun range for target practice with other types of firearms. The peak of lead concentration is quite narrow because targets are generally set in or very close to the center of the range. The breadth results from some spacing of targets, ricochet, and use of shotguns that spread the shot over some width. The total amount of lead dispersed on the cleared area of the shooting range (approximately 3,600 m^2) is estimated to be 1.72 t, which is equivalent to approximately 15.5% of the total lead dispersed at the shotgun range.

The high lead concentration at ~80 m apparently results from the accumulation of lead fired at elevated trajectories in attempts to hit clay targets that have been launched or thrown. Because the launching pad is approximately 7 m to the right of the shooting box, most pigeons are moving from right to left in front of the shooter. They are, however, moving in a very wide range of trajectories – from nearly straight up over the shooter to very low across in front of the shooter. Even when shooters are successful in hitting the flying targets, most of the shot do not strike the target, but rather travel well beyond it. The 80-m anomaly is wider than the closer one because of the spread of the shot at a greater distance and because shooters are tracking a moving target across the range as they are firing. The peak at approximately 80 m apparently results from the combined effect of the normal low trajectory of much of the shot and from the slowing of some of the shot by leaves and branches of trees at the edge of the cleared area. There is a slight right-hand bias to the peak of concentration, probably resulting from the tendency of the shooters to fire early in the flight of the flying targets.

The cause of the third, and much smaller anomaly, at approximately 180 m out from the shooting box is not so clear as the two nearer and larger anomalies. The tree trunks precluded any of the shot in a low trajectory from reaching the site, so it must result from a higher trajectory that arcs up over the first line of trees and falls at that distance. There is no clear explanation why there is a minimum between the second large anomaly at about 80 m and the third anomaly, but the data clearly define these features.

Shot sizes and distribution of fine lead particles

Throughout most of the cleared surface and surrounding forested area, more than 90% of the shot is number 6 to 8 pellets; this is consistent with information on the large number of discarded shot boxes and shot gun casings. These pellets are generally 2–3 mm in diameter, as shown in Fig. 8a. Occasionally there are smaller birdshot and larger 4–5-mm buckshot. More than 95% of the pellets appear as standard lead pellets; only about 5% are copper jacketed shot and the number or steel shot is trivially small. Sectioning and examining many shot reveals that at least some contain hardening agents such as copper, arsenic, and antimony; data in hand are insufficient to determine the quantities of those metals presently on the range.

Careful examination of the shot recovered from the range surface near the shooting box revealed that those samples contained significant quantities of fine particulate lead as shown in Fig. 8b. These samples were carefully panned to insure a high recovery of these fine materials. The "fine" materials shown in Fig. 8b have passed through a 1-mm sieve and range in size down to less than 0.01 mm. They are apparently formed either as the result of lead shot colliding with other as they exited the gun, or as the result of abrasion on the choke of the guns as they were fired. A series of samples were taken at 4-m intervals along the center axis (Fig. 9) to specifically determine the quantity of the fine lead particles. These data are shown in the insert in Fig. 10 and reveal that the amount of fine particulate lead rises until about 30 m and then declines rapidly. The importance of these particles is that they have a much larger surface area per gram of lead than do the complete lead shot and, hence, could leach more lead per gram than intact shot. An additional consideration is that some recovery methods that sieve shot and bullets out of soils as a means of recovery or cleaning will probably not recover the fine particulate lead present near the shooting box.

Effects on the trees

The cleared surface of the shotgun range has been cut out of a 60-year-old second growth mixed hardwood forest (see Fig. 2) and is bounded by forest on all sides. The trees along the forest margin of the cleared area at approximately 65 m from the shooting box and along the sides of the cleared area range from 1 to 35 cm in diameter and are primarily oaks. There are, however, scattered pine, maple, gum, dogwood, and minor amounts of other hardwoods. When the trees are leafed out, it is apparent that some of the trees along the back margin of the open area are distressed as evidenced by fewer live branches and leaves than are present on the trees along the sides. Examination of the trees in the first 5 m beyond the back margin of the developed area reveals that much of the lead shot has sufficient velocity to penetrate the smooth bark of 1- to 10-cm diameter maples and to penetrate the somewhat cork-like bark of the pines. Leaves of trees and shrubs along the back margin have numerous holes from shotgun pellets. At distances of ≥70 m from the shooting box (that is more than about 5 m into the forest beyond the margin of the cleared area), there is no visible evidence of shotgun pellet damage to the hardwoods, although a few scattered trees have bullets stuck in them. Out to distances of more than 100 m from the shooting box, the softer cork-like bark of the pines does contain numerous embedded shotgun pellets (Fig. 13a). The number of pellets embedded and the small impressions left by shot that bounced off the pine trees declines with distance (Fig. 13b) until about 130 m, beyond which there is no longer any visible effect on the trees.

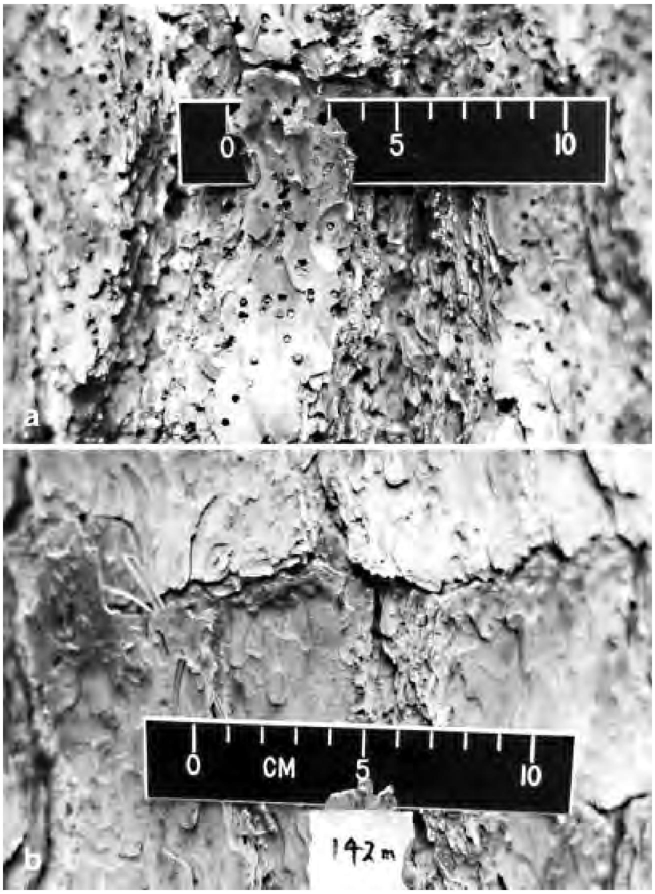

Fig. 13a,b
Trees in the forest beyond the cleared area of the shotgun range contain embedded shotgun pellets and small impressions from the pellets out to a distance of approximately 130 m from the shooting box. The intensity of the visible impacts declines with distance as evidenced by photographs of the bark of Virginia pines at **a** 91 m, and **b** 142 m

Summary and conclusions

The Blacksburg Shooting Range in the George Washington and Jefferson National Forests is a typical public recreational shooting area with a rifle range and a shotgun range. It has similar characteristics with many outdoor ranges in the United States. More than 100 separate 50×50cm sites have been sampled on the shotgun range area to determine the area impacted by lead shot dispersal, the patterns of lead dispersal, and quantity of lead present. Lead has been dispersed over an area approximately 220 m wide by 300 m in length. The total quantity of lead in the shotgun range area is estimated as 11.1 t. The highest concentrations of lead occur along the center axis of the range at a distances of approximately 30 and 80 m; a lesser concentration occurs along this axis at about 180 m. These concentrations result from shooting patterns at stationary targets and at air-borne targets.
The geostatistical analysis yielded an estimate of total lead on the range surface of 11.1 t, which is considerably less than a biased overestimate obtained from extrapolating the sample mean to the reference area of 220×300 m^2. This estimate is a conservative assessment for several reasons. Lead can only be lost from a sample during sampling, not added to it. Great care has been exercised in the collection and processing of the samples to minimize losses, but some small losses can not be ruled out. Shot lodged in the vegetation, such as pine bark, was not been collected and collection areas in front of tree trunks in the forested area were avoided. Shooting has continued since the sample collection and shot continues to accumulate on the range. Finally, the statistical analysis of the lead concentration on the logarithmic scale followed by back transformation (exponentiation) to the original scale is likely to yield slight underestimates of the actual amount. Only in certain special cases, such as normally distributed data, can precise bias corrections be applied. Because the log-lead concentrations were clearly non-normally distributed, these corrections were not applied here. Fortunately, (universal) kriging remains a best linear prediction method, even if the data are not normally distributed (Schabenberger and Pierce 2001).
The average rate of lead accumulation on the shot gun range is approximately 1.4 t/year based upon the total estimated lead and the time since the range was opened in 1993 through to the end of 2000. Periodic range cleaning by Forest Service personnel or volunteers removes much of the larger debris, such as targets and shells, but does not recover much if any of the dispersed shot. Accordingly, it is reasonable to extrapolate that lead will continue to build up on the range area at a rate of at least 1.4 t per year. More than 80% of the lead is dispersed in the forest beyond and adjacent to the ~60×60-m cleared range surface.

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Lead Pollution at Outdoor Firing Ranges

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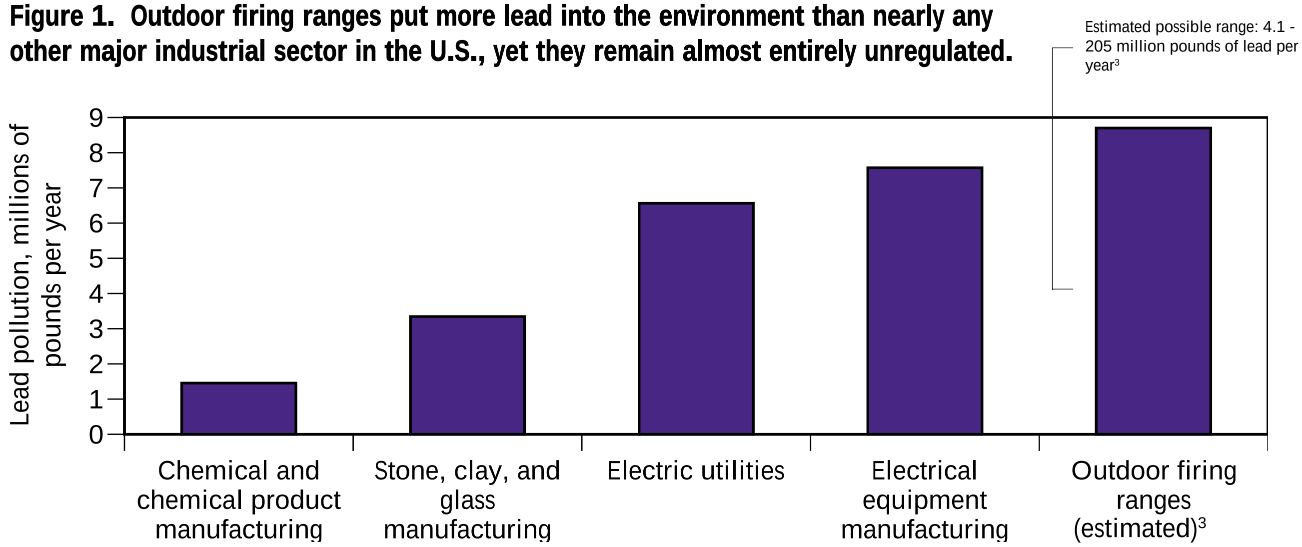
Outdoor firing ranges can be highly contaminated with lead

Lead is the most prevalent contaminant at Superfund sites across the country (EPA 2001a). The highly toxic metal triggers more Superfund cleanups than any other industrial chemical or waste product in the environment. Lead is considered the number one environmental threat to children's health by the federal government, and at very low levels is linked to subtle developmental delays and reduced I.Q. in children (EPA 2001b, 2001c).

Recognition of the toxicity of lead is broad and nonpartisan. On April 17, 2001, the Bush Administration took its first action against lead polluters, in an announcement that the Bush Environmental Protection Agency (EPA) would uphold a Clinton Administration rule requiring all businesses releasing 100 pounds of lead a year (or greater) to report this pollution to the government. The announcement came despite objections raised by affected industries.

Lead contamination has now emerged in another context: firing ranges. The military has been involved in massive lead cleanup efforts for years, at an estimated 700 military firing ranges across the country. In this report, we present the first estimates of lead pollution at commercial and private firing ranges. Our analysis shows that shooting ranges are likely to be one the biggest sources of lead pollution in the country (Figure 1). Assuming a very modest level of activity at the nation's 1,813 firing ranges - just 15 customers shooting 50 rounds a day - firing ranges would put nearly nine million pounds of lead into the environment per year. This is more lead pollution than is produced by any other industry except metals mining and manufacturing, and waste recovery operations. While most of this lead will likely remain on the site, the nation's firing ranges represent a major potential source of lead in water and wildlife, and a potential liability to nearby property owners who may find themselves living next to a hazardous waste site or who might be victims of lead drifting onto their property.

Figure 1. Outdoor firing ranges put more lead into the environment than nearly any other major industrial sector in the U.S., yet they remain almost entirely unregulated.



Notes:
1) This figure represents the top five lead polluting industries in the country after metals mining and manufacturing, and waste recovery operations. 2) Industrial emissions are Toxics Release Inventory reportable emissions for 1999 of lead and lead compounds. 3) Assumes 15 people firing 50 rounds per day at 1,813 ranges nationwide. Estimated possible range of lead pollution produced at 1,813 ranges: minimum value shown represents 10 people firing 20 rounds per day for each range; maximum value shown represents 100 people firing 50 rounds per day for each range.

Source: U.S. Environmental Protection Agency.

Firing ranges are exempt from pollution control laws

In spite of widespread scientific and political agreement on lead toxicity and the need to reduce it, commercial firing ranges are exempt from the EPA's new lead reporting requirements, and virtually every major pollution control law in the United States.

A number of loopholes allow unlimited lead contamination at outdoor firing ranges. In spite of legal precedents to the contrary (VPC 2001), EPA continues its policy allowing firing ranges near water bodies to operate without the pollution discharge permits that are required under the Clean Water Act for all other lead-polluting industries. These ranges present a significant water pollution threat, according to industry sources (NASR 2000). Under the Resource Conservation and Recovery Act, most industries are under strict requirements to dispose of lead waste safely, typically in hazardous waste landfills; shooting ranges are exempt because the act of firing bullets into the soil has not been interpreted by EPA as "discarding" lead.

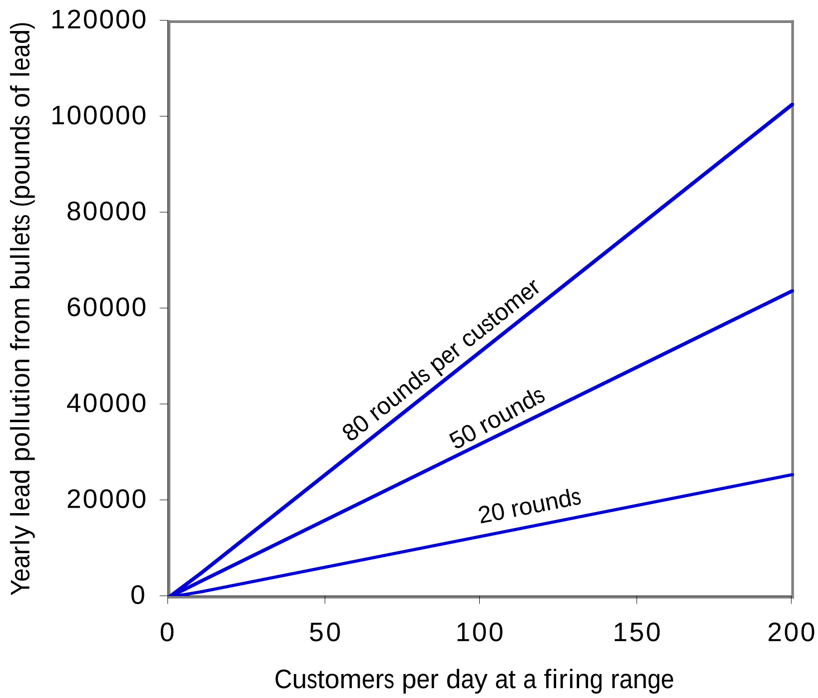
The military's response to contamination at its ranges illustrates the potential magnitude of the problem. The armed forces are involved in massive lead cleanup efforts at an estimated 700 military firing ranges across the country. Private firing ranges enjoy immunity from the environmental laws that drive these cleanups, despite the fact that their operation can result in contamination levels many times what triggers major remediation efforts at industrial and military sites. At very modest levels of activity it is quite possible that every firing range in the U.S. is contaminated with lead at levels that would trigger Superfund cleanups (Figure 2). The threat lead poses to the surrounding environment and communities is not known, but could be substantial. If totally dissolved into the environment:

- A single shot from a 30-30 Winchester containing 8.1 grams of lead could contaminate about 370 cubic feet of soil to Superfund site contamination levels (the equivalent of about 56 bathtubs filled with Superfund site dirt).

- The lead in just one bullet from a 22-caliber rifle (2.6 grams) could contaminate one day's worth of drinking water for the entire population of Salt Lake City with a level of lead deemed unsafe by the EPA. (One bullet weighing 2.6 grams fully dissolved in 51,000 gallons of water results in a lead concentration of 15 parts per billion, the legal limit for drinking water.)

- The amount of lead used in bullet production over a period of four years would be enough to contaminate the entire State of Rhode Island at Superfund levels, to a depth of one foot.

Figure 2. Even at modest levels of activity, a single firing range can become contaminated with tens of thousands of pounds of lead.



Source: Environmental Working Group.

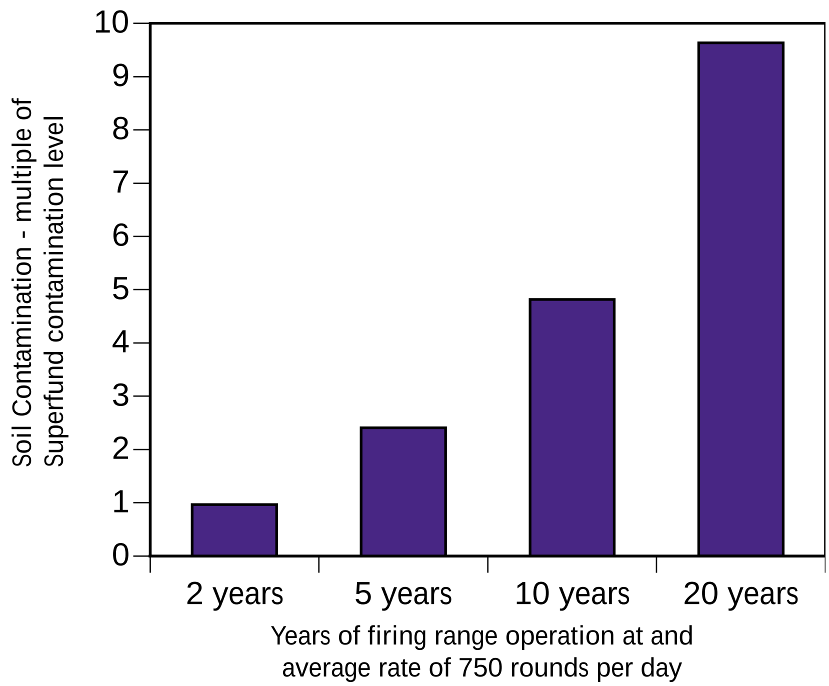
What is a safe level of lead exposure?

There is no amount of lead exposure known to be completely safe for a child. Federal safety standards are based on exposures that present a risk for a child's brain to be measurably harmed. Currently, the Centers for Disease Control and Prevention uses a benchmark safety level of 100 micrograms of lead per liter of a child's blood as an indicator for children at risk for the harmful effects of lead.

The federal government considers that a child playing outdoors is at risk for lead poisoning if concentrations of lead in the soil where the child is playing are higher than 400 parts per million (400 ppm). Through incidental contact with soil from outdoor play, children ingest tiny amounts of soil through what the EPA calls children's normal "hand-to-mouth" activity. In other words, children play in the dirt, get dirt on their hands, and then put their hands and fingers in their mouths, or eat food without washing their hands.

When industrial pollution impacts residential areas - for instance, when soil is contaminated with levels of lead that could put children at risk for lead poisoning - various environmental laws in this country, including the Superfund law, require cleanup actions to make the area safe for children. In contrast, most firing ranges fall outside the purview of environmental statutes. Lead levels can build up to any amount at most privately owned outdoor firing ranges and neighboring properties, with absolutely no requirements for soil testing or remediation until that property is sold. Generally it is only after rivers, streams, or public water supplies have become contaminated that citizen lawsuits can force cleanup actions.

Figure 3. In just 2 years a typical firing range can have lead contamination equivalent to a 5-acre Superfund site.



Source: Environmental Working Group.

Table 1. If totally dissolved in the water supply, the lead contained in a single bullet could contaminate the amount of water consumed daily by hundreds of thousands of people.

	Lead contained in a single shell or bullet (grams)	One bullet can contaminate the amount of water consumed daily by this many people…	Equivalent to the amount of water consumed daily in…
12-gauge shotgun shell	28.0	1,866,667	Houston
45 automatic pistol match ammunition	12.0	799,200	San Francisco
308 Winchester round	9.7	648,000	Baltimore
30-30 Winchester round	8.1	540,000	Seattle
9 mm Luger handgun bullet	7.5	496,800	Denver
22 caliber rifle bullet	2.6	172,800	Salt Lake City

Source: Environmental Working Group. Contamination level was taken as 15 ppb, the action level under the Federal Safe Drinking Water Act.

Outdoor firing ranges can be contaminated with tremendous amounts of lead that can contaminate water supplies and put children at risk

Consider a firing range that has just 15 visitors each day, each of whom fires about 50 rounds or bullets. Assuming an average lead content representative of the common types of ammunition used, in just two years the entire top foot of soil over an area of five acres could be contaminated to Superfund levels. This firing range operating over a period of 20 years would contain about 9.6 times the amount of lead that could trigger a Superfund cleanup (Figure 3). Ranges operating at a higher volume of activity on the same space could easily contaminate the ground to a level where remediation would require the soil to be treated as hazardous waste before it was placed in a double-lined hazardous waste landfill.

The lead found in soil at firing ranges will be in the form of various amounts of dust, small fragments, and nearly intact bullets and pellets. The bullets and pellets will dissolve with time as rain leaches through the soil. Depending on soil type and pH, varying amounts of lead can move off the site, potentially contaminating water supplies. At any given time, the contamination profile at a firing range can include highly contaminated soil in the backstop or berm, more diffuse contamination across the entire extent of soil leading to the backstop, and then some area under the ground in which rainwater has leached lead into the groundwater to form a plume of contamination. Lead will migrate more quickly in sandy soil, with a higher potential to contaminate water supplies. The lead contained in even a single bullet can contaminate the amount of water consumed daily by hundreds of thousands of people (Table 1).

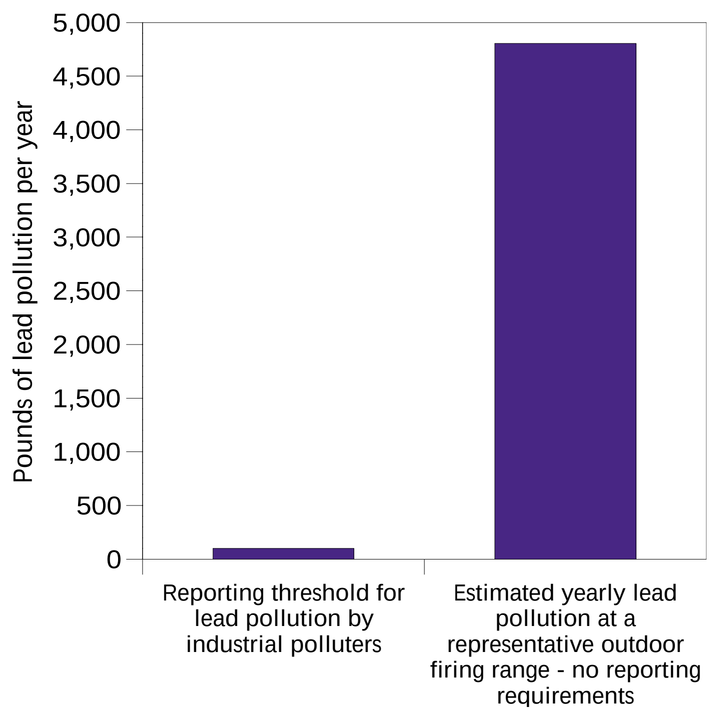
Children living near firing ranges can be exposed to lead through dust that blows off the range to contaminate the air and soil nearby. Families living near firing ranges could be drinking water from their private well that is contaminated with lead that has leached from the range soil. Public water supplies can be contaminated. In the long-term, each firing range in the U.S. almost certainly represents a piece of land so highly contaminated that it would require a massive cleanup effort to be safe for wildlife or any industrial or residential use.

Outdoor firing ranges are exempt from new lead pollution reporting rules

New rules finalized by EPA in January 2001, and supported by the Bush Administration, require industries across the country to report even small amounts of lead pollution to a public database maintained by the government called the toxics release inventory (TRI). Facilities that discharge just 100 pounds of lead each year to the environment are subject to these new, strict reporting requirements.

Private firing ranges are exempt from the new reporting requirements, regardless of how much lead they put in the environment. And the amounts appear to be substantial. A small firing range can emit 100 pounds of lead to the environment (the minimum to trigger reporting for the regulated

Figure 4. A representative outdoor firing range pollutes at 48 times the level that triggers strict reporting requirements for industrial polluters.



Source: Environmental Working Group.

industries) in a matter of days. For example, a range that has 15 customers each day, each of whom shoots 50 rounds or bullets, would create 100 pounds of lead pollution in 7.5 days, or 4,800 pounds of lead contamination in a year (Figure 4).

Despite their significant lead pollution, outdoor firing ranges are exempt from the reporting requirements of EPA's new rules. These ranges are not required to report their pollution, they are not required to get a permit to pollute, and they are not required to clean up the pollution that they cause (unless injured parties bring legal action). This broad exemption from environmental statutes is producing thousands of highly contaminated toxic waste sites at firing ranges across the country.

Recommendations

Private firing ranges are a potentially huge and completely unregulated source of lead pollution in the environment. In order to more fully understand the exact nature of this problem and devise solutions to address it, we recommend that the U.S. EPA, in coordination with state environmental agencies, immediately begin a study of the problem of lead contamination at commercial and private shooting ranges. As a part of that study the U.S. EPA should commission a study of lead levels in the blood of range employees and their children, frequent users of the facilities and their children, as well as children living near these facilities.

Methodology

Estimates of lead pollution presented in this report are based on the following assumptions:

- Soil at firing ranges: Representative unit weight of soil into which bullets are fired — 110 pounds per cubic foot

- Weight of ammunition: taken as representative weight from the range of weights of commonly-used ammunition (Ramage 2000):

  12-gauge shotgun shell – 28 grams
  22 caliber rifle bullet – 40 grains (2.6 grams)
  9 mm Luger handgun bullet – 115 grains (7.5 grams)
  45 automatic pistol match ammunition – 185 grains (12.0 grams)
  30-30 Winchester round – 125 grains (8.1 grams)
  308 Winchester round – 150 grains (9.7 grams).

  For purposes of calculations of total pollution, an average bullet weight, 123 grains (8.0 grams) was assumed. This represents the mean of the 5 lightest types of ammunition shown above (shotgun shells were not included).

- Calculations of contamination relative to Superfund levels: For purposes of discussing the possible extent of contamination at firing ranges relative to that at Superfund sites, lead concentrations were calculated assuming the lead to be concentrated in the upper foot of soil at a range.

- Total number of commercial firing ranges: Calculations of national pollution amounts from firing ranges assume 1,813 operating firing ranges. This is the number of outdoor ranges registered on the National Shooting Sports Foundation web site, but this list is not comprehensive. Catogories of ranges included in the estimated total, as listed on www.nssf.org, are: handgun outdoors, rifle outdoors, skeet shooting, sporting clays, trap shooting, and cowboy action shooting.

- Average amount of water consumed by an individual: Taken as the average population wide consumption in the U.S., one liter (0.29 gallons) per day, from water consumption data presented in EPA 1999.

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WORKPLACE SOLUTIONS

From the National Institute for Occupational Safety and Health

Reducing Exposure to Lead and Noise at Outdoor Firing Ranges

Summary

The National Institute for Occupational Safety and Health (NIOSH) recently published recommendations for reducing exposure to lead and noise at indoor firing ranges [NIOSH 2009]. However, workers and users of outdoor firing ranges may be exposed to similar hazards. This follow-up document examines exposures at these ranges and recommends steps to reduce such exposures.

Description of Exposure

Affected Population

According to the Bureau of Justice Statistics, more than 1.2 million Federal, State, and local law enforcement officers work in the United States [DOJ 2012, 2011]. These officers are required to train regularly in the use of firearms and may be exposed to hazardous levels of lead and noise if they train at outdoor ranges. In addition to law enforcement, NIOSH estimates that shooting ranges employ 40,000–60,000 workers, and that about 15% of the U.S. population, or 34.4 million people, participate in target shooting [NSSF 2010].

Exposure Sources

Several studies of outdoor firing ranges have shown that exposure to lead and noise can cause health problems, particularly among employees and instructors [NIOSH 2011; Tripathi et al. 1991; Goldberg et al. 1991]. Lead exposure occurs mainly through inhalation of lead dust, skin contact with lead from bullets, or ingestion (e.g., eating or drinking with contaminated hands) [NIOSH 2009]. Workers and shooters involved in shooting, cleaning operations, collecting casings, and handling spent bullets may also be exposed to lead.

Indoor vs. Outdoor Ranges

An estimated 9,000 non-military outdoor ranges exist in the United States, with millions of pounds of lead from bullets shot annually. Because outdoor ranges are typically built in an open area, lead and noise are more widely dispersed. Outdoor ranges need less cleaning and maintenance than indoor ranges. However, despite the natural ventilation of outdoor firing ranges, personal breathing zone lead levels can exceed the NIOSH recommended exposure limit (REL) and Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) [Mancuso et al. 2008]. Some outdoor ranges have ballistic baffles overhead and concrete walls and structures on the sides. The air in these spaces can become stagnant and lead to increased exposures.

Exposure Limits

Lead

OSHA has established two different limits for airborne exposure to lead [29 CFR 1910.1025*]. The action level for airborne lead exposure is 30 micrograms per cubic meter of air (μg/m^3) as an 8-hour time weighted average (TWA). The OSHA PEL for airborne exposure to lead is 50 μg/m^3 as an 8-hour TWA. For workers exposed to airborne lead above the action level for more than 30 days per year, OSHA requires blood lead monitoring every 6 months. If an employee's blood lead level (BLL) exceeds 60 μg lead/100 g of whole blood (or the average of the last 3 BLLs is greater than 50 μg lead/100 g), the employee must be removed from further exposure until BLLs decline to 40 μg lead/100 g or less.

The NIOSH REL for airborne lead is 50 μg/m^3 as an 8-hour TWA.

The U.S. Department of Health and Human Services recommends that BLLs among all adults be reduced to <10 μg/dL [DHHS 2011].

Noise

For noise exposure, the OSHA PEL is 90 decibels, A-weighted (dBA), and the action level is 85 dBA both as an 8-hour

*Code of Federal Regulations. See CFR in References.

TWA using a 5-dB exchange rate [29 CFR 1910.95]. The OSHA occupational noise standard states that exposures to impulsive noise should not exceed 140 dB peak sound pressure level (SPL).

The NIOSH REL for noise (8-hour TWA) is 85 dBA using a 3-dB exchange rate [NIOSH 1998]. NIOSH also recommends that peak SPL not exceed 140 dB.

NIOSH Investigations

NIOSH conducted Health Hazard Evaluations that involved exposure to lead and noise to law enforcement officers and employees at outdoor firing ranges (Figure 1).

Lead

At a firing range in California, 16 personal breathing zone (PBZ) air samples and six surface wipe samples were collected for lead. The air samples did not exceed occupational exposure limits (REL or PEL) for lead. The highest lead exposure (15 $\mu g/m^3$) was measured on an instructor at the range. Exposures can vary depending on weather conditions (particularly wind speed and direction) and the shooter's proximity to the gun smoke source. The highest levels of surface contamination were on the firearms. Lead was also found on outdoor picnic tables where employees ate. Colorimetric wipe tests identified lead on hands, but employees had good personal hygiene practices; no lead was found on hand wipes after hand washing [NIOSH 2011].

Noise

NIOSH evaluated the noise exposure of a SWAT team in Fort Collins, CO, during training exercises. Hearing was tested before and immediately after training sessions. Noise measurements were made of firearms and of the protection offered by customized hearing protectors. Most officers did not show any change in hearing after shooting, but the oldest group did show mild hearing loss at higher frequencies. Firearm noise was between 159 and 169 dB, which was greater than the 140 dB peak limit for impulsive noise. Peak noise reductions from the ear plugs, ear muffs, and customized protectors were in the 30 dB range. Double hearing protection (plugs plus muffs) added 15–20 dB of additional protection [NIOSH 2003].

Figure 1. NIOSH exposure assessment of Federal law enforcement officers conducting a live-fire training exercise

Recommendations

Workers and shooters at outdoor firing ranges should take the following steps to protect themselves [NIOSH 2003, 2009, 2011]:

- Attend training, follow safe work practices, and participate in health monitoring programs.
- Report symptoms to your employer and get medical attention when needed:
  - Common health effects of lead poisoning in adults include reproductive effects, nausea, diarrhea, vomiting, poor appetite, weight loss, anemia, fatigue, hyperactivity, headaches, stomach pain, and kidney problems.
  - Exposure to high noise levels can cause hearing loss, tinnitus (ringing in the ear), stress, high blood pressure, fatigue, and gastro-intestinal problems.
  - If you suspect you have had high lead exposure, even if you show no symptoms, get your BLL tested.
- Practice good hygiene:
  - Wash hands and face with soap and water or clean them with lead decontamination wipes after shooting, handling spent cartridge cases, or cleaning weapons, especially before eating, drinking, or smoking. Wipes for cleaning skin without water are commercially available and should be used if access to soap and water is limited [NIOSH 2009].
  - Change clothes before leaving the range and wash clothes separately from other family clothing.
- Use personal protective equipment (PPE):
  - Wear double hearing protection (earplugs and earmuffs) and eye protection when shooting.
  - Wear a brimmed cap and tight-fitting clothes for protection against hot shells and ejected casings if the range's shooting stations are in very close proximity.
  - Wear properly-fitted respirators and full protective outer clothing for maintenance activities that involve close contact with lead dust or spent bullets.
  - Wear gloves and eye protection when using chemicals to clean firearms.

Employers should take the following steps to protect workers and shooters at firing ranges:

- Consider providing non-lead bullets and non-lead primers (often referred to as "green" or non-toxic" ammunition) [NIOSH 2011].
- If state law permits, consider providing noise suppressors for gun barrels [NIOSH 2011].
- Establish effective engineering and administrative controls:
  - Apply appropriate noise control measures, such as sound transmission barriers (i.e., walls, earthen berms), and absorptive materials such as acoustical treatments

and natural vegetative (i.e., plants, trees, grass) buffers to limit noise in nearby areas [MN DNR 2003].

— If possible, use non-porous materials, coatings, or plastic covers on all contact surfaces to make them easier to clean.

— Limit the length of time that workers and shooters use the firing range: rotate assignments and provide quiet, clean, break areas.

— If you operate a range with ballistic or overhead baffles and wall structures, consider using fans behind the shooters and pointed down-range in order to provide sufficient air movement away from the shooters.

— Routinely clean the range using proper techniques and disposal methods. Do not use dry sweeping, wiping, or dusting. Use wet cleaning and HEPA vacuums only [NIOSH2011].

— Consider installing wind speed and direction meters.

- Post range safety rules and provide authority to range masters to enforce them.
- Provide workers and shooters with training and information about hazards:

— Inform workers and shooters about the importance of hygiene in reducing potential lead exposures, post warning signs, and provide convenient washing facilities to encourage frequent hand washing.

— Prohibit eating, smoking, chewing gum, or tobacco use in areas potentially contaminated with lead.

— Inform pregnant workers and shooters about possible risks to the fetus.

— Ensure that workers are aware of symptoms that may indicate a health problem.

— Tell workers about participating in medical surveillance programs and getting their BLLs tested, even if they don't show symptoms.

- Review OSHA requirements for medical monitoring for lead (29 CFR 1910.1025(j)) and noise (29 CFR 1910.95(d)(e)(g)(h)).
- For best medical and lead management practices, consult the Association of Occupational and Environmental Clinics [Kosnett et al. 2007].
- To reduce lead contamination at your range, consult the EPA's Best Management Practices for Lead at Outdoor Shooting Ranges [EPA 2001].
- Establish a hearing conservation program [NIOSH 2011].
- Provide workers with protective equipment:

— Provide and encourage the use of double hearing protection devices (earplugs and earmuffs) along with hygiene and cleaning kits.

— Provide skin protection, eye protection, and NIOSH-approved respirators† for workers who clean lead-contaminated areas.

— Provide knee or full body pads to limit transfer of lead to clothing.

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†A written respiratory protection program should be developed and implemented that meets the requirements of the OSHA respiratory protection standard [29 CFR 1910.134].

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For more information

More information about firing ranges and NIOSH HHEs on firing ranges can be found on the NIOSH firing range topic page:

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General information about noise and lead exposures can be found on these NIOSH topic pages:

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Reducing Exposure to Lead and Noise at Outdoor Firing Ranges

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DHHS (NIOSH) Publication No. 2013–104

Outdoor Notes : Lead Shot Outlawed in Waterfowl Hunting Areas, Starting in 1991

BY EARL GUSTKEY

JUNE 27, 1986 12 AM PT

The U.S. Fish and Wildlife Service has announced that it plans to ban lead shot in federal waterfowl hunting areas throughout the country, starting in 1991.

The service is being sued by the National Wildlife Federation, the nation's largest conservation organization, which seeks a nationwide lead shot ban in 1987. Preliminary arguments in the suit are scheduled to begin today in U.S. District Court at Sacramento.

Both sides said that negotiations for an out-of-court settlement of the long controversy broke down Wednesday night.

The federation, the U.S. Fish and Wildlife Service and many other conservation organizations maintain that spent lead shot in waterfowl areas is responsible for the lead poisoning deaths of bald eagles and waterfowl. Estimates of waterfowl deaths related to lead poisoning range up to 2 million ducks a year. Service biologists say they know of 114 bald eagles killed since 1980 from eating birds carrying lead shot in their bodies.

Some hunting groups maintain that large-scale lead poisoning deaths of bald eagles and waterfowl are unproven, and that converting to less-dense steel shot would result in the crippling of far more waterfowl than is the case when lead shot is used.

The federation contends in its suit that the Endangered Species Act, the Migratory Bird Treaty Act and the Bald and Golden Eagle Protection Act all require that lead shot be banned in the lower 48 states, and that it can be ended by the 1987-88 hunting seasons.

The government's proposal for the lower 48 calls for a ban in 1987 in areas where waterfowl harvests exceed 20 birds per square mile during the hunting season. Each year more areas would be covered until 1991-92, when the ban would reach areas with harvests below five birds per square mile.

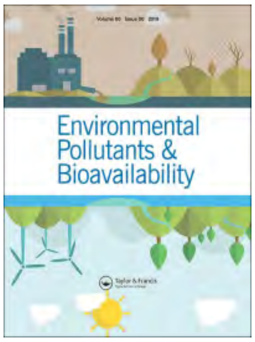
Alaska, where eagles are not endangered, would be exempt from the schedule but would still have to convert to steel shot by 1991.

Department of Fish and Game warden Carol Thompson reminds Salton Sea fishermen that an ocean sportfishing license isn't applicable to the Salton Sea, where a general fishing license is required. Thompson said she has cited more than a dozen fishermen at the sea this month who had only ocean licenses.

"It's the No. 1 violation at the sea presently and the confusion seems to be a misunderstanding in terms," Thompson said. She added that many license agents in Los Angeles, Orange and San Diego counties mistakenly believe only an ocean license is required at the sea.

Briefly

Don Williams of Ceres, Calif., caught a 12-pound 13-ounce largemouth bass at the recent Red Man pro bass tournament at Clear Lake, Calif., which earned him $1,000 and tied a 13-year-old Bass Anglers Sportsman's Society record for the largest bass caught in a BASS tournament. The big bass also helped Williams win the tournament and a first-place check of $1,810. . . . Wyoming biologists report that grizzly bear incidents there this spring were unusually low and attribute the ursine inactivity to an unusually wet, cool spring, which provided good bear forage in remote areas. . . . A Utah game warden recently saw a rare river otter in Morgan County, which expands the areas where the otters are known to exist. . . . David Carradine and Bill Walton are scheduled to participate in a Muscular Dystrophy Assn. celebrity trapshoot July 12 at Prado Tiro in Chino, the Olympic shooting site. . . . The OP Pro Surfing Championships Aug. 26-31 at Huntington Beach will be an "AA" rated event by the Assn. of Surfing Professionals.



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Pollution risk from Pb towards vegetation growing in and around shooting ranges – a review

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REVIEW ARTICLE

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Pollution risk from Pb towards vegetation growing in and around shooting ranges – a review

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ABSTRACT
Commissioned and de-commissioned shooting ranges continue to pose an environmental and human health risk due to the accumulation of toxic Pb emanating from spent munitions. The phytotoxic effects of Pb accumulation in plants include inhibition of root growth and lowering of plant metabolism. The uptake of Pb by plants is directly affected by factors such as plant species and physicochemical properties of the soil. However, scientists and researchers have leveraged on the ability of some plant species to accumulate and tolerate Pb toxicity and applied them in the control and management of Pb pollution of shooting range soils. This technique is called phytoremediation. The objectives of this review are: (i) to assess the prevalence of toxic Pb metal in plant species growing in and nearby shooting ranges, (ii) to establish the soil-plant mechanistic pathway for Pb (iii) discuss the effectiveness of phytoremediation technology towards shooting range soil amendment.

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Lead; shooting ranges; phytoremediation; phytotoxicity; soil pollution

1. Introduction

Vegetation and crops in agricultural fields in the vicinity of shooting ranges are at risk of pollution from Pb emanating from the use of Pb-containing munitions [1–3]. The extended residence time of Pb in soils due to its insoluble mineralogical products and lack of deterioration from microbial activity means that the bioavailability and bioaccessibility of this toxic heavy metal can exist in the soil for a very long time [1]. In addition, the half life of Pb in the soil is approximated to be in the range of 740 to 5900 years [4]. The background concentrations of Pb in soils lie within the range of 10 to 30 mg/kg [4]. The distribution and accumulation of Pb in soils arising from anthropogenic activities such as shooting practices is well documented [5–7]. Total Pb concentrations of up to 1×10^4 µg/g have been reported in shooting range soils [8]. Furthermore, large quantities of used Pb containing projectiles amounting to 1×10^8 spent Pb shots per hectare have been recovered in shooting range soils [8]. In most studies, total Pb concentrations in shooting range soils were found to be exceedingly higher than the set regulatory limits. For example, in Norway, total Pb concentration of 33,000 mg/kg was established in shooting range soil [9]. This shooting range experienced Pb loading of 330 times the set World Health Organization maximum limit of 100 mg/kg. Similarly, the United States Environmental Protection Agency's maximum contaminant limit (MCL) of 400 mg/kg was surpassed 83 times [9]. The use of Pb in industrial and household products is highly controlled and in some cases prohibited due to the detrimental effects from exposure to Pb [10]. Human and animal exposure to Pb through contact with polluted soils or consumption of contaminated plant products such as fruits and vegetables can lead to severe health problems and death [11,12]. Blood Pb concentrations of more than 10 µg/dl have been reported in 42.4% of shooters in South Africa [12].

The bioaccumulation of Pb in plants and crops cultivated near shooting ranges increases the chance of Pb migration through the food chain [13,14]. Total Pb concentration of 1390–1450 ppm/kg has been reported in Vetiver grass tissue in the USA [15]. Similarly, total Pb concentrations of up to 70 mg/kg (dry weight) have been determined in plant leaves [16]. In other studies plant roots have experienced Pb concentrations of the range 1347.2 to 3825.7 mg/kg (DW) in a shooting range soil contaminated with over 5998 mg/kg of Pb [4]. The accumulation of Pb in the different plant tissues is also determined by whether the tissue is an above-ground biomass or below-ground biomass [17]. Additionally, it is important to distinguish the pathway through which Pb reached plant tissues, whether it was through surface deposition on the above-surface portions of the plants or via root absorption [18]. Most of the studies carried out to investigate bioaccumulation of plants growing near

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shooting ranges have discovered that these plants absorbed total Pb concentrations much higher than the maximum permissible limit of 2 mg/kg (in plants) set by WHO [19]. The World Health Organization and the Food and Agriculture Organisation (FAO) have also set maximum permissible Pb concentration of 0.3 mg/kg (DW) in edible vegetables [4]. Most of the studies that have been carried out have not satisfied this limit either. The detrimental effects of Pb absorption by plants are well documented. The accumulation of Pb in plants has been reported to decrease dry weight and photosynthesis process [20]. In the same way, elevated concentrations of Pb in plants have been found to inhibit root growth, lower water absorption and plant metabolism. These observations suggest the severity of this problem to negatively affect the quality of agricultural output and the eventual migration of Pb through the food chain [19].

Quantification of pollution risk from Pb towards plants has been carried out using various risk assessment methods and formulae. Pollution risk assessment indices and factors such as translocation factor (TF), biological concentration factor (BCF), biological accumulation factor (BAF) and hazard quotient (HQ) have all been used to establish the degree of Pb contamination in Plants [19]. The soil physicochemical properties have a bearing on the rate of Pb uptake by plants. Soil pH plays a significant role in the solubility and bioavailability of Pb in shooting range soils. Plants growing in acidic soils tend to absorb more Pb compared to those growing in alkaline soils [6]. This is due to the fact that low soil pH solubilizes Pb minerals and makes Pb bioavailable to plants [6]. In addition, plants growing in sandy soils that are polluted with Pb tend to accumulate higher concentrations of Pb compared to those growing in clay soils. Pb is more bioavailable in sandy soils than in clay soils [6]. On the other hand, high content of organic matter in shooting range soils has been reported to transform Pb into stable Pb-organo complexes. Elevated content of organic matter in the soil produces more carbon dioxide (CO_2) resulting in formation of stable Pb compounds that are less bioavailable [6]. In a related study, Darling et al. (2003), investigated Pb mobilisation in 17 shooting range soils with pH ≤ 6 and discovered that Pb dissolution was favoured in these soils and the solubility was even more in shooting ranges where the soils had low clays and organic matter [21]. Over and above, the type of plant is of great influence on the amount of Pb that it can absorb. There are plants that are very effective phytoextractants and phytoaccumulants of heavy metals in the soil and these kinds of plants have been exploited by scientists and researchers in soil reclamation and remediation efforts [22,23]. The control and management of Pb contamination of shooting range soils by plants take place through processes called phytoremediation and phytostabilisation. These processes are able to reduce the mobility and leaching of Pb in shooting range soils by immobilizing and stabilizing it and thereby minimizing exposure to biota [24]. Furthermore, phytoremediation technique has been found to be cost effective and environmentally friendly since it does not add new pollutants to the soil [25]. The soil structure and composition are not disturbed when this technique is applied [24]. In addition, phytoremediation occurs with the concomitant reduction of other processes such as soil erosion and decrease in dust caused by the wind and thereby reducing the deposition of Pb on above-ground plant parts [18]. The objectives of this review include: (i) to discuss the pathways of Pb in shooting range soils to vegetation growing in shooting ranges; (ii) to investigate the characteristics of plants that make them excellent Pb phytoexctractants; (iii) to examine the effect of soil physicochemical properties on soil-plant Pb pathways; and (iv) to discuss in depth the economic and environmental benefits of phytoremediation strategies.

2. Prevalence of Pb in plants growing in and around shooting ranges

It is a known fact that Pb has no nutritional value in plants [4]. The deposition of Pb in shooting range soils is not restricted only to the soil, plants and microorganisms that have direct and indirect contact with the polluted soils are at risk of absorbing and accumulating this toxic heavy metal in their tissues [18]. In addition, Pb collected in plant tissues can reach human beings and animals through consumption of contaminated plant products [13]. It is against this backdrop that scientists and researchers are continuously screening vegetation growing in shooting range soils and crops grown in agricultural fields near shooting ranges for possible contamination from Pb. A ton of evidence exists that confirms accumulation of Pb and its apparent toxicity towards vegetation found in and around shooting ranges [1,15,16]. Table 1 shows examples of studies carried out in the past 25 years that show that the uptake of Pb by plants growing in shooting ranges is a growing environmental concern.

It can be deduced from Table 1 that most studies around the world are now focussing on Pb pollution risk towards vegetation growing in and around shooting ranges. Most of the studies carried out in some countries have established that concentrations of Pb in plant tissues are higher than the countries' established regulatory and guidance limits. In one of the first studies carried out in Finland where total Pb concentrations in shooting range soil exceeded background soil concentration of 240 mg/kg by more than 200 fold, some edible fruits such as lingonberries accumulated Pb concentrations of up to 0.3 mg/kg [16]. The amount of Pb in these fruits rendered them inedible according

Table 1. Recent studies carried out on Pb uptake by vegetation growing in and around shooting ranges.

Location and year of study	Total Pb concentration in shooting range soil (mg/kg)	Plant tissue studied	Concentration of Pb in Plant tissue (mg/kg)	Reference
Finland (1993)	4,700–54,000	(i) Leaves (ii) Lingoberries	(i) 14–70 (ii) 0.3	[16]
England (1994)	36–10,620	(i) Roots (ii) Stems (iii) Seed pods (iv) Seeds	(i) 470 (ii) 62 (iii) 12 (iv) 148	[1]
New Zealand (1998)	4,000–8,300	(i) Roots (ii) Leaves	(i) 1347.2–3825.7 (ii) 9.6–93.7	[4]
Switzerland (2001)	44–33,600	(i) Leaves	(i) 0.28–1151.5	[26]
USA (2002)	16,200	(i) Beard grass (*polypogon spp.*) and cord-grass (*spartina foliosa*) (ii) Marsh rosemary (*limonium californicum*) (iii) Pickleweed (*s. suberterminalis*)	(i) 2.77–18.1 (ii) 8.96 (iii) 6.25	[6]
South Korea (2002)	78.00–165.85	(i) Root (ii) Shoot	(i) 4.15–6.30 (ii) 3.77–7.30	[17]
USA (2005)	300–4500	(i) Grass tiller	(i) 1390–1450	[15]
Switzerland (2008)	14,000–156,000	(i) Leaves	(i) 50–4640	[18]
Japan (2008)	19,600	(i) Above-ground plant tissue	(i) 166	[48]
Pakistan (2010)	2.0–29.0	(i) Root (ii) Shoot	(i) 1.0–43.0 (ii) 15.0–41.0	[72]
Switzerland (2011)	500	(i) Root (ii) Shoot	(i) 50–200 (ii) 5–18	[75]
Switzerland (2012)	466–644	(i) Shoot	(i) 11–62	[50]
Finland (2012)	50,000	(i) Leaves	(i) 0.97–30	[47]
Switzerland (2013)	500	(i) Shoot	(i) 1.3–5.8	[27]
USA (2016)	10,068–70,350	(i) Root (ii) Shoot	(i) 1893–5021 (ii) 252–880	[35]
Pakistan (2016)	1,331	(i) Stem	(i) 27.71–82.26	[25]
Nigeria (2018)	14.85	(i) Shoot	(i) 12.30	[44]
Norway (2018)	47–7189	(i) Grass	(i) 1.3–29	[13]
USA (2018)	ND (Not Determined)	(i) Root (ii) Shoot	(i) 117 (ii) 81	[28]
Switzerland (2018)	471	(i) Shoot	(i) 6	[78].

to the Finnish food safety guideline of 0.1 mg/kg and the Food and Agriculture Organization (FAO) or World Health Organization (WHO) set limit of 0.3 mg/kg tolerated by a healthy human being [29]. A positive correlation between total Pb concentration in soil, the Pb short fall zone and plant-available Pb was established in a study in England [1]. The highest plant Pb uptake of up to 4102 mg/kg was experienced in soils that accumulated the highest number of Pb shots and pellets at 257 Pb pellets per soil core and highest total Pb concentration of 5000–10,620 mg/kg in the soil. Conversely, a decrease in the number of plants per square meter was experienced in soils with high total Pb concentration. In addition, plants that accumulated the highest amount of Pb (5000–10,620 mg/kg) displayed reduced stem diameters (0.6 mm) compared to plants with stem diameter of 2.88 mm and growing in soils with low Pb content (less than 500 mg/kg) [1]. The most affected plant tissues in this study were the roots which accumulated up to 470 mg/kg and all the plant tissues contained Pb concentrations much greater than the set statutory limit of 20 mg/kg for Pb in edible plants and vegetables [1]. The roots have been found to possess the ability to alter the soil characteristics that aid the roots to retain more Pb [30]. In a similar study, Hui et al. (2002) have also shown that Pb concentration in plants correlated positively with the Pb shot and pellet densities [6]. Plants growing in soil with the highest density of Pb pellets and shots reaching highs of 1,620 shot pellets/kg (dry soil) accumulated Pb concentrations of up to 18.1 mg/kg (soil Pb of 16,200 mg/kg). In contrast, plants growing in soils containing only 4 shots/kg (dry soil) and total Pb concentration of 75.1 mg/kg were able to absorb just 2.77 mg/kg in their tissues [6]. Furthermore, a study in New Zealand has demonstrated a positive linear correlation between the quantity of Pb in the roots and leaves of all five plants studied and the amount of Pb discovered in the soil [4]. The concentrations of Pb in the plant tissues were much greater than the WHO set critical limit of 0.3 mg/kg, reaching highs of 3825.7 mg/kg [4].

The uptake of Pb by vegetation has been found to be one of the routes through which Pb moved through the food chain. Studies have been carried out that indicate that areas highly polluted with Pb pose risk to uptake of Pb by animals grazing in those areas [13]. In a study by Robinson et al. (2008), Pb concentration of up to 4,640 mg/kg was recovered in the leaves of plants and this concentration was much greater than the 30 mg/kg indicated to be toxic to livestock [18]. As a result, strict majors need to be taken in order to control and manage the mobility, bioavailability and bioaccessibility of Pb in shooting range soils.

3. Soil-plant Pb mechanistic pathways

Plants absorb Pb from the soil through a passive ion exchange process that takes place at an accelerated rate up to a point where ion exchange sites in the spaces not occupied by the roots are well equilibrated with the soil liquid mixture [31]. There are various routes through which Pb accumulated in shooting range soils reach plant tissues [1,16]. After absorption by the roots, Pb is translocated into shoots through the xylem [32]. It has also been established that various classes of proteins are also responsible for the translocation of Pb from the roots into the shoot [32]. Proteins belonging to the CPx-type ATPases protein class have been linked to the transport of toxic heavy metals such as Pb using ATP across cell membranes [33]. A large quantity of Pb is harvested from the soil through plant roots and translocated to the shoots, branches and leaves [4,34]. A study by Rooney et al. (1999) established higher concentration of Pb in the plants roots measuring up to 3825 mg/kg compared to 100 mg/kg in stem tissues [4]. In a related study, Cao et al. (2003) recovered 750 mg/kg of Pb in plants roots compared to 420 mg/kg in the shoots [5]. In another study by Fayiga et al. (2016), the roots of grasses found in three shooting ranges in Florida, USA, collected Pb concentrations of the range 1,893–5,021 mg/kg compared to the shoots that accumulated 252–880 mg/kg of Pb [35]. Furthermore, in a shooting range in Spain, Pb concentrations of 33.30–1,107.42 mg/kg have been determined in the roots of *A. capillaris* species compared to 10.90–135.23 mg/kg found in the roots [36]. Pb concentrations absorbed by plant roots and shoots were much higher than those observed in the control sites of 9.82 mg/kg in the roots and 6.43 mg/kg in the shoots [36]. A more pronounced Pb content has been reported in tuberous plants such as carrots, sweet potatoes, cassava, yam and dahlias [34].

The accumulation of Pb in the plant roots is made possible through the binding of Pb to ion-exchangeable sites on the cell wall and formation of Pb precipitates such as Pb-carbonates and Pb-oxides outside the cells [37]. The transport of Pb from the soil into the plant roots takes place across the root-cell plasma membrane through voltage gated plasma membrane cation channels such as Ca-channels [38]. Significant amount of Pb is normally found in the surface and sub-surface soil layers and a reduction in Pb concentration is observed with increasing soil depths [37]. The amount of Pb absorbed by plants through the roots is largely dependent on Pb concentration in soil at the depths reached by the plant roots [6]. After absorption by the roots, Pb is largely restricted to the roots because of strong Pb binding to the carboxyl groups of galacturonic acid and glucuronic acid in the cell walls of the root cells [39]. The consequence of this strong binding is the restricted migration of Pb via apoplast [39]. Various plant root factors directly affect the absorption of Pb from the soil by the roots. These factors include root surface area, root exudates, degree of transpiration and mycorrhization process [37]. A general observation is that monocotyledons accumulate less amounts of Pb in their roots compared to dicotyledons [38]. Pb translocated to other parts of plant from the roots is normally of lower amounts because of Pb precipitation and immobilisation in the cell walls of plant roots [20]. Pb translocation to the shoot takes place via the root apoplast and across the cortex, collecting near the endodermis that functions as a semi-barrier to the transport of Pb from the plant roots to shoots [40]. This factor contributes to higher Pb concentrations observed in plant roots than shoots [41]. The casparian strips of the root endodermis are the main obstacles for Pb migration across the endodermis into the plant middle cylindrical tissue [42]. The predominant pathway of Pb transport from the root to shoot is via the apoplast at lower Pb concentration. However, as the concentration of Pb increases in the roots, the restriction in mobility function of the plasmalemma is destroyed leading to large quantities of Pb entering the cells [43]. This causes damage to the cell and interrupts the efficacy of the plasmalemma to act as a barrier towards Pb transport from root to shoot and intercepts the discriminatory porosity of the plasmalemma and tonoplast [43].

In most cases, a decrease in the concentration of Pb in plant tissues away from the roots is observed, with relatively lowest Pb concentrations in plant tissues furthest away from the plant roots. The main reason for this observation is the increased restriction of Pb in plant root cell walls than in other organs of the plant. This is caused by strong binding of Pb in lignified root tissues than non-lignified plant tissues such as the shoots, branches and leaves [43]. Contrastingly, there are cases where the translocation rate of Pb from the plant roots into the shoots may be high resulting in higher total Pb concentrations in the shoots than in the roots. This observation was made by Magaji et al. (2018) in which two of the eight plant species studied accumulated higher concentrations of Pb in the plants shoots compared to the roots [44]. Pb concentrations of 12.30 and 11.01 mg/kg were discovered in the shoots of *A. zygia* and *V. paradoxa* plants respectively, compared to 8.71 mg/kg (*A. zygia*) and 9.02 (*V. paradoxa*) mg/kg found in the roots [44]. However, in some cases, total concentration of Pb in plant leaves may be relatively high due to Pb deposited on the leaves surface emanating from dust collecting in the waxy cuticles of the leaves [4]. The ability of plant leaves to absorb Pb depends on the morphology of the leaves [37]. Furthermore, the age of the leaves can determine their ability to absorb and accumulate Pb [45]. Aging leaves tend to accumulate high concentrations of Pb compared to younger leaves [45]. Robinson et al. (2008) have reported concentrations in the range 50–4640 mg/kg in the leaves of 10 plant species growing in shooting range soils with Pb loading of 14,000–156,000 mg/kg [18]. Pb concentrations in some of the plant leaves were reported to be 10 to 50 times higher than the set maximum toxicity level of 30 mg/kg for consumption by livestock and substantially higher than the European Union established maximum level of 0.2 mg/kg in cereal grains [18,46]. In a study by Selonen et al. (2012), Pb concentrations of 0.97–30 mg/kg were reported in the grass leaves growing in Pb polluted shooting range soils in Finland and providing a pathway through the food chain by being available to herbivores grazing the contaminated grass [47]. Robinson et al. (2008) made an important observation, whereby Pb uptake increased acutely when total Pb concentrations in the soil reached a specific threshold of 60,000 mg/kg [18]. This has an implication on the rate of Pb transport through the food chain as the rate of Pb uptake by plants increased beyond this concentration and thereby making Pb more available to herbivores. The degree and rate of Pb uptake from the soil by plants depends on factors such as plant species and the physical and chemical properties of the soil [31]. In general, the concentration of Pb in different plant tissues decreases in the order: roots>leaves>stem>seeds [37]. The abilities of these different plant organs to absorb Pb from the soil have been applied towards shooting range soil remediation and reclamation strategies [36,48].

The accumulation of Pb in above ground plant biomass can exacerbate the migration of Pb through the food chain when herbivores feed on contaminated plant materials [13]. In a study by Johnsen et al. (2019), Pb concentrations of up to 5 mg/kg were determined in the faeces of sheep after consuming grasses contaminated with Pb reaching highs of 29 mg/kg [13]. The livers obtained from over 32 slaughtered sheep were found to contain Pb concentration in the range 0.19–0.3 mg/kg and it is fortunate that this Pb concentration was not greater than the Pb concentration of 0–3 mg/kg (dw) regarded to be standard in the sheep livers [13]. Therefore, under favourable Pb soil-plant mechanistic pathways, the rate of Pb uptake by plant would be higher resulting in higher concentrations of Pb in above ground plant organs and increased migration through the food chain.

4. Pb toxicity and tolerance in plants

Studies have shown that Pb is not an essential element in plants and does not have any nutritional value [4]. However, this element has been found to occur naturally in plants, with some plants containing background concentrations of 2.1–2.5 mg/kg (DW) [49]. Total Pb concentrations of 100–500 mg/kg in the soil have been reported to be toxic to plants [49]. In addition, Pb concentrations of 30–300 mg/kg in plant tissues are regarded to be toxic and can lead to harmful effects such as decrease in plant dry weight, photosynthesis, root growth and a diminishing ability by the plant roots to absorb water from the soil [3,50]. In Finland, the growth of the pine tree was significantly reduced in an active shooting range compared to the trees growing in an abandoned shooting range [51]. The stunted growth of the pine trees was believed to have been caused by the damaged roots and root connecting mycorrhizal fungi [51]. The growth of the pine tree was observed after few years since cessation of shooting activities at the shooting range, an indication of reduced exposure to toxic Pb [51]. The pine plants even grew taller than those found at the control site [51].

Root growth is hindered by Pb accumulation in plant roots due to Pb-induced impedance of cell division in the tips of the plant roots [52]. In a study by Lago-Vila et al. (2019), inhibition of root elongation was observed in three plant species growing in Pb polluted soils obtained from three shooting ranges [53]. A decrease in plant root elongation from 6.66 cm to a range of 4.07–5.47 cm was observed for the *sinapis alba* plant species growing in three contaminated soils obtained from a Pb polluted trap shooting range (TSR). Likewise, a decrease in root elongation from 6.66 cm to the range of 3.75–4.87 cm was also observed for the same plant species growing in Pb polluted soils of a small arms firing range (SFR) [53]. Root growth inhibition was also observed in the other two plant species, *Lactuca sativa* (1.05–42.87% root growth inhibition) and *Festuca ovina* (6.80–34.98% root growth inhibition) used in the same study [53]. In other studies, high Pb concentrations in plant roots were found to damage the microtubules of the mitotic spindle resulting in blockage of the pro-metaphase cells caused by the induced c-mitoses [54]. Other detrimental effects of Pb exposure in plants include stunted plant growth and chlorosis [55]. The toxicity of Pb towards plant physiological processes is summarized in Table 2.

A study in Australia observed reduction in the growth of the lettuce (*Latuca sativa*) shoot biomass grown for eight weeks in three different Pb polluted shooting range soils [56]. The lettuce plants were able

Table 2. Effect of Pb accumulation on plant physiological processes [55].

	Effect on the plant physiological process	
Physiological process	Increase	Decrease
Hormonal functions		√
Enzyme activity	√	√
Electron transport		√
Membrane structure		√
Water absorption		√
Mineral nutrients		√
Photosynthesis		√

to accumulate 500–3,710 mg/kg DW of Pb and the total Pb concentrations at the four shooting ranges studied were in the range 2,330–12,167 mg/kg [56].

The accumulation of Pb in plants can activate the enzyme activity or can inhibit it [37]. An inhibition of most physiological processes such as hormonal functions, electron transport, membrane structure and water absorption is observed. Accumulation of Pb in plant tissues lowers the water absorption ability of the plant by destroying the cell turgidity and the flexibility of the cell walls and thereby reducing the capacity of the cells to store water [57]. Stomatal closure due to increased and uncontrollable concentrations of abscisic acid (ABA) has been reported in plants with elevated concentrations of Pb [58]. Pb is classified as a soft metal that has high affinity for soft donor ligands [37]. Enzymes containing the thiol group (–SH) in their structure are at risk of inhibition of their activities due to complexation of Pb with thiol group of the enzyme [59]. These thiol groups are usually located in the active site of the enzyme and are responsible for the enzyme functions. The thiol groups are also important stabilizers of the enzyme tertiary structure [37]. Furthermore, Pb ions accumulating in plant tissues can block the carboxyl groups (–COOH) found in enzymes and thereby inhibiting the enzyme activity [37]. The deposition of Pb in plant roots negatively affects their branching pattern [37]. Degradation of protein molecules in plant tissues has been observed with accompanying remarkable modifications to the composition of triglyceride macromolecules [60]. In plant leaves, Pb toxicity has been linked to reduced rate of chlorophyll synthesis due to its impedance of the plant uptake of nutritional elements such as magnesium and iron [61]. Pb loading in plants has been reported to reduce the rate of photosynthesis due to degradation of the chloroplast, chlorophyll, carotenoids and plastoquinone [3,62]. Elevated concentration of Pb in plants also affects the photosynthesis chemical process through shortage of supply of carbon dioxide (CO_2) caused by Pb-induced closure of the stomata [62]. The complexation of Pb with protein molecules bearing the soft nitrogen (N–) and sulfur (S–) donor atoms in the chlorophyll leads to destruction of photosynthesis tools [63]. The inhibition of electron transport has also been reported in the donor and acceptor sites of PSI, PSII and cytochrome b_6f complex enzymes [64]. Moreover, Pb has been found to occupy the place of Ca, Cl^- and Mn in the oxygen-emitting extraneous polypeptide of PSII leading to the degradation of the oxygen-producing complex [65]. Disruption of the respiration processes and lowering of the adenosine 5`-triphosphate (ATP) have been observed with increasing concentration of Pb in plants [66]. The suppression of these processes has been linked to the disconnection of the oxidative phosphorylation [66,67]. The pronounced effect of Pb on the nutritional sufficiency of plants has been associated with the obstruction of entry of the cations K, Ca, Mg, Zn, Cu and Fe and nitrate ions from the soil solution into the plant roots [49]. Pb is able to achieve this by altering the size of the active sites on the root surface for entry of essential elements and through Pb-induced changes in the activities and structure of enzymes found in the root membrane [68]. The absorption of nitrate from the soil is also significantly lowered by Pb toxicity due to the inhibition of the activity of the nitrate reductase enzyme. This has also been linked with the disruption of the nitrogen metabolic processes [69]. Elevated levels of reactive oxygen species (ROS), such as superoxide ion (O_2^-), hydroxyl free radicals ($^{\cdot}OH$) and hydrogen peroxide (H_2O_2) have been reported in plant tissues due to the harmful effects of Pb [41]. Increased concentrations of these oxygen species lead to unbalanced redox reactions inside plant cells and thereby causing oxidative stress in young and developing plant organs [41]. The deposition of reactive oxygen species such as hydrogen peroxide can induce oxidative deterioration of polyunsaturated fatty acids in plant tissue membrane, resulting in oxidative stress to the plant [70].

Even though the toxicity of Pb towards plants is conspicuous, some plants are able to tolerate the accumulation of high levels of Pb in their tissues [36,44]. The translocation of Pb from the roots into above ground biomass is usually followed by sequestration and detoxification of Pb in the vacuoles of plants [32]. The transportation of Pb into plant vacuole takes place via various transporter gene families including the ATP-binding cassette transporters (ABC), cation diffusion facilitator (CDF), heavy-metal ATPase (HMA) and natural resistance-associated macrophage protein (NRAMP) [32]. Such plants are able to survive in Pb contaminated shooting ranges and without displaying any toxic effects from exposure to Pb. As a result, these types of plants have found use in the control and management of pollution from Pb in shooting ranges through a process called phytoremediation [22,25]. Plants that tolerate Pb are able to do that in two ways; (i) the 'excluder' technique and (ii) the accumulator technique [71]. In the excluder technique, the total concentration of toxic Pb is kept at an unchanging low level up to the point of critical soil concentration when toxicity emerges and unhindered Pb transport takes place [71]. The excluder plants are able to get rid of Pb through discharge of Pb precipitating chemical species such as oxalate that keeps Pb in a less toxic precipitate form inside plant tissues [71]. The toxicity of Pb towards plant tissues can also be excluded by binding the Pb to carboxylate groups (–COOH) of uronic acid which prohibits its uptake by the roots [71]. In a study by Robinson et al. (2008), the *Equisetum arvense* species displayed the excluder characteristics in which Pb concentration in plant tissues was kept unchanging at low levels of less than 100 mg/kg for soil Pb concentrations of up to 60,000 mg/kg [18]. Pb can also be prohibited from reaching plant tissue through root avoidance of highly contaminated points within the soil core [18]. On the other hand, the accumulator technique involves the active concentration of Pb inside plant tissues covering a full spectrum of the soil concentration which is associated with highly peculiar plant physiology [71]. Plants that employ the accumulator technique are able to compensate for the accumulation of Pb in plant tissues through production of chemicals that lessen the toxic effects of Pb. These plants are able to produce antioxidant defence chemicals, elevate levels of polyamine and amino acids and drastic changes in hormonal balance [71]. In a study by Lago-Vila et al. (2019), the *Lactuca sativa L.* species demonstrated tolerance of Pb toxicity due to the presence of high amounts of organic matter that complexed Pb and minimized its toxicity [53]. Pb toxicity tolerance by *Lactuca sativa L.* species had seen an increase in the germination index (G_{index}) of these plants in six shooting ranges polluted with 161.0–10,873 mg/kg of Pb [53].

Other plants are able to deal with elevated levels of toxic Pb through a detoxification strategy that involves transformation of toxic Pb into a less toxic complex through binding of Pb to chemical species in plant tissues and converting it into less toxic Pb-complexes [37]. The detoxification process can take the form of isolating the Pb and its chemicals in the cell vacuoles so that it does not reach plant tissues. In addition, the toxicity of Pb can be subdued through binding Pb with glutathione antioxidant and amino acids. In a study by Magaji et al. (2018), Pb tolerance by eight plant species was observed in which some plant species accumulated up to 12.30 mg/kg in the shoot [44].

5. Quantification of Pb pollution risk towards plants

The toxicity of Pb and hence its pollution risk towards receptors such as plants can be assessed using various pollution risk assessment indices and factors such as translocation factor (TF), biological concentration factor (BCF), biological accumulation factor (BAF), hazard quotient (HQ), germination index (GI), root growth inhibition (GI) and bioaccessibility as shown in Table 3 [25,36,50,72,73]. The hazard quotient (HQ) is used to estimate ecological risk of Pb towards receptors such as plants growing in Pb polluted shooting range soils [73]. It is defined as the ratio of exposure concentrations to a toxicological benchmark [74]. Hazard quotient of greater than one indicates possible toxicity risk and its pronounced effects and hence further assessment of the plant is required (Table 3) [73].

Bioaccessibility studies have been carried out towards establishing and estimating the bioavailability

Table 3. Risk assessment of Pb towards plants.

Pollution Risk Index	$[Pb]_{total}$ in soil (mg/kg)	Inference	Reference
Bioconcentration factor (BCF)	500	BCF < 1 (low Pb bioavailability)	[75]
Translocation factor (TF)	12.30–14.85	TF = 2.91 (efficient translocation of Pb from the root to the shoot)	[44]
Translocation factor (TF)	82.36–724.85	TF = 0.11–0.66 (low Pb translocation from roots to shoot)	[36]
Biological absorption coefficient (BAC)	82.36–724.85	BAC = 2.06 (the plants showed good Pb phytoextraction)	[36]
Bioaccessibility index	21,900	66% of Pb bioaccessible to plants	[73]
Hazard Quotient (HQ)	16,400–27,600	0.109–4.10 (low to high Pb risk to plants)	[73]
Bioconcentration factor (BCF)	12,167	BCF = 0.22–1.5 (low to medium Pb bioavailability)	[77]
Germination Index (G_{index})	161–10,873	G_{index} = 62–82% (inhibition of germination and plant growth due to Pb)	[76]

of Pb to plants [73]. Bioaccessibility analysis helps allay the assumption that the amount of Pb accumulated in shooting range soils will all be absorbed by plants growing in the polluted soils. As a result a more realistic estimate of Pb uptake by plants is ascertained and its concomitant toxicity risk [73]. The uptake and accumulation of Pb in plants can also be expressed through the bioconcentration factor (BCF) [75]. Bioconcentration factor describes the quotient of plant tissue Pb concentration to soil total Pb concentration [75]. BCF < 1 implies low bioavailability of Pb in the plants.

The translocation of Pb from the roots to different plant tissues such as the shoots can be estimated using the translocation factor (TF) [36]. Translocation factor is defined as the quotient of total Pb concentration (mg/kg) in shoots to that in the roots [36]. A translocation factor greater than one (TF > 1) denotes efficient translocation of Pb from the root to the shoot. Furthermore, (TF > 1) translate to high chances of Pb being available to animals that feed on the polluted plant and thereby increasing migration of Pb in the food chain (Table 3). In addition to using translocation factor (TF), Seijo et al. (2016) also applied bioconcentration factor (BCF) and biological absorption coefficient (BAC) to evaluate Pb translocation in plants growing in polluted shooting range soils [36]. Plants with BAC > 1 and BCF > 1 tend to be good extractants and phytostabilizers of Pb respectively (Table 3). Plants that are excellent the phytostabilizers make them good candidates for phytoremediation of polluted shooting range soils through immobilization of Pb in the roots and reduces migration of Pb through the food chain.

The detrimental effects of Pb on plants can also be assessed by studying the growth of the roots for a particular plant growing in a Pb polluted shooting range soil compared to the unpolluted control soils. Pb toxicity can therefore be quantified through determination of the germination index (G_{index}) and root elongation index (RI) [53]. Germination index describes the product of seed germination (%) and root elongation (mm) of plants in shooting range soils relative to the product of seed germination (%) and root elongation (mm) of the same plant species growing in control soils [76]. Germination index (G_{index}) of 90–110% indicates no Pb toxicity, $G_{index} < 90\%$ indicates inhibition effect to the germination and root elongation of plants whereas $G_{index} > 110\%$ refers to plants with a stimulation effect. Two shooting ranges situated in Monforte de Lemos, Spain, were found to contain Pb deposition of 161–10,873 mg/kg. Toxicity of Pb towards three plant species growing in the two shooting ranges was studied. The findings indicated $G_{index} <$ 90% (62% and 82%) for the *S. alba* plant species sampled from two sites on the trap shooting range (TSR1 and TSR2), demonstrating inhibition of germination and plant growth due to Pb toxicity as shown in Table 3 [76].

The hyperaccumulative properties of plants towards Pb have been exploited by scientists and researchers in the phytoremediation efforts towards the control and mitigation of Pb pollution of shooting range soils [23,25,36,44,78]. Phytoremediation strategies have been regarded as green techniques since they do not produce or add any toxins to the environment. Moreover, such soil amendment applications are non-intrusive since they cause little to no destruction to the ecological make-up of the shooting range soils providing little upset to biota.

6. Factors affecting the uptake and translocation of Pb in plants

The bioavailability and bioaccessibility of Pb in shooting range soils depends, to a large extent, on the physicochemical properties of the soil and the plant species itself [36,50]. The soil physicochemical properties have a significant impact on the weathering and speciation of Pb in the soil [79,80]. The uptake of Pb by plants is influenced largely by soil physical and chemical properties such as soil pH, moisture, cation exchange capacity, organic matter content and soil texture [75]. In addition, the plant species, root zone and root structure also do have significant impact on the rate of Pb uptake and its translocation in plants [81].

6.1. Plant species

The uptake of Pb from the soil is to a large extent influenced by the plant species [81]. Plants that have the capacity to uptake large quantities of Pb from the soil are referred to as metallophytes or hyperaccumulators [32]. The hyperaccumulators do not store the absorbed toxic Pb metal in their roots, but rather translocate it to above ground plant parts such as shoots and leaves at concentrations of 100–1000 times higher than in non-hyperaccumulator plants [32]. In addition, the uptake of this high concentration of Pb does not present any toxic results in plants. Hyperaccumulators possess three characteristics that distinguish them from their non-hyperaccumulator counterparts. These include; (i) greater ability for heavy metal uptake such as Pb, (ii) root-to-above ground biomass translocation of heavy metal, and (iii) sequestration and detoxification of heavy metal as shown in Figure 1 [32,82]. Moreover, the amount of

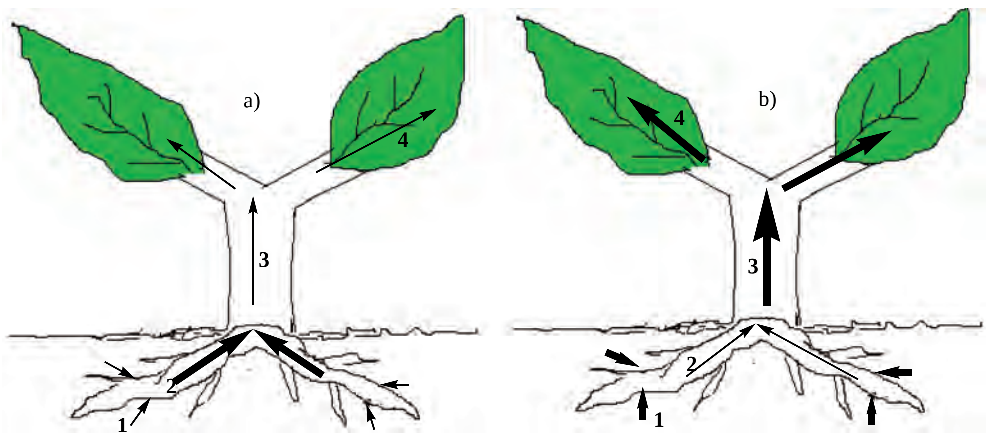

Figure 1. Processes of heavy metal distribution and tolerance in a)non-hyperaccumulator and b) hyperaccumulator plants. (1) indicates heavy metal uptake by the plant roots, (2) heavy metal sequestration in root vacuoles (3) root-to-shoot heavy metal translocation and (4) heavy metal binding to the cell walls and sequestration in vacuoles. The bold arrows indicate a stronger process while the thin arrows show a less strong process.

Pb accumulated may differ between varieties of the same plant species that have been exposed to the same concentration of Pb [25]. This can give insight into Pb-specific hyper-accumulators that can be applied towards control and management of Pb pollution in shooting range soils [25].

Three different plant species growing in Switzerland were investigated in a pot experiment towards uptake of Pb in shooting range soil contaminated with about 500 mg/kg of Pb [75]. It was established that three plant species; *Plantago lanceolata, Lolium perenne, and Triticum aestivum* displayed significant Pb uptake in their roots and shoots. *T. aestivum* was able to absorb the highest concentration of Pb (~200 mg/kg) in the roots compared to *L. perenne (*~130 mg/kg) and *P. lanceolata* (~110 mg/kg). The translocation of Pb from the roots to the shoots also varied with the plant species. *P. lanceolata* experienced the highest translocation of Pb to the shoot which saw its shoot accumulating ~15 mg/kg of Pb compared to ~10 mg/kg and ~5 mg/kg in the respective shoots of *L. perenne* and *T. aestivum* [75]. In addition, the study by Conesa et al. (2011) was also able to establish that all the three plant species investigated had bioconcentration factors below one, a general indication of low root-to-shoot Pb transfer [75]. This implies that the possible use of these three plant species in phytoremediation of Pb polluted shooting range soils would not pose a significant risk of Pb transfer into the food chain. In a related study carried out in the same country, Switzerland, the shoots of the following plant species; *Chenopodium album, Grasses, Trifolium spp., Persicaria lapathifolia palida* and *Persicaria lapathifolia lapathifolia* were harvested from the shooting range sites at which soil samples were collected [50]. This study further investigated the impact of the soil characteristics such as the acidic soils versus calcareous soils on the uptake of Pb by the plants. The *C. album* species accumulated the highest concentration of Pb (~60 mg/kg) in the shoot followed by *Trifolium spp*. (~22 mg/kg), *Grasses* (~18 mg/kg) and *Persicaria lapathifolia palida* absorbed the lowest concentration of Pb (~10 mg/kg) in its shoot. It is worth noting that the uptake of Pb took place under acidic soil conditions. In contrast, the uptake of Pb by the plant species growing in calcareous soils was lower compared to acidic soils. Under calcareous soils, *C. album* accumulated the least amount of Pb (~2 mg/kg) compared to the other three plant species studied. On the other hand, *Trifolium spp., Persicaria lapathifolia palida* and *Grasses* growing in calcareous soils accumulated 3, 4 and 6 mg/kg of Pb [50]. This study was able to demonstrate the effectiveness of the acidic soils towards the dissolution of Pb minerals and making it available for uptake by plants compared to the calcareous soils with its pH in the alkaline (pH ~ 8.5) region. The elevated pH of the calcareous soil may have exacerbated the partitioning of Pb on Fe and Mn hydroxides and thereby restricting its mobility and bioavailability. Furthermore, the transformation of Pb into less soluble Pb-carbonates in the presence of high content of calcium carbonate may have made Pb less available for uptake by plants in the calcareous soil.

In a study by Tariq and Ashraf (2016), the uptake of Pb by four different plant species; *Brassica campestris, Helianthus annuus, Pisum sativum* and *Zea mays* growing in shooting range soil with high Pb loading (1,331 mg/kg) were compared [25]. Out of the four plant species studied, *P. sativum* was able to absorb over 96.23% of Pb from the shooting range soil, an indication of high Pb removal efficiency. In addition, these plant species exhibited the highest bioconcentration factor (BCF), a confirmation that it is a hyper-accumulator. On the other hand, *Z. maize* displayed the second highest extraction efficiency towards Pb with a phytoextraction capacity of 66.36% [25]. The *H. annus* and *B. campestris* were the least effective towards Pb uptake from the soil achieving Pb removal efficiency of 48.86% and 33.85% respectively. This study showed the varying capabilities of the four hyper-accumulators towards the uptake of Pb from polluted shooting range soils.

More studies have been carried out in recent years in order to determine the applicability of phytoremediation as a substitute for the control and management of Pb pollution in shooting range soils [23]. This form of shooting range pollution management strategy has been found to be cost effective and environmentally friendly compared to other techniques such as chemical stabilization and soil removal [83–85].

6.2. *Effect of soil pH*

The uptake of Pb by plants from the soil takes place through the Langmuir process that is largely affected by pH [86]. The pH has been found to play a significant role in proton production by the roots leading to acidification of the rhizosphere and thus favouring Pb dissolution [32]. The absorption of Pb in the soil by plants has been found to increase with increasing pH in the range 3.0–8.5 [86]. The low pH inhibits precipitation of Pb in the plant cell walls and its retention and thereby facilitates its translocation to the shoots [87]. In a study by Robinson et al. (2008), elevated soil pH of 6.9 and high organic carbon of up to 7.3% lowered the phytotoxicity of Pb towards plants leading to revegetation of the shooting range [18]. The high pH reduces the weathering, transformation and dissolution of Pb and thereby restricting its availability for uptake by plant roots [79]. In addition, Pb chemical species such as hydrocerussite [$Pb_3(CO_3)_2(OH)_2$] and cerussite ($PbCO_3$) are stable at elevated pH making Pb not available for absorption by plants roots [5].

Evangelou et al. (2012) determined high concentrations of Pb in plants growing in acidic soils, which were 1.7 times higher than the Pb concentrations in calcareous soil [50]. The high pH of the calcareous soils decreased the mobility and availability of Pb through its adsorption in the Fe and Mn oxides and hydroxides that were formed at elevated pH levels. Furthermore, the calcareous soil contains high concentrations of $CaCO_3$ that is able to precipitate Pb and transform it into the less soluble Pb-carbonates resulting in reduced availability of Pb for plant uptake [50]. The findings by Evangelou et al. (2012) were in agreement with the study carried out by Conesa et al. (2011) in which *Plantago lanceolate L*. plant species accumulated same range of Pb concentrations under similar calcareous soil conditions of the shooting range [50,75]. The impact of pH on Pb uptake by plants has seen the adjustment of soil pH with chemicals such as lime to pH range of 6.5 to 7.0 in order to minimize Pb absorption by plants [22].

Pb toxicity in plants has been shown to be directly related to plant available Pb fraction in the soil due to favourable conditions of pH, electrical conductivity, composition of soil solution and mineralogical composition of the soil [56]. Formation of chelates between ligands such as histidine or citrates and Pb is pH controlled and this establishes an equilibrium between the chelators and hydrated Pb cations moving along the transpiration path and the immobile Pb binding sites in the plant cell wall surrounding the xylem vessels [88].

Changes in the soil pH to more alkaline levels due to addition of soil amendments such as lime and MgO promoted the formation of insoluble Pb-hydroxides, leading to reduction in exchangeable Pb in the studied shooting range soils [56]. The formation of hydr(oxide) precipitates is responsible for the immobilisation of Pb and reduction of its plant uptake from the soil. In a study by Magaji et al. (2018), a weakly alkaline soil pH (7.2) coupled with electrical conductivity of 8.11 μS/cm favoured plant Pb uptake by eight plant species growing in a Pb polluted shooting range soils [44]. Translocation factors (TF) of up to 1.76 were determined for the studied plant species. The acidic pH of the trap shooting range (TSR) soil found in Spain provided suitable conditions for the dissolution, transformation, mobility and bioavailability of Pb resulting in enhanced plant Pb uptake [53]. The uptake of Pb by seedlings of three different plant species, *Sinapis alba* L, *Lactuca sativa* L and *Festuca ovina* L, growing in acidic shooting range soils lowered their germination index an indication of manifestation of Pb toxicity. The plants also experienced inhibition of root growth caused by Pb phytotoxicity from Pb uptake under favourable conditions of acidic soils [53].

6.3. Effect of soil cation exchange capacity

In addition to the soil pH, cation exchange capacity (CEC) has also been found to play a crucial role in the mobility, bioavailability and eventual uptake of Pb by plants from shooting range soil [5]. The soil CEC describes the number of exchangeable cations that can be taken up by a specified mass of soil and therefore determines the binding ability of such soil [89]. It is influenced to a large extent by the concentration of negative charges on soil colloidal surfaces and the comparative density of positive charges arising from metal species in soil solution [90,91]. In some cases, the negative charges on soil colloidal surfaces may be controlled by the pH of the soil solution while in some situations cationic substitution of Si^{4+} by Al^{3+} would have occurred in clay minerals based on their similar shapes [91]. As a result, the negative charges on the soil colloidal surfaces have to be cancelled out by a corresponding equal number of cationic species from the soil solution. This process is called cation exchange and it is reversible due to the formation of weak electrostatic bonds between the cations and the negatively charged soil colloidal surfaces [90]. The attached cations can therefore be replaced by other loosely adsorbed cations and this process is largely dependent on the cation charge and it is negatively affected by the hydration of the ionic radius [91]

Furthermore, elevated soil pH may inhibit Pb uptake by plants due to increased adsorption of Pb within the soil cation exchange sites [89]. In consequence, soils with high CEC experience enhanced binding capacity towards Pb resulting in its reduced mobility and availability for plant uptake [92]. The binding of metal cations by soils rich in clay minerals decreases in the order $Cu^{2+} > Cd^{2+} > Fe^{2+} > Pb^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+} > Zn^{2+}$ [93]. In a study by Conesa et al. 2011, Pb uptake by three plant species was significant due to prevailing favourable soil physicochemical properties such as the high soil CEC of 10.3 cmol/kg [75]. High cation exchange capacity of the soil provides for an enhanced exchange of Pb ions sorped into the soil fraction and release of these Pb ions into soil solution and their ultimate uptake by plants [75]. This exchange of Pb ions between the soil exchange sites and the soil solution accelerates the dissolution of Pb into the soil solution and its absorption by plant roots. It is worth noting that soil CEC alone cannot be a major determinant of the effectiveness of Pb uptake by plants since other soil properties such as pH, texture and moisture content should be at play. As indicated in a study by Conesa et al. (2011), the shooting range soils were found to possess other favourable physicochemical properties such as high clay and silt fractions of 45% and 52% respectively [75]. Such soils have demonstrated enhanced Pb uptake by plant roots. Rodriguez-

Seijo et al. (2016), discovered high translocation factors of 0.43 and 0.66 for soils with respective high CEC of 6.03 and 9.51 cmol/kg. Soils that experienced low CEC values translocated less concentrations of Pb from their roots to shoots such as soil with CEC of 2.65 cmol/kg and corresponding translocation factor of 0.13 [36].

6.4. Effect of soil organic matter

Soil organic matter refers to the fraction of the soil that comprises the remains of plants and animals that have been returned to the soil and are at various states of decomposition [24,94]. This decomposition process of the once living organism results in the formation of a dark coloured and porous material called humus [94]. The rate of decomposition of dead organism remains is influenced by various factors such as the quantity of animal and plant residues in the soil and the physicochemical properties of the soil such as soil pH and moisture [24].

Organic matter is important to the soil in that it serves as a nutrient reservoir and helps improve the soil structure, reduce erosion [94]. It also plays a crucial role in the evolution of the soil separates, strengthens infiltration rate and water-holding capacity of the soil [95]. The resultant increase in the water-holding capacity of the soil due to elevated levels of organic matter is caused mainly by the concomitant increase in the quantity of micropores and macropores in the soil that are formed from the agglomeration of soil particles [94]. A study by Hudson et al. (1994) has shown that water-holding capacity in the soil can increase by 3.7% for a corresponding increase of 1% in the soil organic matter [96]. Elevated levels of organic matter in the soil have the tendency to increase soil pore volume leading to an increase in the adhesive and cohesive forces inside the soil and an accompanying expansion in the water-holding capacity of the soil [94,97].

The decomposition process of the dead plant and animal materials leads to the liberation of various products such as CO_2, H_2O, energy and essential nutrients [90]. In addition, the humus consists of the acids fulvic, hymatomelanic and humic which contain acidic functional groups and can therefore form organo-metal complexes with toxic heavy metals such as Pb and thereby controlling their solubility, mobility and bioavailability [24]. In a study carried out by Ma et al. (2007), at a shooting range in Florida (USA), the binding of Pb in the sorption sites of the bio-chemicals found in the organic matter resulted in the formation of water-soluble organo-Pb complexes that made Pb more mobile and bioavailable for plant uptake [98]. In a similar study by Rodriguez-Seijo et al. (2016), the high organic matter content (12.32%) in an old trap shooting range soil found in Spain played a significant role in the uptake of Pb (1,107 mg/kg) from the soil into the roots [36]. In the same study, organic matter of 6.20% recorded at a different sampling site translated into only 694 mg/kg of Pb absorbed by the roots. It is also important to note that organic matter works in conjunction with other soil physicochemical properties to effect an efficient and effective Pb uptake by plants.

6.5. Effect of root structure

Plant characteristics such as root cross-sectional and surface area, root secretions, mycorrhization and transpiration rate have significant impact on the absorption rate and uptake of Pb [37]. The solubility of Pb in the soil also has a marked influence in the absorption and uptake of Pb from the soil by plants [99]. Pb that exists in the form of carbonate and phosphate precipitates in the soil is not readily available for uptake by plants. It is worth noting that Pb in the soil is categorized as Lewis acid and it is able to make strong covalent and ionic bonds with organic ligands and chemical species in soils and plants [37]. The presence of microorganisms in the soil also affects Pb uptake and translocation by plants through processes such as bioaccumulation and biosorption [100].

6.6. Effect of soil texture

Soil texture describes the relative fraction of particulate matter of various dimensions which may include sand, silt and clay that constitute the mineral component of the soil [24,94]. The corresponding particle sizes for sand, silt and clay are >50 µm, 2–50 µm and < 2 µm respectively [90]. Soil texture has a great influence on the moisture-holding capacity of the soil and sandy soils have been found to possess the lowest moisture-holding capacity compared to clay soils. Silt soils on the other hand have lower moisture-holding capacity compared to clay soils [94]. Soil texture also plays a significant role in Pb availability in plants such that plant Pb uptake in fine sand fraction was more pronounced compared to other soil fractions that were mostly clay and course sand [56]. The findings by Sanderson et al. (2014), were in agreement with those by Qian et al. (1996) in which the highest extractability of Pb was observed in the fine sand fraction [56,101]. It has been established that sandy soils make Pb more available to plants and thereby increasing their uptake by plants and subsequent translocation to above ground biomass [6]. On the other hand, clay soils demonstrate strong binding affinity towards Pb and thereby immobilize Pb and make it less available for plant uptake [90]. The mechanism through which clay soil fraction binds Pb is thought to occur through the adsorption of Pb via ion exchange and distinct sorption process [102]. The mechanism for the specific adsorption of Pb has been established to involve the initial adsorption of the hydroxyl ions by the clay soil fraction followed by the electrostatic interaction between Pb and the adsorbed hydroxyl ions [102]. This binding of Pb by clay soil fraction, as stated above, restricts the availability of Pb for plant uptake and translocation to above ground plant organs.

7. Phytoremediation approach

Scientists and researchers are continuously searching for eco-friendly techniques and methods for the control and management of Pb pollution of shooting range soils. The cost implications of such methods have also been a topical discussion for sustainable soil remediation and reclamation efforts. In recent years, phytoremediation has become an increasingly cost effective, efficient and environmentally friendly technology for the amendments of highly polluted soils [22,23,36,103]. Phytoremediation describes application of engineered green plants to remove, immobilize, contain and stabilize environmental pollutants such as trace and heavy metals, organic substances and radioactive compounds found in the soil [104,105]. This technique utilizes processes in the plant that may be chemical, biological or physical that assist in the uptake and translocation of pollutants through the plant resulting in improved quality of the soil [104]. Plants are able to achieve these processes by employing such mechanisms as phytostabilization, phytoextraction, phytovolatilization and rhizofiltration [104]. Phytostabilization involves the immobilization of Pb in the soil by plants through absorption and precipitation in the root zone and thereby limiting its mobility in the soil [22,106]. On the other hand, phytoextraction mechanism entails the uptake of Pb by plant roots and its translocation into above ground plant biomass [106]. In contrast, phytovolatilization involves the uptake of Pb by plants and its loss as secondary Pb species through transpiration into the atmosphere. This process is usually more pronounced in growing plants that uptake water along with Pb species and their loss through the plant leaves via transpiration [106]. Lastly, there are instances whereby the control of Pb pollution in soil may be mitigated through rhizofiltration in which Pb in soil solution surrounding the plants root zone is absorbed and sequestrated within the roots [106].

There has been a surge, in recent years, in the number of studies that assessed the effectiveness of vegetation towards shooting range soils amendments and reclamation efforts [22,23,36,103]. Examples of studies where phytoremediation strategies have been effective include such studies as those carried out by Tariq and Ashraf (2016), Rodriguez-Seijo et al. (2016) and Sneddon et al. (2009). Tariq and Ashraf (2016) reported the phytoextraction ability of Pisum sativum that demonstrated Pb removal efficiency of 96.23% from shooting range soil polluted with over 1,331 mg/kg of Pb [25,36,107]. In a study by Rodriguez-Seijo et al. (2016) in a shooting range in Spain, the phytoremediation effectiveness of *Agrostis capillaris L.* grass towards Pb immobilization in which 1,107 mg/kg of Pb was absorbed by the roots of the grass with about 135 mg/kg translocated into the shoots in a [36]. In the United Kingdom, a study by *Sneddon et al. (2009)* established a concentration of 38 mg/kg in the shoots of *L. Perenne* growing in soils containing contaminated with 43.89–159.98 mg/kg of Pb emanating from ammunition [107]. The advantage of phytoremediation technology to other soil remediation techniques such as chemical and physical amendments is that it is less disruptive to the ecosystem [104]. There is no destruction of the soil structure and loss of habitat for living organisms compared to soil removal techniques [22,36]. Above all, this method is cost effective and does not introduce foreign chemicals into the environment compared to chemical amendments [22]. In addition, to the control and management of pollutants in the soil, phytoremediation serves another purpose in that plants prevent soil erosion by holding the soil together with their roots and reduce the impact from runoff water from rainfall. Plant roots also produce into the soil chemicals that serve as a source of nutrients for the microbes found in the rhizosphere [108]. As a result, the density of microbial communities is usually higher in the rhizosphere than in the soils furthest away from the plant roots. This describes the interdependence between the soil microbial populations and plants [108]. The multifaceted benefits of phytoremediation has led to its recommendation by the United States Environmental Soil Protection Agency (USEPA) as one of the methods that can be employed for the control and management of Pb pollution in shooting range [106].

8. Conclusion

Shooting ranges do not only pose pollution risk to the soils found in shooting range premises but to the vegetation growing in and nearby these shooting ranges as well. The uptake of Pb by plants takes place through various chemical and physical processes. The efficiency of Pb uptake by plants depends on many factors such as the plant species itself and the soil physicochemical properties. Lead pollution of shooting range soils has deleterious effects on plants due to the uptake of this toxic heavy metal by plants. Most of the shooting ranges are not fenced and therefore act as grazing fields for livestock and animals. This may result in the migration of Pb through the food chain. In addition, arable farming activities taking place nearby shooting ranges are also at risk of crop contamination from this deadly heavy metal.

However, the uptake of Pb from the soil by plants has manifested into the application of plants towards control and management of Pb pollution in shooting range soils. This technique is called phytoremediation and it has been widely accepted by environmental protection agencies such as the USEPA as a technology to remediate Pb polluted soils. Phytoremediation technology makes use of plants that are hyper-accumulators and significant strides have been made in the application of this technology towards shooting range soils amendments and reclamation efforts. Investigation into possible pollution of both surface and underground water sources found near shooting ranges is a continuous process.

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No potential conflict of interest was reported by the author(s).

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