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An overview of soil contamination in shooting ranges and chitin as a potential amendment

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Abstract— Soil contamination with heavy metals has become a serious concern all over the globe, threatening the ecosystem and human health. Soil and groundwater pollution near shooting ranges has been observed recently in different regions worldwide. Shooting ranges, where soldiers are trained and people do shooting as a hobby and a sport, are marked with high loading of bullets and partially degraded bulletins. As bullets consist of heavy metals such as lead (Pb), copper (Cu), antimony (Sb), arsenic (As), nickel (Ni) and zinc (Zn), there is a high risk of releasing these metals into soils and surrounding ecosystem during natural degradation. Several studies found heavy metals at high concentrations at or nearby shooting ranges. As noticed in this review study, Pb, Cu, As, and Sb was found in top soils, alongside the lateral distances up to 400m revealing the environmental damage caused by the shooting ranges. Several studies suggest different techniques in shooting soil remediation. Chemical and Physical treatments, ex-situ soil washing phytoremediation technologies, and application of natural adsorbents were noticed as possible remediation technologies. Chitin, a natural polymer, was also found as a potential metal trapper in soil remediation, which can be collected as waste material from fish markets. The functional groups and chelation properties of chitin have proven its metal mobilization capacity in many studies.

Keywords –Shooting ranges, soil, contamination, chitin

1 Introduction

Soil contamination is the occurrence of a particular substance in soil exceeding its tolerable limits [1]]. Intensive agriculture, forestry, metal mining, transport, industrialization and urbanization have led to inter-related contamination and other forms of land degradation [2]]. Long term continuation of releasing contaminants may lead to an accumulation of hazardous substances in soils. When the buffering capacity of soil is exceeded, the mobility of the contaminants boosts up, resulting in surface water and/or groundwater contamination.

1.1 Heavy metals in soils

Heavy metals are chemical elements present in all kinds of soils, and very low general levels of heavy metals are found in soils and plants. Heavy metals occur naturally but rarely at toxic levels. The biological role of a few of these chemical elements has led to them being grouped under the generic name of “microelements”, and some of those are highly toxic at lower levels of exposure [3]–[5]].

Accumulation of heavy metals in the soil is a huge problem with industrialization. Soil may be contaminated by the accumulation of metal or the metalloids through mine tailings, land application of fertilizers, sewage sludge discharge, pesticide application, wastewater irrigation, coal combustion residues, spillage of petrochemicals, atmospheric deposition and shooting practices etc.[6]–[9]]. Heavy metals in the soil from anthropogenic sources tend to be more mobile, hence bio-available than pedogenic or lithogenic [10], [11]].

The toxicity and the mobility of toxic metals depend on their specific chemical forms, amounts present in the ecosystem, some external factors such as temperature, oxidation-reduction potential, the presence of anions and cations of other metals and soil pH. Lower soil pH causes increased mobility and availability of most heavy metals [12]–[14]].

The heavy metals essentially become contaminants in the soil environments because their rates of generation via man-made cycles are more rapidly relative to natural ones; those become transferred from mines to random environmental locations where higher potentials of direct exposure occur. Furthermore, the concentrations of the metals in discarded products are relatively high compared to those in the receiving environment, and the chemical form in which a metal is found in the receiving environmental system may render it more bio-available [6], [8], [15]]. Accumulation of excess heavy metal amounts in the soils may harm humans, other animals and plants. Exposure to heavy metals for a more extended period of time may lead to chronic health effects. Heavy metal toxicity can result in damaged or reduced mental and central nervous function, damage to blood composition, and lower energy levels. Lungs, kidneys, liver and other vital organs can damage due to defects produced through heavy metal accumulation [8], [16]].

The presence of metals in water streams and marine water causes a significant health threat to the aquatic community, most common being the damage to the fish's gill [17]]. Heavy metal bioaccumulation is possible through the food chain (soil-plant-human or soil-plant-animal-human), direct ingestion or contact with contaminated soil, and drinking contaminated groundwater. This may reduce food safety and marketability. Phytotoxicity also reduces agricultural land productivity leading to food insecurity and land tenure problems [18]]

2 SHOOTING RANGES AS A SOURCE OF HEAVY METALS

Shooting ranges are defined as the sites where soldiers are trained, and people do shooting as a hobby and a sport. Shooting ranges are characterized by high loading of bullets, which releases lead (Pb), copper (Cu), antimony (Sb), arsenic (As), nickel (Ni) and zinc (Zn) into the soil. Lead (Pb) and, to lesser extent, antimony (Sb) are common contaminants in areas adjacent to the stop butts of military shooting ranges [19]]. On average, new bullets and pellets consist of over 90% Pb, 7% Sb, <2% arsenic (As) and <0.5% nickel (Ni) [20]]. Low-quality Pb, from which bullets are made, may also contain bismuth (Bi) and silver (Ag). Zinc (Zn) and copper (Cu) covers to improve the ballistic properties of high-velocity rounds. Tracer and incendiary bullets contain strontium (Sr), barium (Ba) and Zn. Shooting soil is the second-largest Pb contaminated range in the world; vary from 10 to 60,000 tons of annual deposition, which is extremely higher than the allowable levels [19]]. Lead contamination of the shooting ranges has increased rapidly during the last few years in many countries. Approximately 80,000 tons/year of Pb were used to produce bullets and shots in the United States [21]]. As shown in table 1 the heavy metals present in shooting range soils are considerable. Fig. 1 shows possible contaminant sources coming from shooting ranges.

Fig. 1. Possible contaminant sources coming from shooting ranges

Table 1. Heavy metals present in different shooting range soils

References	Location (shooting range)	Distances from the firing line	Soil sampling depth (cm)	Heavy Metal (mg/kg)					
				Pb	**Sb**	**As**	**Cu**	**Ni**	**Zn**
[22]	Alytus, southern Lithuania	45m	10	53,023	599.78	NM	20.3	8.2	2.7
[23]	Cho-do is in the southern part of South Korea	Backstop area in shooting range	30	21,824	117	NM	443	NM	120
[24]	5km East of Kachia, Kaduna State, Nigeria	200m and 400m	15	14.85	NM	NM	0.55	ND	1.04
[25]	Pantex Firing Range, Amarillo, Texas	Random sampling	10 -25	5560	20.24	10.10	2916	NM	353.1
[26]	New Jersey,USA	Behind the firing position	0-15	397,840	845	1,057	318	NM	NM
[27]	Losone, Southern Switzerland	Random sampling in the firing range	0-30	620	17	NM	63	61	100
[28]	Siena in Tuscany in central Italy	125m	Surface soil	1898	16.3	NM	54	65.7	142
[2]	Shooting range and training centre of El Telenor, León, Spain	Backstop area in shooting range	0-15	4451.57	96.10	62.47	88.52	46.30	31. 68
[29]	Terningmoen military shooting range in Elverum, Norway	trial pits located between the firing line and the backstop berm	0-15	1400	110	NM	843	NM	NM
[30]	Lahore, Pakistan	Random sampling in the firing range	0-3	1331	NM	NM	84.50	2.83	NM

3. SOIL REMEDIATIONS

Remediation of contaminated soils is costly and difficult. Although the prevent entering contaminants is a must, it is hard to manage the non-point contaminant sources in the environment. Therefore, implementing soil remediation techniques to reduce metal contamination in soils is necessary to protect human and ecosystem health. The remediation technology should meet the maximum tolerable limits of toxic metals. The regulatory limits of a few trace metals reported by the U.S.EPA are shown in table 2.

Table 2. Regulatory limits of a few heavy metals present in soils [31]

Heavy metal	The maximum concentration in sludge (mg/kg or ppm)	Annual pollutant loading rates		Cumulative pollutant loading rates	
		(kg/ha/yr)	(lb/A/yr)	(kg/ha)	(lb/A)
As	75	2	1.8	41	36.6
Cd	85	1.9	1.7	39	34.8
Cr	3000	150	134	3000	2679
Cu	4300	75	67	1500	1340
Pb	420	21	14	420	375
Hg	840	15	13.4	300	268
Mo	57	0.85	0.80	17	15
Ni	75	0.90	0.80	18	16
Se	100	5	4	100	89
Zn	7500	140	125	2800	2500

3.1 Chemical and physical methods of soil remediation

Chemical and physical treatment methods of soil remediation are high-cost processes which need high-end technical inputs. High-temperature treatments (produce a vitrified, granular, non-leachable material), use of solidifying agents (produce cement-like material), and washing soils are practiced as ex-situ treatment methods [32]].

Elevating soil pH reduces the metal availability and therefore limits the plant uptake, making it less likely to be incorporated in their tissues and ingested by humans. Draining soils is well-practiced physical soil treatment; drainage improves soil aeration and allows metals to oxidize, making them less soluble. However, the effectiveness of metal immobilization through facilitating drainage or oxidation depends on the type of the contaminant. Some metals, such as Chromium, increase their mobility when oxidized [33], [34]].

Applying Phosphate rich amendments is the commonly practiced chemical treatment method for heavy metal immobilization. However, this is not applicable for the soils contaminated with As; mobility may enhance with the addition of Phosphate [35]]. Furthermore, the addition of Phosphate might be resulting surface water pollution via eutrophication [36]].

Phytoremediation is a low-cost, practical and technically feasible method for heavy metal removal in contaminated soils that uses plants in metal mining, stabilizing, volatilizing or degrading contaminants via biochemical processes inside the plants [4], [15], [37]]. Different kinds of pollutants, including heavy metals, can be remediated using this technique. However, the use of non-edible plants is encouraged considering the risk of entering these contaminants into the food chain. Selecting plants is essential as different plant species show different metal extractability and metals toxicities. Furthermore, the safe disposal of contaminated biomass is necessary [3], [38]].

Soil amendments reduce the bioavailability and mobility of heavy metals and another pollutant in the soils. In addition to that, amendments restore soil quality by balancing pH, the addition of organic matter into the soil can increase the water holding capacity and re-establish the microbial communities. The use of soil amendments enables site remediation, revitalization, re-vegetation and reuse of lands [39], [40]].

The application of appropriate soil amendments may reduce the metal mobility. Precipitation, sequestration and sorption of contaminants are possible with the addition of soil amendments. The application of soil amendments is identified as an effective method in soil remediation that is often use. Commonly used amendments are animal manures and litters, municipal biosolids, sugar beet lime, coal combustion products, wood ash, log yard waste, composted biosolids, lime products, agricultural byproducts, traditional agricultural fertilizers etc. Naturally-occurring waste materials are cost-effective amendments for immobilizing shooting range soils. Eggshells and oyster shells [41]], Cow bone [42]], and poultry litter based biochar [43]] have been studied to minimize metal mobility at shooting ranges. However, Amendments are not always positive in heavy metal removal. Therefore, care should be taken when selecting the appropriate amendments to contaminated sites. The effects of olive husk and cow manure on metal availability in a Pb, Zn and Cu-contaminated soil were investigated by [44]], and they reported that amending contaminated soil with olive husk increased metal solubility in soil, while cow manure treatment did not sufficiently alter metal bioavailability and plant metal accumulation.

3.2 Remediation of shooting soils

The high mobility of heavy metals such as Pb is a severe problem of shooting ranges. Due to the bullet fragmentation and withering, the availability of Pb, Cu, Sb and other heavy metals may present in high concentrations in shooting ranges [45]]. Bioaccumulation of heavy metals in plants grown nearby shooting ranges [46]] and the ruminants grazed in shooting ranges [47]] were reported. Therefore, an effective method for shooting soil remediation is considered essential.

There are limited remediation options disused for shooting range soils. Reprocessing all the earth or capping the entire shooting range with non-contaminated material is impractical [48]]. Usage of naturally occurring waste materials which have the potential to adsorb heavy metals is considered more cost-effective compared to the other soil treatment methods [49]]. Increasing soil pH, with the addition of $CaCO_3$ containing food waste materials such as waste eggshells, oyster shells, poultry waste, and mussel shells [41]–[43]] have been tested in immobilizing metals in polluted soils. Among natural sorbents, chitin has shown potential in heavy metal removal, especially for Cr, Cu, and Mn [50], [51]].

3.3 Use of chitin as a soil amendment in environmental remediation

Agricultural residues and fishery wastes, available in large amounts, can be considered effective and alternative technologies for the remediation of polluted environments. The fishery waste may contain prawn shells which primarily consist of Chitin. Chitin, a natural polymer extracted from crustacean shells, such as prawns, crabs, insects, and shrimps, is a white, hard, inelastic, nitrogenous polysaccharide [52]]. In addition, chitin is the second most abundant, naturally- occurring polysaccharide polymer containing amino sugars [53], [54]].

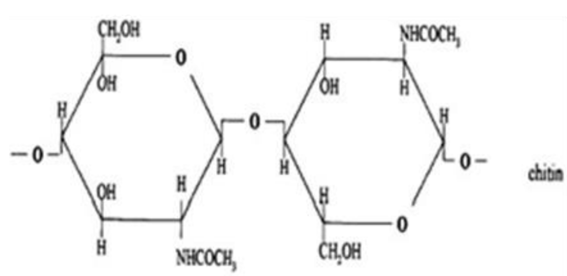

Fig. 2. Chemical formulas of chitin

Chitin is recognized as excellent metal ligand, forming stable complexes with many metal ions. Chitin has a high percentage of nitrogen (6.9%); amine and hydroxyl groups in their chemical structures act as chelation sites for metal ions, making them beneficial chelating agent. Other than that, those are considered natural polymers with excellent properties such as biocompatibility, biodegradability, non-toxicity, metal adsorption, etc. [52]]. The coordination complex formation between the metal and the chitin nitrogen or oxygen is the possible bond. Ion exchange has also been suggested as a process that may be active in taking certain metals by chitin [52], [53]]. Chitin helps to immobilize several toxic metals such as Pb, Zn, and Cd

by forming stable compounds to immobilize the metals [50], [51]]. Further, to improve metal-binding abilities, some chemical modifications such as increasing the degree of deacetylation, cross-linking between the polymer chains or grafting of functional groups can be made [54]].
For heavy metals, chitin amendment can have contradicting effects on mobility, bioavailability, and toxicity. Further, breakdown products (e.g. acetate and fructose) from chitin degradation may be ideal carbon sources for anaerobic and facultative microorganisms capable of metal reduction. Hence, chitin has been explored for wastewater treatment, such as removing toxic metals and radionuclides, recovering precious metals, and recycling metals from industrial wastewater for reuse to reduce operational costs.

4. Conclusion:

The potential ecosystem risk caused by heavy metals released from shooting ranges was well notified in this study. Considering the negative impacts of boosting up metal mobility and bioaccumulation risk, implementing remediation technologies at shooting ranges was considered essential. Chitin was identified as a potential polymer that can be collected as waste material in fish industries in immobilizing metals released from the shooting ranges.

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