

Heavy Metal Soil Contamination



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This is the third note in a series of Soil Quality-Urban technical notes on the effects of land management on soil quality.



Introduction

Soil is a crucial component of rural and urban environments, and in both places land management is the key to soil quality. This series of technical notes examines the urban activities that cause soil degradation, and the management practices that protect the functions urban societies demand from soil. This technical note focuses on heavy metal soil contamination.

Metals in Soil

Mining, manufacturing, and the use of synthetic products (e.g. pesticides, paints, batteries, industrial waste, and land application of industrial or domestic sludge) can result in heavy metal contamination of urban and agricultural soils. Heavy metals also occur naturally, but rarely at toxic levels. Potentially contaminated soils may occur at old landfill sites (particularly those that accepted industrial wastes), old orchards that used insecticides containing arsenic as an active ingredient, fields that had past applications of waste water or municipal sludge, areas in or around mining waste piles and tailings, industrial areas where chemicals may have been dumped on the ground, or in areas downwind from industrial sites.

Excess heavy metal accumulation in soils is toxic to humans and other animals. Exposure to heavy metals is normally chronic (exposure over a longer period of time), due to food chain transfer. Acute (immediate) poisoning from heavy metals is rare through ingestion or dermal contact, but is possible. Chronic problems associated with long-term heavy metal exposures are:

- Lead – mental lapse.
- Cadmium – affects kidney, liver, and GI tract.
- Arsenic – skin poisoning, affects kidneys and central nervous system.

The most common problem causing *cationic* metals (metallic elements whose forms in soil are positively charged cations e.g., Pb^{2+}) are mercury, cadmium, lead, nickel, copper, zinc, chromium, and manganese. The most common anionic compounds (elements whose forms in soil are combined with oxygen and are negatively charged e.g., MoO_4^{2-}) are arsenic, molybdenum, selenium, and boron.

Prevention of Heavy Metal Contamination

Preventing heavy metal pollution is critical because cleaning contaminated soils is extremely expensive and difficult. Applicators of industrial waste or sludge must abide by the regulatory limits set by the U.S. Environmental Protection Agency (EPA) in Table 1.

Table 1. Regulatory limits on heavy metals applied to soils (Adapted from U.S. EPA, 1993).

| Heavy metal | 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) |
| Arsenic | 75 | 2 | 1.8 | 41 | 36.6 |
| Cadmium | 85 | 1.9 | 1.7 | 39 | 34.8 |
| Chromium | 3000 | 150 | 134 | 3000 | 2,679 |
| Copper | 4300 | 75 | 67 | 1500 | 1,340 |
| Lead | 420 | 21 | 14 | 420 | 375 |
| Mercury | 840 | 15 | 13.4 | 300 | 268 |
| Molybdenum | 57 | 0.85 | 0.80 | 17 | 15 |
| Nickel | 75 | 0.90 | 0.80 | 18 | 16 |
| Selenium | 100 | 5 | 4 | 100 | 89 |
| Zinc | 7500 | 140 | 125 | 2800 | 2500 |

Prevention is the best method to protect the environment from contamination by heavy metals. With the above table, a simple equation is used to show the maximum amount of sludge that can be applied. For example, suppose city officials want to apply the maximum amount of sludge (kg/ha) on some agricultural land. The annual pollutant-loading rate for zinc is 140 kg/ha/yr (from Table 1). The lab analysis of the sludge shows a zinc concentration of 7500 mg/kg (mg/kg is the same as parts per million). How much can the applicator apply (tons/A) without exceeding the 140 kg/ha/yr?

Solution:

- (1) Convert mg to kg (1,000,000 mg = 1kg) so all units are the same:

$$7500 \text{ mg} \times (1 \text{ kg}/1,000,000 \text{ mg}) = 0.0075 \text{ kg}$$

- (2) Divide the amount of zinc that can be applied by the concentration of zinc in the sludge:

$$(140 \text{ kg Zn/ha}) / (0.0075 \text{ kg Zn/kg sludge}) = 18,667 \text{ kg sludge/ha}$$

- (3) Convert to lb/A: $18,667 \text{ kg/ha} \times 0.893 = 16,669 \text{ lbs/A}$

$$\text{Convert lbs to tons: } 16,669 \text{ lb/A} / 2,000 \text{ lb/T} = 8.3 \text{ T sludge per acre}$$

Traditional Remediation of Contaminated Soil

Once metals are introduced and contaminate the environment, they will remain. Metals do not degrade like carbon-based (organic) molecules. The only exceptions are mercury and selenium, which can be transformed and volatilized by microorganisms. However, in general it is very difficult to eliminate metals from the environment.

Traditional treatments for metal contamination in soils are expensive and cost prohibitive when large areas of soil are contaminated. Treatments can be done *in situ* (on-site), or *ex situ* (removed and treated off-site). Both are extremely expensive. Some treatments that are available include:

1. High temperature treatments (produce a vitrified, granular, non-leachable material).
2. Solidifying agents (produce cement-like material).
3. Washing process (leaches out contaminants).

Management of Contaminated Soil

Soil and crop management methods can help prevent uptake of pollutants by plants, leaving them in the soil. The soil becomes the sink, breaking the soil-plant-animal or human cycle through which the toxin exerts its toxic effects (Brady and Weil, 1999).

The following management practices will not remove the heavy metal contaminants, but will help to immobilize them in the soil and reduce the potential for adverse effects from the metals – Note that the kind of metal (cation or anion) must be considered:

1. Increasing the soil pH to 6.5 or higher.

Cationic metals are more soluble at lower pH levels, so increasing the pH makes them less available to plants and therefore less likely to be incorporated in their tissues and ingested by humans. Raising pH has the opposite effect on anionic elements.

2. Draining wet soils.

Drainage improves soil aeration and will allow metals to oxidize, making them less soluble. Therefore when aerated, these metals are less available. The opposite is true for chromium, which is more available in oxidized forms. Active organic matter is effective in reducing the availability of chromium.

3. Applying phosphate.

Heavy phosphate applications reduce the availability of cationic metals, but have the opposite effect on anionic compounds like arsenic. Care should be taken with phosphorus applications because high levels of phosphorus in the soil can result in water pollution.

4. Carefully selecting plants for use on metal-contaminated soils

Plants translocate larger quantities of metals to their leaves than to their fruits or seeds. The greatest risk of food chain contamination is in leafy vegetables like lettuce or spinach. Another hazard is forage eaten by livestock.

Plants for Environmental Cleanup

Research has demonstrated that plants are effective in cleaning up contaminated soil (Wenzel et al., 1999). Phytoremediation is a general term for using plants to remove, degrade, or contain soil pollutants such as heavy metals, pesticides, solvents, crude oil, polyaromatic hydrocarbons, and landfill leachates. For example, prairie grasses can stimulate breakdown of petroleum products. Wildflowers were recently used to degrade hydrocarbons from an oil spill in Kuwait. Hybrid poplars can remove ammunition compounds such as TNT as well as high nitrates and pesticides (Brady and Weil, 1999).

Plants for Treating Metal Contaminated Soils

Plants have been used to stabilize or remove metals from soil and water. The three mechanisms used are *phytoextraction*, *rhizofiltration*, and *phytostabilization*. This technical note will define rhizofiltration and phytostabilization but will focus on phytoextraction.

Rhizofiltration is the adsorption onto plant roots or absorption into plant roots of contaminants that are in solution surrounding the root zone (rhizosphere). Rhizofiltration is used to decontaminate groundwater. Plants are grown in greenhouses in water instead of soil. Contaminated water from the site is used to acclimate the plants to the environment. The plants are then planted on the site of contaminated ground water where the roots take up the water and contaminants. Once the roots are saturated with the contaminant, the plants are harvested including the roots. In Chernobyl, Ukraine, sunflowers were used in this way to remove radioactive contaminants from groundwater (EPA, 1998).

Phytostabilization is the use of perennial, non-harvested plants to stabilize or immobilize contaminants in the soil and groundwater. Metals are absorbed and accumulated by roots, adsorbed onto roots, or precipitated within the rhizosphere. Metal-tolerant plants can be used to restore vegetation where natural vegetation is lacking, thus reducing the risk of water and wind erosion and leaching. Phytostabilization reduces the mobility of the contaminant and prevents further movement of the contaminant into groundwater or the air and reduces the bioavailability for entry into the food chain.

Phytoextraction

Phytoextraction is the process of growing plants in metal contaminated soil. Plant roots then translocate the metals into aboveground portions of the plant. After plants have grown for some time, they are harvested and incinerated or composted to recycle the metals. Several crop growth cycles may be needed to decrease

contaminant levels to allowable limits. If the plants are incinerated, the ash must be disposed of in a hazardous waste landfill, but the volume of the ash is much smaller than the volume of contaminated soil if dug out and removed for treatment. (See box.)

Example of Disposal

Excavating and landfilling a 10-acre contaminated site to a depth of 1 foot requires handling roughly 20,000 tons of soil. Phytoextraction of the same site would result in the need to handle about 500 tons of biomass, which is about 1/40 of the mass of the contaminated soil. In this example, if we assume the soil was contaminated with a lead concentration of 400 ppm, six to eight crops would be needed, growing four crops per season (Phytotech, 2000).

Phytoextraction is done with plants called hyperaccumulators, which absorb unusually large amounts of metals in comparison to other plants. Hyperaccumulators contain more than 1,000 milligrams per kilogram of cobalt, copper, chromium, lead, or nickel; or 10,000 milligrams per kilogram (1 %) of manganese or zinc in dry matter (Baker and Brooks, 1989). One or more of these plant types are planted at a particular site based on the kinds of metals present and site conditions. Tables 2 and 3 demonstrate the importance of using hyperaccumulators.

Table 2. Percentage decrease in water-extractable zinc and cadmium in three soils after growth of Alpine pennycress (*Thlaspi caerulescens*) (McGrath, 1998).

| Site Sampled | Zn | Cd |
|--------------|----|----|
| Farm | 28 | 10 |
| Garden | 17 | 22 |
| Mountain | 64 | 70 |

Table 3. Removal of zinc in a hypothetical 4.5 T/A (dry matter) crop growing in soil contaminated with 1000 (ppm) zinc with a target of 50 ppm, showing the importance of hyperaccumulation (>10,000 ppm zinc) (McGrath, 1998).

| ppm Zn in plant | Lbs. of Zn removed | % of soil total in one crop | years to target |
|-----------------|--------------------|-----------------------------|-----------------|
| 100 | 0.9 | 0.04 | 2470.0 |
| 1000 | 9 | 0.38 | 247.0 |
| 10,000 | 90 | 3.85 | 24.7 |
| 20,000 | 179 | 7.69 | 12.4 |
| 30,000 | 268 | 11.54 | 8.2 |

Phytoextraction is easiest with metals such as nickel, zinc, and copper because these metals are preferred by a majority of the 400 hyperaccumulator plants. Several plants in the genus *Thlaspi* (pennycress) have been known to take up more than 30,000 ppm (3%) of zinc in their tissues. These plants can be used as ore because of the high metal concentration (Brady and Weil, 1999).

Of all the metals, lead is the most common soil contaminant (EPA, 1993). Unfortunately, plants do not accumulate lead under natural conditions. A chelator such as EDTA (ethylenediaminetetraacetic acid) has to be added to the soil as an amendment. The EDTA makes the lead available to the plant. The most common plant used for lead extraction is Indian mustard (*Brassica juncea*). Phytotech (a private research company) has reported that they have cleaned up lead-contaminated sites in New Jersey to below the industrial standards in 1 to 2 summers using Indian mustard (Watanabe, 1997).

Plants are available to remove zinc, cadmium, lead, selenium, and nickel from soils at rates that are medium to long-term, but rapid enough to be useful. Many of the plants that hyperaccumulate metals produce low biomass, and need to be bred for much higher biomass production.

Current genetic engineering efforts at USDA in Beltsville, MD, are aimed toward developing pennycress (*Thlaspi*) that is extremely zinc tolerant. These taller-than-normal plants would have more biomass, thereby taking up larger quantities of contaminating metals (Watanabe, 1997).

Traditional cleanup *in situ* may cost between \$10.00 and \$100.00 per cubic meter (m^3), whereas removal of contaminated material (*ex situ*) may cost as high \$30.00 to \$300/ m^3 . In comparison, phytoremediation may only cost \$0.05/ m^3 (Watanabe, 1997).

Future Prospects

Phytoremediation has been studied extensively in research and small-scale demonstrations, but in only a few full-scale applications. Phytoremediation is moving into the realm of commercialization (Watanabe, 1997). It is predicted that the phytoremediation market will reach \$214 to \$370 million by the year 2005 (Environmental Science & Technology, 1998).

Given the current effectiveness, phytoremediation is best suited for cleanup over a wide area in which contaminants are present at low to medium concentrations. Before phytoremediation is fully commercialized, further research is needed to assure that tissues of plants used for phytoremediation do not have adverse environmental effects if eaten by wildlife or used by humans for things such as mulch or firewood (EPA, 1998). Research is also needed to find more efficient bioaccumulators, hyperaccumulators that produce more biomass, and to further monitor current field trials to ensure a thorough understanding. There is the need for a commercialized smelting method to extract the metals from plant biomass so they can be recycled.

Phytoremediation is slower than traditional methods of removing heavy metals from soil but much less costly. Prevention of soil contamination is far less expensive than any kind of remediation and much better for the environment.

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