SOIL-PLANT-ANIMAL PATHWAY

SOIL REMEDIATION USING BIOSOLIDS

Two risk assessment pathways were evaluated at sites where biosolids and alkaline by-products were used to remediate mine spoils and metal contaminated soils.

Part I

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METAL contaminated soils have prevented revegetation at many locations where smelter emissions or mine wastes caused contamination and soils were acidic. Such metal toxic soils can be revegetated effectively using mixtures of biosolids and alkaline by-products so that the soil metals are no longer phytotoxic, and nutrient deficiencies of such disturbed soils are corrected. Concerns have been expressed that revegetation of such highly contaminated soils may solve one environmental problem but create another because of the potential for harm to wildlife returning to the lushly vegetated, remediated sites.

These issues were raised during consideration of a Superfund site remediation project in Jasper County, Missouri. Jasper County is located in the center of what is referred to as the "Old Lead Belt." For over a century, small-scale mining and milling operations of lead and zinc-rich ores dotted the landscape. As the ore bodies became depleted, the county was left with a rich history and over 7,000 acres of barren soil to restore. In Joplin, the largest town in Jasper County and also the location of the main lead smelter, over 2,000 yards of soils have been excavated and replaced with clean fill. This type of remedy is not only impractical, it is potentially impossible on a large scale.

As part of the development of remediation alternatives for the Jasper County mine wastes and contaminated soils, *in situ* remediation has been considered. A report —on which this two-part article is based — was prepared to address the question of potential harm to wildlife that would return to the remediated site. The report discusses the results of a risk assessment undertaken to see what available data indicate about hazard remediation by use of biosolids plus alkaline by-products to revegetate such soils. Limits to protect wildlife on biosolids-amended soils were developed, and may prove to be a solid technical basis for protecting wildlife when remediating soils.

Determining the best practical approach to restore an active plant and animal community on the mine wastes at a particular site, such as in Jasper County, is a complicated decision. It is desirable to both limit the risks posed by the metal contaminants and to create a functional ecosystem on the denuded areas in a manner that is both protective and cost-effective. Risk assessment using relevant data should clarify whether *in situ* remediation of the Jasper County soils would be expected to protect highly exposed organisms or require further demonstration with full wildlife testing on such remediated sites.

TAILOR-MADE MIXES

There are three general approaches to remediation of sites such as Jasper County. The default option is soil removal and replacement, a very expensive and very disruptive approach. A second method for revegetation is domestication of metal tolerant cultivars of red fescue and bentgrass, which requires annual N fertilizer applications because there are no metal tolerant legumes. A third method, and one researched extensively by two coauthors of this report (Chaney and Brown), involves applications of "tailor-made" mixes of biosolids plus alkaline by-products to remediate the toxicity and infertility (rather than seeding metal resistant grasses on minimally fertilized soils) so that these factors do not limit any plants from growing on the remediated soil. To prevent pH from dropping in a few years after treatment, enough limestone equivalent is added to make the topsoil calcareous (neutralize acidity plus 50 to 100 t/ha of $CaCO_3$-equivalent); this residual limestone in the soil can prevent pH decline for very long periods if the acidification from fertilizers does not occur. A fuller consideration of any nutrient imbalances of the amended soil allows selection of

These before (left) and after (right) views of an "Old Lead Belt" site in Jasper County, Missouri show effects of applying biosolids and alkaline by-products to revegetate such soils.

additional alkaline by-products for use as element fertilizers to be included in the remediation mixtures.

The combination of biosolids and limestone can inactivate soil zinc, cadmium and lead, allowing effective plant growth and potentially reduce bioavailability of soil elements to animals that consume soils. The biosolids provide both organic and inorganic binding sites for the metals. These inorganic binding sites consist primarily of amorphous metal oxide minerals. These minerals have a very high surface area that is also very reactive at high soil pH. Increasing the pH of the systems increases metal binding capacity and therefore lowers metal availability.

Application of biosolids in combination with limestone has been used on a number of metal contaminated sites to restore a plant cover. These sites include Palmerton, Pennsylvania (zinc smelter), Katowice, Poland (zinc, lead slag and waste piles), Bunker Hill, Idaho (zinc, lead smelter deposition and tailings materials) and Leadville, Colorado (alluvial lead and zinc pyritic tailings). In addition to use on metal contaminated sites, there is a relatively long history (30-plus years) of biosolids use to reclaim lands disturbed by a range of mining activities. At many of these biosolids-revegetated metal rich soil sites, wildlife have thrived. Small mammals are so successful in Palmerton, for example, that predator birds have become established on previously barren smelter killed soils. Rabbits and birds are common soon after the severe metal phytotoxicity and nutrient deficiency of the acidic contaminated soils is remediated by the mixture of biosolids and alkaline by-products.

By evaluating potential for adverse effects of mine wastes, a decision can be made on which remedial alternative is acceptable.

REMEDIATION RISK ASSESSMENT

As part of the process to determine appropriate metal concentrations for biosolids during the development of the 40 CFR 503 regulations, scientists working with the U.S. Environmental Protection Agency attempted to define the range of pathways where elements in land applied biosolids could cause harm to highly exposed and sensitive species. The species evaluated for this process were the most sensitive potential receptors for each pathway. Species for the risk assessment included humans, plants, soil organisms and a range of livestock and wildlife.

For the risk assessment process for remediated soils in Jasper County, we have tried to use a similar approach to that used in the Part 503 regulation development. Metals of concern in Jasper County contaminated mine wastes and soils are zinc, lead and cadmium. Recognizing that the application of biosolids and limestone can restore a vigorous plant cover to these sites, there are potentially two pathways that these elements might cause damage to an ecosystem — Soil to Plant to Animal (herbivore exposure) and Remediated Soil to Animal. When information on similar sites where biosolids have been used is available, that information has been the basis for risk estimates. In cases where such directly applicable information is not available, the existing literature on ecological effects of lead, zinc and cadmium from contaminated sites or from biosolids amended sites has been used to outline potentially acceptable soil concentrations that should protect highly exposed and sensitive species from adverse effects as a result of exposure to these elements in the remediated mine wastes. Application of biosolids to these sites has consistently resulted in a reduction in phyto- and bioavailability of these metals. By evaluating the potential for adverse effects of the unremediated mine wastes — and taking into account the experience that biosolids and limestone application should reduce this risk — it may be possible to decide if this remedial alternative is acceptable.

Part I of this article looks at the first pathway, soil to plant to animal. Part II, to appear in the next issue, examines the second pathway, remediated soil to animal. Overall conclusions will be in Part II.

PATHWAY: SOIL TO PLANT TO ANIMAL — RISKS FROM ZINC

In cases where a plant cover has been restored to contaminated sites without prior remediation, zinc (Zn) levels in plants are near phytotoxic levels in surviving plants. In general, restoring a plant cover to sites without soil amendment has had limited success. Plant species are often limited to metal tolerant ecotypes. The alternative was applying very high rates of clean material over the surface of the contaminated soils. The problems associated with each of these options were reasons that the application of tailor-made biosolids mixtures were developed for these sites (thus data is available for this pathway). Amendment mixtures have included 50 (Palmerton, Joplin, Bunker Hill) to 100 (Leadville, Katowice) tons/acre of biosolids and in some cases biosolids compost (Bunker Hill wetlands). In each case, a high rate of limestone or high calcium carbonate residual also has been used to raise soil pH so that metals are precipitated or adsorbed more strongly. In Palmerton, coal fly ash (100 tons/acre) was mixed with Class B biosolids. In Katowice, a residual from acetylene production was used as a lime source. In Leadville, sugar beet lime was mixed with Class B biosolids or biosolids compost (for use directly on the river banks) at 100 tons/acre to neutralize existing and potential acidity. In the wetland at Bunker Hill, wood ash was mixed with compost before application to provide a lime source.

Livestock graze in Leadville, Colorado after plant cover is restored on once-contaminated sites.

Zinc is phytotoxic when leaves reach high Zn concentrations. Different plant species have different thresholds for soluble soil Zn at which Zn phytotoxicity occurs. Plant tissue concentrations reported to cause phytotoxicity range from 200 to 1,200 mg kg^{-1} with smaller variation within species. As a general rule, nearly all plant species have very strong yield reduction when foliar Zn exceeds 500 mg kg^{-1}; in acidic soils, this Zn causes yellowing of young leaves due to Zn-induced iron deficiency. In most of the studies of metal uptake by mammals in the vicinity of zinc-lead (Zn-Pb) smelters, vegetation of the heavily contaminated areas is sparse and limited to metal tolerant grasses that survive by excluding Zn from shoot tissue. Once this specialized tolerance mechanism fails and plant shoot tissue Zn exceeds about 500 ppm, these plants will also suffer from Zn toxicity and die. Despite increased tolerance, the foliar Zn concentration threshold for phytotoxicity for these plants is similar to that of crop plants.

For Zn to pose a threat to animals which ingest such high Zn plants, higher plant Zn levels would be required than the phytotoxic threshold concentration of 500 mg kg^{-1}. Because plants are injured at lower Zn concentration than required to harm animals which consume the plants, Zn risk to animals is prevented by this soil-plant barrier.

In cases where biosolids have been used to restore Zn-Pb contaminated soils, Zn concentrations in vegetation have been under the diagnostic threshold phytotoxic concentrations and fall within the normal range for healthy crops. This indicates that if plants are growing well on the treated soils, the potential for Zn contamination of plants growing on remediated Jasper County contaminated soils is very unlikely to result in a food chain threat to livestock or wildlife.

ZINC RISK TO LIVESTOCK AND WILDLIFE

Plant Zn has been linked to fatality or injury in horses in several cases. In Palmerton, foals that grazed on pastures with elevated Zn concentration (1000 mg Zn kg^{-1} dry forage largely the result of smelter deposition on plant tissue compared to normal levels < 50 mg kg^{-1}) suffered from Zn-induced copper (Cu) deficiency. In Leadville, horses also suffered Zn-induced Cu deficiency as a result of grazing on Zn contaminated pastures. Cu supplementation reversed injury to foals in both locations. Beef and dairy cattle performed normally even though their forages were grown on contaminated soils. In 1980, the National Research Council's (NRC) recommended limits for maximum dietary Zn considered that marginal Cu supply increased risk from high diet Zn to ruminant livestock. If dietary Cu was marginal for growth, the forage Zn maximum recommended was 300 mg kg^{-1}, while with adequate Cu, most species tolerate over 1000 mg Zn kg^{-1} in diets, according to the NRC. When forages are grown on biosolids amended soils, forage Cu will be in the normal rather than marginal level for ruminants, reducing the potential for risk from high dietary Zn.

The potential for Zn-induced Cu-deficiency to occur in nonruminants appears to be very limited. In nonruminants, Zn accumulation by the body appears to be regulated by homeostasis mechanisms (the tendency to maintain, or the maintenance of, normal, internal stability in an organism by coordinated responses of the organ systems that automatically compensate for environmental changes).

PATHWAY: SOIL TO PLANT TO ANIMAL — RISKS FROM CADMIUM

Excess Cadmium (Cd) in diets of subsistence rice farmers has caused renal proximal tubular dysfunction and occasionally an osteomalacia called *itai-itai* disease. A recent study reported that Cd (10 mg kg^{-1}) in willow buds on trees growing in alluvial mine tailings rich in Zn, Cd and Pb (and a wetland soil) was sufficient to cause negative health effects in ptarmigan. These birds eat willow buds in the early spring. For this study, excess Cd in the buds was associated with reproductive problems in the ptarmigan. Zinc concentrations in the buds were not reported. Because of this data omission, it isn't possible to see if Zn content of the foliage also was elevated. In cases where Zn content is also high, Cd absorption may be reduced. In this study, it seems likely that limited Zn uptake from these wetland soils allowed more Cd to be absorbed by the birds. This suggests that this pathway may be pertinent for an ecological hazard in Jasper County.

Two factors need to be considered with these examples. First, in the case of human food-chain Cd health effects, the rice was grown in flooded soils contaminated by mining and smelting waste. Rice was the staple food in the farmers' diets. Rice is a unique grain as concentrations of other essential elements in polished rice such as Ca, Fe, and Zn are generally present in deficient concentrations for humans. The same amount of Cd that caused health effects to subsistence farmers in Japan was not associated with any observed Cd accumulation or health effects when other foods (shellfish, vegetables, wheat, sunflower kernels) carried increased Cd to humans.

Second, in both rice cultivation and in willow habitat, soils generally alternate between anaerobic and aerobic conditions. Under anaerobic conditions, sulfide can form, and the metal ions (Zn, Pb, and Cd) can be precipitated as metal sulfides. When aerobic conditions return, the sulfides can be oxidized and the metals transformed to more soluble forms. Because of the soil chemistry of Cd and Zn, and the large amount of zinc sulfides (ZnS) that must be oxidized to free all soil Zn, the cadmium sulfides (CdS) dissolve before ZnS. The absence of Zn to inhibit Cd uptake and translocation within the rice plant leads to excess Cd uptake without Zn phytotoxicity — which would be expected when Cd and Zn are in the ratio found from mine waste contamination (about 1 Cd to 100 Zn). Increased grain Cd without a corresponding increase in grain Zn eliminates the protection from excess Cd accumulation that is generally seen in all other crops when Zn is a cocontaminant. In aerobic soil environments, when Zn and Cd are present in ratios >100:1, uptake and accumulation of Cd are quite limited. Thus, soil chemistry of wetland environments may cause Cd to pose a greater risk than in aerobic environments.

For use of biosolids compost in normal wetland restoration, this should not be an issue. It would only be a factor in cases where wetlands have metal contamination and go through seasonal fluctuations in the water table. The varying water level will result in alternating aerobic and anaerobic conditions, which can result in dissolution of metal sulfides.

There is one example of metal uptake by plants in a wetland environment where

At metal-contaminated sites in Bunker Hill, Idaho, composted biosolids and limestone were applied in drained wetlands (above). The wetlands were readily revegetated (below).

biosolids compost and limestone were used to restore a vegetative cover. In the Page Swamp, a wetland developed in Zn-Pb mine waste near Kellogg, Idaho, barren mine wastes were readily revegetated. Plant Cd concentrations in this case are below the level that was associated with negative health effects to ptarmigan. Levels of Zn and Pb also are reduced compared to samples collected from the unremediated mine waste area.

For aerobic soil environments in acidic contaminated soils which allow higher uptake of Cd and Zn, plant uptake of Cd is generally inhibited by Zn. Because Zn is usually 100-fold higher than Cd in the soil, and a similar relationship is translocated to plant shoots, Zn causes important yield reduction before Cd is greatly increased. In addition, absorption of Cd by animals consuming forages grown on Zn and Cd contaminated soils may be restricted because these forages are rich in Zn, which can inhibit Cd absorption.

In other cases where high Zn, Cd, and Pb soils have been remediated using a biosolids-lime mixture, plant Cd is reduced compared to control unremediated soils. Concentrations are sufficiently reduced to suggest that the potential for food chain transfer of Cd is limited.

FOOD CHAIN TRANSFER OF SOIL LEAD

Plant uptake of Pb to plant shoots is generally limited both by the insolubility of Pb in soils and the precipitation of Pb with phosphates in plant roots. Extensive evaluation of risks from Pb in vegetable garden soils has shown limited uptake of soil Pb by lettuce and similar plant species which accumulate higher Pb levels than other garden and field crops. Application of limed biosolids compost to high Pb urban garden soils strongly reduced Pb uptake by lettuce. Thus, the hazards associated with excess Pb in soils are generally agreed to be associated with direct ingestion of soils rather than from plant accumulation of soil Pb. Plant uptake of Pb from mine waste sites remediated with a biosolids-limestone amendment is also reduced compared to unremediated soils. ■

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