Bioresource Technology 101 (2010) 5667–5676

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Phytoavailability and fractionation of lead and manganese in a contaminated soil after application of three amendments

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ARTICLE INFO

Article history:
Received 11 June 2009
Received in revised form 23 December 2009
Accepted 29 January 2010
Available online 9 March 2010

Keywords:
Phytostabilisation
Soil-amendment-plant interaction
Metal fractionation
Translocation properties
Biometric characters

ABSTRACT

Studies were conducted to determine the best management practice for immobilisation of toxic Pb and Mn in soil and the interaction of these metal contaminants with the associated plants. The research protocol comprises addition of soil amendments to accelerate physico-chemically driven sorption processes and growth of appropriate plant species to reduce physiologically driven uptake of Pb and Mn. *Lolium perenne* L (perennial rye grass), *Festuca rubra* L (creeping red fescue) and *Poa pratensis* L (Kentucky blue grass) were tested in the presence of soil amendments (lime, phosphate and compost, both individually and in combination). The effectiveness of treatments in stabilizing metals was assessed on the basis of metal speciation in soil, partitioning of metals in plants, and metal uptake. Significant partitioning of Pb in immobile forms was noticed by the growth of *P. pratensis* and Mn by the growth of *L. perenne*. Lime application lowered plant Pb and Mn, while phosphate decreased plant Pb and increased plant Mn. Combined amendment addition resulted in a significant decrease in the exchangeable (mobile) metal fraction in soils growing *Poa* for Pb and in soils growing *Lolium* for Mn. EC_{root} (ratio of root concentration to soil concentration) and EC_{shoot} (ratio of shoot concentration to soil concentration) for Pb in *Poa* decreased by 72% and 60% with combined application of amendments, while the corresponding decreases for Mn in *Lolium* were 48% and 43%.

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1. Introduction

Pb and Mn have been used extensively in transportation systems during the past few decades. Both are of considerable concern, since toxic effects of these metals are linked to many ecological and human health risks. The use of tetraethyl lead (TEL) as an antiknock compound for gasoline engines in the early 1980s and the subsequent replacement of methyl cyclopentadienyl manganese tricarbonyl (MMT) have led to considerable exhaust emissions of Pb and Mn. Both are also released to the environment by other anthropogenic activities. For example, Pb contamination results from mining and smelting activities, use in paints, as well as from disposal of municipal sewage sludge and industrial wastes enriched in Pb (Joint FAO/WHO Expert Committee on Food Additives, 2000; Ma et al., 1995). Because of the high binding strength of Pb to soil fractions, Pb is highly immobile in soil and it becomes virtually permanent, with a soil retention time of 150–5000 years (Friedland, 1990). Hence, even though the use of leaded gasoline was suspended several decades ago in North America and most of the industrialized world, many roadside soils remain contaminated with Pb (Sezgin et al., 2003). In Canada, the anthropogenic emissions of Mn amounted to 1225 tons, with approximately 75% from industrial facilities and 20% from gasoline-powered motor vehicles using MMT (Environment Canada, 1987).

Contamination of soil by lead is of major concern due to its high toxicity to humans and animals and its bioavailability through ingestion or inhalation. Relatively low concentrations of Pb in the blood can affect children's mental development, an effect that persists into adulthood (Needleman et al., 1990; Laidlaw et al., 2005). Exposure to high concentrations of Mn can cause numerous health problems, including neurodegenerative disorders (such as manganism) similar to Parkinson's disease (US EPA, 2003).

Phytoremediation is a cost-effective, environmentally friendly and ecologically sound remediation method (Baker et al., 1994) for metal-contaminated sites. Depending upon the conditions of the site, level of clean-up required and plant species, the remediation method can be either containment or removal (Padmavathiamma and Li, 2007). Containment by *in situ* immobilisation or in-place inactivation of contaminants using plants and amendments is phytostabilisation (Smith and Bradshaw, 1979; Arienzo et al., 2003). This may be suited for busy contaminated sites such as highway soils, where contaminant removal is neither feasible nor practical due to physical and financial constraints.

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0960-8524/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.biortech.2010.01.149

Many amendments and plants have been reported to be effective for the stabilisation of metal-contaminants (Simon, 2005; Kumpiene et al., 2007). But a holistic approach involving suitable plants and natural amendments that can remediate the metal-contaminated sites, retaining the functional and ecological integrity of soil is still lacking. The present study was undertaken in the contaminated acidic soils of coastal British Columbia using natural agricultural amendments such as lime, phosphate and compost individually and in combination, together with plant species: *Lolium perenne* L (perennial rye grass), *Festuca rubra* L (creeping red fescue) and *Poa pratensis* L (Kentucky blue grass). These plants were found to be suitable for phytostabilisation by Padmavathiamma and Li (2009).

The objectives were: (1) to assess the effect of soil-amendment–plant interaction on the partitioning of Pb and Mn in various soil fractions and to evaluate the mobility and phyto-availability of these metals in soil; and (2) to assess the effect of soil improvement or amelioration on the accumulation characteristics and translocation properties of these metals in the plants. The studies generated sufficient data to suggest a cost effective package that not only reduce the hazard associated with excess Pb and Mn, but also improve soil quality and restore its functionality.

2. Methods

The present study was performed on soil collected from the backyard of Surrey Fire hall No. 5, near the main intersection of highway 1 with 176th Street in Surrey, British Columbia. This represents a busy site with respect to traffic counts (>80,000 vehicles/day), and it is highly contaminated with Cu, Pb, Mn and Zn (Preciado and Li, 2006). This paper focuses on Pb and Mn, whereas an earlier paper considered Cu and Zn. The metal interaction studies by Padmavathiamma and Li (2009) revealed a high degree of correlation between Cu and Zn, and limited correlation between Pb and Mn. Gasoline combustion may be the main source of Pb and Mn in highway soils. The original soil (B0) containing 52 mg/kg Cu, 93 mg/kg Pb, 215 mg/kg Mn, and 70 mg/kg Zn, was spiked with further Cu, Pb, Mn and Zn, resulting in total measured Cu, Pb, Mn, and Zn concentrations of 80, 146, 408 and 148 mg/kg, respectively (designated BA), approximately matching the British Columbia (Ministry of Environment, 1995) A-level limits for contaminated sites. Details on spiking the soil with multi-metals and addition of amendments are given in Padmavathiamma and Li (2010). The plant species investigated were *L. perenne* L (perennial rye grass), *F. rubra* L (creeping red fescue) and *P. pratensis* L (Kentucky blue grass). The study was conducted as a pot experiment in a completely randomized design with 18 treatments and three replications (Table 1). The nomenclature used for various treatments/conditions is given in Table 1. The experiment was conducted in a greenhouse from August 2006 to November 2006. Soil and plant samples were collected at 90 DAS (days after sowing). Shoots and roots were then separated and oven dried (70 °C) to constant weight. Various biometric characters such as length of root, number of branches per root, root weight, length of shoot, number of leaves per plant, shoot weight and root/shoot ratio were recorded at harvest.

Basic characteristics of the soil such as pH, electrical conductivity, total carbon, available P and texture were estimated using standard procedures. The procedure of Tessier et al. (1979), as modified by Preciado and Li (2006), was adopted for selective sequential extraction. The different metal fractions estimated were: exchangeable, carbonates and oxides, organic and residual. The plant samples were air dried and ashed by the method outlined by Lintern et al. (1997). The ash was dissolved in 10 mL 1 M HCl and diluted to 50 mL with de-ionized water. Soil and plant extracts were analysed for Pb and Mn using a Varian Spectre AA 220 Multi-element Fast Sequential Atomic Absorption Spectrometer.

The statistical significance of differences among means was determined by one-way analysis of variance (ANOVA) followed by least significant difference (LSD) tests. ANOVA was performed to compare the treatment effects on soil metal speciation, plant metal concentration as well as metal uptake by plants. Correlation and regression analyses were conducted to establish the relationship between different parameters. When *R* was statistically significant at $P \leqslant 0.05$, an asterisk ($*$) is provided to denote the statistical significance. In order to assess the efficiency of plants for phytostabilisation, the Enrichment Coefficient (EC) of root (C_{roots}/C_{soil}, the ratio of root concentration to soil concentration) and shoot (C_{shoots}/C_{soil}, ratio of shoot concentration to the soil concentration) and Translocation Factor ($TF = C_{shoots}/C_{roots}$, ratio of shoot concentration to the root concentration) were calculated (Kumar et al., 1995).

3. Results and discussion

The soil was sandy clay loam, classified as Luvisolic Humoferric Podsol according to the Canadian System of Soil Classification. Basic characteristics were: pH 5.4, electrical conductivity = 0.61 dS/m, % carbon = 1.5 and available phosphorus = 10.4 mg/kg. The metal concentrations in the original (B0) and spiked soil (BA) were: Cu = 52 and 80 mg/kg, Pb = 93 and 146 mg/kg. Mn = 215 and 408 mg/kg and Zn = 70 and 148 mg/ kg, respectively.

3.1. Metal concentrations and uptake in plants

The plant concentration (mg/kg) and plant uptake (μg/pot) of Pb and Mn (both root and shoot) are given in Table 2. The concentration is the quantity of metal accumulating in plants per unit weight (i.e. mg/kg dry weight), whereas the uptake by plants in a pot indicates the total metal removal/pot. In Table 2, the means in the same column followed by a common lower case superscripted letter do not differ significantly from each other according to the least significant difference (LSD) test ($P \leqslant 0.05$). The lowest plant concentrations, as well as uptake (both root and shoot) (significant

Table 1
Experimental program.

Conditions/treatment	Nomenclature
Original soil with multi-metal concentrations (52 mg/kg Cu, 93 mg/kg Pb, 215 mg/kg Mn and 70 mg/kg Zn)	B0
Original soil spiked with multi-metals to give total concentrations (80 mg/kg Cu, 146 mg/kg Pb, 408 mg/kg Mn and 148 mg/kg Zn)	BA
BA plus lime (10 tons/ha), source – finely ground dolomite	BAL
BA plus phosphate (135 kg P_2O_5/ha), source – Ca $HPO_4 \cdot 2H_2O$	BAP
BA plus compost (10 tons/ha), source – city of Vancouver Yard trimming compost with pH 6.4; E.C – 3.2 dS m^{-1}; *C*/*N* ratio – 21.3, Cu – 1.2 mg/kg, Zn – 42 mg/kg, Fe – 61 mg/kg and Mn – 146 mg/kg	BAO
BA plus lime plus phosphate plus compost (combined application)	BALPO

Plants studied – *Lolium perenne*, *Festuca rubra* and *Poa pratensis*. Metals studied – Cu, Pb, Mn and Zn. Stage of sampling – 90 DAS. Design – completely randomized design. Eighteen treatments (six conditions for each of three plant species) with three replications.

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