Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Science of the Total Environment 367 (2006) 732 – 744
Science of the Total Environment
An International Journal for Scientific Research into the Environment and its Relationship with Humankind
www.elsevier.com/locate/scitotenv

Assessing nickel bioavailability in smelter-contaminated soils

Jeffrey L. Everhart [a,*], David McNear Jr. [a], Edward Peltier [a], Daniel van der Lelie [b], Rufus L. Chaney [c], Donald L. Sparks [a]

[a] *Department of Plant and Soil Sciences, University of Delaware, Newark, DE 19717, USA*
[b] *Brookhaven National Laboratory, Building 463, 50 Bell Avenue, Upton, NY 11973, USA*
[c] *Animal Manure and By-Products Laboratory, Animal and Natural Resources Institute, Bldg. 007, US Department of Agriculture Henry A. Wallace Agricultural Research Center, Beltsville, MD 20705, USA*

Received 10 October 2005; received in revised form 6 December 2005; accepted 14 December 2005
Available online 24 February 2006

Abstract

Metal contaminants in soil environments derived from industrial pollution have clearly established the need for research on bioavailability and potential health risks. Much research has been conducted on metal sorption in soils. However, there is still a need to better understand the availability of metal contaminants to plants and microbes. Such information will enhance both human health and decisions about remediation efforts. In this study, Welland Loam (*Typic epiaquoll*) and Quarry Muck (*Terric haplohemist*) Ni contaminated soils from Port Colborne (Canada) which had been treated and untreated with limestone, were employed in greenhouse and bioavailability studies. These soils varied in pH from 5.1 to 7.5, in organic matter content from 6% to 72%, and in total Ni from 63 to 22,000 mg/kg. Oat (*Avena sativa*), a nonhyperaccumulator, and *Alyssum murale*, a hyperaccumulating plant species, were grown on these soils in greenhouse studies for 45 and 120 days, respectively, to estimate Ni accumulation. A Ni specific bacterial biosensor was also used to determine Ni bioavailability, and the results were compared to those from the greenhouse studies and more conventional, indirect chemical extraction techniques (employing $MgCl_2$ and a $Sr(NO_3)_2$). Results from the greenhouse, chemical extraction, and biosensor studies suggested that as the pH of the soil was increased with liming, Ni bioavailability decreased. However, the phytoextraction capability of *A. murale* increased as soil pH increased, which was not the case for *A. sativa*. Furthermore, the Ni specific bacterial biosensor was successful in predicting Ni bioavailability in the soils and suggested that higher Ni bioavailabilities occur in the soils at pH values of 5.1 and 6. The combination of plant growth, chemical extraction, and bacterial biosensor approaches are recommended for assessing bioavailability of toxic metals.

Keywords: Nickel uptake; Bioavailability; *Alyssum murale*; *Avena sativa*; Hyperaccumulators; Phytoremediation

1. Introduction

Emissions from a Ni smelting facility in Port Colborne, Ontario, Canada have left the nearby farmland with elevated Ni levels. Extremely high soil Ni concentrations have been detrimental to the agriculture industry in this region and have left the neighboring farmland unsuitable for growing fruits and vegetables (McLaughlin, 2002). In situ remediation is considered as the only means of cleanup due to the scale of the contamination and the cost effectiveness of the strategy. In order to restore the productivity of the elevated metal contaminated soils, the bioavailability of Ni in these soils needs to be defined to understand the fraction accessible to the food chain and to the plants used for

* Corresponding author.
E-mail address: everhart_jeff@yahoo.com (J.L. Everhart).

0048-9697/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.scitotenv.2005.12.029

phytoremediation. This study will define bioavailability as the fraction of Ni available to biological systems. The first adverse affect of soil Ni in acidic soils is phytotoxicity and toxicity to microbes. Various chemical extraction methods have been developed to indirectly assess the association of metals with various soil components (Madden, 1988; Tessier et al., 1979). Also, field and greenhouse studies can provide total metal uptake information, which defines the metal fraction available to plants and microbes (Chaney et al., 2003). The application of bacterial biosensors, obtained by placing a luciferase reporter system under the transcriptional control of bacterial heavy metal resistance operons, has been developed to quantify the metal fraction in a contaminated soil that is bioavailable to the bacteria and causes toxicity, thus inducing the metal specific resistance operon. This induction can be directly measured via the transcription of the coupled luciferase reporter system, which results in a quantitative light signal. This novel technique is, depending on the resistance operon, element specific (Corbisier et al., 1999; Tibazarwa et al., 2001). A comparison between the data obtained with the Ni specific biosensor on the Ni fraction that caused induction of the Ni-resistance operon and the fraction of Ni taken up by corn, showed that there was a linear correlation between the two data sets (Tibazarwa et al., 2001). In this paper we used a combination of the above mentioned methods as a means of risk assessment to investigate nickel bioavailability.

In situ remediation to reduce Ni bioavailability in industrially contaminated soils is very important due to the Ni's phytotoxic effects. Soil amendments have been used to alter the pH of the soil, thus altering Ni speciation and consequently its bioavailability (Kukier and Chaney, 2001). However, one of the most effective strategies is the use of hyperaccumulating plants, for example *Alyssum murale*, to phytoextract the Ni from the soil (Chaney et al., 1997; Li et al., 2003) and remove the fraction of Ni that can be taken up by these plants (McGrath, 1998; Salt et al., 1998). Brooks et al. (1977) were the first to refer to a Ni hyperaccumulator plant as one that had the ability to accumulate more than 1000 mg/kg Ni of dry weight in their shoots. The most numerous metal accumulating plants are the Ni hyperaccumulators, which currently contain 318 taxa, many of them belonging to the *Alyssum* genus (Baker et al., 2000). The species *A. murale*, a known Ni hyperaccumulator, evolved on serpentine soils and has the ability to exist on these soils, even though they have elevated Ni levels that cause strong phytotoxicity effects in other plant species under acidic soil conditions. Recently, this species has been shown to phytoextract Ni from nonserpentine soils (Li et al., 2003). Furthermore, rhizobacteria isolated from the rhizosphere of *A. murale* contributed to an increase in Ni availability and an increase in Ni phytoextraction (Abou-Shanab et al., 2003). However, the phytoextraction performance of this species is not known for metal contaminated soils treated to circum neutral pH.

The high organic muck soils present in the Port Colborne region are ideal for vegetable production. However, this agricultural industry was adversely affected by the Ni emissions from the refinery. Therefore, much interest has been devoted to various crops, identifying toxicity symptoms and investigating losses of their marketable yields (Temple and Besessar, 1981; Frank et al., 1982; Bisessar, 1989). A very important crop that has been studied for its growth on the Port Colborne contaminated soils is *Avena sativa* (Oat) (Kukier and Chaney, 2000, 2001). Like all Gramineous plant species, Oat has an Fe chelating mechanism that unlike most other plants releases phytosiderophore and solubilizes Fe, making it available for plant uptake. Oat secretes a phytosiderophore known as avenic acid, which chelates soil Fe that is absorbed by the root of the plant in the rhizosphere (Römheld and Marschner, 1986). However, Chambers et al. (1998) concluded that phytosiderophore chelation of ferric iron was not a selective process and Ni may have the ability to compete with Fe, only to accumulate in elevated levels in the grasses. Classic symptoms of Ni toxicity in oats are interveinal chlorosis and the development of perpendicular white strips on the above ground biomass (Hunter and Vergnano, 1952). However, it has recently been noted that the classic Ni toxicity symptom of perpendicular white banding in the shoots of grasses is due to the diurnal secretion of phytosiderophores contributing to Fe deficiencies during plant development. When phytosiderophore secretion is minimal, usually during the dark hours when photosynthesis is halted, Fe cannot be taken up by plant. Therefore, perpendicular white banding appears when plant development is occurring under Fe stress deficiency (Marschner et al., 1987; Takagi et al., 1988). The ecological advantages observed in the Poaceae families of plants provide more questions on their existence at or tolerability of elevated Ni levels in contaminated soils. There is a need to explore the possibilities of *A. sativa* surviving in highly bioavailable Ni soils and determining the effects Ni has on this plant at different pH levels. Finally, this marketable plant, when grown on Ni contaminated soils, may have the ability to transfer Ni into the food chain thus identifying a health risk associated with the Port Colborne region.