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Soil Pollution by Heavy Metals and Remediation (Mazandaran-Iran)

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Abstract: Heavy metals and metalloids are an increasing environmental problem worldwide. Some industrial activities and agricultural practices increase their level in the substrate and the possible introduction of these elements in the food chain is an increasing human health concern. The protection and restoration of soils and water contaminated with heavy metals generate a great need to develop efficient adsorbents for these pollutants. Agricultural fertilizers which contain small amounts of cadmium and lead is widely applied and used in Iran. However, both these heavy metals remain below toxic levels. In contrast, contamination of lowland rice fields by sewage sludge from textile plants and some mining has increased the heavy metal content of the soil and reduced rice yields in these areas (Mazandaran province). Currently remediation of polluted soil is being carried out, using plants such as *Vetiveria zizanioides* and *Eichornia crassipes*, plus applications of zeolite in some areas of Meandering province of Iran. This mini review firstly indicate general objectives about remediation and then deal with to some activies about agricultural soil remediation that contaminated with some heavy metals (specially, Pb and Cd in Mazandaran province of Iran. We conclude that above mentioned species, may be an effective species for phytoextraction and should be tested for this purpose in field conditions.

Key words: Soil pollution, heavy metals, remediation, Iran

INTRODUCTION

Heavy metals and metalloids are an increasing environmental problem worldwide. Some industrial activities and agricultural practices increase their level in the substrate and the possible introduction of these elements in the food chain is an increasing human health concern (Cakmak *et al*., 2000). Engineering industrial techniques may efficiently be used to clean up contaminated soils but most of them require sophisticated technology and are therefore expensive and suitable only for small, polluted areas (Moffat, 1995). In modern economics, various types of activity, including agriculture, industry and transportation, produce a large amount of wastes and new types of pollutants. Soil, air and water have traditionally been used as sites for the disposal of all these wastes. For example, beef cattle in the United States are estimated to produce 92 million mt/year of manure, while dairy cattle produce 27 million mt/year (Tan, 1995). Some of this manure may wash into nearby streams and pollute rivers, lakes and soil (Alloway, 1990; Ebadi *et al*., 2005; Amini *et al*., 2005).

In all countries and Iran, the most common kinds of waste can be classified into four types: agricultural, industrial, municipal and nuclear (Amini *et al*., 2005). Agricultural wastes include a wide range of organic materials (often containing pesticides), animal wastes and timber by-products. Many of these, such as plant residues and livestock manure, are very beneficial if they are returned to the soil. However, improper handling and disposal may cause pollution (Celine *et al*., 2005; Biasioli *et al*., 2006). Industrial waste products may be in gas, liquid or solid form. The most important gases are carbon dioxide (CO_2), carbon monoxide (CO), nitrogen dioxide (NO_2) and sulfur dioxide (SO_2). They are produced by combustion in industry and by automobiles and they pose a hazard to the environment (Rozen, 2006). Another part is food pipal garbage that made up of materials discarded by homes and industry. It conrocessing plants produce both liquid and solid wastes. Another urban waste is munictains paper, plastic and organic materials. Some of these can be recycled by composting or they may be burnt or disposed of in landfills.

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Sewage sludge is the product of treatment plants. The materials processed in the treatment plants are domestic and industrial wastes. They are usually liquid mixtures, composed both of solids and of dissolved organic and inorganic materials. The water is separated from the solid part by a number of treatments before it is environmentally safe for discharge into streams or lakes (Liao and Xie, 2006; Magiera *et al*., 2006; Leung and Jiao, 2006; Marchand *et al*., 2006). The content of major nutrients and micronutrients in sewage sludge varies depending on the source. Data indicates that the nitrogen content of textile sludge is generally high. However, the heavy metal content is also high. Some trace elements are required in small amounts by plants and animals, whereas others are hazardous to human health.

Phytoextraction implies the use of plants to remove pollutants from the environment and has been proposed as an interesting alternative solution for the decontamination of large areas (Cunningham and Berti, 1993; Brooks, 1998). Most studies dealing with phytoextraction focus on hyperaccumulating plants able to concentrate high levels of heavy metals in their aerial parts without showing any symptom of injury. The strategies of resistance in those plants involve several mechanisms such as the vacuolar sequestration of heavy metals linked to overproduced organic acids (malate, citrate, or oxalate) or phytochelatins produced from glutathione (Salt *et al*., 1998). Heavy-metal-tolerant plants belonging to the genus Alyssum, Thlaspi, or Silene have been identified for a long time (Brooks, 1998) and their use for phytoextraction purposes has been recommended (Schwartz *et al*., 2003; Zhao *et al*., 2003). Most hyperaccumulators, however, are difficult to manage and have a shallow root system and their interest is therefore limited in the case of deep contamination (Keller *et al*., 2003).

The first step to assess the potential interest of a plant species for phytoextraction is to quantify, in a fully controlled environment, the mean level of toxic metal accumulation in relation to the growth rate. The present study deals with Pb and Cd, two elements sharing numerous similar chemical properties that are often present concomitantly in polluted areas. Accumulations of these elements were quantified in the two species, *Vetiveria zizanioides* and *Eichornia crassipes*, plus applications of zeolite in some areas of Meandering province of Iran.

Contamination from industrial wastes: A study was conducted of industrial pollution in lowland rice areas in the area of Dashte-Naz, Mazandaran and Goharbaran. These areas are being polluted by heavy metals from sewage sludge produced by the Chemical industry. This waste is disposed of directly into agricultural lands, all of which are used to irrigate lowland rice. About 720 ha of lowland of Mazandaran, Iran. The pollution of agricultural areas in Iran (Mazandaran province) is mainly caused by the overuse of fertilizers and pesticides. Another cause of pollution is sewage sludge or municipal garbage that is in irrigation water and flows into lowland rice fields, or is disposed of in landfills. These wastes rice fields were polluted in this way (Amini *et al*., 2005).

Soil surveys by Amini *et al*. (2005) revealed that there were very high concentrations of boron, cadmium and lead in three villages in the Dashte-Naz and Goharbaran areas. Falling soil productivity in these areas caused a reduction in rice yields and farmers' incomes. After 20 years of contamination, the average rice yield had decreased by about 80%. The initial rice yield of about 4-6 mt ha^{-1} had become 1 mt ha^{-1}. However, the heavy metal content in the soil had increased by about 18-98%, compared to unpolluted soil and study using polluted soil from this area showed that high concentrations of lead, cadmium, copper, chromium and boron were found in the plant tissue, roots and grain of rice. Most of the pollutants had accumulated in the root system (Ming-He *et al*., 2006; Querol *et al*., 2006; Huang *et al*., 2006).

Contamination from agricultural wastes: In study carried out by Amini *et al*. (2005) in an area of intensive lowland rice farming in Mazandaran found that the levels of lead and cadmium in the soil were fairly low. Lead was present in soil samples in a range of 10-43 ppm, while the levels of cadmium were 0.19-0.49 ppm. The content of lead and cadmium which were present may have originated in applications of phosphate fertilizer. The cadmium content of phosphate fertilizer in Indonesia is 35-255 g mt^{-1}.

Phosphate fertilizer is essential in intensive agriculture, especially in Indonesia with its high rainfall and rapid leaching. These conditions result in a low soil pH and high levels of iron and aluminum oxide. These in turn immobilize the phosphorus in the soil solution and hinder its uptake by plants (Ming-He *et al*., 2006; Querol *et al*., 2006).

Based on the levels of lead and cadmium in rice, Amini *et al*. (2005) found that intensive lowland rice areas in two districts of Mazandaran could be divided into three categories: Highly polluted soils, soils with medium pollution and unpolluted soils (Table 1). Only 7% of the total lowland areas studied was polluted by lead and about 4% by cadmium. These results indicate that after 30-40 years of phosphate application, the productivity of these soils could still be sustained.

Table 1: Total area of intensive paddy rice contaminated by lead and cadmium in two areas of Mazandaran province-Iran

Percentage	Total area (ha)	Level of pollution	Lead and Cadmium content in rice grain
			Lead (ppm)
60	63,300	Unpolluted	≤0.5
33	35,000	Slightly polluted	0.5.1.0
7	7,200	Polluted	≤1.0
	105,500		Total
			Cadmium
79	83,300	Unpolluted	<0.12
17	18,500	Slightly polluted	0.12. 0.24
4	3,700	Polluted	>0.24
	105,500		Total

Source: Amini *et al.* (2005)

Another study was conducted in tea plantations in an area of Mazandaran which is important for agroforestry and tourism (Mazandaran Environment Agency, 2002). The aim of the study was to see the effect of air pollution by automobiles on soil quality. The results of the soil survey showed that the lead content results of the soil in the plantations increased near main roads (Table 2). The level of soil pollution by lead, most of which was produced by petrol combustion depended on the distance from the main road. However, the cadmium content in soils was not influenced by the distance from the main road. This indicates that the cadmium content in the soil was not the result of air pollution, but may have resulted from the application of high levels of phosphate fertilizer in these areas.

Contamination from sement mining and smelting: Sement mining is carried out by individuals rather than companies in Mazandaran province. They use traditional methods for separating the Sement from the raw material. The main waste product from this process is mud and rubble which contain a high concentration of lead. These wastes are disposed of directly in the Neka River, which is also used as a source of irrigation water in the lowland rice areas around the mining areas.

A soil survey conducted by Mazandaran Environment Agency (2003) in this area found that the soil surrounding the traditional mining was polluted by lead. The pollution covered the land around six villages (Table 3). The concentration of lead in soil near the mining was higher than in more distant soils. A high concentration of lead was found in rice straw and rice grain. All of the values were higher than the maximum permitted level of lead in soils (0.5 ppm).

Remediation and rehabilitation of soils contaminated by heavy metals: The use of deep-rooting halophyte species is of particular interest in this context because these plants are naturally present in environments characterized by an excess of toxic ions, mainly sodium and chloride.

Table 2: Heavy metal content in two paddy rice, Mazandaran province, Iran

Distance from main road (m)	Lead plantation		Cadmium plantation	
	A	B	A	B
0	37	55	0.6	0.4
50	24	30	0.8	0.4
100	23	28	0.7	0.4
200	19	27	0.6	0.4

Source: Mazandaran Environment Agency (2002)

Table 3: Lead content of soil, rice straw and rice grain in area contaminated by sement mining

Villages	Distance from traditional mining location (km)	Soil lead (ppm)	Rice straw lead (ppm)	Rice grain lead (ppm)
A.B	<0.1	6.7	5.3	0.43
C	0.8-1.0	5.6	1.8	<0.0005
D	1.2-1.5	1.8	0.8	<0.0005
E	7.0-7.5	2.4	-	<0.25
F	11.5-12.0	1.3	-	<0.0005

Source: Mazandaran Environment Agency (2003)

Several studies demonstrated that some tolerance mechanisms operating at the whole-plant level are not always specific to sodium and those other toxic elements such as copper, zinc, or cadmium may accumulate in salt glands or trichomes in tamaris [*Tamarix aphylla* (L.) Karst.], marsh-daisy [*Armeria maritima* (Mill.) Willd.] and gray mangrove [*Avicennia marina* (Forsk.) Vierh.] (Hagemeyer and Waisel, 1988; Neumann *et al.*,1995). Among the halophyte flora, species belonging to the genus Atriplex may be of special interest because of their high biomass production associated with a deep root system able to cope with the poor structure and xeric characteristics of several polluted substrates. These species also naturally produce high amounts of oxalic acid, which may assume positive functions in tolerance mechanisms to heavy metal stress (Van Baelen *et al.*, 1980; Mazen and El Maghraby, 1997; Sayer and Gadd, 2001). Fourwing saltbush [*Atriplex canescens* (Pursh) Nutt.)] has been especially recommended for revegetation of mine sites and other harsh environments (Baumgartner *et al.*, 2000; Glenn *et al.*, 2001; Newman and Redente, 2001). Other species, such as Gardner's saltbush [*A. gardneri* (Moq.) D. Dietr.] (Salo *et al.*, 1996), Australian saltbush (*A. semibaccata* R. Br.) (De Villiers *et al.*, 1995), shadscale saltbush [*A. confertifolia* (Torr. and Frem.) S. Wats.] (Wood *et al.*,1995) and Suckley's endolepis [*A. suckleyi* (Torr.) Rydb.] (Voorhees *et al.*, 1991) have been successfully tested for revegetation purposes. Atriplex species are able to accumulate high amounts of Se (Vickerman *et al.*, 2002) and some of them have been shown to accumulate B (Watson *et al.*, 1994) or Mo (Voorhees *et al.*, 1991). To the best of our knowledge, no data are available concerning Zn and Cd accumulation in these species.

Soil contaminated by heavy metals may pose a threat to human health if the heavy metals enter the food chain. Remediation should be carried out to ensure that agricultural produce from such areas can safely be eaten (Ebadi *et al*., 2005).

Remediation can be achieved in several ways: physical, chemical and biological (Ebadi *et al*., 2005). A study has been carried out by Mazandaran Environment Agency (2002) on the use of vetiver grass (*Vetiveria zizanioides*) and zeolite to remediate contaminated soils in Mazandaran, Iran. The results showed that vetiver grass could grow well on soils contaminated with high concentrations of lead and cadmium. By concentrating the contaminants in its roots, the vetiver grass reduced the concentration of lead in soil by as much as 38-60% and cadmium by 35-42% (Table 4). The heavy metals accumulate in the root system (Table 5).

The application of 500 kg ha^{-1} zeolite increased the growth and yield of rice growing in contaminated soils and decreased the total concentration of lead and cadmium by up to 1.5 times. Zeolite reduced the level of available lead and cadmium by half. In addition, the application of zeolite reduced the lead content of rice straw by 56% and of rice grain by 69%. It reduced the cadmium content of the rice grain by up to 67%, compared to the control.

Another experiment by Mazandaran Environment Agency, 2004, was conducted in a greenhouse, using water hyacinth (*Eichornia crassipes*) to remediate soil polluted by lead and cadmium. The results showed that these plants grew well in contaminated soil and were able to accumulate lead and cadmium taken up from the soil (Table 6). The content of lead and cadmium in the plants (on a dry matter basis) reached as high as 400 ppm.

Table 4: Lead and cadmium content in soil before and after remediation by vetiver grass

Treatments	Site A before	Site A after	Site B before	Site B after
Lead (ppm)				
Vitiver	38.0	15.0	14.0	8.0
Vitiver+80 (ppm) lead	118.0	48.0	94.0	58.0
Cadmium (ppm)				
Vitiver	1.2	0.7	0.6	0.4
Vitiver+20 (ppm) Cadmium	21.1	12.7	20.6	13.4

Source: Mazandaran Environment Agency (2002)

Table 5: Levels of lead and cadmium in vetiver grass after remediation by vetiver

Treatments	Site A straw	Site A root head	Site A root	Site B straw	Site B root head	Site B root
Lead (ppm)						
Vitiver	4.6	13.6	9.1	3.2	8.3	6.4
Vitiver +80 (ppm) lead	6.2	18.2	12.1	4.2	11.0	8.8
Cadmium (ppm)						
Vitiver	0.07	0.25	0.19	0.00	0.20	0.11
Vitiver +20 (ppm) Cadmium	0.12	0.98	0.42	0.08	0.54	0.27

Source: Mazandaran Environment Agency (2002)

Table 6: Uptake and levels in water hyacinth of lead and cadmium

Application (ppm)	Level in plant (dry matter basis)	Lead uptake (ppm)	Cadmium uptake (ppm)
Lead			
0	156	2	-
50	155	13	-
100	155	24	-
200	160	45	-
400	150	128	-
Cadmium			
0	130	-	0.3
50	27	-	5.4
100	25	-	9.2
200	27	-	15.5
400	27	-	30.5

Source: Mazandaran Environment Agency (2004)

CONCLUSION

Can *Vetiveria zizanioides* and *Eichornia crassipes* be used for phytoextraction?: The present review shows that above species is tolerant to both Cd and Pb and that it may accumulate these elements in the aerial part without showing any significant decrease in terms of biomass production during a time exposure to high concentrations in nutrient solution.

According to Cunningham and Berti (1993), plants may be suitable for phytoextraction purposes if they contain more than 10000 mg toxic elements per kg of dry matter. The putative interest of a given species, however, depends on the best quantitative compromise between metal concentration and biomass production. Plants are considered as hyperaccumulators if they contain more than 10000 mg kg^{-1}Pb or 100 mg kg^{-1} Cd and if the shoot to root ratio for heavy metal concentration is greater than 1 (Brooks, 1998). The usual level of biomass production of above plants in Mazandaran Province is around 5 mg dry matter ha^{-1} $year^{-1}$, which corresponds to a mean yield of more than 30 mg fresh matter ha^{-1} $year^{-1}$ (Mazandaran Environment Agency, 2003). Proper management of the culture by application of fertilizers and chemicals and increase of the density of plants in the field should lead to an increase of biomass production by a factor of 3 (Mazandaran Environment Aagency, 2003). If we assume that growth of Above plants is not inhibited by the external dose of Pb and Cd that used in this study and considering that plants accumulate 830 mg kg^{-1} dry matter Cd and 440 mg kg^{-1} dry matter Pb (taking into account the proportions of leaves and stems at the time of harvest), one may expect to remove 4.15 kg ha^{-1} Cd and 2.2 kg ha^{-1} Pb per year for a basal biomass production of 5 mg dry matter ha^{-1} $year^{-1}$. The potential of Cd tolerance is of particular interest if we assume that the dose of Cd used in the present work exceeds by far the value found in soil solution, even for highly polluted substrate. It is also obvious that the above-reported value corresponds to a theoretical value quantified in nutritive solution and that removal of Cd from a soil would be expected to be substantially lower as uptake largely depends on the availability of Cd in polluted substrates. On another hand, it has to be mentioned that the dose of Pb used in the present work is very low compared with the doses used in other studies or present on contaminated soils (Mazandaran Environment Agency, 2003). Since we intended to compare the specific effects of Cd and Pb on plant behavior, we decided to use similar doses for both elements. Therefore, the data for Pb extraction potential may be underestimated considering the low level of Pb used in our work (Mazandaran Environment Agency, 2004).

Further experiments are necessary to check that there is no growth inhibition on a long-term basis and that the rates of metal uptake and translocation are maintained at subsequent developmental stages. Finally, parameters influencing the bioavailability of heavy metals in soil conditions also have to be tested and potential removal rates should be confirmed by experiments using soil as a substrate for plant growth. Final notes should be considered for more understanding:

- After 30-40 years of intensive use of fertilizer in lowland areas of Mazandaran, including rock phosphate, the concentration in the soil of heavy metals such as lead and cadmium still remains below toxic levels. However, these elements are sometimes present naturally in rock phosphate, so that continuous monitoring is needed (Querol *et al*., 2006; Huang *et al*., 2006; Fenn *et al*., 2006).
- Sewage sludge from the textile industry contains high concentrations of elements such as boron, lead, cadmium, copper and chromium. Disposal of these wastes into rivers decreased rice production and was a potential cause of environmental degradation (Huang *et al*., 2006; Fenn *et al*., 2006).
- Air pollution from the exhaust of cars driving through tea plantation areas increased the lead content of the soil. The concentration of the lead was highest in the soil nearest the main road (Querol *et al*., 2006).
- Sement mining and smelting in Neka was a significant cause of pollution for lowland rice around this area and increased the lead content of rice (Huang *et al*., 2006; Fenn *et al*., 2006).
- The remediation of soil contaminated by lead and cadmium by growing water hyacinth or vetiver grass, with an application of zeolite, significantly reduced the level of these two heavy metals in the soil (Fenn *et al*., 2006).

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