Arch. Biol. Sci., Belgrade, 66 (4), 1457-1464, 2014 DOI:10.2298/ABS1404457S

HYPERACCUMULATORS OF MERCURY IN THE INDUSTRIAL AREA OF A PVC FACTORY IN VLORA (ALBANIA)

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Abstract - Contamination by heavy metals is one of the major threats to soil and water as well as human health. Much attention is being paid to metal-accumulating plants that may be used for the phytoremediation of contaminated soils. Some plants can accumulate remarkable levels of metals, 100-1000-fold the levels normally accumulated in most species. This study evaluated the potential of mercury accumulation of 17 plant species growing on contaminated sites in the ex- industrial area of the PVC Factory, Vlora, Albania. Plant roots, shoots and soil samples were collected and analyzed for the selected metal concentration values. The biological accumulation coefficient (BAC) was calculated to evaluate the potential use of plant species for phytoremediation purposes. The concentration of Hg in soils inside the contaminated area varied from 45-301 mg/kg^{-1}. The concentration of Hg in plant shoots and roots varied from 0.1 to 12.9 mg/kg^{-1} and 0.1 to 4.2 mg/kg^{-1}, respectively. Species *Medicago sativa* L. and *Dittrichia viscosa* (L.) W. Greuter were found to be the most suitable plants for phytoremediation of the site contaminated with mercury (BAC values varied from 30-10 percent, respectively). Considering the BAC values, none of the plant species was found to be a hyperaccumulator; however, plants with high BCF (metal concentration ratio of plant root to soil) and low BTC (metal concentration ratio of plant shoots to roots) have the potential for phytostabilization and phytoextraction. The results of this study can be used for the management and decontamination of soils with mercury using plant species having phytoremediation potential/characteristics.

Keywords: hyperaccumulators; mercury; phytoremediation.

INTRODUCTION

Heavy metals are a major environmental concern. They are harmful to humans and animals, and tend to bioaccumulate in the food chain. The threat that heavy metals pose to humans is aggravated by their long-term persistence in the environment (Chaney et al., 1995). Industrial and municipal wastes generate a great deal of particulate emissions and waste slag enriched in heavy metals that contaminate the surrounding soil, water and air. Such effects are particularly serious and pose a severe ecological and human health risk when smelting works are located in the vicinity of urban environments (Gutiérrez-Ginés et al., 2010).

In Albania there are many sites heavily polluted by harmful substances released into the environment. One of these sites is the former Soda-PVC plant, a factory that produced polyvinylchloride (PVC), chlorine, caustic soda, hydrogen, hydrochloric acid and other chemicals. The plant is located four kilometers north of Vlora, an important city in southern Albania, center of an industrial and tourist area, where serious problems with mercury contamination have been reported (UNEP/MAP GEF/ME/6030-00-08. 2000). The contamination arises from the use of metallic Hg for the electrolytic production of chlorine, that in turn was used for the production of vinyl chloride monomer (VCM) and eventually PVC. The factory was closed in 1992, and was substantially destroyed during civil unrest in 1997. Extensive soil pollution has been caused in the wider area of Vlora by the disposal of mercury compounds and other heavy metals from the factory during its operation and later on. Therefore, high levels of mercury, well above the accepted limits, are anticipated on this site (UNEP/MAP GEF/ME/6030-00-08. 2000), UNEP/IAEA (UNEP 1985). There is a rural area around the factory currently inhabited by about 180 families. The site has been recognized by the United Nations Environment Program report as one of the five "hot spots of pollution" in Albania, with serious contamination problems that pose immediate risks to human health and the environment, and require urgent remedial action (UNEP/IAEA, UNEP 1985). Traditionally techniques of soil remediation are costly and may cause secondary pollution. Phytoremediation is a new evolving field of science and technology to clean up polluted soil, water or air (Gutiérrez-Ginés et al., 2010, Meagher et al., 2005). It can be defined as the use of plants to remove, destroy or sequester hazardous substances from environment. Phytoremediation can provide a cost-effective, long-lasting and aesthetic solution for the remediation of contaminated sites (Lazo et al., 2008).

Some plants can accumulate remarkable levels of metals – 100-1000-fold the levels normally accumulated in most species (Gutiérrez-Ginés et al., 2010, Meagher R. B., et al., 2005). Metal hyperaccumulating species have been identified and at least 45 plant families and individual species (or even populations) can accumulate different metals such as Zn, Cd, Cu, Co, Ni, Se and As, or particular combinations of these (Öbek, 2009). New metal-hyperaccumulating species or populations continue to be identified (Prasad, 1997).

Here we present preliminary results of a study of Hg accumulation and tolerance in different naturally growing plant species in one of the areas most polluted by mercury, located in the city of Vlora, Albania.

MATERIALS AND METHODS

Site description

The investigated site (40°28.572' N, 19°27.106' E) lies at an elevation of 17 m, close to the seaside. The climate is temperate humid (average annual temperature 10°C; average annual rainfall 1 058 mm (min) to 1 562 mm (max). The main wind direction is from the northeast. Soil and plant samples were collected within the factory site, and at different locations within a distance of 0 to 5 km in the main wind direction (Fig. 1). The site is situated 5 km from the city of Vlora (Albania). During the plant's operation, chlorine-alkali electrolysis was conducted using excessive quantities of mercury; about 70 tons of mercury was released from the production into the vicinity. The contamination has affected approximately 5-6 ha of the soil near the former factory. Despite the high contamination level, families and animals live on and around the industrial site in extremely hazardous conditions (Kabata-Pendias et al.,1989).

Soil and plant sampling

Sampling was conducted in June 2011 at different points in the area. Soil samples were collected in the contaminated area described by a square, as well as at four different points at increasing distances from the factory (from 0-5 km), in the northeast wind direction.

The sample taken furthest from the site, located near the Orikumi, was used as the control (Fig. 1). Soil was collected from the upper horizon (0-15 cm depth), air-dried and sieved through a 2-mm sieve.

Spontaneously growing plant species were collected mainly in the contaminated area, whereas a smaller number was collected at three other stations. After plant species identification (Demiri 1981), they

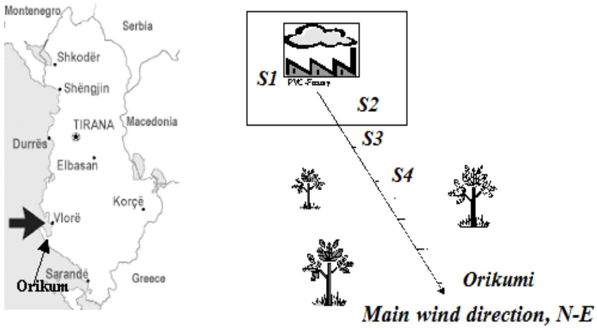

Fig. 1. Sampling area with stations of soil and plant sampling points.

were thoroughly washed with deionized water, dried until constant weight at 40°C, ground and analyzed for mercury content.

Plant species were collected from different parts of the contaminated zone, in order to assess the impact of mercury in different areas as well as its transport to the sea. Consequently, plants were collected inside the contaminated area, in a cultivated zone near the area as well as two species were collected in the sea (sea algae).

Inside the contaminated area, 17 plant species were chosen: *Dittrichia viscosa* (L.) W. Greuter, *Echium plantagineum* L., *Tamarix dalmatica* Baum., *Limonium anfractum* Salmon., *Crithmum maritimum* L., *Saccharum ravennae* (L)., *Phragmites communis* Trin., *Typha angustifolia* L., *Salix alba* L., *Imperata cylindrica* (L.) P.B., *Populus alba* L., *Euphorbia paralias* L.; three species were collected in a cultivated area *Zea mays* L., *Medicago sativa* L., *Allium cepa* L. and two species from the sea, *Posidonia oceanica* (L.) Delile and *Cymodocea nodosa* (Ucria) Asch.

Chemical analysis of soil samples

A modified procedure based on UNEP/IAEA Reference Method for Pollution Studies No. 26 (1985) was used to determine the content of mercury in the soil samples. About 0.3 g (thoroughly ground and sieved through a 63-μm nylon sieve) of soil was treated with a mixture of 9 ml HCl and 1 ml of HNO_3 and left overnight at room temperature. After that, samples were digested in a hot plate at 70-80°C for 3-4 h. After cooling, 1 ml of 5% $K_2Cr_2O_7$ was added and water up to 50 ml. An aliquot of 5-40 ml of clear solution was used for determination of mercury content by cold vapor atomic absorption spectrometry. Blank samples were prepared from distilled water and treated in the same way as samples. The average value as well as the standard deviation of mercury content was calculated analyzing two parallel samples. IAEA 405 soil certified reference material was used in order to control the accuracy of the results.

Analytical procedure of plant samples analyses (Based on the UNEP/IAEA Reference Method for contamination studies).

About 1 g of plant sample was left for seven days to be treated with a mixture of HCl:HNO_3 (3:1) at room temperature in half-pressure PTFE vessels. Samples were treated heated for 3 h at 70-80^{0}C. After cooling, 1 ml of 5% $K_2Cr_2O_7$ was added and water to 50 ml. Depending on the mercury content in the sample, an aliquot of clear solution was used for the determination of mercury content by cold vapor atomic absorption spectrometry using a Varian AA 10+ spectrometer.

RESULTS AND DISCUSSION

Mercury content in soil.

The mercury contents in soil samples are summarized in Table 1.

The highest concentration of mercury in soils was found inside the contaminated area of the PVC Factory, about 301.5 mg/kg^{-1}, whereas at the Orikumi station, located 5 km from the factory, the mercury content was 0.39 mg/kg^{-1}. The content of mercury at this station was below the permitted levels of mercury content in soils, according UNEP 2002, which determines that the levels of mercury that do not have ecological impact vary from 0.07 to 0.4 mg/kg. The content of mercury at the station 400 m from the factory was more than 20 times higher than the permitted value, whereas inside the polluted area its levels varied from 2-15 times higher than the limit determined for contaminated soils (20 mg/kg^{-1}) according to UNEP 2000.

Mercury content in plants

Results of mercury content in plant species (Table 2)

Table 1. Mercury content in soils (mg.kg^{-1})

Stations	C mg/kg	S_{dev}
Orikum	0.392	*0.12*
1000m	1.805	*0.18*
400m	9.140	*2.82*
PVC 1	44.970	*0.58*
PVC 2	301.540	*37.83*
CRM 405 IAEA	0.780	*0.01*

show that the highest concentration of mercury was found in the species *Medicago sativa* L, about 12.92 mg/kg, as well as in *Tamarix dalmatica* Baum, *Dittrichia viscosa* (L.) W. Greuter, *Crithmum maritimum* L. and *Zea mays* L. where the levels of mercury varied from 3.33-5.34 mg/kg. Levels of mercury present in these plant species show a very high pollution of the plants (Kabata-Pendias, 2001). The concentration of mercury in the sea plants was lower than the detection limit of the method CV-AAS, probably because the pollution has not been transported toward the sea. The level of mercury in some plant species was lower than the limits of detection, such as in *Saccharum ravennae* (L.), *Allium cepa* L, *Populus alba* L *and Salix alba* L, due to the fact that the accumulation of mercury from plants is very dependent on the kind of species, even though they are growing in a very polluted area (Kabata-Pendias 2001).

Evaluation of the mercury content in plants at different distances from the factory.

Four plant species were chosen in order to study the variations in the mercury content in plants collected at different distances from the polluted area. The selected stations were S1 – Orikum, 5 km from the factory (Hg in soil 0.392 mg/kg), S2 – 400 m from the factory (Hg in soil 9.13 mg/kg) and S3 – inside the polluted area (Hg in soil 45.0 mg/kg). Results are presented in Table 3.

Table 2. Mercury content in plants (mg/kg) DW.

Plant species	Hg mg.kg^{-1}	S_{dev}
Dittrichia viscosa (L.) W.Greuter	5.14	*1.07*
Echium plantagineum L.	0.19	*0.00*
Tamarix dalmatica Baum.	5.34	*0.77*
Zea mays L.	3.33	*0.05*
Limonium anfractum Salmon.	0.79	*0.02*
Euphorbia paralias L.	1.71	*0.23*
Crithmum maritimum L.	4.36	*1.61*
Medicago sativa L.	12.92	*1.54*
Cymodocea nodosa (L.) Delile	ND*	-
Saccharum ravennae (L.)	ND	-
Allium cepa L.	ND	-
Posidonia oceanica (Ucria) Asch	ND	-
Phragmites communis Trin.	0.21	*0.02*
Typha angustifolia L.	0.20	*0.04*
Salix alba L.	ND	-
Imperata cilindrica (L.) P.B	0.64	*0.05*
Populus alba L.	ND	-

*ND = Not Detected.

As can be seen in, the distance from the polluted area did affect the content of mercury in plants. The concentration of mercury in plants grown inside the polluted area was from 1.3-5.3 mg/kg^{-1} for the species *Dittrichia viscosa* (L.) W. Greuter, *Tamarix dalmatica* Baum and *Echium plantagineum* L., classifying these plants as heavily polluted, whereas the level of mercury in species *Limonium anfractum* Salmon was higher than the allowed critical level of mercury in plants.

The levels of mercury decrease with the distance from the contaminated area, ranging from 0.667 mg/kg^{-1} at 400 m distance to lower than 0.2 mg/kg^{-1} (maximum allowed level of mercury in plants) at the Orikumi station.

Bioaccumulation coefficient

Values of the bioaccumulation coefficient, BAC, were calculated as the percentage of the mercury content in plants (grown inside the contaminated area) versus its content in soils. Results are presented in Fig. 2. As can be seen, the species *Medicago sativa* L. is

Table 3. Content of mercury in plants grown in three different stations.

STATION	S1	S2	S3
Plant species	Hg mg.kg^{-1}	Hg mg.kg^{-1}	Hg mg.kg^{-1}
Dittrichia viscosa (L.) W.Greuter *(areal part)*	0.152	0.667	5.136
Echium plantagineum L. *(areal part)*	0.032	0.206	1.310
Tamarix dalmatica Baum. *(areal part)*	0.084	0.194	5.340
Limonium anfractum Salmon. *(areal part)*	ND	ND	0.790

Table 4. Mercury content in different parts of the plant.

Station	S 1	S3
Plant species	Hg mg/kg	Hg mg/kg
Dittrichia viscosa (L.) W.Greuter areal	0.152	4.202
Dittrichia viscosa (L.) W.Greuter roots	0.141	4.008
Echium plantagineum L. areal	0.032	0.169
Echium plantagineum L. roots	0.147	0.171

characterized by the highest BAC value (28%), followed by *Tamarix dalmatica* Baum. and *Dittrichia viscosa*(L.) W. Greuter., with BAC values more than 10%.

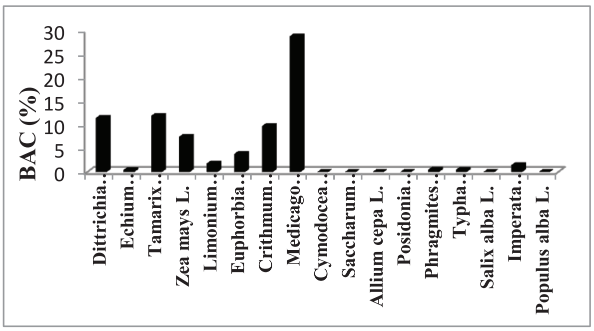

Fig. 2. Values of BAC (%)

Two species were chosen to evaluate the part of the plant where mercury was accumulated in higher levels, *Dittrichia viscosa* (L.) W. Greuter and *Echium plantagineum* L. The content of mercury was determined in the aerial part as well as in the roots of the plant species grown in two different stations: Orikumi (0.4 mg/kg Hg in soil) and inside the contaminated area (45.0 mg/kg Hg in soil). Results are shown in Table 4.

Results of mercury content in the different parts of plant species show that the accumulation process is dependent on the kind of species as well as on its content in soil. Consequently, mercury was found almost in the same levels in the roots and aerial part of *Dittrichia viscosa* (L.) W. Greuter, whereas it was more concentrated in the roots of *Echium plantagineum* L. Results obtained for plants grown inside the contaminated area show that they accumulate mercury in the roots and aerial part in the same content. The reason of such results could be the volatile properties of mercury, causing plants to accumulate the metal from both soil and air.

The effect of vegetative phase in mercury accumulation

The effect of mercury accumulation in plants at different vegetative phases of growth was also evaluated. The content of mercury was determined in *Dittrichia viscosa* (L.) W. Greuter in three vegetative phases: before flowering, during flowering and during fructification. Plants were collected inside the contaminated area. Results are presented in Table 5.

Results of mercury accumulation in three different vegetative phases of plants show that the concentration of mercury was higher before the flowering

Table 5. Mercury content in three vegetative phases

Plant species	Hg $mg.kg^{-1}$
Dittrichia viscosa (L.) W.Greuter (before flowering)	5.136
Dittrichia viscosa (L.) W.Greuter (during flowering)	4.202
Dittrichia viscosa (L.) W.Greuter (fructification)	ND

phase of *Dittrichia viscosa* (L.) W. Greuter, whereas its content decreased during the flowering phase and waslower than the limit of detection during the phase of fructification. The reason of these results is that during the fructification the number of leaves is smaller, taking into account that for this evaluation only the aerial part of the plant was analyzed.

DISCUSSION

The results obtained in this study reveal that the accumulation levels of mercury in plants are not uniform, either within or among the plant species. As was observed, the species *Dittrichia viscosa* (L.) W. Greuter accumulated comparatively greater amounts of mercury in the roots than in the aerial parts (stem and leaf) compared to *Echium plantagineum* L. when grown in the uncontaminated area. Conversely, both plant species accumulated higher levels of mercury in the aerial part when grown inside the contaminated area. The reason for these results may be the possible mercury uptake from the air taking into account that mercury could be found in atomic form at ambient temperature. Mercury mobility appears to be greater when it enters the plant through the stem or leaf (Peterson et al., 1984).

The metal entry into plants through the leaves is more significant for pollution elements because of aerosol deposits (Fergusson, 1984). A number of reports revealed that metal accumulation levels in plants are influenced by their distance from the source of the metal and also seasonal effect (Kabata-Pendias et al., 1989). The content of mercury in *Dittrichia viscosa* (L.) W. Greuter, *Echium plantagineum* L., *Tamarix dalmatica* Baum and *Limonium anfractum* Salmon decreased with the distance from the polluted area, even though not proportionally for all species. This may be partly due to plant varieties and their ability to absorb and accumulate heavy metals in their tissues (Fergusson, 1984). In addition, the vegetative phase influenced the level of mercury accumulation in plant species. Species *Dittrichia viscosa* (L.) W. Greuter accumulated higher levels of mercury before and during the flowering phase, whereas after fructification the mercury levels were lower than the detection limit of the method.

CONCLUSIONS

In this study, the mercury content in some selected plant species grown inside one of the sites most contaminated with mercury in Albania was evaluated. The measured levels of mercury in soils from the polluted area are apparent evidence of the heavy pollution caused by the uncontrolled discharge of metallic mercury in the area. The mercury content ranged from 301.5 to 45.0 mg/kg^{-1}, being 15 times higher than the normal allowed value (20 mg/kg^{-1}).

Even though most of the plants chosen in this study were grown inside the polluted area, they did not show any affinity for mercury accumulation. This supports the fact that many factors such as the fluctuating environment (temperature, soil pH, soil aeration, soil moisture), root system, availability of the element in the soil, etc., influence the uptake and accumulation of this element (Fergusson, 1991).

The increased levels of mercury in plants were not in good correlation with its content in soils, which indicates that the accumulation process is dependent not only on its content in soils but also on plant species cytology (Kabata-Pendias et al., 1989).

Inside the contaminated area, *Medicago sativa* showed the highest value of BAC, about 30%, followed by *Tamarix dalmatica* Baum and *Dittrichia viscosa* (L.) W. Greuter, resulting in approximately 10% of the BAC value.

The content of mercury varied in different parts of the plant species, such as the roots and aerial parts. Its accumulation in each part was also very dependent on the content of mercury in the soil. Inside the contaminated area, plants accumulated more mercury in their aerial parts.

In addition, the vegetative phase of plant growth affected mercury accumulation. *Dittrichia viscosa* (L.) W. Greuter accumulated more mercury before the flowering phase and smaller quantities in the phase after flowering and fructification.

Studies examining mercury accumulation could be very helpful in the future in the fields of phytoremediation and phytoextraction. Plant species with large biomasses and shorter reproductive periods are preferred for these processes

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