Original Research

Bioavailability of Lead, Cadmium, and Nickel in Tatra Mountain National Park Soil

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Abstract

Our research investigated the bioavailability of Pb, Cd, and Ni in the soil of Tatra Mountain National Park (Chochołowska Valley, Kościeliska Valley, Małej Łąki Valley, and Strążyska Valley). The content of Pb, Cd, and Ni was estimated using the ASA method with accuracy of 0.1 μg/g. Rudd's methodology was applied to estimate direct and indirect bioavailability of the metals in question. Ions of Pb in prevailing amounts occur in indirectly bioavailable forms of carbonates and organic compounds. Content of Pb and Ni as scarce particles is much higher in comparison to an average content of Cd in the soil. The amounts measured corresponding to 10 percentile and geometric mean can be used as a reference value in prospective research held in Tatra Mountain National Park or in other protected areas.

Keywords: Tatra Mountain National Park, soil, metals, bioavailability, speciation analysis

Introduction

Increasing awareness of the dangers arising from natural environmental pollution makes it necessary to maintain regular checkups of the content of toxic elements and compounds in air, soil, and food [1].

From among substances that have the most negative influence on the natural environment, ions of metals of toxic character have been in the center of attention recently. Their toxicity consists in the ability to cumulate in living organisms and their chronic toxicity [2]. A natural source of metals for people and animals together with particular matter absorbed while breathing is plant material [12]. The main source of contamination of plants with the metals in question on territory beyond the reach of industrial pollution, municipal waste, and that created by motorization is dust settled on leaves and on the soil itself, and the content of metals in it depends on the geochemical characteristics of the host rock and pedogenesis [3, 13, 14]. Compounds of most metals, especially the most toxic ones, are easily soluble in soil solution and therefore are easily absorbed by plants.

Distribution of different types of contamination in the natural environment takes place between: atmospheric falls and soil onto which also fall dusts from the air. The migration of the metals in the soil is determined by the soil's chemical, biological, and physical characteristics.

In the processes of metal distribution in the system: atmospheric fall – soil, the phenomenon of bioavailability in toxicological phase is of major importance. This phenomenon consists of the form change of the xenobiotic, e.g. lead carbonate, which is less soluble, takes the form of a chloride in consequence of the processes taking place in the surface layer, and therefore is easily soluble. Another manifestation of this phenomenon is the different characteristics of the way the chosen elements co-exist separately, e.g. in the dust suspended in the air or in the total fall in comparison to soil solution. This leads to the fact that in

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consequence of accumulation by subterranean parts of plants, a phenomenon of competition for the receptor, which might be a root for example, may occur [15-18].

Besides, in the territory of Tatra Mountain National Park long range emission has been observed, frequently with a source located hundreds of kilometers away. The occurrence of this phenomenon is proven by research on radium 226 distribution, namely on the glacier in Pod Chłopkiem Pass at Morskie Oko. The amount of this radioisotope, as a result of permanent emission is comparable to amounts occurring on the surroundings of Zabrze [3].

Those dust pollutants mainly come from the emission processes taking place while burning coal for heating.

Having taken into account contemporary publications, in order to characterize the phenomenon of migration and accumulation of specific ions of metals it is necessary to become familiar with their chemical forms in which they occur in soil. In this context, with regard to specific research goals there are a few speciation methods available that concern soil. These fixed forms of occurrence decide about ecotoxicological or physiological importance of a particular element in a trophic chain of plants, animals and humans [3-5, 19].

An illustration to that issue may be the outcome of research showing the content of those elements in a shinebone head among the inhabitants of Zakopane. The amounts were as follows: Pb (12.92 µg /g), Ni (0.79 µg/g), and Cd (0.77 µg/g) [6]. Attention should be drawn to the fact that there are similarities between inhabitants of Zakopane and those living close to industrial plants: 20.95 µg/g as a result of car fume emissions as well as low emissions within the grounds of Zakopane.

Speciation analysis is contemporarily considered an appropriate method to specify the metal content in soil [6]. The synthetic remarks justify research, and as may be concluded from publications, the first of its kind dealing with bioavailability of Pb, Cd, and Ni in the soil of Tatra Mountain National Park. The information obtained makes a solid basis to estimate the real ecotoxicological quality of soil in relation to specific properties of their accumulation by various plants.

The point of our research was to estimate the quantity of directly and indirectly bioavailable Pb, Cd, and Ni in the soil from the Park.

Research Methodology

Pb, Cd, and Ni content was marked in 60 samples of soil taken in 2008 from four sites: Chochołowska Valley, Strążyska Valley, Kościeliska Valley, and Małej Łąki Valley.

Specifying the chemical form of the metals present in soil was done using Rudd's method (1988), consisting of a sequenced extraction using appropriate solutions at ratio 1:40 at the mass of a 1g of soil with the following solutions:

- for exchangeable form: 1.0 M KNO_3 ratio 1:40
- for adsorbed form: 0.5 M KF (pH=6.5) ratio 1:40
- for organic solution: 0.1 M $Na_4P_2O_7$ ratio 1:40
- for carbonates: 0.1 M EDTA (pH=6.5) ratio 1:40
- for sulphides: 6.0 M HNO_3 ratio 1:40
- for residues: 5 ml HNO_3 (twice)

Soil sample was 10 cm×10 cm, taken in an open area, without the undergrowth from a surface layer at a depth of 5 cm. Air dried, crushed, and screened with a 1 mm sieve, soil was exposed to respective solutions for 24 hours, then centrifuged for 10 minutes (4,000 rpm), flushed with 25 cm^3 of redistilled water, and centrifuged for 5 min (4,000 rpm). The obtained extracts were acidified with 1% HNO_3. The reagents used were spectrally pure made by Merck's (Supra Pure).

For each series of measures taken there were three blank tests. The results coming out of 6 samples were corrected with regard to values of blank tests.

The content of heavy metals in the tested samples was marked using flame method ASA, with the use of a Philips Pye Unicam SP-9 spectrophotometer at accuracy of 0.01 µg/g. Recovery for the analytical procedures applied was in-between 97-102% and controlled using pattern solutions produced by WZORMAT containing Pb, Cd, and Ni within the range of concentration in soil.

Results

Content values found in our research comply with nonparametric distribution. Therefore, to discuss the issue of bioavailability of the metals in question, geometrical average was applied (Table 1). The results presented show variation with regard to the area of occurrence in respective chemical forms.

Considering the average values of metal content in the soil, the following may be presented respectively to the place of occurrence [µg/g].

Chochołowska Valley:

- exchangeable form: Pb (5.78) > Cd (0.22) > Ni (0.02)
- adsorbed form: Pb (1.98) > Ni (1.97) > Cd (0.31)
- organic solution: Pb (19.01) > Cd (1.47) > Ni (1.33)
- carbonates: Pb (34.05) > Ni (4.06) > Cd (1.07)
- sulphides: Pb (6.73) > Ni (4.12) > Cd (0.91)

Kościeliska Valley:

- exchangeable form: Pb (2.19) > Ni(1.01) > Cd (0.11)
- adsorbed form: Ni (1.89) > Pb (1.67) > Cd (0.35)
- organic solution: Pb (18.48) > Ni (2.32) > Cd (2.26)
- carbonates: Pb (55.52) > Ni (5.91) > Cd (1.66)
- sulphides: Ni (10.80) > Pb (7.87) > Cd (0.98)

Strążyska Valley:

- exchangeable form: Pb (4.23) > Ni (0.21) > Cd (0.00)
- adsorbed form: Pb (1.77) > Ni (0.82) > Cd (0.23)
- organic solution: Pb (17.76) > Cd(1.93) > Ni (0.85)
- carbonates: Pb (37.54) > Ni (3.07) > Cd (1.31)
- sulphides: Pb(5.16) > Ni(1.51) > Cd (0.98)

Małej Łąki Valley:

- exchangeable form: Pb (2.22) > Ni (0.74) > Cd (0.14)
- adsorbed form: Pb (1.80) > Ni (0.92) > Cd (0.45)
- organic solution: Pb (21.81) > Cd (2.38) > Ni (1.81)
- carbonates: Pb (49.11) > Ni (5.63) > Cd (1.53)
- sulphides: Ni (9.53) > Pb (7.96) > Cd (1.10)

Table 1. Average metal content values at different sites [µg/g].

Metal	Chochołowska Valley	Kościeliska Valley	Strążyska Valley	Małej Łąki Valley
Exchangeable form				
Pb	5.78	2.19	4.23	2.22
Cd	0.22	0.11	0.00	0.14
Ni	0.02	1.01	0.21	0.74
Adsorbed form				
Pb	1.98	1.67	1.77	1.80
Cd	0.31	0.35	0.23	0.45
Ni	1.97	1.01	0.82	0.92
Organic solution				
Pb	19.01	18.48	17.76	21.81
Cd	1.47	2.26	1.93	2.38
Ni	1.33	2.32	0.85	1.81
Carbonates				
Pb	34.05	55.52	37.54	49.11
Cd	1.07	1.66	1.31	1.53
Ni	4.06	5.91	3.07	5.61
Sulphides				
Pb	6.73	7.87	5.16	7.96
Cd	0.91	0.98	0.98	1.10
Ni	4.12	10.80	1.51	9.53

The average values of Pb, Cd, and Ni are presented in Table 1. They clearly indicate a parallel occurrence of Pb in different forms, while in Chochołowska Valley the top amount of directly bioavailable forms is 7.76 µg/g, where indirectly bioavailable forms reach the value of 53.06 µg/g. The amounts of Pb in exchangeable form are approximately 25 times higher in comparison to amounts of Cd, and 280 times higher in comparison to the amount of Ni. In an adsorbed form the amounts of Pb and Ni are comparable end equal to 2 µg/g, being six times higher when compared to Cd. In an area scope, the highest amounts of Pb were found in directly bioavailable form in Strążyska Valley (6 µg/g) and the amounts of indirectly bioavailable compounds of Pb are comparable to those from Chochołowska Valley. However, it must be stressed that indirectly bioavailable Pb in Małej Łąki Valley was 73 µg/g. Similar amounts in indirectly bioavailable forms were found in soil from Kościeliska Valley (73 µg/g). As may be concluded from Table 1. the main problem of Pb, Ni, and Cd migration is connected with potentially exploiting their sources from organic amalgames or their carbonate forms.

The highest amounts of Cd in an adsorbed form were found in the soil from Małej Łąki Valley, and they are about 0.15 µg/g higher in comparison to other examined locations in the park. Indirectly bioavailable amounts of Cd prove these remarks. Very characteristic for Ni is its significant occurrence in the form of carbonates in Kościeliska Valley (5.91 µg/g), in Małej Łąki Valley (5.61 µg/g), and minor amounts in Strążyska Valley (3.07 µg/g). While an average range of occurrence for Pb is 2.2-7.78 µg/g in the exchangeable form and 1.67-1.98 µg/g in the adsorbed form, the average level of occurrence of Cd in both forms equals from 0.3 µg/g to 0.45 µg/g. A bigger variation in Ni occurrence in those forms was observed in an area scope. It is even more visible in the example of Ni occurrence in the form of organic solution and carbonates.

The above statistical characteristics of element occurrence illustrates the values corresponding to 10 and 95 percentile and geometrical average for all Tatra Mountain National Park areas (Table 2) and variation factors.

Table 2. Statistical characteristics of metal occurrence in speciation forms in in Tatra Mountain National Park soil [µg/g].

Metal	10 percentile	Geometrical average	95 percentile	Variation factor [%]
Exchangeable form				
Pb	1.31	3.60	8.53	125
Cd	0.05	0.12	0.85	270
Ni	0.05	0.5	1.93	188
Adsorbed form				
Pb	0.61	1.80	4.55	69
Cd	0.05	0.33	0.81	105
Ni	0.05	1.40	3.17	83
Organic solution				
Pb	9.23	19.27	32.37	47
Cd	1.17	2.01	3.17	34
Ni	0.05	1.58	3.56	78
Carbonates				
Pb	22.71	44.06	68	48
Cd	0.91	1.39	1.99	37
Ni	1.78	4.67	8.51	57
Sulphides				
Pb	2.62	6.93	11.06	76
Cd	0.89	0.99	1.17	17
Ni	0.05	6.49	21.81	111
Residues				
Pb	2.01	4.06	8.50	46
Cd	1.05	1.16	1.30	19
Ni	1.90	6.66	23.87	140

The content values of the elements contained in soil in their speciation forms clearly indicate that content values of Pb, Cd, and Ni in directly available form can be reference values as occurring in an area anthropogenically unchanged. But indirectly bioavailable forms of Pb with their values at 10 percentile indicate the long-term influence of car tourism that has been increasing. In the past 15 years Pb transferred to a soil environment mainly as a result of using lead tetraethyl in petrol. Comparing the content values of Pb in an interchangeable form or the adsorbed one, as well as in the form of sulphides and so-called rest, it may be assumed that these forms are of geochemical origin, while Pb compounds in the form of organic solution and carbonates are the result of car and industrial as well as household fume emissions. Furthermore, it is proven by the fact that the variation factor is similar and equals for Pb 47% for organic amalgames and for carbonates 48%. The constant influence of pollutant emissions containing Pb, Cd, and Ni, which are characteristic for automobile emission, according to publications, take effect in less variability in occurrence of these forms in comparison to directly bioavailable forms. For example, variations in occurrence of Pb in its interchangeable form is three times higher in comparison to organic compounds and carbonates of that metal. Variation in occurrence of Cd and Ni is much higher as well in both forms, interchangeable and adsorbed and values, respectively (Cd 270% and 105%), in comparison to organic amalgames 33% and carbonates 36%. Likewise, the variation of Ni in directly bioavailable form equals, respectively, 188% and 82%, and is much higher in comparison to directly bioavailable forms.

As characteristic content values for the elements researched in soil from Tatra Mountain National Park, the following may be assumed: Pb in exchangeable form (3.6 μg/g), in adsorbed form (1.50 μg/g), in organic solution (19.3 μg/g), and in the form of carbonates (4.0 μg/g).

The amounts of Cd in respective forms reach: 0.12 μg/g, 0.33 μg/g, 2.0 μg/g, and 1.4 μg/g. An average value of Ni content in exchangeable form and the adsorbed one equals 0.5 μg/g and 1.40 μg/g. In organic solution and carbonates the values are 1.58 μg/g and 4.67 μg/g.

It must be stressed that for the purpose of forecasts of ecological changes for this area or for any other protected areas the content values corresponding to 95 percentile are of significant importance, and it must be noted that they are reasonable at a level of contemporarily observed local emissions and the intensity of traffic.

As the soil is an element of the environment characterized by remarkable ability of bio-chemical changes taking place, for example, in a plant root zone, it might be expected that chemical phenomena characteristic by their number will occur. Their illustrations are not only average levels of occurrence and their variation, but the character of co-occurrence of Pb, Cd, Ni in a particular speciation form with other metals in Tatra Mountain National Park (Figs. 1-6, Table 3).

It turned out that Pb content changes remarkably, in a directly proportional way in exchangeable form, with Zn, where the occurrence of Ni is inversely proportional with Cr.

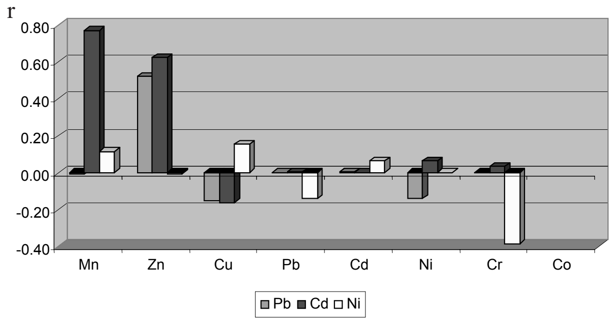

Fig. 1. Co-occurrence of Pb, Cd, and Ni in exchangeable form with other metals in the soil in Tatra Mountain National Park for $r \geq 0.3$ $p < 0.05$; $r \geq 0.5$ $p < 0.01$; $r \geq 0.7$ $p < 0.005$.

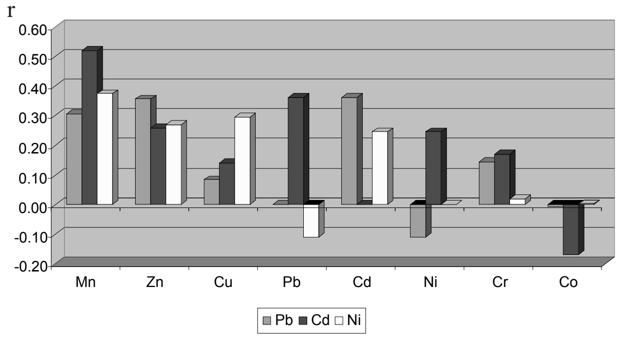

Fig. 2. Co-occurrence of Pb, Cd, and Ni in adsorbed form with other metals in the soil in Tatra Mountain National Park for $r \geq 0.3$ $p < 0.05$; $r \geq 0.5$ $p < 0.01$; $r \geq 0.7$ $p < 0.005$.

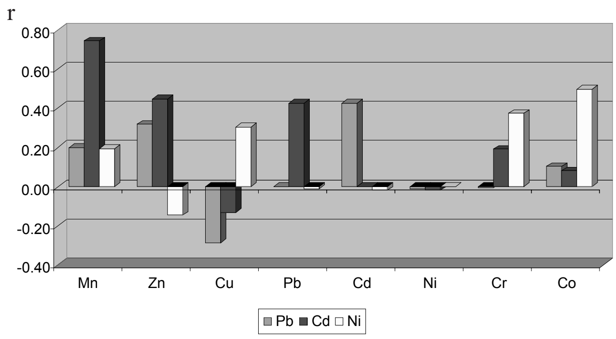

Fig. 3. Co-occurrence of Pb, Cd, and Ni in organic solution with other metals in the soil in Tatra Mountain National Park for $r \geq 0.3$ $p < 0.05$; $r \geq 0.5$ $p < 0.01$; $r \geq 0.7$ $p < 0.005$.

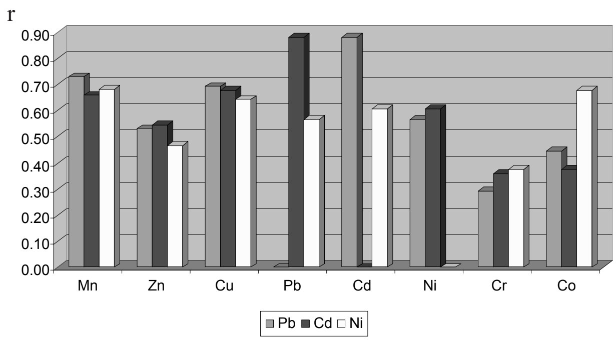

Fig. 4. Co-occurrence of Pb, Cd, and Ni in form of carbonates with other metals in the soil in Tatra Mountain National Park for $r \geq 0.3$ $p < 0.05$; $r \geq 0.5$ $p < 0.01$; $r \geq 0.7$ $p < 0.005$.

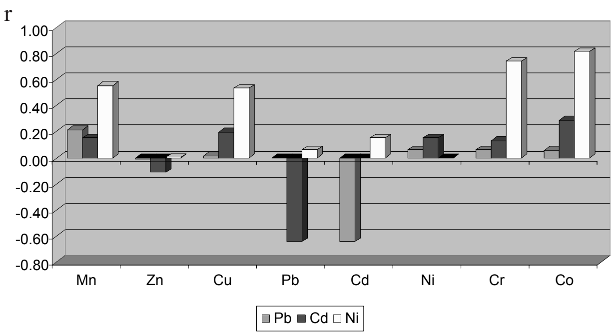

Fig. 5. Co-occurrence of Pb, Cd, and Ni in the form of sulphides with other metals in soil in Tatra Mountain National Park for $r \geq 0.3$ $p < 0.05$; $r \geq 0.5$ $p < 0.01$; $r \geq 0.7$ $p < 0.005$.

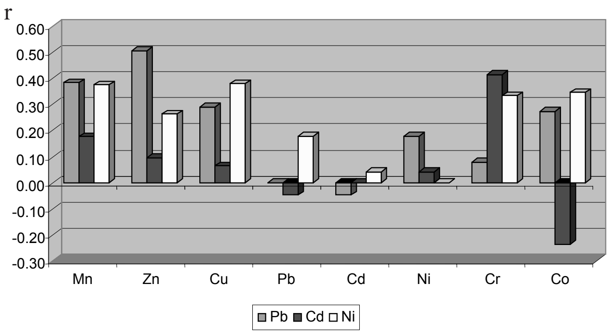

Fig. 6. Co-occurrence of Pb, Cd, and Ni in rest forms with other metals in soil in Tatra Mountain National Park for $r \geq 0.3$ $p < 0.05$; $r \geq 0.5$ $p < 0.01$; $r \geq 0.7$ $p < 0.005$.

Amounts of exchangeable Cd forms change directly proportionally with Mn and Zn. The number of significant interactions with other elements is greater in the case of adsorbed forms.

Adsorbed forms of Pb, Cd, and Ni decide largely about their chemical interactions. The great relationship of Ni with Co and Cr and forms of organic solution appeared to be interesting as well as in cases of Cd with Mn, Zn, and Pb. Pb showed high relation to changes in Zn and Cd content, which are characteristic for dusts produced while brake pads are grinding. The analysis of the character of co-occurrence of Pb, Cd, and Ni present in particular speciation forms clearly suggests an order that involves not only all the elements, but also the strenght of their interdependence with carbonates of the metals in question. Very strong interdependence of directly proportional character of Pb, Cd, and Ni concern Mn (0.65-0.73) and Cu (0.64-0.68). It must be stressed that the strongest relationships characterized by common correlation above 0.85 concerned Cd with Pb and Ni with Pb and Cd (0.55-0.60). Comparing the diagrams presented concerning Ni, two proportional changes with carbonates Mn (0.67), Cu (0.64), Co (0.65), and Cd (0.6) of that element can be indicated. The smallest relation from among the elements examined (Pb, Cd, and Ni) is to carbonate compounds of Cr.

A supplement of the issue discussed are the results showing interdependence of Cd, Pb, and Ni with sulphides and so-called rest. Two are the most significant. Directly proportional changes of Ni with Cr, Co, Cu, and Mn in the form of sulphides, and to a lesser extent in the form of so-called rest. In a form of rest, two proportional changes stand out in the occurrence of Pb with Cd and Zn, and to a lesser extent with Cu and Co. Attention must be paid to inversely proportional changes of Pb and Cd in the form of sulphides.

Discussion

Research concerning the occurrence and co-occurrence of Pb, Cd, and Ni in park soil refers to contemporarily observed research trends concerning protected areas, as well as to 12 theses included in the European Soil Chart. Every protected area is influenced by a specific dust emission that differs not only at their dispersibility but also at their percentage of occurrence of each of the elements mentioned, their function, and average dust diameter. The area of the park is differentiated when it comes down to the content of Zn and Cr (57 µg/g). Additionally, these soils differ in their surface layer density that varies from 0.7 g/cm^3 for the soil in Kuźnice and Myślenickie Turnie to 0.57 g/cm^3 for the soil from Świnicka Pass. Research conducted by Stobiński indicates the increasing tendency in Zn and Cr content following the depth at which the samples were taken. This very fact, and the growing automotive presence in Zakopane Valley, directed interest to Pb, Cd, and Ni as elements characteristic of automotive emissions. Zn and Cr content change, according to Stobiński's research, shall be connected with their content in parent rock.

What is more, Pb, Cd, and Ni content values were measured in relation to the species of trees present in a particular area, unlike in Kościeliska Valley, where Pb content in directly available forms was 2.5 times higher in comparison to Pb content in the same form in Chochołowska Valley. The differentiating factors were predominant maples and sycamores in Chochołowska Valley, while beeches dominated Kościeliska Valley. That observation also proved to be right in the case of Strążyska Valley, where soils from the beech habitat also contained higher amounts of interchangeable forms of Pb, similar to Chochołowska Valley. However, maple and sycamore habitats were affected, as it turned out, in higher amounts of Pb and Ni in adsorbed form. Indirectly bioavailable content values of Pb in soil varied from 22-499 µg/g, Cd: 1.53-2.38 µg/g, and Ni: 1.8-5.6 µg/g, and was getting homogenous as a result of the presence of three species of sycamore trees, beech, and spruce. That specific average may be observed on the example of content values of Pb, Cd, and Ni in all forms of occurrence (Table 1) in the soil from Małej Łąki Valley.

Physiographic characteristics of the four valleys from Tatra Mountain National Park clearly indicated the possibility of the penetration of the valleys by pollution in indirectly bioavailable forms. The valleys in question are of closed character and contemporary winds make them exposed to prevailing pollution from car emissions [7].

The problem of heavy metals present in plants may also be connected with food poisoning. Contaminants and adulterants of medicinal plants can be pharmacologically active

Table 3. Co-occurrence of Pb, Cd, and Ni with other metals in different chemical forms.

Metal	Mn	Zn	Cu	Pb	Cd	Ni	Cr	Co
Exchangeable form								
Pb	-0.01	0.52	-0.15	1.00	0.01	-0.14	0.00	
Cd	0.77	0.63	-0.16	0.01	1.00	0.07	0.03	
Ni	0.12	-0.01	0.15	-0.14	0.07	1.00	**-0.38**	
Adsorbed form								
Pb	0.31	0.36	0.08	1.00	**0.36**	-0.11	0.14	-0.01
Cd	0.52	0.26	0.14	0.36	1.00	0.25	0.17	-0.17
Ni	0.37	0.27	0.30	-0.11	0.25	1.00	0.02	0.00
Organic solution								
Pb	0.20	0.32	-0.29	1.00	**0.43**	-0.01	-0.01	0.10
Cd	0.75	0.45	-0.13	0.43	1.00	-0.02	0.19	0.08
Ni	0.20	-0.14	0.31	-0.01	-0.02	1.00	**0.37**	**0.50**
Carbonates								
Pb	0.73	0.53	0.69	1.00	**0.88**	**0.57**	**0.29**	**0.45**
Cd	0.66	0.55	0.68	0.88	1.00	**0.61**	**0.36**	**0.37**
Ni	0.68	0.47	0.64	0.57	0.61	1.00	**0.38**	**0.68**
Sulphides								
Pb	0.21	-0.01	0.02	1.00	**-0.64**	0.06	0.06	0.06
Cd	0.15	-0.11	0.20	-0.64	1.00	0.15	0.13	**0.29**
Ni	0.56	0.00	0.54	0.06	0.15	1.00	**0.74**	**0.82**
Residues								
Pb	0.38	0.51	0.29	1.00	-0.05	0.18	0.08	0.28
Cd	0.18	0.10	0.06	-0.05	1.00	0.04	**0.42**	-0.24
Ni	0.38	0.26	0.38	0.18	0.04	1.00	**0.33**	**0.35**

and responsible for unexpected toxicity. Plants used in traditional medicine may be harvested from contaminated soils or cleaned improperly such that they may contain illness-producing microorganisms. Ayurvedic medications, for example, have been known to cause lead poisoning in children because of their contamination with this heavy metal and others, such as arsenic and mercury, as has been signaled by Bashar Saad et al. Contamination of crop and medicinal plant samples by organic chemicals has become a pressing problem in many Arab countries. This problem, however, does not concern Tatra Mountains National Park and is quoted here merely in order to indicate potential risk involved while discussing the link between traditional medicine and heavy metals contamination. Most reports of toxic effects due to the use of herbal medicines and dietary supplements are associated with hepatotoxicity (HT), although reports of other toxic effects, including kidney, nervous system, blood, cardiovascular and dermatologic effects, mutagenicity, and carcinogenicity, have also been published in medical literature. Hepatic impairment resulting from the use of conventional drugs is widely acknowledged, but there is less awareness of the potential HT of herbal preparations and other botanicals, many of which are believed to be harmless and are commonly used for self-medication without supervision [8].

Wu et al. in their paper present how *Pseudomonas putida*, a robust and versatile antifungal rhizosphere bacterium, is engineered to produce MBP-EC20, a metal-binding peptide that has high affinity for cadmium. *P. putida* is also modestly cadmium resistant, due to the presence of an efflux pump in the metalloregulatory *cad* operon. Production of MBP-EC20 in *P. putida* not only enables enhanced cadmium binding but also protects the engineered strain and the colonized sunflower plants against the toxic effects of cadmium. These results demonstrate that a combination of enhanced microbial biosorption and plant-bacterium symbiosis is a promising strategy for heavy-metal cleanup [9].

If other plants were to illustrate the presence of heavy metals in particular parts, a tea plant would be a good example to show that prevailing metals are accumulated in subterranean parts. Tea plants grown on un-contaminated soil showed similar As and Cd distribution. Concentrations of As and Cd in feeding roots were 2~50 times higher than those in stems or main roots, 5~100 times higher than those in old leaves, and 25~600 times higher than those in young shoots, suggesting that feeding roots were the main accumulation organ. The concentration of As and Cd in tea plants was in the order: feeding roots > stems ≈ main roots > old leaves > young shoots [10].

Another plant that had been examined in order to find a relationship between metals present in it was rice Genotypic and environmental variation in Cd, Cr, As, Ni, and Pb concentrations of grains, and the relationships between these heavy metals and Fe and Zn were investigated in 2006 by Cheng et al. using 9 rice genotypes grown in 6 locations for two successive years. Significant genotypic variation was detected in the five heavy metal concentrations in grains, indicating the possibility of reducing the concentration of these heavy metals in grains through breeding approach. The environmental effect varied with metal, with Pb and Ni having greater variation than the other three metals. There was significant genotype-environment (location) interaction of the concentrations of all five heavy metals in grains, suggesting the importance of cultivar choice in producing rice with low heavy metal concentrations in grains for a given location. Correlation analysis showed that Cd and As, Cr and Ni, and As and Pb concentrations in rice grains were closely associated, and that Ni concentration in grains is negatively correlated with Zn concentration [11].

Conclusions

1. For the need of estimating the tendency in changes of metals of anthropogenic origin content in soil in Tatra Mountain National Park a statistical characteristics of occurrence and co-occurrence was established for Pb, Cd, and Ni with other metals. That characteristics may be applied to estimate the pollution level of protected areas.
2. In protected areas, on the example of Tatra Mountain National Park, indirectly bioavailable forms of metals will be predominant over the forms directly bioavailable as a result of a complex influence of local car emission, heating emissions from individual households and secondary forest dusting Pb.
3. Co-occurrence of Pb and Cd was differentiated in terms of form of occurrence, the kind of metal and the sample site location as well as a tree habitat and species content of trees.

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