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Factors influencing uptake of contaminated particulate matter in leafy vegetables

Research Article

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Abstract: The contents of cadmium, iron, lead and zinc in the biomass of two species of leafy vegetables after urban particulate matter (PM) application was investigated in lettuce (*Lactuca sativa var. capitata*) and chard (*Beta vulgaris var. cicla)*. The experimental design consisted of four variables: i) two different soil types, ii) two vegetables, iii) two size fractions of contaminated particulate matter (PM) (0.063-0.119 mm, and <0.063 mm), and iv) foliar and soil application of the PM. The aliquots of the PM samples were applied to the soil before the experiment and as a foliar suspension during plant growth. The element uptake by plant biomass was significantly higher *via* foliar application, simulating the atmospheric deposition, than *via* the roots from the soil application treatment. The content in plants increased rapidly compared to the control treatment for the elements iron, lead and zinc. Gently washing the leaves only slightly reduced the amounts of Fe and Zn. However, the majority of Pb was removed by washing with the concentration dropping from 3000% to 500%. The effect of PM application on Cd contents in plant leaves was negligible, in most cases. Lettuce exhibited higher element uptake compared to chard. No adverse effects of PM application on growth parameters of the vegetables were observed. No significant differences were reported for particle size fractions of PM. Fluvisol soils had a higher element uptake *via* roots than Chernozem soils. Moreover, the addition of PM into the Fluvisol altered the sorption properties of the soil resulting in a lower Cd uptake by plants growing in PM amended Fluvisols.

Keywords: *Risk elements • Leafy vegetable • Urban particulate matter*

1. Introduction

Particulate matter (PM) is associated with relatively high contents of risk elements bound onto particles differing in site, traffic level, seasonal variability, meteorological parameters and size [1]. These risk elements are released into the atmosphere due to the combustion of fossil fuels, wood, and wastes, as well as due to intensive industrial activities. Fossil fuel combustion is a main source of Be, Co, Hg, Mo, Ni, Sb, Se, Sn, and V; elements such as As, Cr, Cu, Mn, and Zn are also present in relatively high levels. Conversely, industrial processes produce the highest levels of As, Cd, Cu, Ni, and Zn emissions. Elements such as Pb, Fe, Cu, Mo, Zn, Ni, Cd, Cr, Ba, Br, Sb, Fe, Na, Ca, Al, Mg, and Mn are usually associated with intensive automobile traffic [2-5].

At industrial and urban sites, mainly influenced by steel and aluminium production and petroleum refinement, most elements were significantly more concentrated (by factors varying between 3 to 10 for elements like Mn and Fe) when compared to rural aerosols. Concerning particle size, many elements are attached with fine particles rather than to coarse ones [6,7]. Sutherland *et al*. [8] applied nine partial decomposition procedures and a total digestion treatment road-deposited sediments. The nine digestions varied from weak single reagents (0.11 $mol.l^{-1}$ acetic acid) to strong multi-step procedures. Eight metals were examined: Al, Co, Cu, Fe, Mn, Ni, Pb, and Zn. Cold (room temperature) 0.5 mol l^{-1} HCl was judged superior based on the defined criteria. This simple, rapid treatment had limited impact on the

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residual matrix (mean and 95% confidence interval for Al recovery was 6.1%); recoveries of all elements examined were independent of $CaCO_3$ content; the treatment produced high mean extraction efficiencies for Cu (58.9%), Pb (84.5%), and Zn (73.7%), and produced high anthropogenic signals.

Both wet and dry deposition can result in PM transport from the atmosphere to soil or plants where high contents of potential contaminants in PM can be a source of potential ecotoxicological problems. The intensity of soil and plant contamination is dependent on the distance of the contamination source. In the case of intensive traffic, increased Cd and Zn levels in soil were observed up to 160 m from the highway, whereas elevated Pb contents were reported as far as 320 m from the highway [9]. In the soil, however, a different pattern of the individual elements was observed for different soil pH, organic matter content, content of Fe, Mn, Al hydro(oxides), soil microbial activity *etc*. [10]. The soil type and composition plays an important role for heavy metal retention. As reviewed by Bradl [11], the soil particles with large surface reactivities and large surface areas such as clay minerals, iron and manganese oxyhydroxides, humic acids, *etc*. can enhance adsorption properties. Clays are known for their ability to effectively remove heavy metals by specific adsorption and cation exchange as well as metal oxyhydroxides. Soil organic matter shows a large number and variety of functional groups and high CEC values, which results in enhanced heavy metal retention ability mostly by surface complexation, ion exchange, and surface precipitation.

PM can affect green plants either *via* deposition on the aboveground biomass, where the contaminants can penetrate the leaf surface, or indirectly *via* soil-root interaction. The ability of the individual plants to absorb risk elements is determined by plant species and/or genotype. The main source of elements for plants is the growing medium – soil, soil solution, fertilizers *etc*. The elements are taken up by the roots and then transported to the leaves. A potential risk of soil elements presented by plant species, individual elements, and its level in soil, and soil properties [12,13].

However, foliar plant uptake must be also taken into account. Rodriguez *et al*. [14] observed a positive association of Zn, Fe, Cu, Ni, Br, Pb, Co, and Mn contents in *Tillandsia capillaris* and *Lolium multiflorum* biomass with vehicular traffic. Kabata-Pendias and Pendias [10] accentuated two phases of foliar element uptake: i) non-methabolic penetration of the cuticule and ii) methabolic, representing element accumulation against the concentration gradient. The foliar uptake of the risk elements is also affected by the morphology of leaf surface. Various plant species such as bryophytes, lichens, mushrooms, higher plants (*Taraxacum sp.*) *etc*. are considered species with the ability to absorb the elements from wet and/or dry deposition. However, the absorbed elements can be leached with rainwater, especially in the case of acid rain. In this context, the more leachable elements seemed to be those bound on the rough particles kept close to leaf surface. The elements attached to the small particles are able to penetrate the leaves more deeply, and therefore are protected against leaching [10,15].

In our research, a model pot experiment was carried out to demonstrate and evaluate two possible ways of environmental impact of element content in airborne particulate matter on plants: i) possible contamination of the human food chain *via* soil pollution followed by plant uptake of these elements; in this case the influence of the addition of two PM samples into the soil on cadmium, iron, lead, and zinc uptake by lettuce (*Lactuca sativa* L. *var. capitata*) and chard (*Beta vulgaris* L. *var. cicla*) was investigated and ii) the effect of foliar application of the PM samples on two vegetable species was investigated, as well. Among the leafy vegetables available, the species with high leaf surface but differing in leaf architecture and cuticle composition were preferred. The main objective of the investigation was to compare potential risk of PM uptake-associated elements as affected by PM particle size, soil properties and plant species. The hypotheses that uptake of contaminants depends i) on sorption efficiency of the soil types under study, ii) on size of the PM, iii) on plant specific uptake mechanisms, and iv) on differences in root *vs*. foliar uptake were tested.

2. Experimental Procedures

2.1 Pot experiment

The PM sample (PKC) was prepared from urban dust collected from filters of the air-conditioner system in the Prague Congress Center buiding close to the highway. It was dried at laboratory temperature and sieved twice. Finally, the physical fractions labelled A (particle size 0.063–0.119 mm), and B (particle size <0.063 mm) were used for the pot experiments. The following two soil samples differing in their physicochemical characteristics were selected for the experiment: i) uncontaminated Chernozem with a cation exchange capacity (CEC) of 255 mmol kg^{-1}, a pH level of 7.2, and an total organic carbon content (TOC) of 2.3%, and ii) slightly contaminated Fluvisol with a CEC of 201 mmol kg^{-1}, a pH level of 6.8, and a TOC of 2.6%. The total element content in both PM and soil samples are summarized in Table 1. The *Aqua Regia*

Total	Cd	Fe	Pb	Zn
Fluvisol	2.64±0.14	25906±714	106±10	268±6
Chernozem	0.686±0.072	25595±452	47±2	119±1
PM A	2.33±0.12	32598±1	140±14	1392±13
PM B	1.78±0.14	35703±3	123±4	1363±51
2 mol.l^{-1} HNO_3 extractable	Cd	Fe	Pb	Zn
Fluvisol	1.63±0.03	4592±47	58.9±1.1	161±3
Chernozem	0.30±0.01	1969±48	18.3±0.3	37.5±0.7
PM A	1.71±0.1	12377±152	73.3±1.3	890±14
PM B	1.45±0.1	12946±121	66.4±1.0	731±13

Table 1. Total and potentially mobilizable (extractable with 2 mol l^{-1} HNO_3) element content in soil and PM samples (mg kg^{-1}).

soluble element concentrations in loamy soils cannot exceed a maximum of 1.0 mg kg^{-1} Cd, 140 mg kg^{-1} Pb and 200 mg kg^{-1} Zn [16]. In sandy soils, the maximum allowable limits are as follows: 0.4 mg kg^{-1} Cd, 100 mg kg^{-1} Pb and 130 mg kg^{-1} Zn. Fe contents in soils are not limited. Therefore, Fluvisol element contents exceed the maximum permissible limits for Czech soils.

Lettuce (*Lactuca sativa* L. *var. capitata*) and chard (*Beta vulgaris* L. *var. cicla*) were cultivated in pots filled with 5 kg of air-dried soil wherein three replications of each treatment were used. Two approaches of PM application were carried out as follows: either 30 g of the individual PM samples was applied to each pot prior to sowing, and later thoroughly mixed with the experimental soil; or a suspension of 7.5 g of the PM and 200 ml of deionized water was prepared for foliar PM amendment and applied successively over a one week period on developed plant leaves. The application was repeated over the next four weeks for the total addition of 30 g PM. The plants were treated with deionized water, and soil moisture was kept at 60% of its maximum water holding capacity. Plants were harvested at the top of vegetation and the aboveground biomass of the plants (amended *via* foliar PM application) was then cut in two, with one half left unwashed and the other carefully washed with deionized water. Both the aboveground biomass and roots were dried at 60°C, grounded, and analyzed for Cd, Fe, Pb, and Zn content. Immediately upon harvesting of the plants, soil samples were taken from the bulk, air-dried at ambient temperature, ground in a mortar, passed through a 2-mm plastic sieve, and analyzed for mobile portions of the elements.

2.2 Analytical methods

Total concentrations of the elements in PM followed microwave assisted oven digestion of 20 mg dust samples in a mixture of concentrated acids HNO_3, HF and H_2O_2 (5:1:1). SRM 1648 Urban Particulate Matter (NIST, USA) was used as the control. In this material, the certified value of elements represented 75±7 mg kg^{-1} Cd, 6550±17 mg kg^{-1} Pb, and 4760±140 mg kg^{-1} Zn. In our experiment 66±3 mg kg^{-1} of Cd, 6470±4 mg kg^{-1} of Pb, and 4612±6 mg kg^{-1} of Zn was determined.

The Cd, Fe, Pb, and Zn concentrations in the digests were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Varian VistaPro, Varian, Australia), previously described [17]. Comparative data were obtained by instrumental neutron activation analysis (INAA) and particle induced X-ray emission (PIXE) techniques in accordance with the procedure described earlier [18].

The total concentrations of Cd in the soils was determined in the digests obtained by the following decomposition procedure: Aliquots (0.5 g) of air-dried soil samples were decomposed in a digestion vessel with a mixture comprising 8 ml of concentrated nitric acid, 5 ml of hydrochloric acid, and 2 ml of concentrated hydrofluoric acid. The mixture was heated in an Ethos 1 (MLS GmbH, Germany) microwave assisted wet digestion system for 33 min at 210°C. After cooling, the digest was quantitatively transferred into a 50 ml Teflon® vessel and evaporated to dryness at 160°C. The digest was then dissolved in a 3 ml nitric and hydrochloric acid mixture (1:3), transferred into a 25 ml glass tube, filled with deionised water, and kept at laboratory temperature until downstream measurements. A certified reference material RM 7001 Light Sandy Soil (Analytika, Czech Republic) was applied for the quality assurance of analytical data. In this material, the certified value of elements represented 0.32±0.05 mg kg^{-1} Cd, 43.8±3.7 mg kg^{-1} Pb, and 120±7 mg kg^{-1} Zn. In our experiment 0.30 mg kg^{-1} of Cd, 45.2 mg kg^{-1} of Pb, and 119 mg kg^{-1} of Zn was determined.

The Cd concentrations in the digests were determined by ICP-OES (Varian, VistaPro, Australia). The following non-destructive analytical techniques were applied for the determination of total Fe, Pb, and Zn contents in soils: INAA and PIXE for Fe and Zn, and PIXE for Pb. The soil pH was determined using deionised water or 0.2 M KCl (w/v=1+2.5). Cation-exchange capacity (CEC) was calculated as the sum of Ca, Mg, K, Na, Fe, Mn, and Al extractable in 0.1 M $BaCl_2$ (w/v=1+20 for 2 hours) [19]. Total organic carbon (TOC) was determined spectrophotometrically after the oxidation of organic matter by $K_2Cr_2O_7$ [20].

Potentially mobilizable portions of elements in soils and PM extraction with 2 mol L^{-1} solution of HNO_3 in ratio 1:10 (w/v) at 20°C for 6 hours [21] was applied (Table 1). The mobile portions of elements in soils was determined by extraction with a 0.11 mol l^{-1} solution of CH_3COOH at a ratio of 1:20 (w/v) for 16 hours [22] (Table 2). Each extraction was provided in three replicates. For the centrifugation of the extracts, a Hettich Universal 30 RF (Germany) device was used. Following extraction, samples were centrifuged at 3000 rpm for 10 minutes and the supernatants stored at 6°C prior to measurement. Cd, Fe, Pb, and Zn concentrations were determined by ICP-OES (Varian, VistaPro, Australia). Element contents in aboveground biomass and roots of vegetables were determined for 500 mg of plant material. Concentrated nitric acid (8.0 ml) (Analytika Ltd., Czech Republic) and 30% H_2O_2 (2.0 ml) (Analytika Ltd., Czech Republic) were added. The mixture was heated in an Ethos 1 (MLS GmbH, Germany) microwave assisted wet digestion system for 30 min at 220°C. After cooling, the digest was quantitatively transferred into a 20 ml glass tube filled with deionized water. Cd, Fe, Pb, and Zn concentrations in the digests were determined by ICP-OES (Varian, VistaPro, Australia).

2.3 Statistics

The Dixon's test was applied for identification of outliers followed by a one-way Analysis of Variance (ANOVA) at a significance level of α=0.05. For comparison of element uptake intensity among the plant species, a Biological Absorption Coefficient (BAC), defined as the ratio of total element content in aboveground biomass and soil, was used. This model has been used successfully for example, Ge *et al*. [23] determined a BAC index of up to 10 in the case of Cd for green plants growing at an element contaminated site, as well as indexes of 0.7 for Cu, 0.08 for Ni, 0.7 for Pb, and 1.0 for Zn. In our case, mobile portions of elements extractable with a 0.11 mol l^{-1} solution of CH_3COOH (Table 2) was applied for BAC level calculation to simulate plant-availability of soil elements and/or PM added to the soil. In the case of foliar PM application, the BAC level was calculated as a ratio of the total amount of the elements in the aboveground biomass of one plant and the total amount of the elements in the PM applied.

Lettuce Soil	Treatment	Cd	Fe	Pb	Zn
Fluvisol	control	0.617±0.014	37.8±0.7	0.188±0.040	54.6±0.4
	PM A in soil	0.598±0.101	38.8±19.8	0.173±0.034	56.4±8.1
	PM B in soil	0.615±0.020	36.6±10.6	0.198±0.068	56.5±1.6
Chernozem	control	0.080±0.002	29.2±0.2	0.200±0.009	7.29±0.11
	PM A in soil	0.082±0.022	25.9±5.1	0.205±0.613	7.58±2.44
	PM B in soil	0.088±0.016	29.7±3.4	0.201±0.447	6.82±1.08
Chard Soil	**Treatment**	**Cd**	**Fe**	**Pb**	**Zn**
Fluvisol	control	0.547±0.014	24.8±0.7	0.188±0.040	52.6 ± 0.4
	PM A in soil	0.538±0.041	23.1±10.2	0.206±0.090	52.7±4.9
	PM B in soil	0.492±0.012	22.5±12.9	0.135±0.076	46.0±1.0
Chernozem	control	0.068 ± 0.002	15.2 ± 0.2	0.142 ± 0.009	5.29 ± 0.11
	PM A in soil	0.070±0.021	19.0±2.7	0.128±0.020	6.53±0.89
	PM B in soil	0.058±0.012	13.8±2.5	0.219±0.050	4.07±0.75

Table 2. Soil element portions at the end of the pot experiment extractable with 0.11 mol l^{-1} CH_3COOH (mg kg^{-1}).

3. Results and Discussion

3.1 Element contents in plants

3.1.1 Cadmium

When comparing cadmium content in plant roots (Tables 3 and 4), soil amendment with PM showed a significant increase compared to control, with the exception of lettuce roots grown in the soil amended by PM sample A (particle size 0.063 – 0.119 mm). Potentially mobilizable portion of Cd in PM samples was higher (reaching 80% of the total content in PM B) compared to the soil where mobilizable Cd contents varied between 45% in Chernozem and 60% in Fluvisol (Table 1). The results indicated a joint influence of PM derived Cd and higher mobilizable Cd portion in the Fluvisol. In the case of chard, root cadmium uptake was lower in PM amended Chernozem than in the unamended Chernozem. A similar pattern was observed in foliar PM application on the chard leaves. With the Fluvisol, higher cadmium levels were determined when compared to Chernozem due to a higher Cd levels in the Fluvisol as well as its higher mobility (Table 2). Zehetner *et al*. [24] reported that traffic-born heavy metals in the immediate roadside zone tend to be more mobile than geogenic heavy metals at greater distances from the road. Although mobilizable portions of Cd in PM samples exceeded these in the soils no significant effects of PM added to the soil on element mobility were observed in our case. Moreover, the mobile portion of Cd in PM itself is relatively high compared to other elements such as lead [25]. Harrison and Chirgawi [26] demonstrated the translocation of Cd to the unexposed plant parts, such as radish leaves and inner lettuce leaves, where the ratio of the translocation represented *ca*. 30% of the total atmospherically derived Cd on plants.

In the aboveground biomass (Tables 5 and 6), the effect of PM particle size was negligible. Expectedly, foliar application of PM suspension significantly increased the Cd content in lettuce and chard leaves. Washing the leaves sufficiently released the cadmium added *via* the PM suspension indicating facile leachability of this

Soil	Treatment	Cd	Fe	Pb	Zn
Fluvisol	control	0.930±0.108	128±3	1.25±0.28	43.7±6.1
	PM A in soil	0.957±0.054	119±13	1.78±0.16	57.2±5.7
	PM B in soil	1.13±0.13	142±42	1.88±1.21	59.9±18.9
	PM A foliar	1.29±0.03	150±15	1.80±0.34	63.0±3.0
	PM B foliar	1.43±0.16	186±28	2.31±0.11	70.3±16.9
Chernozem	control	0.250±0.037	143±16	1.82±0.61	40.9±2.1
	PM A in soil	0.387±0.042	123±38	1.67±0.65	40.3±6.3
	PM B in soil	0.417±0.043	111±9	1.87±0.23	36.2±4.8
	PM A foliar	0.476±0.072	175±3	1.46±0.21	37.9±5.6
	PM B foliar	0.543±0.085	161±63	2.42±1.15	37.7±0.3

Table 3. Element content in roots of lettuce (mg kg^{-1}).

Soil	Treatment	Cd	Fe	Pb	Zn
Fluvisol	control	0.587±0.015	344±85	0.672±0.103	46.4±0.2
	PM A in soil	0.989±0.177	393±23	1.88±0.51	38.7±1.8
	PM B in soil	0.884±0.111	326±29	1.17±0.03	46.6±6.9
	PM A foliar	0.778±0.227	374±70	1.75±0.60	37.6±0.6
	PM B foliar	0.779±0.026	440±46	1.55±0.05	40.9±6.0
Chernozem	control	0.371±0.087	471±30	1.17±0.25	29.9±7.6
	PM A in soil	0.213±0.081	297±54	1.06±0.01	25.1±7.9
	PM B in soil	0.265±0.134	354±6	1.02±0.17	21.3±3.6
	PM A foliar	0.196±0.003	240±79	1.01±0.06	24.6±4.0
	PM B foliar	0.215±0.037	256±1	1.03±0.24	27.8±8.9

Table 4. Element content in roots of chard (mg kg^{-1}).

Soil	Treatment	Cd	Fe	Pb	Zn
Fluvisol	control	1.03±0.05	128±31	0.898±0.267	47.8±0.0
	PM A in soil	0.740±0.01	157±16	0.901±0.170	48.4±4.0
	PM B in soil	0.800±0.07	263±33	0.858±0.019	53.3±2.5
	PM A foliar a)	1.49±0.034	6014±355	22.0±0.6	300±2
	b)	1.19±0.089	1316±143	3.96±0.10	105±24
	PM B foliar a)	1.26±0.183	5951±135	19.1±1.8	196±16
	b)	0.850±0.000	1603±1	4.06±0.08	77.6±5.4
Chernozem	control	0.345±0.103	428±39	0.663±0.029	24.2±4.5
	PM A in soil	0.314±0.018	207±48	1.07±0.00	35.7±0.4
	PM B in soil	0.423±0.047	223±5	1.05±0.09	36.1±2.8
	PM A foliar a)	0.911±0.148	4969±1168	20.0±0.4	214±4
	b)	0.444±0.039	1015±76	3.88±0.13	69.9±1.1
	PM B foliar a)	0.876±0.151	5167±1006	15.6±3.2	174±30
	b)	0.415±0.045	899±82	3.53±0.37	67.1±0.5

Table 5. Element content in aboveground biomass of lettuce; a) unwashed part of leaves, b) washed part of leaves (mg kg^{-1}).

Soil	Treatment	Cd	Fe	Pb	Zn
Fluvisol	control	1.15±0.11	281±45	1.24±0.12	133±7
	PM A in soil	1.02±0.07	302±50	1.60±0.01	110±10
	PM B in soil	0.830±0.039	250±96	1.54±0.14	115±20
	PM A foliar a)	1.18±0.27	3252±226	11.5±0.2	203±1
	b)	0.849±0.071	379±33	1.58±0.20	124±28
	PM B foliar a)	1.42±0.18	1789±550	5.43±1.50	185±17
	b)	0.975±0.416	287±53	1.16±0.08	116±5
Chernozem	control	0.567±0.112	262±56	1.43±0.22	108±6
	PM A in soil	0.219±0.024	250±76	1.61±0.29	94.1±18.3
	PM B in soil	0.234±0.013	344±23	1.41±0.08	51.7±10.3
	PM A foliar a)	0.633±0.224	2571±330	8.61±0.73	138±14
	b)	0.272±0.058	641±182	2.26±0.45	61.6±0.3
	PM B foliar a)	0.624±0.061	3477±425	10.5±1.6	159±11
	b)	0.278±0.039	312±1	1.32±0.03	62.4±9.4

Table 6. Element content in aboveground biomass of chard a) unwashed part of leaves, b) washed part of leaves (mg kg^{-1}).

element from the leaf surface. The results indicated high efficiency of washing of the leaves as well as relatively low impact of PM amendment on total Cd contents in the leaves. Low migration of Cd throughout the whole lettuce plant after foliar Cd application was observed by Fismes *et al*. [27]. Atmospheric deposition of cadmium on herbage from long-term experimental plots at the Rothamsted Experimental Station in the UK was evaluated by Nicholson *et al*. [28]. Their study indicated that washing mixed herbage samples prior to analysis did not affect measured Cd concentrations. It can be inferred that Cd deposited and retained on herbage makes a minor contribution to the total plant Cd detected in the above-ground vegetation sampled from these Rothamsted plots over time. These results seemed to be contradictory to our findings, however, the total Cd deposition was probably significantly higher in our model experiment.

As documented by other authors, the cadmium content in lettuce growing in uncontaminated and/or industrial areas varies between 0.4 and 0.6 mg kg^{-1} [13,29]. From local retailers in Manisa, Turkey, Bagdatlioglu *et al*. [30] found 0.05±0.01, and 0.07±0.01 mg kg^{-1} of cadmium in lettuce and chard (if *ca*. 10% of dry matter in plant leaves is calculated); these values are lower when compared to the levels mentioned above, indicating contamination levels playing a role within the particular areas of the investigation. Our results indicated elevated Cd contents and high mobility in Fluvisol confirming better Cd plant-availability in sandy soils as documented by Table 1 [10].

3.1.2 Iron

As compared to cadmium, the potentially mobilizable and mobile portion of the total iron content in soil was significantly lower (Tables 1 and 2). Therefore, plant iron concentrations confirmed limited plant-availability of this element whereas chard showed a greater ability in iron uptake. Similarly as in the case of cadmium, a lower root uptake of Fe was observed in PM amended soils than in the control even in chard roots of plants amended *via* the foliar application (Tables 3 and 4). Due to high Fe contents in the PM, a substantial increase in the Fe content of chard leaves (and especially lettuce) was reported (Tables 5 and 6). Moreover, washing the leaves did not result in complete removal of Fe, indicating substantial iron penetration *via* the leaf surface.

Cawse [31] determined an average Fe content of 130 mg kg^{-1} dry matter in lettuce growing in uncontaminated soils, and Panagiotopoulos *et al*. [32] determined a content of 180 mg kg^{-1} dry matter. In industrial areas the Fe levels varying between 100 and 330 mg kg^{-1} dry matter were determined in lettuce biomass [13,33,34] in accordance with our plants from control and PM amended soils. However, a comparison of the results from different locations is difficult in principle due to various soil physicochemical properties and/or Fe contents and mobility, as well as sources of anthropogenically derived iron. Bagdatlioglu *et al*. [30] reported a wide range of Fe contents in both lettuce (245±223 mg kg^{-1}) and chard (532±585 mg kg^{-1}) originating from various locations with *ca.* 10% of dry matter in plant leaves.

3.1.3 Lead

The Pb levels in roots of lettuce did not differ significantly from those in chard roots (Tables 3 and 4). The PM amendment significantly affected lead levels in plant roots growing in Fluvisol with the exception of lettuce in PM amended soil. A low uptake of soil lead by the aboveground biomass of tested vegetables was apparent but a significantly increased Pb content in lettuce leaves at Chernozem and chard leaves at Fluvisol was observed (Table 5 and 6). A lower mobility and/or plant-availability of lead compared to other elements such as Cd and Zn was confirmed in this experiment as well as by Huang *et al*. [35] and Sawidis *et al*. [36]. The lead content in lettuce was variable by location and affected by individual soil physicochemical conditions, especially pH levels and clay content in the soils [12]. In our case, lead uptake by plants was influenced by soil type and was affected predominantly by differing mobile content of lead. Golia *et al*. [12] determined Pb levels in the range from 0.01 to 0.12 mg kg^{-1} dry matter in lettuce leaves growing in uncontaminated areas, Kabata-Pendias and Pendias [10] reported a concentration range between 0.7 and 3.6 mg kg^{-1} dry matter. Also, Bagdatlioglu *et al*. [30] determined low levels of Pb in lettuce (1.63±0.70 mg kg^{-1}) and chard (1.06±0.67 mg kg^{-1}) if *ca.* 10% of dry matter in plant leaves was calculated. In industrial areas, the Pb contents in lettuce leaves varied between 0.17 and 15.3 mg kg^{-1} dry matter [13]. As documented in Table 1, the mobility of Pb in the soils was one order of magnitude lower compared to cadmium. According to Vodyanitskii [37], lead is stable in organic soils with an average lifetime varying from hundreds to thousands of years, and its low mobility is due to the formation of stable Pb^{2+} organic complexes.

The foliar PM application resulted in a 20-fold increase of Pb content in lettuce and a 10-fold increase in chard leaves, while no significant differences were observed between PM physical fractions (Tables 5 and 6). The washing of leaves was successful only in the case of chard leaves, whereas with lettuce leaves a substantial portion of PM-originating Pb was retained. Roberts *et al*. [38] determined 1506 mg kg^{-1} of Pb and 596 mg kg^{-1} of Pb in lettuce leaves (growing in extremely contaminated conditions) before and after washing, respectively. Uzu *et al*. [39] exposed lettuce plants to atmospheric fallouts from a lead-recycling plant for 43 days, and the Pb content in plant biomass reached 335±50 mg kg^{-1}. They also found Pb-rich spots of a few hundred of micrometers in diameter located in necrotic zones. In addition, submicrometric particles were observed inside stomatal openings. Hu and Ding [40] used isotopic ratio for the identification of lead contamination sources in peri-urban area in China. They speculated that the Pb isotopic content in various vegetables is possibly a combination of soilborne Pb being taken up through the soil-to-root pathway, and airborne Pb assimilated *via* the atmosphere-to-leaf pathway. These findings correspond to our observations.

3.1.4 Zinc

Zinc contents in plant roots were comparable within the same experimental soil (Tables 3 and 4) and lower in the case of Chernozem, which corresponds to the lower mobility of Zn in this soil (Table 2). Increased root Zn content was observed only in lettuce growing in Fluvisol, and after foliar PM amendment. After the soil PM application a lower zinc uptake by chard aboveground biomass compared to control was observed, whereas Zn levels in lettuce leaves tended to increase after PM amendment (Tables 5 and 6). The obvious Zn levels determined in lettuce leaves vary from 45 mg kg^{-1} [41] and 75 mg kg^{-1} [13,42]. Bagdatlioglu *et al*. [30] reported Zn levels in lettuce from various locations ranging from 18.6 to 36.3 mg kg^{-1}, and in chard from 17.1 to 42.4 mg kg^{-1} if *ca.* 10% of dry matter in plant leaves was calculated. Zinc content in chard and lettuce determined previously [43] were similar to our findings.

Foliar PM application resulted in a significant increase in the Zn content of unwashed leaves, however, this increase did not reach the levels of the element inputs comparable to Fe and Pb (Tables 5 and 6). In the case of chard, washing the leaves removed the PM-derived Zn quantitatively, whereas a substantial amount of Zn was retained in lettuce leaves, indicating that this element penetrated the lettuce leaf surface more easily than the chard leaf surface. No significant differences were observed between PM physical fractions. The range of Zn concentrations in lettuce was comparable to those determined by Preer *et al*. [44].

3.2 Biological Absorption Coefficients

3.2.1 Soil PM application

The soil application of PM represented an increase in total element content of the experimental pots by 0.014 mg of Cd, 200 mg of Fe, 0.8 mg of Pb, and 8 mg of Zn per kg of soil. BAC levels were calculated according to Ge *et al*. [23] but mobile portions of individual elements (Table 2) were used instead of total element content in soil due to different mobility and/or plant-availability of the individual elements (Table 7). Among the elements, the highest BAC factors were observed for iron (between 3,4 and 25) and lead (between 2 and 21); when comparing the soils, higher BAC factors were calculated for Chernozem due to the lower element mobility. These results also suggested higher portions of plant-usable Fe and Pb from the extractable pool of these elements as compared to Cd and Zn. In the case of Cd and Zn the high extractable portions of elements in soil did cot represent the real plant-available portion of these elements as evident especially in the case of Zn in Fluvisol. With the exception of Cd, chard exhibited higher BAC factors when compared to lettuce. The effect of PM soil application was negligible. Ge *et al*. [23] reported the following BAC factors for plants: 10 for Cd, 0.7 for Pb, and 1.0 for Zn. Voutsa *et al*. [13] calculated BAC factors up to 1.5 for carrot and leek whereas low uptake of Cd, Zn, and Pb was determined for lettuce, cabbage, and chicory. Pandey *et al*. [45] determined BAC factors of Cd for spinach and radishes ranging from 0.17 to 0.20; for Pb the levels were 5-fold lower. These results were not comparable to our findings because BAC levels were calculated using total element content in soil. However, an effect of vegetable species and/or different element levels in soils is evident from the cited works.

Lettuce					
Soil	Treatment	Cd	Fe	Pb	Zn
	control	1.67	3.38	4.77	0.88
Fluvisol	PM A in soil	1.34	3.44	5.36	0.90
	PM B in soil	1.28	6.70	5.42	0.94
	control	4.31	14.66	3.32	3.32
Chernozem	PM A in soil	4.57	9.70	1.94	5.82
	PM B in soil	4.85	9.47	2.71	5.44
Chard					
Soil	Treatment	Cd	Fe	Pb	Zn
	control	1.86	7.43	6.60	2.44
Fluvisol	PM A in soil	1.90	14.53	7.25	2.13
	PM B in soil	1.68	9.77	14.92	2.51
	control	4.34	17.24	10.07	20.42
Chernozem	PM A in soil	2.66	13.51	21.00	14.94
	PM B in soil	4.01	27.29	12.11	13.23

Table 7. Bioconcentration factors of elements in plant aboveground biomass growing in PM amended soil.

3.2.2 Foliar application of PM suspension

The foliar application of PM suspension represented the addition of 0.07 mg Cd, 980 mg Fe, 4.2 mf Pb, and 42 mg Zn from the physical fraction A, and 0.05 mg Cd, 1000 mg Fe, 3.7 mf Pb, and 41 mg Zn from the physical fraction B. The highest BAC factors were determined for Cd, the lowest for Fe and Pb (Table 8), and no significant differences were found between plant species, PM physical fraction, and soil type. A significant pool of elements released by washing the leaves was evident, as well. The BAC factors derived from foliar PM application could be roughly compared with the Air Accumulation Factors (AAF) derived from element concentrations in ambient air. However, Pandey *et al*. [45] and Voutsa *et al*. [13] determined AAF levels significantly higher than those from our results, confirming a better uptake of airborne elements compared to soilborne ones. Pandey *et al*. [45] calculated the following AAF levels for spinach: 286 for Cd, and 37 for Pb. Voutsa *et al*. [13] determined AAF levels for lettuce and cabbage of 242 and 138 (Cd), 84 and 4 (Pb), and 37 and 60 (Zn), respectively. The calculation of AAF factors are based on the element concentrations in the atmosphere given in μg m^{-3}. Therefore, a different approach was used for the calculation where total amount of elements applied on plant leaves in our experiment exceeded the levels used by the abovementioned authors. In our case, higher amounts of elements were applied to the plant leaves *via* PM suspension compared to element concentration in the atmosphere, even higher than element levels reported by Wang *et al*. [46] in water at polluted sites in China.

Concluding the research, foliar application of PM suspension resulted in a significant increase of element content in plant leaves. A comparison of root and foliar uptake of Cd and Pb was performed by Salim *et al*. [47] with radish plants and their results are in agreement with our findings. The differences in foliar element penetration among individual plant species are given by the external tissues cuticle, *etc*.) of epidermis cells [48]. Greger *et al*. [49] determined low foliar Cd uptake of *Beta vulgaris* compared to *Pisum sativum* due to lower permeability of the cuticular membrane. However, most of the elements were removed by plant washing. In this context, Fe and Zn tended to penetrate the leaf surface more deeply than Cd and Pb. Low efficiency of Fe and Zn removal by washing of the plant leaves by deionized water was also observed [50]. Alfani *et al*. [51] determined the Fe transfer from the surface deposit to the leaf tissue whereas, the Pb content was

Lettuce					
Soil	Treatment	Cd	Fe	Pb	Zn
Fluvisol	PM A foliar a)	0.639	0.184	0.157	0.215
	b)	0.512	0.040	0.028	0.076
	PM B foliar a)	0.710	0.167	0.155	0.129
	b)	0.477	0.045	0.033	0.057
Chernozem	PM A foliar a)	0.391	0.152	0.143	0.154
	b)	0.191	0.031	0.028	0.050
	PM B foliar a)	0.492	0.145	0.127	0.128
	b)	0.233	0.029	0.029	0.049
Chard					
Soil	Treatment	Cd	Fe	Pb	Zn
Fluvisol	PM A foliar a)	0.506	0.100	0.082	0.146
	b)	0.364	0.012	0.011	0.089
	PM B foliar a)	0.797	0.050	0.044	0.136
	b)	0.548	0.008	0.009	0.085
Chernozem	PM A foliar a)	0.272	0.079	0.061	0.099
	b)	0.117	0.020	0.016	0.044
	PM B foliar a)	0.351	0.097	0.086	0.117
	b)	0.156	0.009	0.011	0.046

Table 8. Bioconcentration factors of elements in plant aboveground biomass amended by foliar application of PM suspension.

higher in the leaf surface deposit than in the leaf tissue. The effect of PM physical fraction was negligible, soil element level and/or mobility were the dominant factor affecting plant-availability of the soil risk elements. The direct comparison of soil and foliar PM application indicated a higher potential risk of foliar application. In the case of soil amendment, a low availability of PM-derived risk elements and even improved soil sorption capacity were demonstrated, resulting in a lower root uptake of the elements. However, long-term observation of PM behavior in soil is recommended due to possible decomposition of PM organic matter and the subsequent release of risk elements into soil solution.

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References

[1] Varrica D., Dongarrà G., Sabatino G., Monna F., Inorganic geochemistry of roadway dust from the metropolitan area of Palermo, Italy, Environ. Geol., 2003, 44, 222-230
[2] Allen A.G., Nemitz E., Shi J.P., Harrison R.M., Greenwood J.C., Size distributions of trace metals in atmospheric aerosols in the United Kingdom, Atm. Environ., 2001, 35, 4581-4591
[3] Norra S., Stüben D., Trace element patterns and seasonal variability of dust precipitation in a low polluted city – the example of Karlsruhe/Germany, Environ. Monit. Assess., 2003, 93, 203-228
[4] Birmili W., Allen A.G., Bary F., Harrios, R.M., Trace metal concentrations and water solubility in size-fractionated atmospheric particles and influence of road traffic, Environ. Sci. Technol., 2006, 40, 1144-1153
[5] Gaudry A., Moskura M., Mariet C., Ayrault S., Denayer F., Bernard N., Inorganic pollution in PM10 particles collected over three french sites under various influence: rural conditions, traffic and industry, Water, Air, Soil Pollut., 2008, 193, 91-106
[6] Shaheen N., Shah M.H., Jaffar M., A study of airborne selected metals and particle size distribution in relation to climatic variables and their source identification, Water, Air, Soil Pollut., 2005, 164, 275-294
[7] Charlesworth S.M., Lees J.A., The distribution of heavy metals in deposited urban dusts and sediments, Coventry, England, Environ. Geochem. Health, 1999, 21, 97-115
[8] Sutherland R.A., Tack F.M.G., Ziegler,A.D., Bussen, J.O., Metal extraction from road-deposited sediments using nine partial decomposition procedures, Appl. Geochem., 2004, 19, 947-955
[9] Viard B., Pihan F., Promeyrat S., Pihan J.C., Integrated assessment of heavy metal (Pb, Zn, Cd) highway pollution: bioaccumulation in soil, Graminaceae and land snails, Chemosphere, 2004, 55, 1349-1359
[10] Kabata-Pendias A., Pendias H., Trace elements in soils and plants, 3rd ed., CRC Press, Boca Raton, 2001
[11] Bradl H.B., Adsorption of heavy metal ions on soils and soils constituents, J. Coll. Int. Sci., 2004, 277, 1–18
[12] Golia E.E., Dimirkou A., Mitsos I.K. Influence of some soil parameters on heavy metals accumulation by vegetables grown in agriculture soil of different soil orders, Bull. Environ. Contam. Toxicol., 2008, 81, 80-84
[13] Voutsa D., Grimanis A., Samara C., Trace elements in vegetables grown in an industrial area in relation to soil and air particulate matter, Environ. Pollut., 1996, 94, 325-335
[14] Rodriguez J.H., Pignata M.L., Fangmeier A., Klumpp A., Accumulation of polycyclic aromatic hydrocarbons and trace elements in the bioindicator plants Tillandsia capillaris and Lolium multiflorum exposed at PM10 monitoring stations in Stuttgart (Germany), Chemosphere, 2010, 80, 208–215
[15] Wood T., Bormann F.H., Increases in foliar leaching caused by acidification of an artificial mist, Ambio, 1975, 4, 169-171
[16] Public notice No. 13/1994, regulating some details concerning the preservation of agricultural lands available. Czech Ministry of the Environment, Prague, 1994
[17] Sysalová J., Száková J., Mobility of important toxic analytes in urban dust and simulated air filters determined by sequential extraction and GFAAS/ICP-AES methods, Chem. Pap., 2007, 61, 271 - 275
[18] Sysalová J., Kučera J., Kotlík B., Havránek V., Quality control materials for the determination of trace elements in airborne particulate matter, Anal. Bioanal. Chem., 2002, 373, 195-199

[19] ISO 11260, Standard of Soil Quality — Determination of Effective cation Exchange Capacity and Base Saturation Level Using Barium Chloride Solution, International Organization for Standardization, 1994
[20] Sims J.R., Haby V.A., Simplified colorimetric determination of soil organic matter. Soil Sci., 1971, 112, 137–141
[21] Borůvka L., Huanwei C., Kozák J., Krištoufková S., Heavy contamination of soil with cadmium, lead and zinc in the alluvium of the Litavka river, Rostl. Výr., 1996, 42, 543-550
[22] Quevauviller P., Ure A., Muntau H., Griepink B., Improvement of analytical measurements within the BCR – program – Single and sequential extraction procedures applied to soil and sediment analysis, Int. J. Environ. Anal. Chem., 1993, 51, 129–134
[23] Ge Y., Murray P., Sauvé S., Hendershot W., Low metal bioavailability in a contaminated urban site, Environ. Toxicol. Chem., 2002, 21, 954-961
[24] Zehetner F., Rosenfellner U., Mentler A, Gerzabek M.H., Distribution of road salt residues, heavy metals and polycyclic aromatic hydrocarbons across a highway-forest interface, Water Air Soil Pollut., 2009, 198, 125–132
[25] Komarnicki G.J.K., Lead and cadmium in indoor air and the urban environment. Environ. Pollut., 2005, 136, 47-61
[26] Harrison R.M., Chirgawi M.B., The assessment of air and soil as contributors of some trace metals to vegetable plants II. Translocation of atmospheric and laboratory-generated cadmium aerosols to and within vegetable plants, Sci. Tot. Environ., 1989, 83, 35-45
[27] Fismes J.F., Echevarria G., Leclerc-Cessac E., Morel J.L., Uptake and transport of radioactive nickel and cadmium into three vegetables after wet aerial contamination, J. Environ. Qual., 2005, 34, 1497-1507
[28] Nicholson F.A., Jones K.C., Johnston A.E., The significance of the retention of atmospherically deposited cadmium on plant surfaces to the cadmium content of herbage, Chemosphere, 1995, 31, 3043-3049
[29] Fleischer M., Sarofim A.F., Fassett D.W., Hammond P., Shacklette H.T., Nisbet I.C.T., et al., Environmental impact of cadmium: A review by the panel on hazardous trace substances, Environ. Health Persp., 1974, 7, 253-323
[30] Bagdatlioglu N., Nergiz C., Ergonul P.G., Heavy metal levels in leafy vegetables and some selected fruits, J. Verbrauch. Lebensm., 2010, 5, 421–428
[31] Cawse P.A., Trace and major elements in the atmosphere at rural locations in Great Britain, 1972-81, In: Kabata-Pendias A., Pendias H. (Eds.), Trace elements in soils and plants, 3rd ed., CRC Press, Boca Raton, 2001
[32] Panagiotopoulos K., Sakelariades S., Polyzopoulos N., Vouzoulidou-Alexandrou E., Concentrations of Zn, Cd, Cu, Ni, Mn, Pb, and Fe in vegetables and soils from three locations in N. Greece, Annals. Fac. Agric. Forestry, 1976, 18, 159-198
[33] Gantides N., Bladenopoulou S., Kandylakis Ch., Spyropoulos A., Investigation of the heavy metal pollution of the vegetative land of West Thessaloniki, In: Proceedings of the 4th Greek Conference on Soil and Environment, Hellenic Soil Science Society, Thessaloniki, Greece, 1992, Vol. A, pp. 401-425
[34] Samara C., Misaelides P., Tsalev D., Anousis I., Kouimtzis T., Trace element distribution in vegetables grown in industrial area of Thessaloniki, Greece, Fresenius Environ. Bull., 1992, 1, 577-582
[35] Huang B., Kuo S., Bembenek R., Availability to lettuce of arsenic and lead from trace element fertilizers in soil, Water, Air, Soil Pollut., 2005, 164, 223–239
[36] Sawidis T., Metentzoglou E., Mitrakas M., Vasara E., A study of chromium, cooper, and lead distribution from lignite fuels using cultivated and non-cultivated plants as biological monitors, Water, Air, Soil Pollut., 2011, 220, 339–352
[37] Vodyanitskii Y.N., Arsenic, lead, and zinc compounds in contaminated soils according to EXAFS spectroscopic data: A review, Eur. Soil Sci., 2006, 39, 611-621
[38] Roberts T.M., Gizyn W., Hutchinson T.C., Lead contamination of air, soil, vegetation and people in the vicinity of secondary lead smelters, In: Kabata-Pendias A., Pendias H., (Eds.), Trace elements in soils and plants, 3rd ed., CRC Press, Boca Raton, 2001
[39] Uzu G., Sobanska S., Sarret G., Muñoz M., Dumat C., Foliar lead uptake by lettuce exposed to atmospheric fallouts, Environ. Sci. Technol., 2010, 44, 1036-1042
[40] Hu, X. Ding Z., Lead/Cadmium Contamination and Lead Isotopic Ratios in Vegetables Grown in Peri-Urban and Mining/Smelting Contaminated Sites in Nanjing, China, Bull Environ Contam Toxicol., 2009, 82, 80–84
[41] Warren H.V., Delavault R.E., Fletcher K., Wilks E., Variation in the copper, zinc, lead and molybdenum content of some British Columbia vegetables, In: Kabata-Pendias A., Pendias H., (Eds.), Trace elements in soils and plants, 3rd ed., CRC Press, Boca Raton, 2001

[42] Shlacklette H.T., Elements in fruits, and vegetable from areas of commercial production in the Conterminous United States, In: Kabata-Pendias A., Pendias H., (Eds.), Trace elements in soils and plants, 3rd ed., CRC Press, Boca Raton, 2001
[43] Madejón P., Barba-Brioso C., Lepp N.W., Fernández-Caliani J.C., Traditional agricultural practices enable sustainable remediation of highly polluted soils in Southern Spain for cultivation of food crops, J. Environ. Manag., 2011, 92, 1828-1836
[44] Preer J.R., Sekhon H.S., Stephens B.R., Collins M.S., Factors affecting heavy-metal content of garden vegetables, Environ. Pollut. 1980, 1, 95-104
[45] Pandey J., Pandey R., Shubhashish K., Air-borne heavy metal contamination to dietary vegetables: A case study from India, Bull. Environ. Contam. Toxicol., 2009, 83, 931-936
[46] Wang Q.R., Cui I.S., Liu W.M., Dong Y.T., Christie P., Soil contamination and plant uptake of heavy metals at polluted sites in China, J. Environ. Sci. Health, 2003, 38, 823-838
[47] Salim R., Alsubu M.M., Atallah A., Effects of root and foliar treatments with lead, cadmium, and copper on the uptake distribution and growth of radish plants, Environ. Int., 1993, 19, 393-404
[48] Marschner H., Mineral nutrition in higher plants, Harcourt Brace Jovanovich Publ., Academic Press, London, 1986
[49] Greger M., Johansson M., Stihl A., Hamza K., Foliar uptake of Cd by pea (Pisum sativum) and sugar-beet (Beta vulgaris), Physiol. Plant., 1993, 88, 563-570
[50] Moraghan J.T., Removal of endogenous iron, manganese and zinc during plant washing, Commun. Soil Sci. Plant Anal., 1991, 22, 323-330
[51] Alfani A., Maisto G., Iovieno P., Rutigliano F.A., Bartoli G., Leaf contamination by atmospheric pollutants as assessed by elemental analysis of leaf tissue, leaf surface deposit and soil, J. Plant Physiol. 1996, 148, 243-248