

Direct and Subsequent Effects of Contaminated Urban Particulate Matter on Risk Element Mobility and Plant-Availability in Soil

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Abstract

The effect of soil amendment by different physical fractions (0.063-0.119 mm, and < 0.063 mm) of urban particulate matter (PM) on mobility of potentially risky elements in soil and/or element uptake by plants was investigated in a pot experiment, in which spinach (*Spinacia oleracea* L.) was cultivated on two different soils. The cadmium (Cd), iron (Fe), lead (Pb), and zinc (Zn) levels were determined in plant biomass and soil after direct and subsequent (evaluated after second vegetation period) soil amendment by PM. Three soil extraction procedures ($2 \text{ mol}\cdot\text{l}^{-1} \text{ HNO}_3$, $0.11 \text{ mol}\cdot\text{l}^{-1} \text{ CH}_3\text{COOH}$, $0.01 \text{ mol}\cdot\text{l}^{-1}$, and CaCl_2) were used for the extraction of mobile portions of elements in PM-amended soils. Additionally, the diffusive gradient in thin films (DGT) technique was applied for the assessment of bioavailable pools of the elements in soil. Element mobility decreased in the following order: $\text{Cd} > \text{Zn} > \text{Pb} \approx \text{Fe}$. The effect of soil physicochemical properties were determinative for extractability as well as for plant uptake of these elements. Neither in the first nor in the second vegetation period did the soil amendment by PM result in significant changes of mobility and plant-availability of the investigated elements which confirms a relatively high stability of PM in the soil and a weak plant uptake of PM-derived risk elements via roots.

Keywords: urban particulate matter, risk elements, mobility, extractability, spinach

Introduction

The risk elements in the atmosphere represent a serious potential impact on other components of the environment [1]. The total contents of certain potentially toxic elements in urban particulate matter as affected by site, traffic level, seasonal variability, meteorological parameters (air humidity and temperature, wind direction, rainfall), and particle size were intensively investigated through the use of various instrumental analytical techniques [2, 3]. Seasonal vari-

ations of urban dust precipitation and chemical dust composition were intensively investigated by Norra and Stueben [4]. Annual courses of metal depositions correlated positively with dust precipitations, and negatively with trace metal concentrations in dusts. In this context, traffic-derived PM is considered the most significant source of risk for human health in the affected areas [5-8].

Roadside surface soils are among the suitable indicators of risk elements of emissions from traffic [9, 10]. Sharma et al. [11] observed a decrease in concentrations of Cd and Pb with increasing distance from the highway, indicating their relation to traffic. Higher metal accumulation has been

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observed in vegetation and soil samples near highways (0-5 m) when compared to such samples from sites located slightly further from thoroughfares (at 5-10 m and 10-15 m). Similarly, Aydinalp [12] observed soil Pb contents ranging from 30 to 1210 mg·kg⁻¹. Zinc concentrations varied from 62 to 493 mg·kg⁻¹ and copper concentration ranged from 20 to 251 mg·kg⁻¹. Cadmium concentrations were lowest in the soil and varied from 0.5 to 5 mg·kg⁻¹. In this case, higher levels of risk elements were associated with roadside soils as compared to their natural background levels. Moreover, an increased risk element content in roadside soils was described by many authors [13-15].

The plant-availability of elements is affected by the physicochemical parameters of the soils (soil pH, sorption capacity, organic matter content, etc.), climatic conditions, plant genotype, and plant management [1, 16, 17]. Generally, the method most commonly used to assess the distribution of elements in environments of solid samples (soil, sediment, sewage sludge, urban dust, atmospheric deposit, coal fly ash, etc.) is the chemical fractionation of elements. This is a process performed through a sequence of different leaching or selective extraction procedures to determine element forms as an important factor in assessment of the potential health impact. The basic method of sequential leaching was developed by Tessier et al. [18] for sediments. Currently, the BCR (now the Institute for Reference Materials and Measurements) scheme is usually applied to different types of solid samples [19]. Various extraction procedures (using e.g. CaCl₂, Ca(NO₃)₂, NaNO₃, BaCl₂ solutions) were described for the determination of mobile portions of elements in soils using different extractants. The extractability of elements depends on the extractant, source of soil pollution, and the nature of the soil [20]. Single soil extraction procedures were recently evaluated by Menzies et al. [21] and Száková et al. [22]. They confirmed the suitability of neutral salt extractants (0.01 mol·l⁻³ CaCl₂, 0.1 mol·l⁻³ NaNO₃) in assessing the available pool of elements in soil.

In our previous experiment, the effect of three rural dust samples (applied to soil) to the uptake of As, Cd, Pb, and Zn by the aboveground biomass of oat plants (*Avena sativa* L.) were assessed in a pot trial. Although element content in dust samples significantly affects the total element content in soil, element content in plants was not affected. Soil sorption capacity and the neutral pH of the experimental soil (7.0) was sufficient for element immobilization. However, potentially mobilizable portions (0.005 mol·l⁻¹ DTPA extractable) of elements significantly increased (Cd by 116%, Pb by 39%, Zn by 50%) in the treated soil, suggesting a possible release of these elements in the future [23]. De Temmerman and Hoenig [24] investigated the potential uptake of airborne trace elements by leaves of leafy vegetables (*Spinacia oleracea*, *Lactuca sativa*, *Cichorium endivia*, *Valerianella locusta*), and subsequently proved that dust deposition significantly increases Pb concentrations in such vegetables. Contrarily, Žalud et al. [25] observed that element uptake by plant biomass was significantly higher *via* foliar application of PM suspension, sim-

ulating atmospheric deposition. In the case of Fe and Zn, the content in plants increased rapidly when compared to the control treatment. Even gently washed leaves contained elevated amounts of Fe and Zn. In the case of Pb, a 30-fold increase of this element was reported in treated leaves compared to the untreated control group. However, the majority of Pb was removed by washing, and the Pb levels dropped, containing 5-fold more Pb than the control. The effect of PM application on Cd content in plant leaves was negligible in most cases. Lettuce tended to exhibit a higher element uptake when compared to chard, and no adverse effect of PM application on growth parameters of the vegetables was determined.

In our study, a model pot experiment was carried out to demonstrate and evaluate the effect of PM amended soil on:

- i) cadmium, iron, lead, and zinc mobility and plant-availability in this soil
- ii) the uptake of investigated elements by spinach (*Spinacia oleracea* L.) plants

The main objective of the investigation was to compare the potential long-term effects of PM uptake-associated risk elements on their mobility and plant-availability in two consecutive vegetation periods.

Materials and Methods

Pot Experiment

The PM sample (PKC) was prepared from urban dust collected from filters of the air-conditioner system in the Prague Congress Center building, located close to the thoroughfare. It was dried at laboratory temperature and sieved twice. Finally, the most abundant physical fractions, labeled A (particle size 0.063-0.119 mm) and B (particle size <0.063 mm), were used for the pot experiments. Two of the following soils differing in their physicochemical characteristics were selected for the experiment:

- i) uncontaminated Chernozem with a cation exchange capacity of (CEC) 255 mmol·kg⁻¹, a pH level of 7.2, and an oxidizable carbon content (Cox) of 2.3 %
- ii) slightly contaminated Fluvisol with a CEC of 201 mmol·kg⁻¹, a pH level of 6.8, and a Cox of 2.6%

Total element content in both PM and soil samples is summarized in Table 1. According to Public notice [26] giving the maximum levels of risk elements in agricultural soils in the Czech Republic, the “pseudo-total“ (Aqua

Table 1. Total element content in soils and PM samples (mg·kg⁻¹); n=3, data expressed as mean±standard deviation.

Soil	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

Regia soluble) element concentrations in loamy soils cannot exceed a maximum of $1.0 \text{ mg}\cdot\text{kg}^{-1}$ Cd, $140 \text{ mg}\cdot\text{kg}^{-1}$ Pb and $200 \text{ mg}\cdot\text{kg}^{-1}$ Zn, and $0.4 \text{ mg}\cdot\text{kg}^{-1}$ Cd, $100 \text{ mg}\cdot\text{kg}^{-1}$ Pb, and $130 \text{ mg}\cdot\text{kg}^{-1}$ Zn for sandy soils. Iron (Fe) contents in soils are not limited. Therefore, Fluvisol element contents exceed the maximum permissible limits for Czech soils for Cd and Zn.

Spinach (*Spinacia oleracea* L.) was cultivated in pots filled with 5 kg of air-dried soil, in which three replications of each treatment were made. Thirty grams (30 g) of the individual PM sample was applied to one pot before sowing and being thoroughly mixed with the experimental soil. Two approaches were applied for cultivation of the spinach plants:

- spinach plants were sown directly after soil amendment,
- lettuce (*Lactuca sativa* L.) was planted directly after soil amendment [25]

Spinach was cultivated subsequently in the second vegetation period without additional PM application to encourage the changes in element mobility due to PM-soil-plant rhizosphere interactions. The plants were treated with deionized water and soil moisture was kept at 60% of its maximum water-holding capacity. Plants were harvested on the top of vegetation, dried at 60°C , ground, and analyzed for Cd, Fe, Pb, and Zn contents. Soil samples were immediately taken from the bulk after plant harvesting, then air-dried at ambient temperature, ground in a mortar, passed through a 2-mm plastic sieve, and analyzed for mobile portions of the elements.

Analytical Methods

The determination of the total concentrations of the elements in PM was done after microwave-assisted oven digestion of 20 mg dust samples in the following mixture of concentrated acids – HNO_3 , HF and H_2O_2 (5:1:1). The procedure was controlled by SRM 1648 Urban Particulate Matter (NIST, USA). The Cd, Fe, Pb, and Zn concentrations in the digests were determined by ICP-OES (Varian, VistaPro, Australia). (Details are described in one of our previous papers [27]). Comparative data were obtained by instrumental neutron activation analysis (INAA) and particle-induced x-ray emission (PIXE) techniques, according to the procedure described earlier [28].

The total concentration of Cd in the soils was determined in 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 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 deionized water, and kept at laboratory temperature until measurement. A certified reference material RM 7001 Light Sandy Soil was applied for quali-

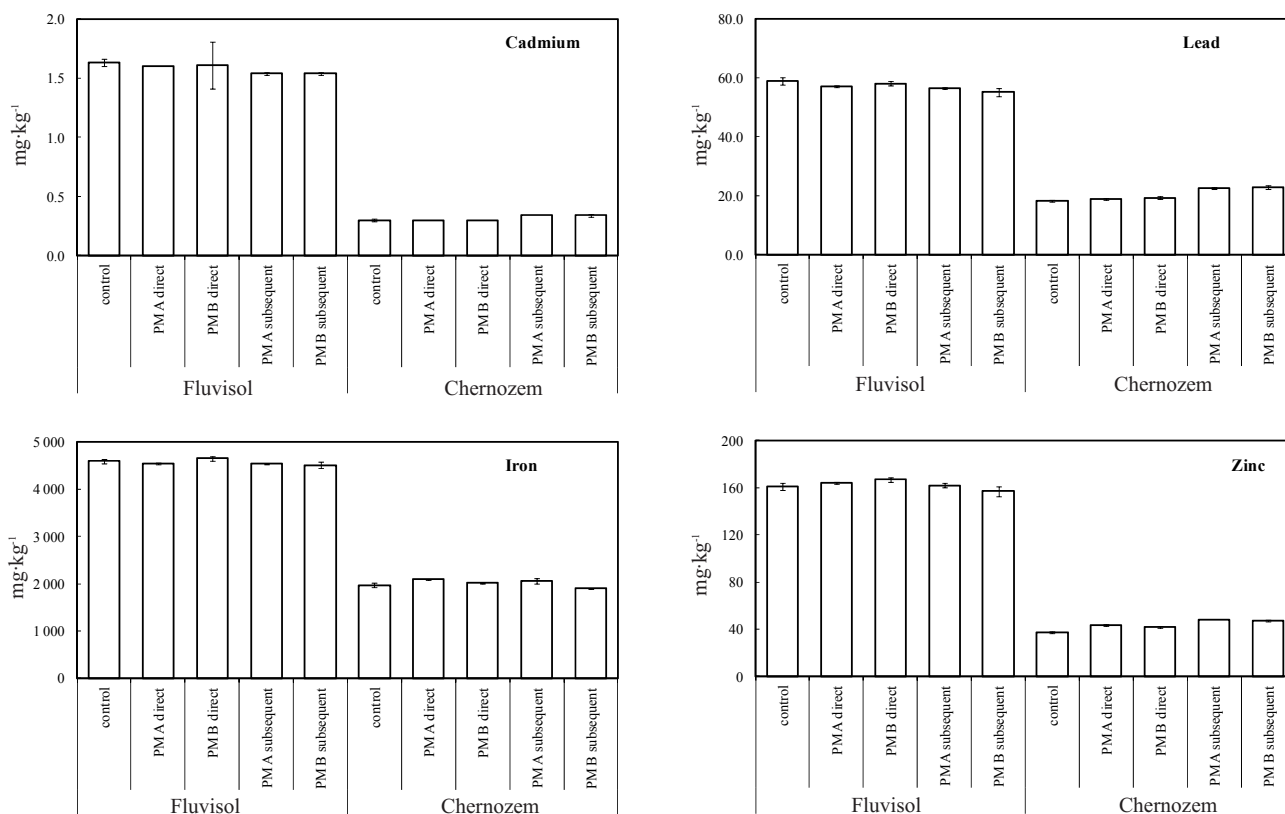


Fig. 1. The potentially mobilizable portions of elements in soils after harvest; extractable with $2 \text{ mol}\cdot\text{l}^{-1}$ HNO_3 ($\text{mg}\cdot\text{kg}^{-1}$); $n=3$, data expressed as mean±standard deviation.

Table 2. The mobile portions of elements in soils after harvest; extractable with $0.11 \text{ mol}\cdot\text{L}^{-1} \text{ CH}_3\text{COOH}$ ($\text{mg}\cdot\text{kg}^{-1}$); $n=3$, data expressed as mean \pm standard deviation.

Soil	Treatment	Cd	Fe	Pb	Zn
Fluvisol	control	0.67 \pm 0.01	4.8 \pm 0.7	0.19 \pm 0.04	52.6 \pm 0.4
	PM A direct	0.69 \pm 0.00	4.5 \pm 0.3	0.24 \pm 0.03	61.2 \pm 0.5
	PM B direct	0.71 \pm 0.01	5.3 \pm 0.1	0.24 \pm 0.01	59.8 \pm 0.7
	PM A subsequent	0.71 \pm 0.01	3.9 \pm 0.1	0.39 \pm 0.06	55.9 \pm 0.7
	PM B subsequent	0.65 \pm 0.01	4.4 \pm 0.4	0.40 \pm 0.04	55.7 \pm 0.7
Chernozem	control	0.12 \pm 0.00	1.2 \pm 0.2	0.14 \pm 0.01	3.3 \pm 0.0
	PM A direct	0.12 \pm 0.00	0.7 \pm 0.2	0.11 \pm 0.02	4.7 \pm 0.1
	PM B direct	0.13 \pm 0.00	0.5 \pm 0.0	0.21 \pm 0.04	4.5 \pm 0.1
	PM A subsequent	0.12 \pm 0.00	0.9 \pm 0.3	0.18 \pm 0.02	4.7 \pm 0.1
	PM B subsequent	0.12 \pm 0.00	1.1 \pm 0.1	0.24 \pm 0.04	3.4 \pm 0.3

ty assurance of analytical data. 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.

For the determination of element contents in above-ground biomass and spinach roots, an aliquot ($\sim 500 \text{ mg}$ of dry matter) of the plant sample was weighed into a digestion vessel. Concentrated nitric acid (8.0 ml) (Analytika Ltd., Czech Republic), and 30% H_2O_2 (2.0 ml) (Analytika Ltd., Czech Republic) were added, and 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 up to volume with deionized water. Cd, Fe, Pb, and Zn concentrations in the digests were determined by ICP-OES (Varian, VistaPro, Australia).

For determination of mobile portions of elements in soils, three soil extraction procedures were applied as follows:

1. extraction with $2 \text{ mol}\cdot\text{L}^{-1}$ solution of HNO_3 at a ratio of 1:10 (w/v) at 20°C for 6 hours [29]
2. extraction with $0.43 \text{ mol}\cdot\text{L}^{-1}$ solution of CH_3COOH at a ratio of 1:40 (w/v) for 5 hours [19]
3. extraction with $0.01 \text{ mol}\cdot\text{L}^{-1}$ aqueous CaCl_2 solution at a ratio of 1:10 (w/v) for 6 hours [30]

Each extraction was provided in three replicates, all the chemicals used were of analytical grade purity, and were purchased from Analytika and Lach-Ner Ltd., Czech Republic. For centrifuging the extracts, the Hettich Universal 30 RF (Germany) device was used. The reaction mixture was centrifuged at 3,000 rpm (i.e. 460xg) for 10 minutes at the end of each extraction procedure, and supernatants were kept at 6°C prior to measurement. Blank extracts representing 5% of the total number of extracts were prepared using the same batch of reagents and the same apparatus; they were also analyzed at the same time and in the same manner as with the soil extracts. Cd, Fe, Pb,

and Zn concentrations in the digests were determined by ICP-OES (Varian, VistaPro, Australia).

The DGT technique was used to determine the bioavailable portion of metals in soils and PM samples. DGT units (DGT REsearch Ltd., Lancaster, GB) consisted of a Diffusive Gel Disc (0.8 mm) in $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ NaCl}$, a Chelex Gel Disc (0.4 mm) in deionized water (Millipore[®]) and a Tuffryn[®] Membrane Filter (25 mm, $0.45 \mu\text{m}$, Pall Corporation). The DGT units were exposed to the soil for 24 hours, where the units were placed on the surface of the soil portion taken off from the individual pots. The average exposure temperature in soil was $23\pm 4^\circ\text{C}$. After exposure, the chelex gel discs were leached for 48 hours (at 4°C) in 1.5 mL vials containing 1 mL $2 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$ [31]. The total metal content in digests (3-times diluted) was determined by ICP-MS (Elan DRC-e, Perkin-Elmer, Norwalk, CT, USA).

The bioavailable concentration of elements C_b [$\mu\text{g}\cdot\text{L}^{-1}$] is calculated by Zhang et al. [32] as follows:

$$C_b = \frac{M\Delta g}{DtA} \quad (1)$$

...where: M [μg] is the element mass adsorbed on exposure area A [3.14 cm^2] within the time period, t [s], Δg [cm] is the thickness of diffusive layer (0.093 cm), and D [$\text{cm}\cdot\text{s}^{-1}$] is the diffusive coefficient of metal in the gel (www.dgtresearch.com)

M is calculated by Zhang et al. [32]:

$$M = C_e \frac{V_g + V_e}{f_e} \quad (2)$$

C_e is the measured element concentration [$\mu\text{g}\cdot\text{L}^{-1}$] (by ICP-MS) in the $2 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$ elution solution, V_g [L] is the volume of the resin gel (0.15 ml), V_e [L] is the volume of elution solution, and f_e is the elution factor for each metal and elution reagent (typically for $1 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$ $f_e = 0.8$).

Table 3. The mobile portions of elements in soils after harvest; extractable with 0.01 mol·l⁻¹ CaCl₂ (mg·kg⁻¹); n=3, data expressed as mean±standard deviation.

Soil	Treatment	Cd	Fe	Pb	Zn
Fluvisol	control	0.04±0.00	0.08±0.04	0.17±0.02	0.20±0.08
	PM A direct	0.04±0.00	0.02±0.00	0.11±0.03	0.21±0.05
	PM B direct	0.04±0.00	0.02±0.01	0.03±0.00	0.15±0.02
	PM A subsequent	0.05±0.00	0.36±0.00	0.24±0.04	0.15±0.04
	PM B subsequent	0.04±0.00	0.22±0.01	0.13±0.02	0.16±0.01
Chernozem	control	0.03±0.00	0.01±0.01	0.03±0.01	0.05±0.03
	PM A direct	0.03±0.00	0.05±0.00	0.06±0.02	0.03±0.02
	PM B direct	0.03±0.00	0.03±0.01	0.02±0.00	0.01±0.00
	PM A subsequent	0.03±0.00	0.04±0.00	0.13±0.02	0.07±0.03
	PM B subsequent	0.03±0.00	0.02±0.00	0.14±0.00	0.04±0.01

For statistical evaluation of the data, Dixon's test was applied for identification of outliers followed by a two-way Analysis of Variance (ANOVA) at a significance level of $\alpha=0.05$ using the Statistica 2011 version 9.1 program (StatSoft, USA).

Results and Discussion

The Mobility of Risk Elements in Soils

The potentially mobilizable portions of investigated elements, i.e. extractable with 2 mol·L⁻¹ solution of HNO₃, are summarized in Table 2. The nitric acid extractable portions were predominantly affected by soil type and physico-chemical characteristics, whereas the effects of PM physical fraction were negligible. Diluted nitric acid is able to dissolve an element portion comparable to the sum of the labile soil element fractions [29, 33] and, in the case of cadmium, this element portion can be accepted as the approximation of the total element content in soil, especially in anthropogenically contaminated soils. In our case the extractable portions of Cd reached 50%, confirming a dominating geogenic source of soil contamination. The extractable portions of Zn and Pb were comparable to those of Cd, whereas Fe was less extractable, reaching 20% in the case of Fluvisol and 10% in the case of Chernozem. Although the contents of Fe and Zn in PM were significant, the element content in PM-amended soils was not significantly altered. The application of PM to soil 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. In the case of Fluvisol, the extractable element portions remained unchanged after direct PM application, and tended to decrease after the subsequent planting. An opposite pattern was observed in the case of Chernozem, in which the extractable element contents tended to increase after both direct and subsequent planti-

ng. Alloway [34] highlighted a high sorption capacity of soil organic matter, resulting in a low mobility of elements, especially with regards to lead. However, Zehetner et al. [35] proved that traffic-born heavy metals in immediate roadside zones tend to be more mobile than geogenic heavy metals found at greater distances from the road. Contrarily, Li [36] observed higher organic matter content in highway soils, resulting in 3-10 times higher Pb adsorption capacities and limited mobility. Our results suggested an increased sorption capacity of Fluvisol due to the addition of PM characterized by high organic matter content and/or small particle size of this material. In a previous experiment [23], three rural dust samples applied to uncontaminated Luvisol were assessed, and potentially mobilizable portions (0.005 mol·l⁻¹ DTPA extractable) of elements significantly increased (Cd by 116%, Pb by 39%, Zn by 50%) in treated soil, suggesting a possible release of these elements in the future. Evidently, the effect of individual soil physicochemical parameters and PM composition are the determining factors for element mobility in the amended soils.

Diluted acetic acid is characterized as an extractant that releases element fractions specifically sorbed on soil clay minerals. Therefore, this extractant is recommended as a suitable test in predicting changes in element mobility in soil amended by sludge occurring from mining exploitation [37]. In our experiment (Table 3), results confirmed a dominating role by element and/or soil properties on mobile portions released by this extractant. In the case of Cd, no significant differences were found between the element portions extracted with this agent from Fluvisol and Chernozem reaching up to 45% of the total content. Meers et al. [38] documented that few or no differences between acidic and alkaline soils were observed when the more aggressive extractants, such chelate-based (DTPA, EDTA) and acid-based (acetic acid, HCl, HNO₃) procedures, as well as stronger extractions used to estimate exchangeable Cd in soil (ammonium acetate, magnesium chloride), were used. In the case of Zn and Fe, a lower extractability was

Table 4. The plant-available concentrations of elements in soil solution after harvest; determined by using the DGT technique ($\mu\text{g}\cdot\text{l}^{-1}$); $n=3$, data expressed as mean \pm standard deviation.

Soil	Treatment	Cd	Fe	Pb	Zn
Fluvisol	control	0.391 \pm 0.034	92.4 \pm 15.5	0.022 \pm 0.012	21.3 \pm 4.4
	PM A direct	0.604 \pm 0.113	87.2 \pm 3.6	0.010 \pm 0.002	25.6 \pm 3.5
	PM B direct	0.577 \pm 0.095	80.0 \pm 6.8	0.010 \pm 0.002	26.9 \pm 8.6
	PM A subsequent	0.358 \pm 0.079	69.1 \pm 0.7	0.011 \pm 0.002	16.7 \pm 8.2
	PM B subsequent	0.481 \pm 0.059	85.8 \pm 34.5	0.020 \pm 0.014	19.3 \pm 2.9
Chernozem	control	0.028 \pm 0.004	121.3 \pm 36.1	0.030 \pm 0.011	10.3 \pm 2.4
	PM A direct	0.050 \pm 0.008	175.3 \pm 23.4	0.052 \pm 0.010	19.6 \pm 4.1
	PM B direct	0.066 \pm 0.007	100.8 \pm 13.8	0.055 \pm 0.021	23.7 \pm 8.3
	PM A subsequent	0.052 \pm 0.013	68.6 \pm 3.7	0.014 \pm 0.003	15.3 \pm 3.1
	PM B subsequent	0.059 \pm 0.008	78.7 \pm 13.7	0.008 \pm 0.003	16.9 \pm 3.4

reported for Chernozem, reaching 9% of Zn and 0.05% of Fe, whereas the mobile contents of Zn and Fe in Fluvisol represented 35% and 0.1% of the total content. But an opposite trend was evident for Pb, as the extractability of this element in both soils did not exceed 1% of total Pb content. A negligible effect of PM application on acetic acid-extractable portions of Cd, Fe, and Zn was observed. For Pb, the extractable contents tended to increase after subsequent PM applications, especially in the case of Fluvisol, indicating decomposition of the most mobile Pb bound in PM organic matter.

Menzies et al. [21] and Meers et al. [38] confirmed the suitability of neutral salt extractants (0.01 mol \cdot l $^{-1}$ CaCl₂, 0.1 mol \cdot l $^{-1}$ NaNO₃) for the assessment of the available pool of elements in soil. The CaCl₂ soluble contents of elements are summarized in Table 4, which indicates low extractable portions of elements with this extractant and a slight increase in Fe- and Pb-extractable portions after subsequent PM applications. However, the extraction technique using 0.01 mol \cdot l $^{-1}$ CaCl₂ does not reflect the behavior of elements, especially with regards to Pb in soil solution [22, 39]. Different sample pretreatments and/or different mild soil extraction procedures can lead to different absolute values of mobile element content in soils. Therefore, the DGT technique was applied for the assessment of plant-available pools of elements in the soil solution (Table 5). The DGT technique may predict heavy metal rhizosphere concentrations and plant metal uptake better than it could metal concentrations in soil solution [40]. In this case, differences in the behavior of individual elements under various physico-chemical parameters of the investigated soils as well as the influence of roots and root exudates of individual plant species must be taken into account. Theoretically, DGT results should exhibit a depletion of element content in the rhizosphere compared to that of the control pots. However, removal of soil solution elements by plants is balanced by a release of metals bound to solid phase in soil as well as their conversion to exchangeable and plant available forms

due to root exudates [41]. In our case, slightly increasing available element contents were observed after direct PM application compared to control; this was followed by a slight decrease of these concentrations after subsequent planting. The available concentrations of elements in the PM sample itself determined by using the DGT technique were 20.2 \pm 0.1 $\mu\text{l}\cdot\text{l}^{-1}$ of Cd, 8419 \pm 1450 $\mu\text{l}\cdot\text{l}^{-1}$ of Fe, 16721 \pm 3569 $\mu\text{l}\cdot\text{l}^{-1}$ of Zn, and 4.41 \pm 1.08 $\mu\text{l}\cdot\text{l}^{-1}$ of Pb in the case of PM A, and 15.9 \pm 0.5 $\mu\text{l}\cdot\text{l}^{-1}$ of Cd, 7381 \pm 451 $\mu\text{l}\cdot\text{l}^{-1}$ of Fe, 13329 \pm 224 $\mu\text{l}\cdot\text{l}^{-1}$ of Zn, and 3.55 \pm 0.02 $\mu\text{l}\cdot\text{l}^{-1}$ of Pb in the case of PM B. The results confirmed the relatively high mobility of Cd and Zn compared to Fe and Pb [42]. Therefore, an increase in the available Cd and Zn pools after the first vegetation period was expected, as well as a decrease in the mobile pools of all the investigated elements after the second vegetation period, which was most likely due to element depletion from the soil solution after their uptake by plants.

The Contents of Risk Elements in Plant Biomass

The element contents in roots and aboveground biomass of spinach are summarized in Tables 6 and 7, respectively. As in our previous experiments [25], a higher element uptake was observed in plants growing in Fluvisol in comparison to Chernozem with higher sorption capacity and higher total content of organic matter. PM soil amendment did not result in any significant element content increase in vegetables, and in the case of amended Fluvisol, the Cd uptake by plants actually decreased after both direct and subsequent PM applications. Conversely, Cd contents in plants growing in Chernozem tended to increase after the second vegetation period, as did Fe, Pb, and Zn contents in both vegetation periods. The results indicated the effect of changing plant-available element content (Table 5) in which the available element concentrations in soil solution increased after the first vegetation period, being available

Table 5. The elements in spinach roots ($\text{mg}\cdot\text{kg}^{-1}$ of dry matter); $n=3$, data expressed as mean \pm standard deviation.

Soil	Treatment	Cd	Fe	Pb	Zn
Fluvisol	control	0.99 \pm 0.05	361 \pm 2	0.85 \pm 0.12	50.9 \pm 15.1
	PM A direct	0.78 \pm 0.06	866 \pm 105	2.42 \pm 0.51	57.5 \pm 0.6
	PM B direct	0.83 \pm 0.03	492 \pm 10	1.89 \pm 0.50	71.8 \pm 14.0
	PM A subsequent	0.55 \pm 0.23	676 \pm 197	1.62 \pm 0.25	51.0 \pm 7.6
	PM B subsequent	0.87 \pm 0.03	719 \pm 64	2.19 \pm 0.31	65.9 \pm 4.4
Chernozem	control	0.33 \pm 0.07	629 \pm 10	1.34 \pm 0.05	38.6 \pm 2.9
	PM A direct	0.29 \pm 0.03	586 \pm 60	1.16 \pm 0.14	53.6 \pm 8.2
	PM B direct	0.27 \pm 0.01	759 \pm 45	1.15 \pm 0.02	47.4 \pm 3.2
	PM A subsequent	0.34 \pm 0.00	683 \pm 23	1.59 \pm 0.08	60.2 \pm 5.6
	PM B subsequent	0.28 \pm 0.01	507 \pm 37	0.88 \pm 0.00	48.2 \pm 8.3

Table 6. The elements in spinach aboveground biomass ($\text{mg}\cdot\text{kg}^{-1}$ of dry matter); $n=3$, data expressed as mean \pm standard deviation.

Soil	Treatment	Cd	Fe	Pb	Zn
Fluvisol	control	1.20 \pm 0.26	228 \pm 9	0.58 \pm 0.16	72.7 \pm 8.3
	PM A direct	0.86 \pm 0.05	404 \pm 1	1.17 \pm 0.31	62.1 \pm 0.1
	PM B direct	1.10 \pm 0.15	399 \pm 38	1.11 \pm 0.08	91.1 \pm 15.6
	PM A subsequent	0.97 \pm 0.11	347 \pm 26	1.45 \pm 0.09	80.0 \pm 2.7
	PM B subsequent	1.01 \pm 0.02	281 \pm 2	0.86 \pm 0.10	74.1 \pm 5.9
Chernozem	control	0.40 \pm 0.02	350 \pm 4	1.09 \pm 0.34	64.2 \pm 3.7
	PM A direct	0.26 \pm 0.02	335 \pm 72	0.45 \pm 0.01	58.1 \pm 4.5
	PM B direct	0.27 \pm 0.04	298 \pm 59	0.60 \pm 0.04	56.5 \pm 2.6
	PM A subsequent	0.51 \pm 0.04	289 \pm 21	0.72 \pm 0.08	77.3 \pm 0.8
	PM B subsequent	0.40 \pm 0.01	325 \pm 46	0.57 \pm 0.25	67.6 \pm 6.1

for the second vegetation period. The PM physical fraction effect was negligible. Száková et al. [23] assessed the uptake of Cd, Pb, and Zn by aboveground biomass of oat (*Avena sativa* L.) from soil amended by rural PM samples. Although element content in dust samples significantly exceeded the total element content in soil, element content in plants was not affected by single-rate soil amendment. Soil sorption capacity and the neutral pH of the experimental soil (7.0) was sufficient for immobilization of the elements.

Kronemann et al. [43] determined an average dry matter Cd content of $0.12 \text{ mg}\cdot\text{kg}^{-1}$ in spinach leaves growing in uncontaminated soils. Our results exceeded this level with regards to risk elements in leafy vegetables. As given by Anonymous [44] the maximum permissible limit for Pb $0.5 \text{ mg}\cdot\text{kg}^{-1}$, for Cd $0.2 \text{ mg}\cdot\text{kg}^{-1}$, for Fe $50 \text{ mg}\cdot\text{kg}^{-1}$, and for Zn $25 \text{ mg}\cdot\text{kg}^{-1}$ of fresh matter. The average dry matter spinach content was cca 10%. Therefore, fresh matter of spinach had between 22 and $44 \text{ mg}\cdot\text{kg}^{-1}$ of Fe, 0.02 and $0.16 \text{ mg}\cdot\text{kg}^{-1}$

¹ of Cd, 0.02 and $0.15 \text{ mg}\cdot\text{kg}^{-1}$ of Pb, and 5.3 and $10 \text{ mg}\cdot\text{kg}^{-1}$ of Zn. None of the investigated elements in our results reached the maximum permissible limits. Bagdatlioglu et al. [45] found between 13 and $128 \text{ mg}\cdot\text{kg}^{-1}$ of iron, 4 and $14 \text{ mg}\cdot\text{kg}^{-1}$ of zinc, 0.01 and $0.21 \text{ mg}\cdot\text{kg}^{-1}$ of lead, and Cd ranging from pre-detection levels to $0.06 \text{ mg}\cdot\text{kg}^{-1}$ in fresh matter of spinach from local retailers in Manisa, Turkey. Therefore, these results are comparable to our findings.

Conclusions

Summarizing the results, soil contaminated by urban PM did not result in significant changes in risk element mobility and element uptake by spinach plants after either a direct or subsequent application of PM. The addition of PM actually slightly decreased element mobility; this was most probably due to a high total organic matter content in PM. A limited PM-derived risk element effect *via* soil-root

transport was confirmed. The mobility and plant-availability of investigated elements in soils and PM decreased in the following order: Cd > Zn > Pb ≈ Fe. Whereas extractable element content findings in soils using different single soil extraction procedures was ambiguous, the application of the DGT technique suggested increasing element concentrations in PM-amended soil solution after the first vegetation period, in which the potential role of root exudation in element release from soil solid phase can be speculated. The increasing available element concentrations in soil solution after the first vegetation period was followed by an increasing element uptake by plants in the second vegetation period. This suggests the DGT technique's suitability for describing slight changes in soil-soil solution-plant root relationships.

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References

- KABATA-PENDIAS A., PENDIAS H. Trace Elements in Soils and Plants. Third ed. CRC Press, Boca Raton., **2001**.
- VARRICA D., DONGARRÀ G., SABATINO G., MONNA F. Inorganic geochemistry of roadway dust from the metropolitan area of Palermo, Italy. *Environ. Geol.* **44**, 222, **2003**.
- DEBOUDT K., FLAMENT P., BERTHO M.-L. Cd, Cu, Pb and Zn concentrations in atmospheric wet deposition at a coastal station in Western Europe. *Water Air Soil Pollut.* **151**, 335, **2004**.
- 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.* **93**, 203, **2003**.
- JERRETT M., FINKELSTEIN M. Geographies of risk in studies linking chronic air pollution exposure to health outcomes. *J. Toxicol. Environ. Health-Part A.* **68**, 1207, **2005**.
- FINKELSTEIN M.M., JERRETT M., SEARS M.R. Traffic air pollution and mortality rate advancement periods. *Am. J. Epidemiol.* **160**, 173, **2004**.
- HOCHADEL M., HEINRICH J., GEHRING U., MORGENSTERN V., KUHLBUSCH T., LINK E., WICHMANN H.E., KRAMER U. Predicting long-term average concentrations of traffic-related air pollutants using GIS-based information. *Atm. Environ.* **40**, 542, **2006**.
- MORGENSTERN V., CARTY C.L., GEHRING U., CYRYS J., BISCHOF W., HEINRICH J. Lack of spatial variation of endotoxin in ambient particulate matter across a German metropolitan area. *Atm. Environ.* **39**, 6931, **2005**.
- WANG W.H., WONG M.H., LEHARNE S., FISHER B. Fractionation and biotoxicity of heavy metals in urban dusts collected from Hong Kong and London. *Environ. Geochem. Health* **20**, 185, **1998**.
- SERRANO BELLES C., LEHARNE S. Assessing the potential for lead release from road dusts and soils. *Environ. Geochem. Health* **19**, 89, **1997**.
- SHARMA S., PRASAD F.M. Accumulation of Lead and Cadmium in Soil and Vegetable Crops along Major Highways in Agra (India). *E-J. Chem.* **7**, 1174, **2010**.
- AYDINALP C. The status of some selected heavy metals in roadside soils of Bursa province, Turkey. *Environ. Eng. Manag. J.* **9**, 559, **2010**.
- BARRUTIA O., CARRERO J.A., HERNANDEZ A., ARTETXE U., ARANA G., GARCIA-PLAZAOLA J.I., MADARIAGA J.M., BECERRILL J.M. Traffic-Related Trace Metal Accumulation in Soils and Plants in Northern Spain. In: Helmholtz Centre Environmental Research-UFZ, CONSOIL. Theme D - Risks & Impacts, Vols 1 and 2: 391-399, 10th International UFZ-Deltares/TNO Conference on Soil-Water Systems, Milan, June 03-06, **2008**.
- DAO L.G., MORRISON L., ZHANG C.S. Spatial variation of urban soil geochemistry in a roadside sports ground in Galway, Ireland. *Sci. Total. Environ.* **408**, 1076, **2010**.
- KLOS A., RAJFUR M., WACLAWEK M., WACLAWEK W. Impact of roadway particulate matter on deposition of pollutants in the vicinity of main roads. *Environ. Protec. Eng.* **35**, 105, **2009**.
- MENCH M., VANGRONSVELD J., DIDIER V., CLIJSTERS H. Evaluation of Metal Mobility, Plant Availability and Immobilization by Chemical-Agents in a Limed-Silty Soil. *Environ. Pollut.* **86**, 279, **1994**.
- TOKALIOĞLU Ş., KARTAL Ş., BIROL G. Application of a three-stage sequential extraction procedure for the determination of extractable metal contents in highway soils. *Turk. J. Chem.* **27**, 333, **2003**.
- TESSIER A., CAMPBELL P.G.C., BISSON M. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* **51**, 844, **1979**.
- 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. *Intern. J. Environ. Anal. Chem.* **51**, 129, **1993**.
- MORAL R., GILKES R.J., MORENO-CASELLES J. A comparison of extractants for heavy metals in contaminated soils from Spain. *Commun. Soil Sci. Plant Anal.* **33**, 23, **2002**.
- MENZIES N.W., DONN M.J., KOPITTKÉ P.M. Evaluation of extractants for estimation of the phytoavailable trace metals in soils. *Environ Pollut.* **145**, 121, **2007**.
- SZÁKOVÁ J., MIHOLOVÁ D., TLUSTOŠ P., ŠESTÁKOVÁ I., FRKOVÁ Z. Effect of soil properties and sample preparation on extractable and soluble Pb and Cd fractions in soils. *Agric. Sci.* **1**, 119, **2010**.
- SZÁKOVÁ J., SYBALOVÁ J., TLUSTOŠ P. Particular aspects of environmental impact of potentially risk elements from airborne particulate matter *Plant Soil Environ.* **51**, 376, **2005**.
- DE TEMMERMAN L., HOENIG M. Vegetable crops for biomonitoring lead and cadmium deposition *J. Atmos. Chem.* **49**, 121, **2004**.
- ŽALUD P., SZÁKOVÁ J., SYBALOVÁ J., TLUSTOŠ P. The effect of contaminated urban particulate matter on risk element contents in leafy vegetables. *Cent. Eur. J. Biol.* **7**, 519, **2012**.
- ANONYMOUS Public notice No. 13/1994, regulating some details concerning the preservation of agricultural lands available. Czech Ministry of the Environment, Prague. **1994**.
- SYBALOVÁ 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.* **61**, 271, **2007**.

28. SYSALOVÁ J., KUČERA J., KOTLÍK B., HAVRÁNEK V. Quality control materials for the determination of trace elements in airborne particulate matter. *Anal. Bioanal. Chem.* **373**, 195, **2002**.
29. 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.* **42**, 543, **1996**.
30. NOVOZAMSKY J., LEXMOND T. M., HOUBA V. J. G. A single extraction procedure of soil for evaluation of uptake of some heavy metals in plants, *Int. J. Environ. Anal. Chem.* **51**, 47, **1993**.
31. JAKLOVÁ DYTRTOVÁ J., ŠESTÁKOVÁ I., JAKL M., SZÁKOVÁ J., MIHOLOVÁ D., TLUSTOŠ P. The use of differential pulse anodic stripping voltammetry and diffusive gradient in thin films for heavy metals speciation in soil solution. *Cent. Eur. J. Chem.* **6**, 71, **2008**.
32. ZHANG H., DAVISON W., KNIGHT B., MCGRATH S. In situ measurements of solution concentrations and fluxes of trace metals in soils using DGT. *Environ. Sci. Technol.* **32**, 704, **1998**.
33. SZÁKOVÁ J., TLUSTOŠ P., BALÍK J., PAVLÍKOVÁ D., BALÍKOVÁ M. Efficiency of extractants to release As, Cd and Zn from main soil compartments, *Analisis* **28**, 808, **2000**.
34. ALLOWAY B.J. *Heavy Metals in Soils*. Blackie and Son Ltd., Glasgow and London, **1990**.
35. 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.* **198**, 125, **2009**.
36. LI L.Y. Retention capacity and environmental mobility of Pb in soils along highway corridor, *Water Air Soil Pollut.* **170**, 211, **2006**.
37. SASTRE J., HERNÁNDEZ E., RODRÍGUEZ R., ALCOBÉ X., VIDAL M., RAURET G. Use of sorption and extraction tests to predict the dynamics of the interaction of trace elements in agricultural soils contaminated by a mine tailing accident, *Sci. Tot. Environ.*, **329**, 261, **2004**.
38. MEERS E., DU LAING G., UNAMUNO V., RUTTENS A., VANGRONSVELD J., TACK F.M.G., VERLOO M.G. Comparison of cadmium extractability from soils by commonly used single extraction protocols, *Geoderma* **141**, 247, **2007**.
39. SZÁKOVÁ J., TLUSTOŠ P., FRKOVÁ Z., NAJMANOVÁ J., BALÍK J. Effect of soil Sample Treatment on Evaluation of Trace Element (Cu, Fe, Mn, Zn) Mobility in Soils, *Transaction of the Universities of Košice*, 137, **2008**.
40. NOWACK B., KOEHLER S., SCHULIN R. Use of Diffusive Gradients in Thin Films (DGT) in Undisturbed Field Soils. *Environ. Sci. Technol.* **38**, 1133, **2004**.
41. FISCHEROVA Z., SZAKOVA J., PAVLIKOVA D., TLUSTOS P. The application of diffusive gradient technique (DGT) for assessment of changes in Cd, Pb, and Zn mobility in rhizosphere. *Plant Soil Environ.* **51**, 532, **2005**.
42. SYSALOVA J., SZAKOVA J., GOESSLER W., TREMLOVA J. Methodological Study of Extraction Procedures Applied to Urban Particulate Matter. *Centr. Eur. J. Chem.* **9**, 1071, **2011**.
43. KRONEMANN H., ANKE M., GRÜN M., PARTSCHEFELD M. The cadmium concentration of feedstuffs, foodstuffs and of water in the GDR and in an area with nonferrous metal industry. In: Kabata-Pendias A., Pendias H. *Trace elements in soils and plants*. 3rd ed. CRC Press. Boca Raton. pp. 413, **2001**.
44. ANONYMOUS Public notice No. 53/2002 setting maximum levels for certain contaminants in foodstuffs. Ministry of Health of the Czech Republic, Prague. **2002**.
45. BAGDATLIOGLU N., NERGIZ C., ERGONUL P. G. Heavy metal levels in leafy vegetables and some selected fruits. *J. Verbrauch. Lebensm.* **5**, 421, **2010**.

