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Heavy metal accumulation in urban soils and deciduous trees in the City of Bolzano, N Italy

Schwermetallakkumulation in Böden und Laubbäumen der Stadt Bozen, N-Italien

Claudia Dadea, Sara Casagrande Bacchiocchi, Nicoletta La Rocca, Tanja Mimmo, Alessio Russo and Stefan Zerbe

Abstract

*Bioindicators are organisms able to provide indirectly or directly information on the impact of pollutants in the environment. The content of heavy metals or other toxic compounds in these living organisms is of great interest to assess the level of contaminants. Leaves of the most common deciduous trees (*Acer pseudoplatanus *L.,* Betula pendula *Roth,* Carpinus betulus *L.,* Cercis siliquastrum *L.,* Ginkgo biloba *L.,* Liquidambar styraciflua*,* Quercus robur *L. and* Tilia cordata *Miller) and two invasive tree species* Ailanthus altissima *P. Mill. and* Robinia pseudoacacia *L., in the City of Bolzano (southern Alps in Northern Italy), were therefore studied to assess their suitability as bioindicators for the trace elements Cd, Cu, Mn, Pb, and Zn, mainly considered as traffic related elements. Leaves and soil samples were investigated, both from high-density traffic roads and control sites of minor traffic impact, such as parks. Our data reveal that* Betula pendula *has a considerable Zn accumulation potential compared to the other investigated tree species. The maximum value measured for Zn in a* Betula *specimen is 200 mg kg*$^{-1}$ *dry weight. With regard to the soils, considering the geoaccumulation index, most of the analyzed soils belong to the first class, i. e. uncontaminated (*$I_{geo} \le 0$*) for all analyzed elements. Moreover, in several samples collected in high traffic areas, Cu and Zn show values within* $1 < I_{geo} \le 2$ *(moderately contaminated). This allows to hypothesize a traffic-related origin for these elements. For this reason,* B. pendula *can be considered a potential heavy metal accumulator and therefore a good bioindicator for these urban pollutants. Since* B. pendula *is widely distributed in urban areas in Central and Northern Europe, it can be considered a species suitable for a systematic and comparative monitoring network.*

Keywords: *Bioindicators; Biomonitoring; Contaminants; Trace elements; Traffic emission; Urban trees.*

Zusammenfassung

Bioindikatoren sind Organismen, die Informationen über die Auswirkungen von Schadstoffen in der Umwelt direkt oder indirekt bereitstellen. Den Gehalt von Schwermetallen und anderen toxischen Verbindungen in diesen Organismen zu bestimmen, ist von großem Interesse, um die Schadstoffbelastung der Umwelt zu bewerten. Daher wurden Blätter der häufigsten Laubbäume entlang der Straßen in der Stadt Bozen (S-Alpen in Norditalien) untersucht, namentlich von *Acer pseudoplatanus* L., *Ailanthus altissima* P. Mill., *Betula pendula* Roth, *Carpinus betulus* L., *Cercis siliquastrum* L., *Ginkgo biloba* L., *Liquidambar styraciflua*, *Quercus robur* L., *Robinia pseudoacacia* L. und *Tilia cordata* Miller, um deren Eignung als Bioindikatoren für die Spurenelemente Cd, Cu, Mn, Pb und Zn zu bewerten. Blätter und Bodenproben von Straßen mit hoher Verkehrsbelastung wurden mit denen mit geringer Verkehrsbelastung (z. B. Parks) verglichen. Unsere Daten belegen, dass *Betula pendula* ein erhebliches Akkumulationspotenzial von Zn im Vergleich zu den anderen untersuchten Baumarten hat. Der Maximalwert für Zn in einer Blattprobe der Birke beträgt 200 mg kg^{-1} Trockengewicht. Bezüglich des bodenkundlichen *geoaccumulation index* gehören die meisten der untersuchten Böden für alle analysierten Elemente zur ersten Klasse, das heißt „unbelastet“ ($I_{geo} \le 0$). Allerdings weisen Proben von stark verkehrsbelasteten Straßen Cu- und Zn-Werte von $1 < I_{geo} \le 2$, d. h. „mäßig belastet“ auf. Dies lässt auf die Herkunft dieser Elemente aus dem Straßenverkehr schließen. Mit ihrer Eigenschaft Schwermetalle anzureichern, wurde die Birke (*B. pendula*) als ein potenzieller Bioindikator in Städten identifiziert. Da *B. pendula* in Stadtgebieten Mittel- und Nordeuropas weit verbreitet ist, scheint die Art für ein systematisches und vergleichendes Monitoring geeignet zu sein.

Schlüsselwörter: Bioindikatoren; Biomonitoring; Schadstoffe; Spurenelemente; Stadtbäume; Verkehrsemission.

1 Introduction

In urban-industrial areas, pollution originates from both anthropogenic and natural sources. In particular, traffic is the main source of several pollutants (therefore called traffic-related elements, TREs) that can be considered as emerging contaminants (Fujiwara et al. 2011). The most important sources include tailpipes, brake lining, bearings, road surface, corrosion of vehicle components and the resuspension of contaminated soil and road dust. Various studies have dealt with TREs such as Cu, Mo, Pd, Pt, Rh, Sb, Pb, and Zn (Sternbeck et al. 2002, Fujiwara et al. 2011, Calvo et al. 2013, Schiavon et al. 2014).

The information on the content of metals and metalloids in biological matrices can be considered a valuable indicator for environmental pollution. Consequently, bioindication and biomonitoring, respectively, are used as a tool in order to assess various types of environmental mismanagement, including pollution, high-input farming, inappropriate disposal of wastes, contamination, etc. This approach uses the condition and diversity of various organisms, including vertebrates (Beernaert et al. 2008), plants (Serbula et al. 2012) and microorganisms (Käffer et al. 2012, Borruso et al. 2015) as tools to assess natural and/or anthropogenic environmental impact (Samecka-Cymerman et al. 2009, Dmuchowski et al. 2011).

Since the late 1980s, plant species are commonly used for biomonitoring with regard to pollutants in urban-industrial environments (Eriksson et al. 1989). Selected plant species provide information on emission sources, the level (“accumulation bioindicators”) and/or impact (“effect bioindicators”) of pollutants on the environment (Ernst 2003, Remon et al. 2013). For this reason, it is essential to identify bioindicators capable to provide early warning on any change that could result in significant risks to human health and to urban ecosystems (Burger 2006, Pope and Dockery 2006, Remon et al. 2013, Novak et al. 2014). The choice of the right bioindicator is a complex task and may require aspects such as short- to long-term trends as well as element accumulation in leaves (Aničić et al. 2011).

Trees, for example, can be suitable for a long-term monitoring strategy because they are long-living organisms compared to grasses and herbs. Compared to lichens and mosses as bioindicators, trees are advantageous because they are widely distributed in cities as the major plant life-form (Wittig 1993, Pauleit et al. 2002, Nowak et al. 2006). They are continuously exposed to atmospheric pollutants via wet and dry deposition and they can trap or intake contaminants bound to airborne particulate matter or present in the soil through leaves, bark, and through the root system, respectively (Sawidis et al. 2001, Pulford and Watson 2003, Celik et al. 2005, Dmuchowski et al. 2011, Bhargava et al. 2012, Kardel et al. 2012, Ugolini et al. 2013). Moreover, trees are commonly abundant in both urban and rural areas and they often cover a wide geographical range. In addition, sampling, identification and cultivation may be easy and inexpensive (Celik et al. 2005, Samecka-Cimerman et al. 2009). Furthermore, tree species have been studied as potential bioindicators with regard to heavy metal exposure (Aboal et al. 2004, Baycu et al. 2006, Murakami et al. 2012, Samecka–Cimerman et al. 2013, Tomasevic et al. 2011). Several studies indicate that leaves of deciduous trees are useful air pollution biomonitors for trace elements in urban habitats (Monaci et al. 2000, Aksoy and Demirezen 2006, Petrova 2011, Khavanin Zadeh et al. 2013, Petrova et al. 2014). However, the majority of existing studies in Italy focuses on one or on few urban tree species (Monaci et al. 2000, Moreno et al. 2003, Gratani et al. 2008, Francini et al. 2010, De Nicola et al. 2013, Ugolini et al. 2013).

According to Wittig (1993), the criteria for the selection of a species as a biomonitor are (a) presence in large numbers all over the monitoring area, (b) a wide geographical range, (c) ease of differentiation between airborne and soil-borne heavy metals, (d) ease of sampling and (e) no identification problems.

In our study, we focus on the City of Bolzano in the Southern Alps (N Italy) where a comprehensive tree inventory (Città Di Bolzano 2010, see also Russo et al. 2014) and detailed information on air quality are available. Accordingly, the aim was to investigate (1) the amount of heavy metals, which are accumulated in the leaves of the selected tree species and (2) the level of heavy metals in corresponding top soils. Based on our results, we drew conclusions on the biomonitoring with urban trees and, in particular, their different adsorption behavior towards different metals in urban environments.

2 Materials and methods

2.1 Study area

The study area is the City of Bolzano located on 254 m above sea level in the Southern Alps, Northern Italy. The city has an area of about 50 km^2 and a population of around 100,000 inhabitants (Città Di Bolzano 2011). Multi-year climatic data (1983-2013; Provincia Autonoma Di Bolzano 2013) show that the average annual precipitation is about 700 mm, with a max. in July and August (85 mm) and a min. in January and February (20.3 mm). The average annual temperature is 12.3 °C. The coldest month of the year is January with an average temperature of 1.3 °C, the warmest month is July with an average temperature of 23.3 °C. Due to the prevalent mountainous landscape of South Tyrol, economic activities, agriculture (mainly, apple orchards and vineyards) and urbanization are concentrated on the valley floors and, in particular, in and around the City of Bolzano (Piacentini et al. 2012). The particular location of the city, surrounded by mountains up to > 2,500 m a.s.l. and the scarcity of winds, especially during the winter season, avoid the removal of airborne pollutants.

2.2 Plant and soil sampling

Leaves from indigenous and non-native tree species (Celesti-Grapow et al. 2010) together with corresponding top soils (0–10 cm), were collected during summer and early autumn (Aug.–Nov.) in 2012. The sampling sites were chosen considering the traffic emissions as the main source of heavy metals along a gradient representing different levels of contamination. Considering the position of the atmospheric pollution-measure stations of the municipality of Bolzano placed along the main traffic roads, four sampling areas were identified for our study purposes, i.e. 1) medium-low traffic area (max. 5,000 cars per day), 2) medium-high traffic area (5,000–7,500 cars per day), 3) high traffic area (> 10,000 cars per day), and 4) control areas, i.e. mainly parks and cycle paths. Traffic data have been extrapolated from the Urban Mobility Plan (PUM 2010). Indigenous and non-native tree species were selected based on the information of a comprehensive tree inventory of the City of Bolzano (Città Di Bolzano 2010, Russo et al. 2014). The selected tree species were the most dispersed along roads and urban green spaces in the city, i.e. *Acer pseudoplatanus* L., *Betula pendula* Roth, *Carpinus betulus* L., *Cercis siliquastrum* L., *Ginkgo biloba* L., *Liquidambar styraciflua* L., *Quercus robur* L., *Tilia cordata*

Miller and the two invasive tree species *Ailanthus altissima* P. Mill. as well as *Robinia pseudoacacia* L. (Burch et al. 2003, Celesti-Grapow et al. 2010). For each tree species, whenever possible, 10 individuals were chosen along streets with traffic and 10 in the control areas.

A representative sample of leaves (4–5 small branches for each tree) was collected from the crown at about 2 m height. Samples were stored in paper bags, transported to the lab and carefully washed with running tap water first and bi-distilled water in the last rinsing. Then, leaves were oven dried at 50 °C for 72 hours until constant weight.

For each tree stand, top-soil samples were taken with a steel gardening spoon at 0–10 cm depth, taking 3 samples from each site, which were mixed afterwards. Soils were first dried at room temperature and then aggregates were broken with a porcelain pestle and mortar and finally sieved at 2 mm. Both, leaves and soil samples were ground in teflon jars by a Mixer Mill MM 400 (Retsch).

2.3 Elemental analysis

The concentration of main nutrients (Ca, Mg, Na and K) and heavy metals (Pb, Cd, Mn, Cu, Mo, Sb, Zn, Pt, Pd, and Rh as mg per kg dry weight) was determined in all samples after microwave-assisted acid digestion using nitric and hydrochloric acid (1:3 v/v) (methodology according to EPA 3051A 2007) by Inductively Coupled Plasma-Optical Emission Spectrometry with an ICP-OES (methodology according to EPA 6010C 2007) in an accredited laboratory (Laboratorio Analisi Ambientali in Varese, Italy). Following this methodology, a representative sample of 1 g was placed into an inert polymeric microwave digestion vessel with concentrated nitric and hydrochloric acid (respectively 3 and 9 mL). The vessels were sealed and subjected to microwave heating. After cooling, the vessel contents were filtered, transferred into a 25 mL volumetric flask, made up to the volume with deionized water and finally analyzed. In order to assess the accuracy of the digestion and analytical procedures, double samples were inserted as random in each batch. Precision values, related to samples analyzed in duplicate, obtained for Mn, Cu, Pb, and Zn in leaves and soils, were always under 10 %.

2.4 Geoaccumulation index (Igeo)

The heavy metal concentration in the investigated urban soil was calculated using the geoaccumulation index Igeo, a method proposed by Muller (1969). The Igeo is computed using the following equation (Wei et al. 2010):

$$I_{geo} = \log_2 (C_n/1.5B_n)$$

where C_n is the measured concentration of the element in the environment, B_n is its geochemical background value in the soil. The constant 1.5 allows to analyze natural element fluctuations and to detect anthropogenic sources (Wei et al. 2010). In this study, the levels measured in soils collected in a remote control area (n = 3) were assumed as background levels.

According to Muller (1969) and Wei et al. (2010), the I_{geo} value for each metal is classified as uncontaminated ($I_{geo} \leq 0$), uncontaminated to moderately contaminated ($0 < I_{geo} \leq 1$), moderately contaminated ($1 < I_{geo} \leq 2$), moderately to heavily contaminated ($2 < I_{geo} \leq 3$), heavily contaminated ($3 < I_{geo} \leq 4$), heavily to extremely contaminated ($4 < I_{geo} \leq 5$) and extremely contaminated ($I_{geo} \geq 5$).

2.5 Bioaccumulation factor

The bioaccumulation factor (BAF) is defined as the ratio between total metal concentration in leaves and soil and it is computed following the equation:

$$BAF=C_{shoot}/C_{soil}$$

Where C_{shoot} and C_{soil} are respectively the metals concentration in the plant´s shoot (mg kg^{-1}) and soil (mg kg^{-1}).

As highlighted by Ma et al. (2001) and Cluis (2004), BAF values classify plant species respectively as hyperaccumulators and accumulators (BAF > 1 mg kg^{-1}), or excluders (BAF < 1 mg kg^{-1}).

2.6 Statistical analysis

The element concentrations measured in the leaf samples showed non-normal (Shapiro-Wilk test) and non-homogeneous (Levene's test) distributions of the values. To test on the significance of metals' concentration differences among the species and the four sampling areas, i.e. from medium-low to high traffic and control areas, the non-parametric Kruskal-Wallis test was applied. All statistical analyses were carried out with the free software Past 3.01.

3 Results

3.1 Heavy metals in soils

Table 1 shows the mean concentration of the main nutrients in soils. Differences between traffic and control areas are not statistically significant.

The mean metal concentration in high traffic and control areas in the soil samples of the present study are Mn > Zn > Pb > Cu > Sb > Cd (Table 1). The differences between control and high traffic areas, however, are not statistically significant for Mn (398 and 384 mg kg^{-1} dw, in control and traffic areas, respectively), Pb (99 and 105 mg kg^{-1}dw), Sb (2.0 and 2.7 mg kg^{-1}dw) and Cd (0.6 and 0.7 mg kg^{-1}dw). Statistically significant differences (Kruskall-Wallis test, $p < 0.01$) were found for Cu (57 and 104 mg kg^{-1}dw) and Zn (140 and 186 mg kg^{-1}dw).

3.2 Heavy metals in plant leaves and BAF

With regard to the investigated tree species, Mn, Cu, Zn, and Pb concentrations vary considerably between species and among different specimens of the same species. For all leaf samples, the Cd content is always below the detection limit (0.2 mg kg^{-1}dw). The measured values vary between 6.8 and 410 mg kg^{-1} dw for Mn, 3.4 and 32 mg kg^{-1} dw for Cu, 5.0 and 200 mg kg^{-1} dw for Zn, and 0.3 and 14 mg kg^{-1} dw for Pb. The highest concentration of Mn and Zn was found in *Betula pendula*, of Cu in *Cercis siliquastrum* and *Robinia pseudoacacia* and of Pb in *Liquidambar styraciflua* (Tab. 1). Differences in metal contents between species in the high traffic and control areas are significant only for Cu ($p < 0.05$). The majority of the studied species shows a BAF around 0.1.

Tab. 1: Mean metal concentration ± SD (mg kg^{-1} dw) in control areas (n = 38) and in traffic areas (n = 42) in the soil samples (^{a} and ^{b} indicate statistically significant differences, Kruskall-Wallis test, $p < 0.01$). The main nutrient mean values (%) are also reported for Ca, Mg, K and Na.

Tab. 1: *Mittlere Schwermetallkonzentration ± SD (mg kg^{-1} dw) der Bodenproben in der Kontrolle (n = 38) und den Verkehrsstraßen (n = 42); ^{a} und ^{b} indizieren statistisch signifikante Unterschiede, Kruskall-Wallis Test, $p < 0.01$). Für die Nährstoffe Ca, Mg, K und Na sind ebenfalls die Mittelwerte angegeben.*

	Ca	Mg	K	Na	Mn	Cu
Control areas	1.3±0.7^a	0.25±0.04^a	0.14±0.05^a	126±56^a	398±104^a	57±25^a
Traffic areas	1.9±1.2	0.25±0.03^a	0.16±0.06^a	148±82^a	384±125^a	104±124^b

	Zn	Pb	Sb	Cd	Pd	Rh	Mo	Pt
Control areas	140±59^a	99±32^a	2.0±0.6^a	0.6±0.3^a	<5	<5	<5	<5
Traffic areas	186±97^b	105±40^a	2.7±1.5^a	0.7±0.4^a	<5	<5	<5	<5

Tab. 2: Minimum, mean, and maximum concentrations (mg kg^{-1} dw) in the leaves of the studied tree species from traffic streets and from control areas (M_{Co}) in the City of Bolzano. The tree species are *A. pseudoplatanus* (n = 7), *A. altissima* (n = 8), *B. pendula* (n = 12), *C. betulus* (n = 10), *C. siliquastrum* (n = 7), *G. biloba* (n = 9), *L. styraciflua* (n = 9), *Q. robur* (n = 5), *R. pseudoacacia* (n = 7), *T. cordata* (n = 10).

Tab. 2: *Mittlere, Minimal- und Maximal-Konzentrationen (mg kg^{-1} dw) in den Blättern der untersuchten Baumarten an Verkehrsstraßen und den Kontrollen (M_{Co}) der Stadt Bozen; die Baumarten sind A. pseudoplatanus (n = 7), A. altissima (n = 8), B. pendula (n = 12),* C. betulus *(n = 10),* C. siliquastrum *(n = 7),* G. biloba *(n = 9),* L. styraciflua *(n = 9),* Q. robur *(n = 5),* R. pseudoacacia *(n = 7) und* T. cordata *(n = 10).*

Species	Mn				Cu				Zn				Pb			
	Min.	Mean	Max.	M_{co}	Min.	Mean	Max.	M_{co}	Min.	Mean	Max.	M_{co}	Min.	Mean	Max.	M_{co}
A. pseudoplatanus	33	46	66	37	11	16	22	10	20	26	35	20	0.9	2.8	5.9	2.6
A. altissima	6.8	28	58	35	7.6	13	26	13	5.1	14	25	8.3	0.7	2.5	3.9	2.6
B. pendula	29	98	410	71	12	15	19	5.7	50	110	200	99	1.2	2.6	4.7	3.1
C. betulus	27	87	160	99	13	15	18	14	32	45	60	36	1.0	2.2	3.5	3.4
C. siliquastrum	14	26	53	21	8.9	17	32	12	22	40	57	29	1.2	2.6	5.0	2.9
G. biloba	13	16	20	20	3.4	5.4	7.3	5.3	5.0	6.5	8.1	7.3	0.8	2.0	3.5	3.0
L. styraciflua	41	100	170	190	4.7	7.4	11	7.0	36	51	71	50	0.8	4.3	14	6.6
Q. robur	26	73	140	59	6.0	12	18	4.6	24	37	58	36	3.2	3.6	3.8	3.2
R. pseudoacacia	16	52	110	26	8.9	18	32	3.9	11	19	23	23	1.5	1.9	3.1	1.5
T. cordata	22	53	67	40	8.6	11	14	12	14	30	41	24	0.3	2.2	7.2	5.3

4 Discussion

4.1 Soil heavy metal contents

Heavy metal natural contents in soils are highly dependent on the geochemical nature of parent material and are due to the weathering of parent rock material and to the pedogenic processes. Their accumulation is important because they are persistent, non-biodegradable and toxic to the biota, if they exceed threshold values (Massas et al. 2008). In our findings it is interesting to observe (Tab. 1) how Cu, Pb and Zn values are higher in control areas compared to those of the porphyry parents rock (measured in the ranges respectively of 1,9-2,3, 12-16 e 28,2-64,1 mg kg^{-1}, Fuganti et al. 2005) and increase by almost two orders of magnitude in traffic areas. Furthermore, Cu, Zn, and Pb levels in the Bolzano's soils, both in high traffic and in control areas, show an overall enrichment in comparison with other unpolluted soils (Kabata-Pendias 2001, Tab. 3) and are similar to those of small-sized cities (Manta et al. 2002). In addition, the statistically significant differences ($p < 0.01$) in Cu and Zn in the control and high-traffic areas, also suggest an anthropogenic origin for these elements.

Tab. 3: Concentration (mg kg^{-1} dw) range of heavy metals in unpolluted and urban soils according to the literature.

Tab. 3: *Literaturdaten zur Konzentration (mg kg^{-1} dw) von Schwermetallen in nicht verunreinigten und urbanen Böden.*

	Mn	Cu	Zn	Pb	Sb	Cd
Unpolluted soils[1]	270–525[2]	25	70	50	-	0.5
Urban soils[2]	286–1.999	16–47	58–516	53–800	-	0.3–2.2

[1] Kabata-Pendias 2001; [2] Manta et al. 2002.

Tab. 4: Average metal contents (mg kg^{-1} dw) from literature for the studied tree species in urban areas (Publ.) compared to the observed data (Obs.).

Tab. 4: *Durchschnittliche Metallkonzentrationen (mg kg^{-1} dw) der untersuchten Baumarten in Städten nach Literaturangaben, verglichen mit den Werten der vorliegenden Untersuchung.*

	Mn		Cu		Zn		Pb		
Species	**Publ.**	**Obs.**	**Publ.**	**Obs.**	**Publ.**	**Obs.**	**Publ.**	**Obs.**	**Reference**
A. pseudoplatanus	107[7]–211[7]	33–66	3.8[1]–5.1[7]	11–22	15[3]–65[7]	20–35	3.6[3]–21[3]	0.9–5.9	1. Aboal et al.. 2004; 2. Anicic et al.. 2011; 3. Baycu et al. 2006; 4. Celik et al.. 2005; 5. Dmuchowski et al. 2011; 6. Hashemi. 2012; 7. Simon et al.. 2011; 8. Tomasevic et al. 2011
A. altissima	n.k.	6.8–58	n.k.	7.6–26	8.9[3]–42[3]	5.1–25	2.6[3]–19[3]	0.7–3.9	
B. pendula	36[8]–72[8]	29–410	6.0[8]–8.4[8]	12–19	32[8]–64[8]	50–200	1.7[5]–41[5]	1.2–4.7	
Q. robur	n.k.	26–140	3.03[1]–11[1]	6.0–18	4.7[1]–18[1]	24–58	0.05[1]–0.45[1]	3.2–3.8	
R. pseudoacacia	43[4]–229[4]	16–110	5.3[4]–10[4]	8.9–32	12[4]–53[4]	11–23	1.2[3]–34[3]	1.5–3.1	
T. cordata	20[8]–82[8]	22–67	6.4[2]–52[2]	8.6–14	13[2]–35[2]	14–41	1.6[8]–12[2]	0.3–7.2	

Considering the scale of Muller (1969), and Wei et al. (2010) and the traffic levels in the urban area of Bolzano, most of the analyzed soils belong to the first class, i. e. uncontaminated ($I_{geo} \leq 0$), for all analyzed elements.

Regarding Mn, the homogenous values, both in polluted and in traffic areas and the I_{geo} values always < 0, allow hypothesizing a relation to the natural background level of the area. On the contrary, Cu and Zn values vary significantly in traffic and control areas and show in several samples collected in high traffic areas values within $1 < I_{geo} \leq 2$ (moderately contaminated), thus pointing to a traffic-related origin for these elements. Zinc, in particular, is a distinguishing elemental marker of tire wear (Kwak et al. 2014) and Cu of brakes (Thorpe and Harrison 2008). Indeed, traffic bound dust particles are produced and continuously emitted and accumulate in the organic matter of the roadside soils that acts as the first target matrix.

4.2 Leaves heavy metal contents

To distinguish between the foliar contamination caused by airborne particles and that caused by soluble metals absorbed through the root system, collected leaf samples were carefully washed before analysis. Several studies reported that the washing of fresh leaves removed only a minor part of surface contaminants (Kozlo et al. 2000) and that Ca, Na, Cu, and Mn concentrations were not changed by washing and that P, Mg and K were lost from leaves by leaching with severe washing (Wallace et al. 1980). However, differences between the washed and unwashed samples reflect, respectively, airborne and soil entry routes, and vary according to the metal pollutant (Aksoy et al. 1999). High concentrations of some heavy metals were determined in the unwashed plant samples as a result of exposure to aerosols (Kos et al. 1996).

The mean metal contents in the leaves of the investigated urban trees do not exceed, in general, those considered as toxic for sensitive plants as stated by Kabata-Pendias (2001) which is for Mn > 1000 mg kg^{-1} dw, for Cu 15-20 mg kg^{-1} dw, for Zn 150–200 mg kg^{-1} dw, for Pb 30–300 mg kg^{-1} dw and for Cd 5–10 mg kg^{-1} dw. For all the analyzed species, the mean Pb content is around 3 mg kg^{-1} dw, which is considered the normal natural level for plants (Allen 1989). For the species *R. pseudoacacia*, *B. pendula*, *T. cordata* and *A. pseudoplatanus*, the average metal contents are similar, or even higher, compared to those documented in other urban areas (Tab. 4, Celik et al. 2005, Baycu et al. 2006, Anicic et al. 2011, Tomasevic et al. 2011).

There are some analogies between the urban trees metal contents detected in our study and the one stated for the same species in other studies. The Cu content of *R. pseudoacacia* leaves, for example, is higher respect to those reported by Celik et al. (2005), measured in washed leaves coming from an industrial and trade center in Turkey (Tab. 4). Regarding the Zn concentrations, measured values range are close to the data reported for the same species by Sawidis et al. (2001). Moreover, the Zn range measured in *T. cordata* leaves is close to that stated by Anicic et al. (2001). Zn and Cu contents of *Q. robur* leaves in rural areas in Spain (Aboal et al. 2004) are lower than those found for oak in the urban area of Bolzano. Therefore, according to our results, it can generally be stated that the Bolzano's traffic areas are affected by the exhaust emissions as they contain considerable loads of heavy metals.

An accumulation of Zn in leaves of *B. pendula* was detected. Consequently, *B. pendula* leaves accumulate Zn at least twice as high as the other species and in the traffic areas the average concentration is 110 mg kg^{-1} dw. Moreover, the range measured in the urban area of Bolzano varies from 50 to 200 mg kg^{-1} dw and it is significantly higher than those values measured in the urban area of Belgrade with 32–64 mg kg^{-1} dw (Tomasevic et al. 2011). The maximum value measured for Zn in a *Betula* specimen is 200 mg kg^{-1} dw, which is close to the threshold limit for toxic effects on plants (Kabata-Pendias 2000). Compared to the other species, *L. styraciflua* seems to be more efficient in Mn accumulation both in high traffic and in control areas and shows mean concentrations of 100 and 190 mg kg^{-1} dw, respectively. However, due to the lack of studies on heavy metal contents with regard to *L. styraciflua,* we cannot compare our findings with other results.

In this paper, the total metal content in leaf samples was measured without considering specific mechanisms employed for specific metals in tree species. These include mechanisms that reduce uptake into the cytosol by entrapment in the apoplastic space, chelation of metals in the cytosol by a range of ligands or efflux from the cytosol, either into the apoplast or into the vacuole. It is also possible that more than one mechanism may be involved in reducing the toxicity of a particular metal (Hall, 2002).

4.3 Sampling site effect

There was no significant relationship between the heavy metal concentration in the surface soil (depth 0–10 cm) and the washed leaves ($p > 0.05$). In general, our results show that the heavy metal contents vary between and within the tree species, despite not being strictly subjected to toxic levels of metals. We found an overall variability of metal accumulation between species and even between individuals of the same species growing in the same sampling site. The total metal content in leaves appears to be significantly related to the different sampling sites, which are parks, medium-low traffic area, medium-high traffic area, and high-traffic area. Moreover, for several specimens, we do not consider the influence of high traffic in different urban areas a key factor for the total metal content in leaves. In addition, our control samples showed a considerable leaf load with the elements compared to the high-traffic urban sites. This corresponds to findings from Tomasevic et al. (2011), who found a considerable amount of air pollutants also in city parks. In fact, it is not easy to distinguish two main pathways responsible for the element enrichment in trees. Possible ways could be the atmospheric deposition of particles on vegetation and thus a foliar uptake contamination and/or the uptake via roots from the soil.

4.4 Bioaccumulation factor (BAF)

BAF values obtained e. g. for Zn and Cu in *A. pseudoplatanus* specimens are similar to those derived for the same species by André et al. (2006). As stated for *Acer* and other species, obtained BAF´s values can confirm a high phytostabilisation potential and a low phytoextraction potential regarding heavy metals in soils. In contrast, the largest BAF values are found in *B. pendula* (1.8 for Zn and 2.2 for Mn) and correspond to individuals located both in polluted as well as in control areas. Moreover, the highest BAF values are not related to the highest metal levels in soils. In fact, as stated by Mertens et al. (2005), the metal extraction ratio decreases with increasing soil metal concentrations. Gu et al. (2007) also concluded that increased values of Cd concentrations in soils correspond to the decrease of the Cd uptake by *Populus* cultivars.

5 Conclusions

The data presented in this study reveal that the species *Betula pendula* has a Zn accumulation potential compared to other tree species when growing in urban areas. Our results also suggest that the species are in general highly variable in terms of metal accumulation characteristics. Our results can be a useful starting point for further biomonitoring in the City of Bolzano and they could be used as a preliminary reference set for the evaluation of future trends and fate of pollutants. Because the data are related to species frequently used in an urban context, they can be also relevant to create a species list in order to support urban tree planners to select tree species tolerant to pollution in urban areas.

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References

Aboal, J.R., Fernández, J.A., Carballeira, A. (2004): Oak leaves and pine needles as biomonitors of airborne trace elements pollution. Environmental and Experimental Botany **51**: 215-225.

Aksoy, A., Haleb, W.H.G., Dixon, J.M. (1999): *Capsella bursa-pastoris* (L.) Medic. as a biomonitor of heavy metals. Science of the Total Environment **226** (2-3): 177-186.

Aksoy, A., Demirezen, D. (2006): *Fraxinus excelsior* as a Biomonitor of Heavy Metal Pollution. Polish Journal of Environmental Studies **15** (1): 27-33.

Allen, S.E. (1989): Chemical Analysis of Ecological Materials (2nd edn.). Blackwell Scientific, Oxford.

Andre´, O., Vollenweider, P.S., Günthardt-Goerg, M. (2006): Foliar response to heavy metals in Sycamore Maple (*Acer pseudoplatanus* L.). Forest Snow and Landscape Research **80** (3): 275-288.

Aničić, M., Spasić, T., Tomašević, M., Rajšić, S., Tasić, M. (2011): Trace elements accumulation and temporal trends in leaves of urban deciduous trees (*Aesculus hippocastanum* and *Tilia* spp.). Ecological Indicators **11**: 824-830.

Beernaert, J., Scheirs, J., Van Den Brande, G., Leirs, H., Blust, R., De Meulenaer, B., Van Camp, J., Verhagen, R. (2008): Do wood mice (*Apodemus sylvaticus* L.) use food selection as a means to reduce heavy metal intake? Environmental Pollution **151**: 599-607.

Bhargava, A., Carmona, F.F., Bhargava, M., Srivastava, S. (2012): Approaches for enhanced phytoextraction of heavy metals. Journal of Environmental Management **105**: 103-120.

Baycu, G., Tolunay, D., Özden, H., Günebakan, S. (2006): Ecophysiological and seasonal variations in Cd, Pb, Zn, and Ni concentrations in the leaves of urban deciduous trees in Istanbul. Environmental Pollution **143**: 545-554.

Borruso, L., Zerbe, S., Brusetti, L. (2015): Bacterial community structures as a diagnostic tool for watershed quality assessment. Research in Microbiology **166**: 38-44.

Burger, J. (2006): Bioindicators: A Review of Their Use in the Environmental Literature 1970–2005. Environmental Bioindicators **1** (2): 136-144.

Burch, P.L., Zedaker, S.M. (2003): Removing the invasive tree *Ailanthus altissima* and restoring natural cover. Journal of Arboriculture **29** (1): 18-24.

Calvo, A.I., Alves, C., Castro, A., Pont, V., Vicente, A.M., Fraile, R. (2013): Research on aerosol sources and chemical composition: Past, current and emerging issues. Atmospheric Research **120**: 1-28.

Celesti-Grapow, L., Pretto, F., Carli, E., Blasi, C. (2010): Flora vascolare alloctona e invasiva delle regioni d'Italia. Sapienza University, Rome, ISBN: ISBN 978-88-95814-33-9.

Çelik, A., Kartal, A.A., Akdoğan, A., Kafka, Y. (2005): Determining the heavy metal pollution in Denizli (Turkey) by using *Robinio pseudo-acacia* L.. Environment International **31** (1): 105-112.

Città Di Bolzano (2010): Catasto degli alberi. Servizio Giardineria Comunale. Ufficio Tutela dell'Ambiente e del Territorio.

Città Di Bolzano (2011): Censimento della popolazione 2011. Retrieved July 26th 2014 from http://www.comune.bolzano.it/context.jsp?area=154&ID_LINK=3980.

Cluis, C., (2004): Junk-greedy greens: phytoremediation as a new option for soil decontamination. Biotechnology Journal **2**: 60-67.

Dmuchowski, W., Gozdowski, D., Baczewska, A.H. (2011): Comparison of four bioindication methods for assessing the degree of environmental lead and cadmium pollution. Journal of Hazardous Materials **197**: 109-118.

De Nicola, F., Spagnuolo, V., Baldantoni, D., Sessa, L., Alfani, A., Bargagli, R., Monaci, F., Terracciano, S., Giordano, S. (2013): Improved biomonitoring of airborne contaminants by combined use of holm oak leaves and epiphytic moss. Chemosphere **92** (9):1224-30.

Ernst, W.H.O. (2003): The use of higher plants as bioindicators. In: Markert, B.A., Breure, A.M., and Zechmeister, H.G., (Eds.). Bioindicators and biomonitors: Principles, concepts and applications **6**: 423-463.

Eriksson, G., Jensen, S., Kylin, H., Strachan, W. (1989): The pine needle as a monitor of atmospheric pollution. Nature **341**: 42-44.

Francini, A., Lorenzini, G., Nali, C., Loppi, S. (2010): Leaves of *Quercus ilex* as indicators of airborne trace element distribution in Lucca (Central Italy). Acta Horticulturae **881**: 531-534.

Fuganti, A., Morteani, G., Bazzoli, G., Cocco, S., Santuliana, E., Visintainer, M. (2005): L'arsenico nelle rocce, nelle acque superficiali e nelle acque sotterranee della Valle dell'Adige fra Mezzolombardo e Mattarello e presso Roveré della Luna (Trento). Atti della accademia roveretana degli agiati. Classe di scienze matematiche, fisiche e naturali **5**: 59-94.

Fujiwara, F., Jiménez Rebagliati, R., Dawidowski, L., Gómez, D., Polla, G., Pereyra, V., Smichowski, P. (2011): Spatial and chemical patterns of size fractionated road dust collected in a megacity. Atmospheric Environment **45** (8): 1497-1505.

Gratani, L., Crescente, M.F., Varone, L. (2008): Long-term monitoring of metal pollution by urban trees. Atmospheric Environment **42**: 8273-8277.

Gu, J., Qi, L., Jiang, W., Liu, D. (2007): Cadmium accumulation and its effects on growth and gas exchange in for Populus cultivars. Acta Biologica Cracoviensia Series Bot. **49** (2): 7-14.

Hall, J.L. (2002): Cellular mechanisms for heavy metal detoxification and tolerance. Journal of Experimental Botany **53**(366): 1-11.

Kabata-Pendias, A. (2001): Trace Elements in Soils and Plants, Third Edition. CRC Press: 432 p.

Käffer, M.I., Lemos, A.T., Apel, M.A., Vaz Rocha, J., De Azevedo Martins, S.M., Ferrão Vargas, V.M. (2012): Use of bioindicators to evaluate air quality and genotoxic compounds in an urban environment in Southern Brazil. Environmental Pollution **163**: 24-31.

Kardel, F., Wuyts, K., Babanezhad, M., Wuytack, T., Adriaenssens, S., Samson, R. (2012): Tree leaf wettability as passive bio-indicator of urban habitat quality. Environmental and Experimental Botany **75**: 277-285.

Khavanin Zadeh, A.R., Veroustraete, F., Buytaert, J.A.N., Dirckx, J., Samson, R. (2013): Assessing urban habitat quality using spectral characteristics of *Tilia* leaves. Environmental Pollution **178**: 7-14.

Kozlo, M.V., Haukioja, E., Bakthiarov, A.V., Stroganov, D.N., Zimina, S.N. (2000): Root versus canopy uptake of heavy metals by birch in an industrially polluted area: contrasting behavior of nickel and copper. Environmental Pollution **107** (3): 413-420.

Kos, V., Budic, B., Hudnik, V., Lobnik, F., Zupan, M. (1996): Determination of heavy metal concentrations in plants exposed to different degrees of pollution using ICP-AES. Fresenius' Journal of Analytical Chemistry **354** (5): 648-652.

Kwak, J., Lee, S., Lee, S. (2014): On-road and laboratory investigations on non-exhaust ultrafine particles from the interaction between the tire and road pavement under braking conditions. Atmospheric Environment **97**: 195–205.

Ma, L.Q., Komar, K.M, Tu, C., Zhang, W., Cai, Y., Kenelly, E.D. (2001): A fern that hyperaccumulates arsenic. Nature **409**: 579-582.

Manta, D.S., Angelone, M., Bellanca, A., Neri, R., Sprovieri, M. (2002): Heavy metals in urban soils: a case study from the city of Palermo (Sicily), Italy. Science of the Total Environment **300** (1-3): 229-243.

Massas, I., Ehaliotis, S., Gerontids, S., Sarris, E. (2009): Elevated Heavy Metal Concentrations in Top Soils of an Aegean Islan Town (Greece): Total and Available Forms, Origin and Distribution. Environmental Monitoring and Assessment, **151**: 105-116.

Mertens, J., Luyssaert, S., Verheyn, K. (2005): Use and abuse of trace metal concentrations in plants tissue for biomonitoring and phytoextraction. Environmental Pollution **138**: 1-4.

Monaci, F., Moni, F., Lanciotti, E., Grechi, D., Bargagli, R. (2000): Biomonitoring of airborne metals in urban environments: new tracers of vehicle emission, in place of lead. Environmental Pollution **107** (3), 321-327.

Moreno, E., Sagnotti, L., Dinarès-Turell, J., Winkler, A., Cascella, A. (2003): Biomonitoring of traffic air pollution in Rome using magnetic properties of tree leaves. Atmospheric Environment **37** (21): 2967-2977.

Muller, G. (1969): Index of geo-accumulation in sediments of the Rhine River. Geojournal **2**: 108-118.

MURAKAMI, M., ABE, M., KAKUMOTO, Y., KAWANO, H., FUKASAWA, H., SAHA, M., TAKADA, H. (2012): Evaluation of ginkgo as a biomonitor of airborne polycyclic aromatic hydrocarbons. Atmospheric Environment **54**: 9-17.

NOWAK, D.J., CRANE, D.E., STEVENS, J.C. (2006): Air pollution removal by urban trees and shrubs in the United States. Urban Forestry and Urban Greening **4**: 115-123.

PAULEIT, S., JONES, N., GARCIA-MARTIN, G., GARCIA-VALDECANTOS, J.L., RIVIERE, L.M., VIDAL-BEAUDET, L., RANDRUP, T.B. (2002): Tree establishment practice in towns and cities – Results from a European survey. Urban Forestry & Urban Greening **1** (2): 83-96.

PETROVA, S. (2011): Biomonitoring Study of Air Pollution with *Betula pendula* Roth., from Plovdiv, Bulgaria. Ecologia Balkanica **3** (1): 1-10.

PETROVA, S., YURUKOVA, L., VELCHEVA, I. (2014): Possibilities of using deciduous tree species in trace element biomonitoring in an urban area (Plovdiv, Bulgaria) Atmospheric Pollution Research **5**: 196-202.

PIACENTINI, D., TROIANI, F., SOLDATI, M., NOTARNICOLA, C., SAVELLI, D., SCHNEIDERBAUER, S., STRADA, C. (2012): Statistical analysis for assessing shallow-landslide susceptibility in South Tyrol (south-eastern Alps, Italy). Geomorphology **151–152**: 196-206.

POPE III, C.A., DOCKERY, D.W. (2006): Health Effects of Fine Particulate Air Pollution: Lines that Connect. Journal of the Air & Waste Management Association **56** (6): 709-742.

PROVINCIA AUTONOMA DI BOLZANO (2013): Servizio meteorologico della Provincia Autonoma di Bolzano. Dati storici. Retrieved April 18th, 2014 from: http://www.provincia.bz.it/meteo/dati-storici.asp.

PULFORD, I.D., WATSON, C. (2003): Phytoremediation of heavy metal-contaminated land by trees-a review. Environment International **29** (4): 529-540.

PUM (2010): Piano Urbano della Mobilità 2020. Assessorato alla Mobilita´. Comune di Bolzano. Retrieved February 13th, 2014 from http://www.comune.bolzano.it/UploadDocs/7494_PUM2020.pdf.

REMON, E., BOUCHARDON, J.-L., LE GUÉDARD, M., BESSOULE J.-J., CONORD, C., FAURE, O., (2013): Are plants useful as accumulation indicators of metal bioavailability? Environmental Pollution **175**: 1-7.

RUSSO, A., ESCOBEDO, F., TIMILSINA, N., SCHMITT, A.O., VARELA, S., ZERBE, S. (2014): Assessing urban tree carbon storage and sequestration in Bolzano, Italy. International Journal of Biodiversity Science, Ecosystem Services & Management **10** (1): 54-70.

SAMECKA-CYMERMAN, A., STANKIEWICZ, A., KOLON, K., KEMPERS, A.J. (2009): Self-organizing feature map (neural networks) as a tool to select the best indicator of road traffic pollution (soil, leaves or bark of *Robinia pseudoacacia* L.). Environmental Pollution **157**: 2061-2065.

SAWIDIS, T., CHETTRI, M.K., PAPAIOANNOU, A., ZACHARIADIS, G., STRATIS, J. (2001): A study of metal distribution from lignite fuels using trees as biological monitors. Ecotoxicology and Environmental Safety **48**: 27-35.

SCHIAVON, M., ANTONACCI, G., RADA, E.C., RAGAZZI, M., ZARDI, D. (2014): Modeling human exposure to air pollutants in an urban area. Revista de Chimie, **6** (1): 61-64.

SERBULA, S.M., MILJKOVIC, D.D.J., KOVACEVIC, R.M., ILIC, A.A. (2012): Assessment of airborne heavy metal pollution using plant parts and topsoil. Ecotoxicology and Environmental Safety **76**: 209-214.

STERNBECK, J., SJODIN, A., ANDREASSON, K. (2002): Metal emissions from road traffic and the influence of resuspension – results from two tunnel studies. Atmospheric Environment **36**: 4735-4744.

THORPE, A., HARRISON, R.M. (2008): Sources and properties of non-exhaust particulate matter from road traffic: A review. Science of the Total Environment, **400** (1-3): 270-282.

TOMAŠEVIĆ, M., ANIČIĆ, M., JOVANOVIC, L., PERIC-GRUJIC, A., RISTIĆ, M. (2011): Deciduous tree leaves in trace elements biomonitoring: A contribution to methodology. Ecological Indicators **11** (6): 1689-1695.

UGOLINI, F., TOGNETTI, R., RASCHI, A., BACCI, L. (2013): *Quercus ilex* L. as bioaccumulator for heavy metals in urban areas: Effectiveness of leaf washing with distilled water and considerations on the trees distance from traffic. Urban Forestry & Urban Greening **12** (4): 576-584.

WALLACE, A., KINNEAR, J., CHA, J.W., ROMNEY, E.M. (1980): Effect of washing procedures on mineral analyses and their cluster analyses for orange leaves. Journal of Plant Nutrition **2** (1-2): 1-9.

WEI, B., YANG, L. (2010): A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China. Microchemical Journal **94**: 99-107.

WITTIG, R. (1993): General aspects of biomonitoring heavy metals by plants. In: Plants as biomonitors: indicators for heavy metals in the terrestrial environment. (Ed.): B. Markert Weinheim VCH Publisher, pp. 3-28.

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Addresses of the authors:

Dr. Claudia Dadea, Sara Casagrande Bacchiocchi*,
Prof. Dr. Tanja Mimmo, Prof. Dr. Stefan Zerbe
Faculty of Science and Technology,
Free University of Bozen-Bolzano
Piazza Università 5
39100 Bolzano, Italy

Prof. Dr. Nicoletta La Rocca,
Department of Biology
University of Padova
Via U. Bassi 58/b
35131, Padova, Italy

Dr. Alessio Russo
Laboratory of Urban and Landscape Design, School of Arts, Culture and Sports
Far Eastern Federal University
690922 Vladivostok, Russia

* Corresponding author: Sara Casagrande Bacchiocchi