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ORIGINAL PAPER

Metals in pine needles: characterisation of bio-indicators depending on species

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Abstract

Air pollution can be studied by appropriate bio-indicators, such as pine needles due to their waxy surface. Metal uptake and accumulation is determined on growing area, but also on the respective species. Scope of the study was to analyse needles of *Pinus densiflora* Siebold et Zucc., *Pinus nigra* Arnold, *Pinus sylvestris* L., and *Pinus thunbergiana* Franco for metals and metalloids, namely aluminium, arsenic, boron, barium, calcium, cadmium, cobalt, copper, chromium, iron, potassium, lithium, magnesium, manganese, molybdenum, sodium, nickel, lead, selenium, strontium, and zinc. Quantitation of the analytes was performed using inductively coupled plasma atomic emission spectrometry and inductively coupled plasma sector field mass spectrometry after acidic microwave-assisted digestion. The obtained data were checked for statistically significant differences. The metal levels differ between the various species, but no general tendency was found for all metals. Since the environmental conditions were the same for all sampled trees, the differences in metal accumulation are supposed to be linked to species of pine tree. The diverse accumulation behaviour can be used for treating polluted soil.

Keywords Bio-monitoring · Metal content · Pine species · *Pinus nigra* · *Pinus thunbergiana* · *Pinus densiflora* · *Pinus sylvestris*

Introduction

Since metals, especially heavy metals, are persistent in the environment, they have become a serious problem during the last decades due to anthropological pollution. Negative impact on the soil microflora along with influence on ground water is a consequence of concern. Furthermore, harmful effects on humans and animals can be subsequently caused due to accumulation of potentially toxic elements, such as lead, in the food chain. Elevated metal levels are found not only in industrial or urban zones, but also in remote areas. Thus, an increasing number of automobiles have been found to have caused higher concentrations of lead, platinum and palladium in the environment, e.g. air and soil (Heinze et al. 1998; Záray et al. 2004).

Metal entry into plants can occur on the one hand by root uptake from soil and on the other hand by precipitation including wet and dry deposition. Thus, plant material is widely used for monitoring environmental pollution with dependency on time and place. Holoubek et al. (2000) state that pine needles are good bio-monitors of air pollutants due to their waxy surfaces offering the possibility to accumulate lipophilic gaseous pollutants as well as particulate matter.

Metals are furthermore important for plants' physiology. Problems caused by deficiency of certain elements are of concern for agricultural crops (Steinnes 2011). These elements are essential for plants, since they act as structural components in carbohydrates and proteins, as enzyme activators—like potassium, are involved in normal metabolism—such as magnesium in chlorophyll and phosphorus in adenosine triphosphate (ATP), and for ensuring osmotic balance (Soetan et al. 2010). Potassium plays a critical role in stress response of plants (for review, see Wang et al.

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2013), and Ca is an essential part of plants' cell wall and membranes (Hepler 2005). Since Mg is a part of chlorophyll, it is essential for photosynthesis and therefore plants' growth. Fe in plants is necessary for chlorophyll synthesis and regulation of photosynthesis. The most widespread microelement deficiency for plants is related to insufficient Zn supply, resulting in stunted growth, chlorosis and smaller leaves, spikelet sterility (Hafeez et al. 2013). Cu has a major role in root metabolism in plants (Tsui 1955). It is reported that Ni induces maximal growth of wheat shoots and roots at a concentration of 100 mg/kg. Conversely, some metals, such as Cd and Pb, exhibit harmful effects even in very low concentrations, whilst others show neither beneficial nor negative effects.

Apart from growing area (Lehndorff and Schwark 2010), determined by soil composition as well as pollution impact (Serbula et al. 2013), the needle metal concentrations depend on climatic conditions and age of the tree (Varnagiryte-Kabasinskiene et al. 2014). Also hybridisation leads to variances in the accumulation behaviour (Juranović-Cindrić et al. 2018). Furthermore, the pine trees themselves influence the soil properties, especially its acidity which has an impact on the bioavailability of manganese and iron for the root system (Parzych et al. 2017).

Conifer needles are considered worldwide as passive samplers of organic (Herceg Romanić and Krauthacker 2007) as well as of inorganic pollutants in air quality monitoring (Bertolotti and Gialanella 2014), even if they seem less efficient than mosses (Čeburnis and Steinnes 2000). Different working groups in Europe and Asia (Yilmaz and Zengin 2004; Sardans and Peñuelas 2005; Tausz et al. 2005; Al-Alawi and Mandiwana 2007; Lehndorff and Schwark 2010; Sun et al. 2010; Pietrzykowski et al. 2014; Skonieczna et al. 2014; Dmuchowski et al. 2018) have studied heavy metal concentrations in pine needles from different species for assessment investigations. Their results vary over a wide range. Due to different sampling sites, further evaluation of influence of species on the metal accumulation cannot be performed.

The present study is focused on twenty-one metals and metalloids, namely Al, As, B, Ba, Ca, Cd, Co, Cu, Cr, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Se, Sr, and Zn. These elements were determined in 1-year-old needles of different pine species, whereby all trees are growing at the same place in order to avoid influence by mother rock background and climatic conditions. The applied analytical procedure consists of acidic microwave-assisted sample digestion followed by two different multi-elemental analytical methods to cover the concentration ranges of ultra-trace as well as major elements. Inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) were used for quantification of the analytes.

Sampling was carried out in summer 2012 at the Lisičine Arboretum, Croatia. Sample preparation was performed at the University of Zagreb in 2012 and 2013. Measurements took place at the University of Zagreb and the University of Natural Resources and Life Sciences in Vienna in 2013. Data evaluation was started in 2013 at the University of Zagreb and the University of Natural Resources and Life Sciences in Vienna and finished in 2018 at Örebro University.

Materials and methods

Glassware and chemicals

Nitric acid (HNO_3) and hydrochloric acid (HCl), both of p.a. quality, were supplied by Merck (Germany).

Calibration standards were prepared by diluting the multi-element standard (ICP Multielement Standard IV; 1000 mg/L) from Merck (Germany) in the concentration ranges from 0.05 to 5.0 mg/L for ICP-AES and from 0.01 to 100 µg/L for ICP-MS. The standard reference material used for validation purposes was SRM 1575a—Trace Elements in Pine Needles (Gaithersburg, USA).

All used glassware and plasticware were cleaned with half concentrated nitric acid prior to use. Ultrapure water (> 18 MΩ cm) was produced in-house.

Samples

All trees sampled, namely *Pinus nigra* Arnold, *Pinus sylvestris*, *Pinus densiflora* Siebold et Zucc., and *Pinus thunbergiana* Franco, were planted in the experimental plot in the Lisičine Arboretum in triangular-shaped plots with a side length of 6 m. This forestry garden is located at latitude N45°40′ and longitude E17°31′, 150 m above sea level. The entire planting area covers about 0.55 hectares. The soil being the same in the entire area can be characterised as luvisol, medium acid, poor in organic matter, at the lower scale for nitrogen supply, but deficient on available phosphorus (Borzan et al. 1995). Regarding the climate, an average temperature of 10.5 °C and annual precipitation of 918 mm are given. The sampling of the fully developed 1-year-old pine needles of three trees ranging from 23 to 27 years age of each pine species was performed in late June 2012. In all cases, the external and sunlit part of the crown was the source for the shoots. The needles of each tree were pooled; from these bulk samples, three aliquots were taken for analysis.

Sample preparation

All needle samples were dried at 105 °C for 2 h to constant weight, afterwards homogenised and ground using a metal-free mortar. Three aliquots of each dried needle sample with a mass ranging from 0.1 to 0.16 g, weighed to the nearest 0.1 mg, underwent digestion using 5 mL HNO_3 (7 mol/L). The acidic digestion was carried out with a MWS-2 Microwave System Speedwave BERGHOF (Germany) using the following programme: step 1: 150 °C/10 min, step 2: 160 °C/10 min and step 3: 190 °C/20 min. The obtained clear digest solution was then filled up to a final volume of 10.0 mL with ultrapure water. The SRM as well as the blank solutions and SRM underwent the same treatment.

Measurements

The elemental concentrations in all digests, blank and standard solutions were measured in triplicate.

ICP-AES

Simultaneous quantification of the analytes was performed using a Prodigy High Dispersive ICP-AES (Teledyne Leeman, Hudson, NH, USA): The following emission lines were used after appropriate line selection: 396.152 nm for Al, 208.956 nm for B, 455.403 nm for Ba, 396.847 nm for Ca, 214.441 nm for Cd, 228.615 nm for Co, 267.716 nm for Cr, 224.700 nm for Cu, 238.204 nm for Fe, 766.491 nm for K, 280.271 nm for Mg, 257.610 nm for Mn, 202.030 nm for Mo, 589.592 nm for Na, 231.604 nm for Ni, 220.353 nm for Pb, 407.771 nm for Sr, and 213.856 nm for Zn. The actual instrumental settings are given in Table 1.

ICP-MS

An Element 2 ICP-SFMS (Thermo Fisher; Bremen, Germany) was the instrument applied for determining the concentrations of elements present in the μg/L-range. The equipment, including the quartz injector pipe, the quartz torch, the self-aspirating aluminium sampler and skimmer cone, also originates from Thermo Fisher. Table 1 contains the listed instrumental conditions applied.

The isotope ions were analysed at different resolution levels: high ($^{75}As^+$), medium ($^{98}Mo^+$), and low ($^{7}Li^+$, $^{82}Se^+$, $^{111}Cd^+$, $^{208}Pb^+$), nominal mass resolutions being 350, 4500, and 10,000, respectively. Indium added to a final concentration of 1.1 μg/L and measured at $^{115}In^+$ was used as internal standard for all resolution levels.

Optimisation and characterisation of the analytical method

Digest solutions of the used SRM were measured five times in order to get replicate data for the calculation of the precision as relative standard deviations (RSD). Analysing the standard reference material, the trueness of the method was evaluated and presented as recovery. Selected samples ($n = 3$) were analysed on different days to calculate the day-to-day repeatability.

The limits of detection (LOD) and the limits of quantitation (LOQ) for all analytes and both methods were calculated using 3σ or 10σ. The sensitivity of the methods can be seen from the respective slopes of the calibration curves.

Calculation

The obtained elemental concentrations were blank-corrected. Dilution steps and the mass of dried sample were considered for calculating the final results of mass concentrations per dry weight.

ANOVA test, based on 0.05 level of significance and the hypothesis that there is essentially no difference between the mean content, was used for finding statistically significant differences of the element content in needles of different pine species.

Table 1 Operating conditions

	ICP-AES	ICP-SFMS
Instrument	Prodigy High Dispersive ICP	Element 2
Output power	1100 W	1300 W
Argon flow	Coolant: 18 L min^{-1}	Coolant: 16 L min^{-1}
	Auxiliary: 0.8 L min^{-1}	Auxiliary: 0.86 L min^{-1}
	Nebulizer: 1 L min^{-1}	Nebulizer: 1.06 L min^{-1}
Peristaltic pump	1.0 mL min^{-1}	100 μL min^{-1}
Nebulizer	Pneumatic (glass concentric)	PFA microflow nebulizer
Spray chamber	Glass cyclonic	PC^3 cyclonic quartz chamber
Plasma viewing	Axial	–

Results and discussion

Analytical method

The determined LOQs for all analytes in the dried needle material were below 2 µg/g. The recoveries calculated from the results obtained for the standard reference material ranged from 90 up to 111% for ICP-MS and from 92 to 115% for ICP-AES. The precision was determined to range from 0.07 up to 2.3% for both methods. The day-to-day repeatability for all analytes was < 2.9%. The coefficients of determination (R^2) were all beyond 0.999 for all calibration curves.

Metal content of needles

The obtained elemental compositions of the needles of all four pine species are listed in Table 2 as mean with standard deviation along with the determined LOQs.

The macro-elements Ca, K, and Mg are present in g/kg levels. According to ANOVA test, the contents of K and Mg do not differ significantly between the pine species, but Ca is more than twice as high in needles from *P. densiflora* and *P. sylvestris* compared to *P. nigra* and *P. thunbergiana*. These findings are presented in Fig. 1. Calcium is an essential element for plants as structural element of cell walls and membranes. Its uptake mainly occurs via roots from soil. Calcium soil content is determined by the composition of the mother rock. Since all four pine species grow in the same area, the Ca level in the needles is supposed to be similar. Thus, it can be stated that the accumulation of this element depends on tree species. In the literature, similar ranges are reported for Ca. For example, Lehndorff and Schwark (2008) found 1500–12,100 mg/kg in needles from *P. nigra*, a range including also the results of this study. Needles from *P. sylvestris* growing in Poland (Skonieczna et al. 2014) were found to contain 3160 mg/kg Ca, much less than the level of Croatian *P. sylvestris* needles, namely 8400 mg/kg. The Polish working group also reports 4450 mg/kg for K and 650 mg/kg for Mg, whereby the former is approx. twice as high and the latter half of the content of our study.

Figure 2 shows the contents of As, Cd, Co, Cr, Pb, and Se. These trace elements are present in levels up to 1 mg/kg in the needles of the four pine species investigated. In needles of *P. sylvestris*, no Co and Cr were found. Chromium content is statistically significant higher in needles of *P. densiflora* and *P. nigra* than in those of *P. thunbergiana*. The Co needle concentrations do not differ significantly between the pine species. Regarding the essential element Se, for *P. thunbergiana* significant lower values

Table 2 Elemental content in mg/kg dried matter (mean values and standard deviation, SD; $n = 3$)

Content in mg/kg	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	Pb	Se	Sr	Zn
LOQ	2.9	0.058	10.1	1.1	0.42	0.0017	0.011	0.023	0.022	0.19	0.84	0.027	0.61	0.87	0.13	0.20	0.019	0.043	0.016	0.17	1.1
Method	AES	MS	AES	AES	AES	MS	MS	MS	MS	AES	AES	MS	AES	AES	AES	AES	MS	MS	MS	AES	AES
Pinus densiflora																					
Content	128	<LOQ	44.0	33.3	8273	0.16	0.094	0.73	3.57	76.6	2800	<LOQ	1603	459	<LOQ	75.6	0.44	0.18	0.32	28.4	15.5
SD	4	–	5.0	0.3	79	0.1	0.012	0.08	0.10	3.7	67	–	9	4	–	9.2	0.06	0.03	0.01	0.3	2.7
Pinus nigra																					
Content	28.8	0.19	20.8	1.2	2312	0.024	0.080	0.99	6.37	43.5	2517	0.43	1543	22.8	4.03	102	0.53	0.14	0.23	5.68	15.6
SD	3.2		1.1	0.4	14	0.005	0.010	0.06	0.95	0.6	99	0.24	21	0.6	0.04	9.3	0.04	0.06	0.01	0.3	3.2
Pinus sylvestris																					
Content	408	0.082	18.6	9.2	8409	0.264	<LOQ	<LOQ	3.40	66.0	2399	3.6	1381	665	1.25	131	1.27	0.37	0.36	13.1	30.9
SD	7		1.0	0.5	100	0.006	–	–	0.26	4.9	89	1.9	60	22	0.31	9.2	0.05	0.02	0.03	1.4	3.4
Pinus thunbergiana																					
Content	105	<LOQ	11.7	13.8	3309	0.068	0.073	0.065	1.52	27.5	2098	0.18	1207	119	2.23	89.2	0.55	0.31	0.059	13.8	6.93
SD	5	–	1.3	0.7	18	0.030	0.05	0.022	0.24	2.3	35	0.11	32	4	0.59	9.9	0.08	0.21	0.058	0.7	0.7

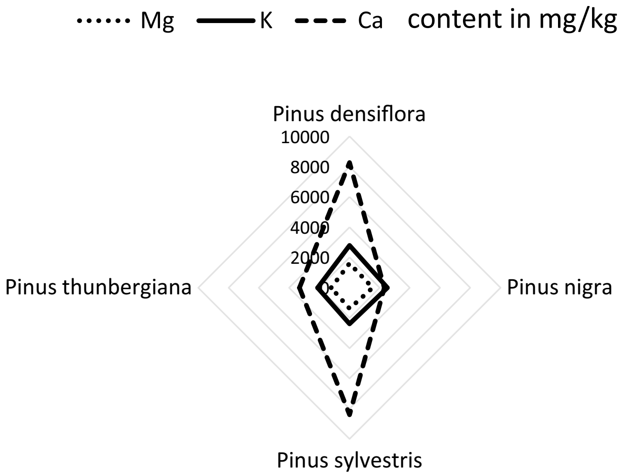

Fig. 1 Macro-elements in needles

were found than for the other species. No comparative data were found in the literature for Co, Cr, and Se. For Pb, two groups were found; needles of *P. densiflora* and *P. nigra* contain less Pb than *P. sylvestris* and *P. thunbergiana*. The concentrations for all pine species are in comparable range to the values published by Lehndorff and Schwark (2008) for *P. nigra* (0.1–4.5 mg/kg). Yilmaz and Zengin (2004) reported much higher Pb contents for needles from *P. sylvestris*. They found Pb levels ranging from 14 up to 30 mg/kg in polluted zones and from 32 to 41 mg/kg in unpolluted areas. Like for Pb, also for Cd the obtained results can be attributed to two groups, whereby in this case *P. nigra* and *P. thunbergiana* have lower contents compared to *P. densiflora* and *P. sylvestris*. These data are in the same range as found in needles of *P. nigra* from urban zone in Cologne, namely 0.005–0.3 mg/kg (Lehndorff and Schwark 2008). Arsenic could not be detected in the samples from *P. densiflora* and *P. thunbergiana*. The contents of the needles of the other two species differ statistically significant. All our results are lower than the content reported by Krachler and Emons (2000), but they do not specify the species of pine tree sampled.

The following trace elements were found to be present in contents ranging from 1 mg/kg up to 45 mg/kg: B, Ba, Cu, Li, Mo, Ni, Sr, and Zn. For B, Li, Ni, and Sr, no data were found in the literature for comparison with ours. Regarding B, three groups were determined, the highest needle concentration was found for *P. densiflora*, followed by *P. nigra* and *P. sylvestris*; *P. thunbergiana* is at the lower end of the

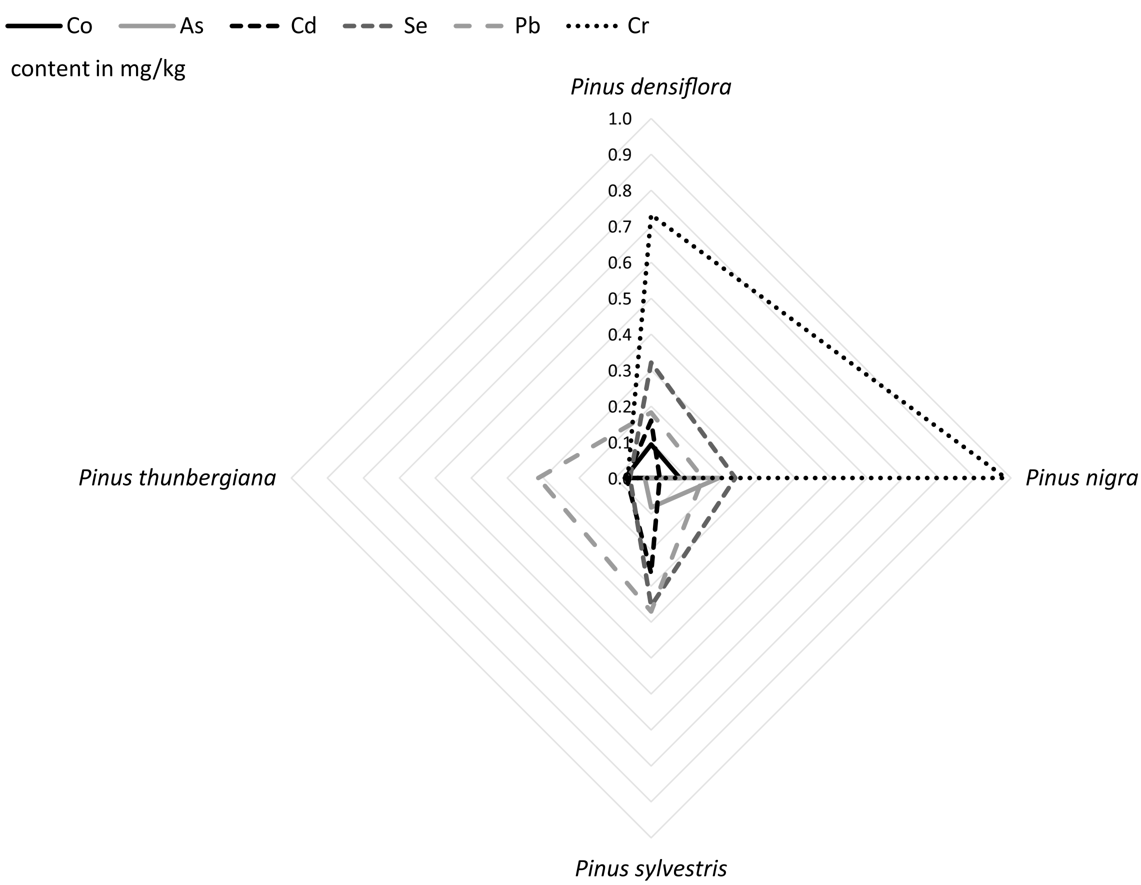

Fig. 2 Trace elements in needles

scale. Also for Sr three clusters were found, whereby again *P. densiflora* shows the highest element level, followed by *P. sylvestris* and *P. thunbergiana*. *P. nigra* needles contain least Sr. The Ni values are clustered in two groups, lower contents were found for *P. densiflora*, *P. nigra* and *P. thunbergiana* than for *P. sylvestris*. Lithium was not detected in the needle samples from *P. densiflora.* The results for the other three pine species can be attributed to two groups, namely *P. nigra* and *P. thunbergiana* having lower levels than for *P. sylvestris*. Reported data of Mo needle content are in the same order of magnitude than those of our study (Lehndorff and Schwark 2008). They found Mo in a range from 0.02 up to 1 mg/kg in needles from *P. nigra* in a polluted area. The four pine species analysed in this investigation grow in a non-polluted area. Nevertheless, we found more Mo in needles of *P. nigra*. Molybdenum is not an element with high abundance in earth crust, and thus its origin is supposed to be linked to anthropological activities. Needles of *P. sylvestris* and *P. thunbergiana*, on the other hand, which grow in the same area with the same environmental conditions, contain less Mo, but also more than reported by Lehndorff and Schwark (2008). Only in the needles of *P. densiflora*, no Mo could be detected. Yilmaz and Zengin (2004) analysed needles of *P. sylvestris* for Cu. They found this element in a range from 2 to 25 mg/kg, whereby the levels are higher in needles from polluted sampling sites. The values determined in our study all fall within this reported range. The dependency on species can be expressed by three groups (in rising order): *P. thunbergiana*–*P. sylvestris* and *P. densiflora*–*P. nigra*. Regarding Ba, except for the needles from *P. nigra*, the levels quantified were all beyond the range given by Lehndorff and Schwark (2008) for polluted area in Germany, namely 0.1–4.5 mg/kg. All four species accumulate this metal in different amounts, no similarities could be found.

Conversely, the Zn data can be clustered in three groups: *P. thunbergiana* < *P. densiflora* and *P. nigra* < *P. sylvestris*. Comparative values are given for needles from *P. sylvestris* collected in Turkey (Yilmaz and Zengin 2004) and Lithuania (Varnagiryte-Kabasinskiene et al. 2014), namely 53–101 mg/kg and 28–36 mg/kg, respectively. Our data fit to those from Lithuania. Iron is an abundant element in the earth, its concentration in the soil being determined by the mother rock composition. Thus, it can be found in almost all plant samples in concentrations beyond LOD. Its soil concentration is determined. Like for other metals already discussed above, also for Fe the accumulation behaviour differs significantly between pine species. Needles of *P. nigra* and *P. thunbergiana* contain less Fe than those collected from *P. densiflora* and *P. sylvestris*.

Sodium was found in needles of *P. sylvestris* in the highest contents, followed by *P. nigra* and *P. thunbergiana*, and *P. densiflora* showing the lowest levels. All obtained values are within the range published for *P. nigra* by Lehndorff and Schwark (2008), namely 2–676 mg/kg. Aluminium and manganese were both determined in needles of *P. nigra* at the lowest level and in needles of *P. sylvestris* at the highest level. Literature data are stated for *P. sylvestris* from Lithuania in similar ranges to our results: 250–340 mg/kg for Al and 250–670 mg/kg for Mn (Varnagiryte-Kabasinskiene et al. 2014). The Al contents in needles of *P. thunbergiana*, and *P. densiflora* are in the middle range and do not differ significantly. Conversely, the Mn levels are different for needles of *P. thunbergiana* and *P. densiflora*.

Pine needles as bio-indicator

Interest in bio-indication of air pollutant effects is rising since decades, already in the 1970s many reviews on this topic were published and can be found summarised by Grodzinski and Yorks (1981). Criterion for bio-indicator species is the fact that semi-quantitative verification of physical and chemical measurements of air quality is possible. Three categories are hereby differentiated—three basic categories for their use— firstly, the so-called indicator species, whereby their presence or absence is noted; secondly, true indicators, i.e. individual species exhibiting damage proportional to dose; and thirdly, accumulators of potentially toxic materials with or without internal damage (Grodzinski and Yorks 1981). Plants showing high concentration of metals, namely more than 1000 mg/kg of Co, Cu, Cr, Pb, and Ni or more than 10,000 mg/kg of Mn and Zn, are considered to be hyper-accumulators (Baker and Brooks 1989). As can be seen from the results on metal content of needles discussed in the previous chapter, none of the analysed species can be classified as hyper-accumulator, not making them useful for soil remediation. Furthermore, no damage was observed at any of the sampled trees. Nevertheless, pine needles provide information on the pollution on their growing site, and these data can be used for assessment studies. It is important to take into account that each species, as shown above, has different uptake and accumulation behaviours, and thus inter-species comparison for long-term or spatial investigations is not recommended. Furthermore, impact of not only air pollution, but also the soil composition with potential contamination has to be considered when performing risk assessments based on needle metal contents. Thus, pine needles' metal content is limited to local pollution studies, such as monitoring changes in time in a certain area.

Conclusion

The pine needle metal content, considered as a valuable marker for pollution, depends not only on the environmental conditions, but is also linked to the species of pine tree. The results discussed above clearly show these findings. Since all trees grow in the same area, influencing parameters such as soil composition, climatic conditions, pollution state, and quality of rain water can be considered to be the same for all sampled trees. Nevertheless, the metal and metalloid levels differ between the various species. No general tendency was found for all analytes, nor for essential and harmful elements as subgroups. Furthermore, the charge of the metals when dissolved in water (+1, +2, or +3) had no influence on the accumulation in the needles.

The diverse accumulation behaviour has to be taken into account when establishing risk assessment studies on polluted areas or estimating the bioavailability of certain elements. None of the species studied shows hyper-accumulator properties, and thus their application for soil remediation is limited. To treat multi-contaminated soils, it is advisable to plant different species in order to cover all pollutants.

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