European spruce as an indicator of environmental pollution: an example from the Vysoké Tatry Mts

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Abstract

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Historical variations of the composition of the environmental compartments can be traced by various methods. One of them is dendrochemistry, the quantitative observation of chemical composition of tree rings. Here we report such study on three selected trees from the National Park Vysoké Tatry Mts in Slovakia. Tree rings were analyzed by laser-ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) and we focus on the concentrations of essential (P, K) and toxic (Pb) elements. All three trees belong to European spruce (*Picea abies*) and the historical variations were strongly overprinted by the intrinsic biological processes within the trees. For the essential elements, especially phosphorus, we see a strong enrichment of this element in the youngest tree rings, owing to the preferential channeling of the fluids along these pathways. The pollutants, such as lead, show a signal smeared by the translocation of the elements within the trees. Only in one tree, the declined signal in the past could be related to the decrease of use of the leaded gasoline in Czechoslovakia. If compared to the literature, one could conclude that the national park was located far away from major pollution sources and therefore the results document only the pristine nature within the park, not the variations of the environmental load over the last decades.

Key words

chemical composition, dendrochemistry, lead, phosphorus, tree rings

Introduction

The past variations in the environment are important clues for the sustainable development of the modern society. Yet, these changes are difficult to monitor. Unless samples have been collected in regular temporal intervals over a longer period, the variations must be deciphered from geological or biological records. The former include sediments (Monecke et al., 2008) or ice cores (Battle et al., 1996), the latter tree rings. Chemical composition of the tree rings is the subject of dendrochemistry, with the aim of detecting natural (Pearson et al., 2006) or man-induced (Watmough and Hutchinson, 1999) fluctuations in the environment. Trees can provide a record of their environment over decades or centuries, reflecting the changes in the concentration of elements but also physical factors (e.g., temperature) of their immediate surrounding. Not all tree species may be suitable for the long-time record as some species exhibit a significant radial translocation of elements across ring boundaries (Cutter and Guyette, 1993).

Materials and methods

In this study, we have examined samples from European spruce (*Picea abies*) trees. The first tree (tree 1) grew near the settlement of Javorina and was cut in 2008. The nearest public road is located about 1 km from the locality where the tree grew. Two trees (tree 2 and 3) grew in a valley called Tichá dolina and fell during a major storm on November 11, 2004. There are no publicly accessible roads in this valley.

The sections cut from the trees were cut and hand-shaven by a jack plane. From these pieces, stripes of ~1 cm thickness were cut. The thickness of the rings was measured under a binocular, and the stripes were cut to smaller pieces to fit into the laser-ablation chamber of the analytical instrument.

For the analysis, we used a laser-ablation inductively-coupled plasma mass spectrometer (LA-ICP-MS) ThermoFisher Scientific with the LA accessory from Merchantek. The instrument is equipped with a Nd:YAG laser. To remove surface contamination, a pre-ablation run was performed before the data were collected. The material ejected by the laser ablation for the data collection itself was fed into the ICP and analyzed by the mass spectrometer. The elements/masses sought were ^{11}B, ^{24}Mg, ^{27}Al, ^{29}Si, ^{31}P, ^{39}K, ^{44}Ca, ^{55}Mn, ^{56}Fe, ^{65}Cu, ^{66}Zn, ^{88}Sr, ^{111}Cd, ^{137}Ba, and ^{208}Pb. All elements were measured relatively to ^{12}C which was determined quantitatively by a separate set of analyses (see below). To quantify the elemental concentrations, we employed a standard Virginia tobacco leaves (CTA-VTL-2) with certified concentrations for the analyzed elements. The validity of the procedure was tested by comparing the LA-ICP-MS data with a digestion of the wood tissues and subsequent analysis by a conventional ICP-MS in a separate set of experiments (Lippelt, 2009) in our laboratory.

The total organic carbon (TOC) content was determined by a multiN/C 2100 (Analytik Jena) instrument on a set of similar wood samples and the standard in our laboratory previously.

Natural settings

The primary goal of this study was to evaluate the environmental variations in the trees which grew in the National Park Vysoké Tatry over the last 100 years. The national park was established in 1949 and was strictly protected as a refuge for rare and endemic natural species since then. The national park is one of the smallest Alpine terrains of the world. The main ridge is only 26 km long; the highest peaks reach over 2,600 meters above the sea level and form a natural barrier between the geological and geomorphogical units of Inner Western Carpathians (mostly in Slovakia) and Outer Western Carpathians (significantly in Poland). There are no major mountain belts north from the Vysoké Tatry; the flat terrain of Poland extends all the way to the Baltic Sea and allows for a free movement of the air masses. On the other hand, there are numerous mountains south of Vysoké Tatry, and the motion of the air is mostly restricted to the W-E direction of the Podtatranská kotlina, a major valley with high population density and abundant industry. Significant industrial parks existed and exist in the cities of Ružomberok and Žilina located west from the national park. Because of the prevalent eastward winds and the high air-borne contamination in these areas, the western part of the national park is relatively polluted. The central and eastern parts, however, where the tree samples were collected, belong to the less polluted portions of Slovakia. Despite of the limited input of pollutants from the Slovak industrial sources, both localities are known to be affected by the imission of the metallurgical industry in Katowice, Poland.

Results and discussion

Based on their mutual correlation, the analyzed elements can be divided into two large groups. In all three trees, there was a relatively strong correlation between Ca, Sr, Mg, Mn, Ba, K, Zn, and P. Additionally, Pb and Cd showed a weak correlation with this group of elements. On the other hand, the elements Si, B, Al, Cu, and Fe showed no correlation to any analyzed element. The numerical values of correlation coefficients are listed in Table 1.

The element from the first group showing the strongest affinity to biological matter is phosphorus (Fig. 1). In all the studied trees, phosphorus shows a marked increase toward the last years of the trees' life span. Although this trend could be interpreted as an increase in phosphorus (phosphate) availability during the last years of the trees' life, it is more likely that this trend reflects the translocation of an essential element such as phosphorus into active parts of the trees. Cutter and Guyette (1993) studied an 18-year old spruce and found out that 10–12 rings were active in the process of water transportation. Therefore, translocation of elements can be expected within such a range and a possible environmental change may not be assigned to a specific year. The translocation smears the signal. Prohaska et al. (1998) studied tree rings from spruce trees which grew under controlled conditions. They observed that not all elements in the tree rings reflected a sudden environmental change (shutdown of the nearby pollution source) for at least 3 years.

Other elements, for example potassium (Fig. 2), show a similar, albeit not as strong increase toward the end of their lifes. In general, elements like potassium, magnesium, and other essential elements, show a steady, uniform concentration across the measured profile, as these concentrations are probably maintained at this level by the biological functions of the trees.

We particularly focused on elements recognized as toxic to biota, such as lead. In the trees 1 and 2, lead behaves similarly as K or Mg (Fig. 3), that is, the concentrations are relatively uniform, with fluctuations between the vegetative period and the offseason. The increased concentrations of Pb in the tree 1 and tree 2

Table 1. Correlation coefficients for the elements analyzed in the studied trees

Tree 1	B	Mg	Al	Si	P	K	Ca	Mn	Fe	Cu	Zn	Sr	Cd	Ba	Pb
B	1.00														
Mg	0.51	1.00													
Al	0.28	0.52	1.00												
Si	0.08	0.07	0.14	1.00											
P	0.48	0.92	0.47	0.23	1.00										
K	0.50	0.96	0.49	0.14	0.91	1.00									
Ca	0.51	0.98	0.53	0.07	0.90	0.94	1.00								
Mn	0.50	0.97	0.51	0.12	0.90	0.94	0.97	1.00							
Fe	0.09	0.16	0.14	0.09	0.17	0.17	0.16	0.14	1.00						
Cu	0.25	0.45	0.33	0.27	0.51	0.44	0.44	0.47	0.11	1.00					
Zn	0.46	0.91	0.54	–0.01	0.77	0.86	0.94	0.90	0.16	0.35	1.00				
Sr	0.51	0.98	0.53	0.09	0.92	0.95	0.99	0.97	0.16	0.47	0.92	1.00			
Cd	0.27	0.57	0.29	–0.01	0.47	0.51	0.56	0.58	0.07	0.35	0.53	0.56	1.00		
Ba	0.50	0.98	0.52	0.07	0.91	0.94	0.99	0.97	0.15	0.44	0.91	0.99	0.56	1.00	
Pb	–0.02	–0.05	0.04	0.11	–0.01	–0.03	–0.03	–0.02	0.08	0.02	0.00	–0.02	–0.07	–0.03	1.00

Tree 2	B	Mg	Al	Si	P	K	Ca	Mn	Fe	Cu	Zn	Sr	Cd	Ba	Pb
B	1.00														
Mg	0.08	1.00													
Al	0.08	0.24	1.00												
Si	0.06	–0.47	0.04	1.00											
P	0.04	0.05	0.18	0.12	1.00										
K	0.08	0.67	0.35	–0.34	0.55	1.00									
Ca	0.05	0.81	0.23	–0.31	–0.18	0.45	1.00								
Mn	0.05	0.91	0.21	–0.54	–0.04	0.65	0.87	1.00							
Fe	0.08	0.08	0.07	0.02	0.02	0.04	0.03	0.03	1.00						
Cu	0.01	0.03	0.04	–0.02	0.01	0.06	0.04	0.04	0.00	1.00					
Zn	0.04	0.78	0.27	–0.41	–0.04	0.52	0.82	0.80	0.05	0.04	1.00				
Sr	0.08	0.86	0.28	–0.51	0.12	0.77	0.78	0.88	0.04	0.06	0.79	1.00			
Cd	0.05	0.18	0.11	–0.10	–0.04	0.16	0.17	0.19	0.04	0.03	0.17	0.24	1.00		
Ba	0.06	0.70	0.19	–0.42	–0.09	0.46	0.76	0.75	0.03	0.04	0.71	0.79	0.21	1.00	
Pb	0.04	0.28	0.10	–0.24	–0.08	0.26	0.26	0.35	0.05	0.01	0.33	0.30	0.04	0.27	1.00

Tree 3	B	Mg	Al	Si	P	K	Ca	Mn	Fe	Cu	Zn	Sr	Cd	Ba	Pb
B	1.00														
Mg	0.04	1.00													
Al	0.05	0.33	1.00												
Si	0.04	0.21	0.38	1.00											
P	0.02	0.43	0.33	0.53	1.00										
K	0.07	0.63	0.36	0.44	0.75	1.00									
Ca	0.02	0.47	–0.01	–0.25	–0.07	–0.08	1.00								
Mn	0.02	0.53	0.01	–0.20	–0.05	–0.02	0.87	1.00							
Fe	0.05	0.08	0.07	0.25	0.06	0.06	0.03	0.01	1.00						
Cu	0.04	0.18	0.23	0.20	0.09	0.14	0.07	0.08	0.05	1.00					
Zn	0.05	0.55	0.15	–0.22	–0.15	0.08	0.60	0.65	0.05	0.16	1.00				
Sr	0.03	0.57	0.12	–0.12	0.13	0.12	0.90	0.82	0.04	0.16	0.62	1.00			
Cd	0.05	0.21	0.07	–0.03	–0.12	0.02	0.28	0.27	0.06	0.26	0.38	0.28	1.00		
Ba	0.05	0.42	–0.02	–0.47	–0.31	-0.02	0.64	0.61	0.02	0.12	0.79	0.62	0.31	1.00	
Pb	–0.02	0.07	0.26	0.58	0.26	0.32	-0.40	-0.31	0.06	0.11	–0.37	–0.28	–0.10	–0.60	1.00

cannot be correlated, and therefore probably do not represent a regional or a large-scale influx of lead into the area where the trees grew. On the other hand, tree 3 shows a much smaller Pb concentrations prior to 1920, with occasional spikes of very short duration. The lead concentration starts to increase around 1925 and continues until mid 1950's where it reaches a concentration comparable to that seen in trees 1 and 2. Because the changes in the observed trees are difficult to correlate to each other, it is not easy to assign the observations from all three trees to a single source; for example, the onset of automobile transportation in Czechoslovakia. In the last decade, however, the lead concentration in the tree rings has been slightly decreasing which could be perhaps explained by the decreased sales of leaded gasoline in Slovakia. An alternative explanation could be the translocation enabling to remove a toxic element such as Pb from the active parts of the trees.

In summary, tree rings have a potential to record the past environmental changes. According to this study, it seems that this potential has been smeared by the translocation of elements within the trees. In a

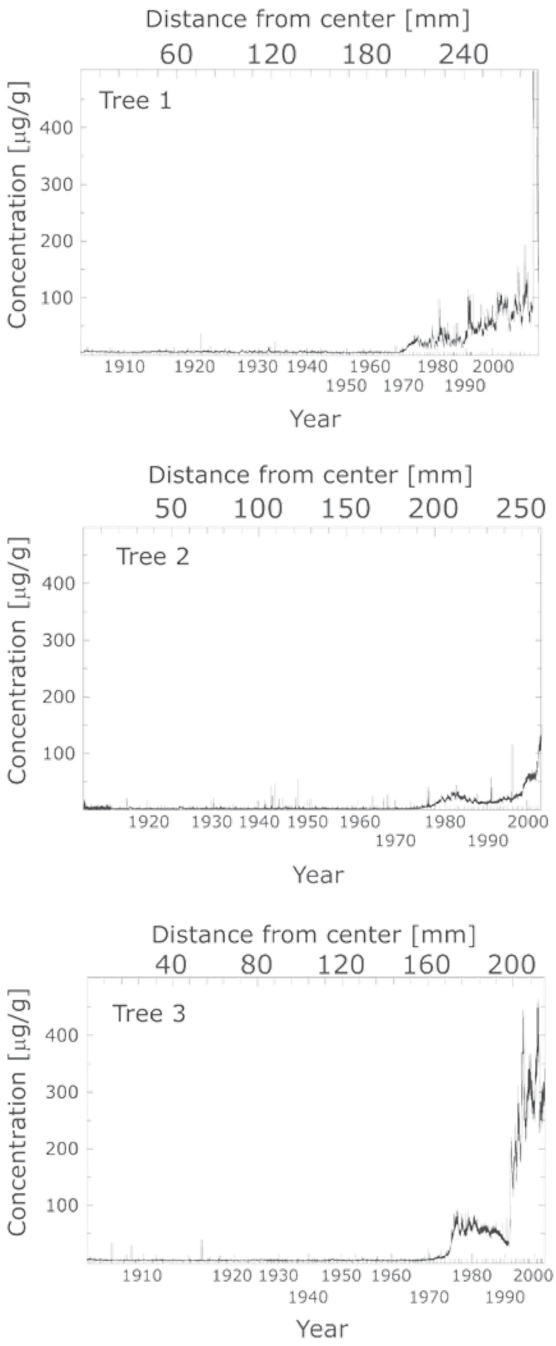

Fig. 1. Concentration profiles of phosphorus in the studied trees.

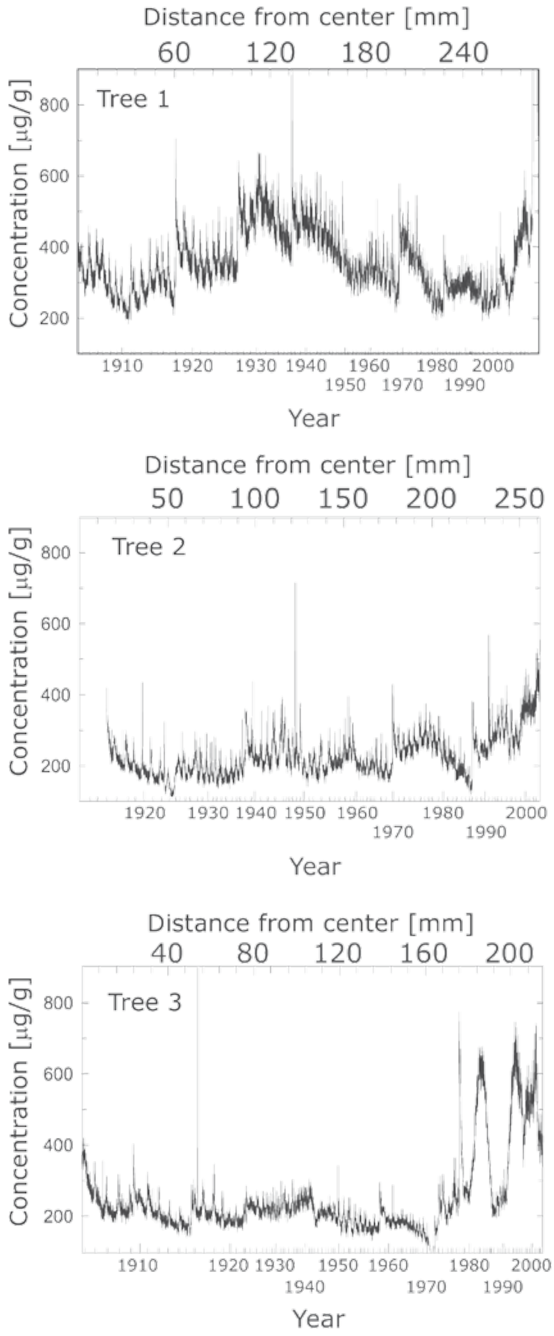

Fig. 2. Concentration profiles of potassium in the studied trees.

single case (tree 3) for one toxic element (Pb), a trend of increase was seen that could be linked to industrial activities. In general, however, the trees studied here do not show any major environmental changes over the past 100 years, either positive or negative. Watmough et al. (1998) have found that the environmental changes associated with Pb can be monitored well in big cities and near major highways, that is, in the immediate vicinity of large sources of this metal. At rural sites, no fluctuations were seen, similarly to our trees 1 and 2. Therefore, we can conclude that the trees in the Vysoké Tatry Mts have not experienced any local drastic environmental changes. For regional and large-scale changes due to metals, they were located too far away from the pollution sources. Gaseous pollutants, such as SO_2, were not addressed in this study, and need to be monitored by different techniques.

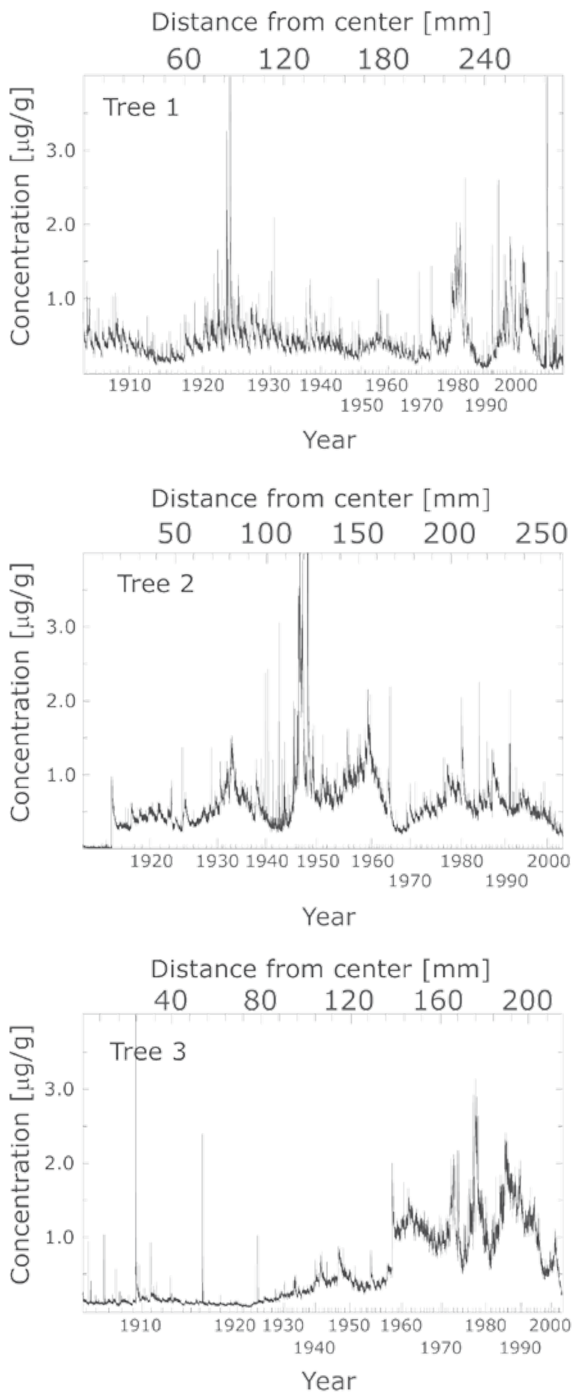

Fig. 3. Concentration profiles of phosphorus in the studied trees.

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Smrek ako indikátor znečistenia životného prostredia: príklad z Vysokých Tatier

Súhrn

Vzorky z troch stromov smreka (*Picea abies*) z Vysokých Tatier boli získané ako odrezané disky na analýzu prvkov. Tieto drevené disky boli analyzované pomocou laserovej ablácie a následnej analýzy s hmotnostnou spektrometriou s induktívne viazanou plazmou. Vzorky boli analyzované na viacero prvkov. Sú medzi nimi elementy, ktoré sú nevyhnutnou súčasťou živých organizmov, napríklad P alebo K, ale aj prvky, ktoré znečisťujú životné prostredie a sú používané ako indikátory stupňa znečistenia, napr. Cd alebo Pb.

Jedna vzorka zo smreka vykazuje podstatné zvýšenie olova v dreve počas svojho života. Zvyšovanie sa začína v 20. rokoch 20. storočia a pokračuje až do 60. rokov.

Obsah draslíka sa mení s časom výraznejšie v jednej vzorke smreka. Od začiatku 70. rokov tu pozorujeme drastické zmeny. Obsah draslíka sa prudko zvyšuje okolo roku 1980 a klesá okolo roku 1990. Potom zase stúpa a za posledných 10 rokov sa stabilizoval.

Obsah kadmia, napríklad, sa vo všetkých troch stromoch počas celého ich života prakticky nemení.

Spomedzi prvkov nevyhnutných pre živé organizmy sú výrazné zmeny pozorovateľné najmä v prípade fosforu. Obsah fosforu prudko stúpa v letokruhoch, ktoré predstavujú posledných približne 30 rokov. V tomto prípade však existujú početné štúdie, ktoré ukazujú na to, že stromy majú tendenciu prenášať niektoré potrebné prvky, napríklad fosfor, zo staršieho dreva do mladšieho a pravdepodobne aj ďalej do vyšších nadzemných častí. Zmeny v prípade fosforu teda určite nepredstavujú zmeny v životnom prostredí.

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