Spatial and temporal trends in winter deposition of Pb, Be, Cu and Zn in selected mountain areas of Central Europe

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Abstract: Bohdálková L., Hruška J. 2017: Spatial and temporal trends in winter deposition of Pb, Be, Cu and Zn in selected mountain areas of Central Europe – *Beskydy,* 10 (1,2): 87–98

Atmospheric depositions of trace metals have been the focus of attention because of their potential toxicity to living organisms. In this paper, winter deposition rates of Pb, Be, Cu and Zn collected from 2009 to 2011 at 10 mountain-top localities in the border area of the Czech Republic were compared and summarized. Across the sites there were up to 7–8fold differences in Pb, Be and Zn deposition rates, and up to threefold differences in their Cu deposition rates. In all cases, rime contained higher amounts of Pb, Be, Cu and Zn compared to snow. More than 92 % of Pb, Cu and Zn occured in soluble (bioavailable) form, whereas only 34 % of Be was in soluble form. Recent trace metal concentrations in precipitation considerably decrease compared to those measured during the period of the highest atmospheric emissions in the 1980s. The industrial region in the northeast of the Czech Republic experienced moderate levels of Pb air pollution, while atmospheric Pb inputs in the rest of the country as well as overall inputs of Cu, Zn and Be were low, representing a low threat to human and ecosystem health. Between-site differences made it possible to classify sites into three categories according to their level of pollution load. A previously-mentioned north-south pollution gradient between the industrial north and rural south of the country was not observed. Sites in the northwest and in the south were among those with the lowest pollution loads. On the other hand, sites in the northeast were the most polluted due to their location near the industrial regions of southern Silesia (Poland) and Ostrava.

Keywords: Lead, Copper, Beryllium, Zinc, Atmosphere, Snow, Ice accretion

Introduction

Industrialization has considerably and irretrievably changed the geochemical cycles of many elements. Anthropogenic activities have increased the amount of several potentially toxic trace metals entering the atmosphere several times higher compared to natural background. For example, the present anthropogenic flux of zinc (Zn) to the atmosphere is threefold higher compared to the natural flux, while lead (Pb) exceeds the natural flux by almost 30 times (Shotyk 1994). The subsequent deposition of these elements to the Earth's surface has caused increased concentrations in the soil system, hydrosphere, terrestrial and aquatic ecosystems, with potentially toxic consequences for living organisms. More than 95 % of the Pb within the biosphere is of anthropogenic origin (Smith, Flegal 1995).

Lead and beryllium (Be) are non-essential and toxic trace metals with cumulative and long-term effects on living organisms at relatively low concentrations. Pb affects the human nervous

and circulatory systems, and may contribute to lowered life expectancies and permanent learning and behavior disorders in children (Nriagu 1978). Exposure to Be affects the respiratory system and causes chronic beryllium disease (Cooper, Harrison 2009).

Although copper (Cu) and zinc (Zn) are essential to most living organisms, elevated Cu concentrations cause liver cirrhosis and aggravate Alzheimer's disease (Flemming, Trevors 1989), while a surplus of Zn may lead to hemolytic anemia and kidney damage (Fosmire 1990).

Considerable water and soil acidification in the Czech Republic, described in numerous studies, has strongly influenced the behavior of trace metals in precipitation, surface water and the soil system because their soluble content is strongly pH-dependent. For example, highly toxic beryllium exponentially increases with pH decreasing from 7 to 4 (Veselý et al. 1989). Drinking water limits (DWL) for dissolved Pb, Be, Cu and Zn concentrations shows Tab. 1.

Tab. 1: Drinking water limits for Pb, Be, Cu and Zn.

Element	DWL
Be	2 $\mu g.L^{-1}$
Pb	10 $\mu g.L^{-1}$
Cu	1 $mg.L^{-1}$
Zn	nd.

nd: not determined

However, systematic direct measurements of trace metal deposition rates in the country were rare before the year 1996. Reconstructions of past atmospheric pollution in the Czech Republic have been studied using geochemical archives such as peat profiles (e.g. Vile et al. 2000, Mihaljevič et al. 2006, Novák et al. 2008), tree-rings (Zuna et al. 2011), lake sediments (e.g. Veselý et al. 1996), upland soils (Ettler et al. 2004) and by the monitoring of small forested catchments (Bohdálková et al. 2014).

Stable isotope ratios of some trace metals are used as a tool for the identification of pollution sources. For example, Pb isotopic ratio ranges of several potential pollution sources depicted in $^{206}Pb/^{207}Pb$ vs. $^{208}Pb/^{207}Pb$ plots and their comparison with the isotope signatures of soil or water samples have enabled the identification and quantification of all Pb sources that have

specific isotope ratios (Komárek et al. 2008). More recently, stable isotopes of other metals (e.g. $\delta^{66}Zn$ or $\delta^{65}Cu$) have also been introduced for pollution source fingerprinting (Novák et al. 2016, Voldřichová et al. 2014).

In 2009, a new monitoring network consisting of 10 remote mountain-top locations was established, and winter horizontal and vertical samples were collected during three consecutive years. Our aim was to i) summarize and compare the Pb, Be, Cu and Zn winter deposition rates in recent studies, ii) evaluate differences in soluble and insoluble trace metal contents in horizontal and vertical precipitation samples, iii) summarize recent studies assessing the sources of pollution, and iv) classify the studied sites into several categories according to their level of pollution load.

Materials and Methods

Study sites

A monitoring network was established to collect vertical and horizontal deposition in the border regions between the Czech Republic, Poland, Germany, Slovakia and Austria. 10 remote mountain-top locations (ca. 1,000 m a.s.l.) located far from local sources of pollutions and at least 5 km from the nearest village or road were selected. The distance between individual sampling sites was about 80 km (Fig. 1). Study site characteristics are described in Tab. 2.

Sampling

Snow and rime samples were collected during three consecutive winters from 2009–2011, every 7 days on average. Snow samples were taken from snowpack surfaces in 30 × 10 × 3 cm volumes and placed in pre-cleaned 1.5-L PP containers. Three identical sampling devices were installed at each site for sampling rime. Each sampling device consisted of two horizontal wooden bars attached to wooden pole 1.5 m above the snow surface. Three pairs of pre-cleaned high-surface area rectangular polyethylene rime samplers were attached to the wooden bars (Fig. 2). Snow and rime samples were taken in triplicate at each sampling site.
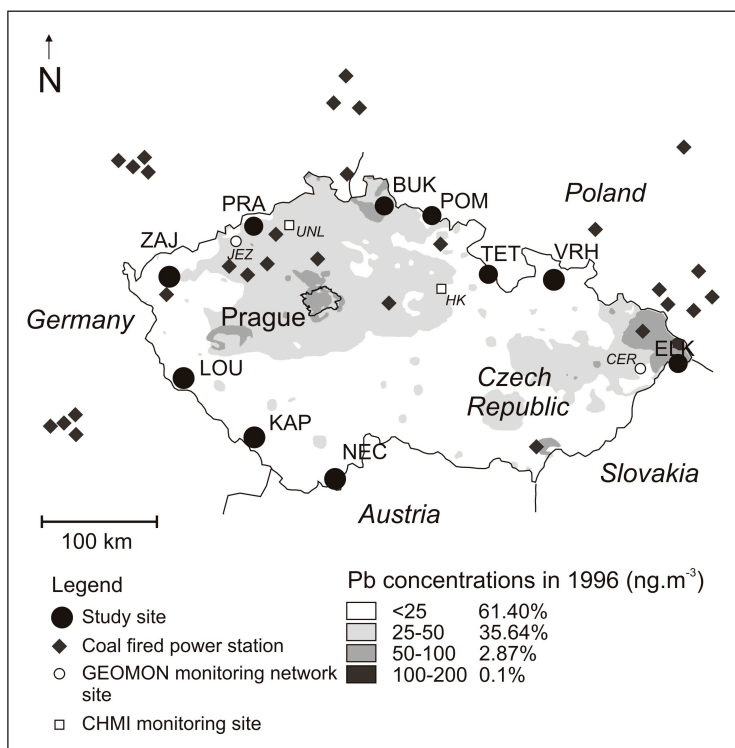
Fig. 1: Location of the study sites and potential sources of pollution. Lead concentrations
in the atmosphere in 1996 (unpublished data, Czech Hydrometeorological Insti-
tute, Prague).

Tab. 2: Description of target study sites.

Site code and name	Geomorphological unit	Elevation (m a. s.l)	Mean annual temperature (°C)	Mean annual precipitation (mm)
ZAJ Zajeci vrch	Ore Mts. (west)	1,008	4.8	982
PRA Pramenac	Ore Mts. (east)	935	4.3	857
BUK Bukovec	Jizerske Mts.	1,006	2.5	1,360
POM Pomezni hreben	Giant Mts.	1,183	1.5	1,415
TET Tetrevec	Eagle Mts.	987	4.7	1,301
VRH Pricny vrch	Jeseniky Mts.	954	4.9	1,018
ELK Velky Polom	Beskydy Mts.	1,006	5.1	1,295
LOU Kamenna loucka	Cesky les Mts.	925	4.8	1,016
KAP Kaprad	Bohemian Forest Mts.	941	4.7	953
NEC Kamenec	Novohradske Mts.	988	4.4	827

Fig. 2: Collecting of rime samples.

Analytical methods

Rime and snow samples were weighed, acidified with HNO_3 and filtered. The filtrate and HF digests of solid particles were analyzed using sector-field ICP MS (Element 2, Thermo Fisher Scientific). Copper and zinc isotope analyses were performed on a double focusing multicollector mass spectrometer with inductively coupled plasma (MC ICP MS Neptune, Thermo Fisher Scientific). Lead isotope analysis was performed with a mass spectrometer with inductively coupled plasma (ICP MS X-series, Thermo Fisher Scientific). Detailed analytical methods and sample processing are described in Čimová et al. (2016), Bohdálková et al. (2012) and Novák et al. (2016).

Evaluation of pollution loads

The considerable between-site variability of winter deposition values described in Čimová et al. (2016), Bohdálková et al. (2012) and Novák et al. (2016) led us to attempt to classify relative pollution load levels into classes according to pollution input amounts. To evaluate the degree of relative pollution load at each individual site i we used the following equations:

$$PR_x(i) = \frac{TDS_x(i)}{TDS_x(\max)} ,$$ (1)

where PR_X is the ratio of the total winter deposition of element X in soluble form (i.e. in both

rime and snow) at individual site i, i.e., $TDS_X(i)$, and the maximal total winter deposition of element X in soluble form detected across the sites, i.e., $TDS_X(max)$. Insoluble fractions were not included because we assumed that under natural conditions they are not in bioavailable form and therefore do not represent a direct threat to the ecosystem. The overall pollution load of n evaluated elements at individual site i (i.e., $L(i)$) is then expressed as:

$$L(i) = \frac{PR_{Pb}(i) + PR_{Be}(i) + PR_{Cu}(i) + PR_{Zn}(i)}{n}, \quad (2)$$

Identification of pollution sources

Recent studies have used two different methods to identify pollution sources of metal deposition: modeling of backward trajectories of air masses and stable isotope determination.

To trace Be pollution sources, Bohdálková et al. 2012 used the HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory) model computing transport trajectories of air masses to selected study sites.

Monitoring of the isotope composition of deposition was used for tracing Pb, Cu and Zn pollution sources (Voldřichová et al. 2014, Novák et al. 2016, Čimová et al. 2016). $^{206}Pb/^{207}Pb$ vs. $^{208}Pb/^{207}Pb$ plots can be used to compare isotope signatures of studied samples with various anthropogenic and geogenic pollution sources (e.g. Vile et al. 2000).

Results and Discussion

Differences in horizontal and vertical deposition during the winter

Mean Pb, Be, Cu and Zn concentrations in vertical and horizontal deposition are shown in Tab. 3. Overall, across the sites there was element enrichment in rime compared to the snow cover. Over the three winters and across the sites, rime had three times higher concentrations of soluble Pb and soluble Zn forms than snow, four times higher concentrations of soluble Cu and seven times higher soluble Be. This phenomenon has previously been described e.g. by Doušová et al. (2007), and has been associated with differences in the origins of individual deposition types (Bohdálková et al. 2012) and/or different pollution sources in individual deposition types (Doušová et al. 2007). Rime

forms when water droplets in fog or the basal cloud layer freeze to the outer surfaces of objects. During atmospheric inversions, fog and the lowermost cloud layers are often enriched in pollutants, which are more efficiently scavenged by the high specific surface of small rime-forming droplets compared to droplets creating the ice crystals of snow (Novák et al. 2016).

Site-specific Pb, Be, Cu and Zn pollution

The total input of individual elements at each site was used to compare between-site variability and to evaluate pollution loads to individual mountain regions. Wintertime in the region is often characterized by increased pollution due to higher energy demands and frequent atmospheric inversions. Fig. 3 shows the total wintertime (mid-November to mid-April) Pb, Be, Zn and Cu deposition at each site for seasons 2009–2011.

Long-term hydrological monitoring of small forested catchments in the Czech Republic (GEOMON network) enabled us to estimate the wintertime proportion to the annual precipitation amount (45 %; see Tab. 2). According to Hindman et al. (1983) rime contributes about 10 % of the snowpack water in mountain areas. The sum of the mean soluble and insoluble element concentrations in both vertical and horizontal depositions (Tab. 3.) in the estimated winter precipitation amount was used to calculate the total winter atmospheric input of individual elements.

The total Pb winter deposition ranged from 450 to 3,700 μg.m^{-2}, total Be deposition varied from 2 to 13 μg.m^{-2} and Zn values ranged from 2,050 to almost 14,000 μg.m^{-2}. Across the sites, KAP had the smallest input of all elements, while the highest winter depositions of Pb, Be and Zn were recorded at ELK. The highest wintertime Cu input of 1,870 μg.m^{-2} was found at BUK, with the lowest values at KAP reaching 620 μg.m^{-2}.
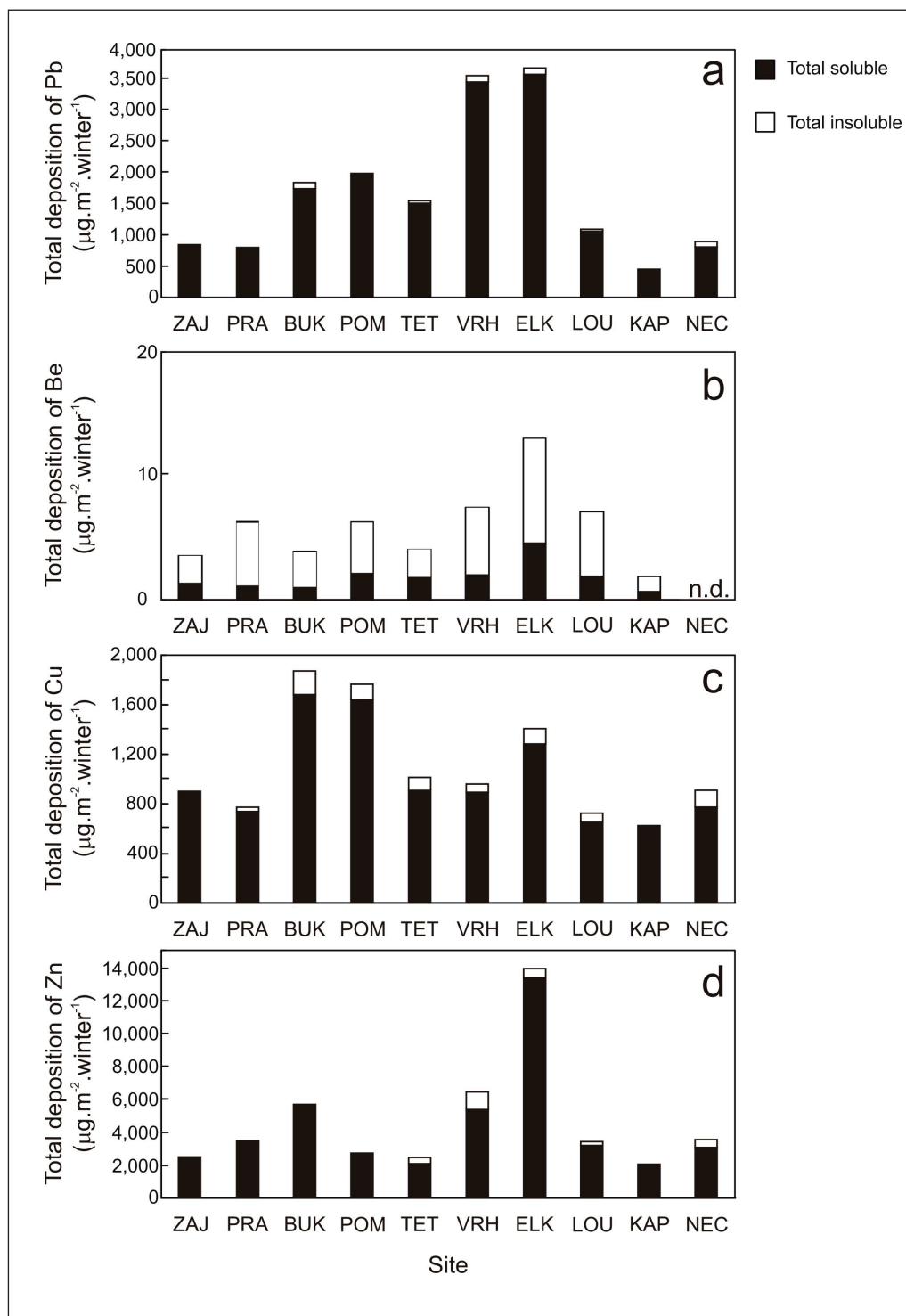
Fig. 3: Total depositions of Pb, Be, Cu and Zn, partitioning of soluble and insoluble fraction (Čimová et al. 2016, Bohdálková et al. 2012, Novák et al. 2016).

Tab. 3: Mean Pb, Be, Cu and Zn concentrations in soluble and insoluble forms in snow and rime for combined winter seasons 2009–2011 (Čimová et al. 2016, Bohdálková et al. 2012, Novák et al. 2016).

Study site	Be (ng.L⁻¹)				Pb (µg.L⁻¹)				Cu (µg.L⁻¹)				Zn (µg.L⁻¹)			
	Snow		Rime		Snow		Rime		Snow		Rime		Snow		Rime	
	Soluble	Insoluble	Soluble	Insoluble	Soluble	Insoluble	Soluble	Insoluble	Soluble	Insoluble	Soluble	Insoluble	Soluble	Insoluble	Soluble	Insoluble
ZAJ	3.0	3.8	8.7	2.9	1.6	0.1	9.4	0.1	1.8	0.1	9.3	0.1	5.9	0.5	41.1	2.2
PRA	3.3	9	8.3	9.8	2.7	0.3	12.2	0.5	2.2	0.5	12.7	0.7	7.5	1.3	46.4	2.2
BUK	2.3	7.8	6.9	4.2	4.3	0.3	16.9	0.3	4.6	0.5	9.2	0.2	9.9	0.7	61.9	0.9
POM	3	9.3	10.6	4.5	3.9	0.2	13.5	0.2	2.7	0.4	14.4	0.3	4.5	0.6	34.2	2.2
TET	2.8	5.5	24.1	21.4	3.6	0.1	26.0	1.3	5.4	0.2	10.9	1.5	54.7	0.9	70.5	3.4
VRH	3.7	8.7	18.6	7.1	8.4	0.6	24.0	1.3	2.1	0.6	7.4	0.7	14.1	2.4	45.6	3.5
ELK	6.7	12.6	17.9	4.6	11.0	0.6	16.3	0.4	3.8	0.9	7.4	0.4	18.8	3.5	86.7	2.7
LOU	2.5	4.6	11.3	2.7	3.2	0.2	7.0	0.2	2.2	0.3	7.3	0.4	8.6	1.0	40.6	1.8
KAP	1.2	4.4	6	5.3	1.1	0.1	6.2	0.2	1.7	0.1	17.5	0.3	9.7	1.8	48.0	1.2
NEC	1.8	28.8			2.1	0.7	8.5	3.5	1.3	1.0	9.5	26.4	62.8	1.7	61.4	36.4

Evaluation of pollution loads

Based on these calculations of pollution loads according to equations (1) and (2) we classified the monitoring sites into three groups (Tab. 4).

The first group ($L \leq 0.33$) included the sites ZAJ, PRA, LOU, KAP and NEC, which are located in the southern and western border regions of the Czech Republic and are characterized by the smallest pollution loads. Sites with intermediate pollution load ($0.34 < L \leq 0.66$) included BUK, POM and TET, situated in the north of the country. The highest pollution load ($L > 0.66$) was observed in the northeast of the Czech Republic (sites VRH and ELK).

Comparisons of soluble and insoluble fractions in rime and snow for individual elements

Proportions of soluble and insoluble fractions in rime and snow in winter atmospheric deposition are shown in Fig. 4.

Across the sites, Pb, Cu and Zn fluxes decreased in the order: soluble element fraction in snow > soluble fraction in rime > insoluble fraction in snow > insoluble fraction in rime. Contrastingly, Be exhibited different proportions compared to Pb, Cu and Zn, with fluxes decreasing in the following order: insoluble Be fraction in snow > soluble fraction in snow > soluble fraction in rime > insoluble fraction in rime.

Lead soluble in diluted HNO_3 made up 96 % of the total Pb deposition, with the remaining 4 % Pb bound mainly in silicates (Čimová et al. 2016). Cu and Zn soluble species also dominated over insoluble species, constituting 92 and 93 %

of the total winter-time flux (Novák et al. 2016). In contrast, only 34 % of the total Be deposition occured in the form of soluble, i.e. bioavailable, form (Bohdálková et al. 2012).

We again note that we assumed that rime contributed 10 % of the snowpack water (Hindman et al. 1983). The actual amount of rime is hard to determine and could have varied among the sites.

Identification of pollution sources

Modeling of backward trajectories of air masses identified southern Silesia, Poland (mostly metallurgy industry) and the industrial city Ostrava (steel and hard coal production) as the sources of Be pollution for the sites ELK, VRH and TET (Bohdálková et al. 2012).

Isotope ratios of winter deposition samples together with the between-site variability of calculated Pb fluxes (Fig. 3a) suggested that the high Pb deposition at ELK and VRH is generated by Pb smelting in Olkusz rather than by coal combustion or remobilized pre-2000 petrol Pb (Čimová et al. 2016). Differences in lead isotope composition in snow and rime could indicate different pollution sources for individual types of deposition (Čimová et al. 2016).

The Lubin black shales deposit in southern Poland was identified as the dominant source of Cu pollution (Novák et al. 2016).

Values of $\delta^{66}Zn$ identified two possible sources of Zn pollution: the Olkusz Mississippi Valley-type Pb-Zn deposit in southern Poland and Ostrava coal.

Tab. 4: Pollution ratios (PR_x) of individual elements, pollution load (L) and classification of the sites into three groups according to the degree of pollution load.

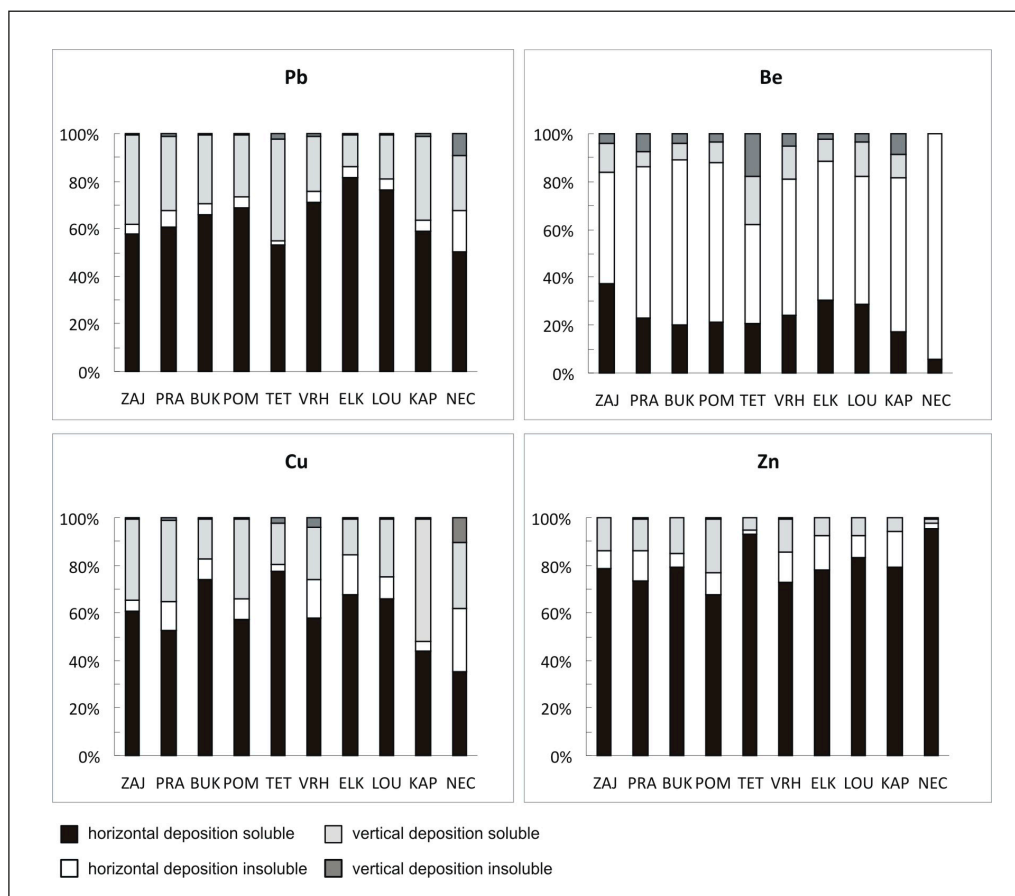| Site	Pb	Be	Cu	Zn	*L* total	Class
ZAJ	0.24	0.29	0.54	0.19	0.27	1
PRA	0.22	0.25	0.44	0.26	0.25	1
BUK	0.49	0.22	1.00	0.43	0.46	2
POM	0.56	0.47	0.97	0.20	0.54	2
TET	0.42	0.39	0.54	0.16	0.41	2
VRH	0.97	0.44	0.53	0.40	0.78	3
ELK	1.00	1.00	0.76	1.00	0.98	3
LOU	0.30	0.42	0.39	0.24	0.33	1
KAP	0.13	0.15	0.37	0.15	0.15	1
NEC	0.23		0.46	0.23	0.25	1

Fig. 4: Partitioning of soluble and insoluble fractions of Pb, Be, Cu and Zn in rime and snow at each study site.

The large isotope differences between soluble and insoluble Zn fractions may be explained by different sources for each fraction (Novák et al. 2016).

Temporal changes in trace metal input fluxes

In Central Europe, considerable air pollution began after World War II. (Vile et al. 2000). Under the former socialist regime, the development of heavy industry, coal mining and combustion and the use of alkyl-lead gasoline additives resulted in some of the highest atmospheric emissions of toxic metals and metalloids in the world (Moldan, Schnoor 1992). Air pollution reached a maximum during the 1980s and then sharply decreased after the Velvet Revolution due to the introduction of state-of-the-art technology in coal-burning power plants, base-metal smelters

and the chemical industry between 1990 and 2005 (Čimová et al. 2016). Fig. 5 shows dramatic temporal change in wet deposition of Pb (dry deposition was not determined) observed at two monitoring sites of the Czech Hydrometeorogical Institute (CHMI) Ústí nad Labem (UNL) and Hradec Králové (HK; Fig. 1) during the years 1991–2010.

On average, recent Pb concentrations in snow were four times lower compared to those measured between 1981–1983 by Král et al. (1992) at seven high-elevation sites in the Czech Republic. However, large between-site differences of the rate of pollution decrease have been observed over more than thirty years. Whereas the southern part of the country had an up to 18-fold pollution decrease, the northeast of the country remained the most polluted region and Pb concentrations in snow decreased only by half (Čimová et al. 2016). Mean concentrations
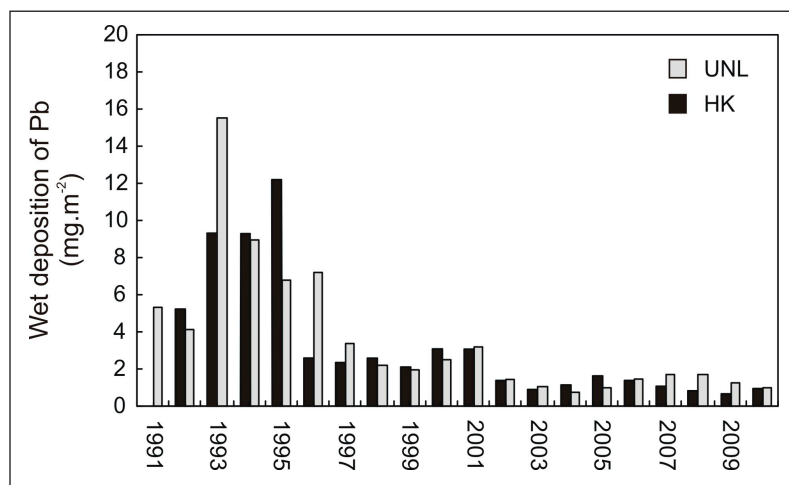
Fig. 5: Temporal changes in wet deposition of Pb measured at Czech Hydrometeorological Institute monitoring sites Ústí nad Labem (UNL) and Hradec Králové (HK).

of soluble Pb in rime samples exceeded the drinking water limit (DWL) for dissolved Pb concentrations ($10 \, \mu g.L^{-1}$) at all group 2 and 3 sites, and exceeded the DWL for mean soluble Pb content in snow at the site ELK. Higher Pb concentrations in rime may not present a direct threat to human health because: (i) rime forms only about 10 % of the total winter deposition (ii) Pb concentrations could be enhanced due to the addition of HNO_3 to precipitation samples (Čimová et al. 2016).

Hydrological data from the year 1996 (GEO-MON) found the highest beryllium deposition rates in the northeast (site CER) and northwest (site JEZ) of the country due to lignite mining and combustion. The CER catchment, situated close to ELK (see Fig.1), exhibited as much as $1,500 \, \mu g.m^{-2}$ of Be in winter. The recorded wintertime Be flux at the JEZ catchment, located close to PRA was $10 \, \mu g.m^{-2}$ (Bohdálková et al. 2012).

Overall, Be, Cu and Zn concentrations in winter precipitation samples were minute compared to DWL and do not present threats to human or ecosystem health (Bohdálková et al. 2012, Novák et al. 2016).

In general, the recent atmospheric deposition of Pb, Be, Cu and Zn did not show a large north-south pollution gradient as has been published in many studies (e.g. Vile et al. 2000, Novák et al. 1996, see also Pb concentrations in 1996 in Fig.1). Sites in the northwest (Ore Mountains) together with the south are now among those

with the lowest pollution loads due to dust removal equipment and desulfurization of power stations, as well as removal of heavy industry from the western part of the country. The most polluted areas are located in the northeast of the Czech Republic where both Czech and Polish industry and coal mining are still active in the close vicinity.

Acknowledgement

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