

Decreased atmospheric deposition of heavy metals shown by long-term monitoring using the moss *Pleurozium schreberi*

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Abstract

In Europe, economical restructuring and technological progress has been aimed at reducing pollution emissions at local, regional and global scales, which has been monitored using standard methods. Among the many methods used to determine deposition of heavy metals, in Europe moss has been used to monitor atmospheric pollution for more than 30 years on a 5-year cycle. Thus, this simple method can be used to assess improvement to the environment after massive economic change. Using PCA analysis, this study examines the long-term trends of heavy metal concentrations (Cr, Cu, Ni, Pb, V, Zn) in Latvia. There has been an decline in heavy metal concentrations in Latvia related to the closure of large industries after the the collapse of the Soviet Union and due to change in fossil fuels in the energy sector from petroleum to natural gas, but past effect from some sources is still evident. Increased quality of automobile fuel led to a decrease of lead concentration, and conversion of fuel source in the energy sector from oil to natural gas caused a decline of V and Ni concentration.

Introduction

Air pollution is a global problem that has a negative impact on the terrestrial environment and living organisms (Koz and Cevik 2014). Among the most significant atmospheric air pollutants are heavy metals, which can have a significant impact on human health (Briffa et al. 2020; Liao et al. 2022), ecosystems (Bjerregaard et al. 2015) and biological and chemical processes in soil (Türtscher et al. 2017). Although declining trends in heavy metals emissions (European ... 2012; European ... 2020) were observed in Europe at the end of the 20th century and in the 21st century, research on heavy metals in different environments have not lost their spotlight (Briffa et al. 2020).

The use of terrestrial moss as bioindicators at different scales is a widely recognized method for studies of atmospheric deposition at international (Harmens et al. 2015; Rühling et al. 1996), national (regional) (Grodzińska and Szarek – Łukaszewska 2001; Napa et al. 2015; Šakalys et al. 2009) and local levels in specific areas (Xiao et al. 2021), and around specific emission sources (Balarama Krishna et al. 2003; rāga et al. 2017) or to monitor the impact of the traffic intensity (Zechmeister et al. 2005). Since the 1970s, Scandinavian countries have used moss species in biomonitoring of trace metal atmospheric deposition (Rühling and Skärby 1979; Steinnes et al. 1997). Expansion of moss monitoring of heavy metal deposition in the Nordic European region to include the Baltic countries occurred in 1990. With further enlargement across Europe, coordinated monitoring using standard methods is undertaken every five years (Frontasyeva et al. 2020; Harmens et al. 2010; Harmens et al. 2011).

Moss is a more efficient chemical deposition accumulator than, for example, leaves of vascular plants, branches, or bark of trees (Brown and Bates 1990). The process of collecting moss samples is not complex and is a relatively inexpensive process (Harmens et al. 2015), and the bioindication method of moss is relatively sensitive to allow determining the level of environmental contamination (Kayee et al. 2015). The accumulated pollutant content in moss represents deposition over the last three to five years (Harmens et al. 2010). The moss bioindication method should utilize a fairly common species, which is dependent on nutrient supply from precipitation (Grodzińska and Szarek – Łukaszewska 2001). The elements identified in precipitation are mostly also found in moss (Schröder et al. 2008), and a linear relationship between content of an element in precipitation and moss was proposed (Rühling et al. 1987). Indeed, significant correlation between the chemical composition of moss and that of precipitation has been observed, and proportion of metals accumulated from precipitation was 40–55% for vanadium, 50% for copper, 35% for zinc, 50–65% for cadmium, and even 100% of lead (Berg et al. 1995). On a European level, the concentrations of Cd and Pb in moss weere significantly correlated with their levels in modelled atmospheric deposition (Holy et al. 2009). However, other studies found no significant correlation between concentrations in wet deposition and moss for

Mn, Cr, and Ni (Ross 1990). Statistical analyses confirmed that concentrations of Cd and Pb in moss are mainly determined by these atmospheric deposition and can therefore be used as bioindicators.

The political and economic transformation after the collapse of the Soviet Union was associated with a rapid decline in atmospheric pollution after 1990 (Cabinet of Ministers 2020; Latvian Environment Agency 2001). Moss monitoring in Latvia has been conducted in Latvia every five years since 1990. Previous results up until 2015 had shown a decrease in the content of heavy metals in the moss *Pleurozium schreberi* (Tabors et al. 2017), which was suggested to be linked to the closure of several industries, a shift in the energy sector from petroleum to natural gas, less emissions in the transport sector, and the reduction of cross-border pollution (Nikodemus et al. 2004; Tabors et al. 2017).

To provide insight on impact of technological improvement in the industrial and decline of long-distance transport on trace metal emissions after entry of Latvia in the European Union, this study provides an analysis of changes in heavy metal content in *Pleurozium schreberi*. We focus on the temporal changes in metal concentrations, rather than the typical spatial analysis of patterns. The study encompasses the period from 1995–2020 when a fixed set of sampling sites were used.

Materials And Methods

Site description

Latvia is located on the eastern coast of the Baltic Sea in the transition zone of the nemoral and boreal zones (Ozenda 1994), called the boreo-nemoral zone (Sjörs 1963). The climate is transitional maritime to continental with mean temperature 3.6 °C in February and 16.9 °C in July. Annual precipitation is 709 mm, of which about 332–441 mm falls in the warm period. The largest amount of rainfall falls in the western part of Latvia and the central part of Latvia on the western slopes of the highlands. The climate is more continental towards the east part of Latvia. Winds dominate from the South-West (Briede and Koreļska, 2018). The forest area is about 52% and the dominant species are pine *P. sylvestris*, birch *Betula* L. spp. and spruce *P. abies*, which contribute 32%, 30% and 19% of the total area (VMD 2021).

During the Soviet occupation, Latvia a developed industrial sector, which accounted for 37.1% of the gross domestic product in 1990, but following the collapse of the USSR demand for Latvian industrial production declined sharply, which continued in the coming years, leading to a shift of industry from the heavy industry to more environmentally friendly, electrical, pharmaceutical industries, and also in replacement of coal and petroleum fossil fuels (Paiders 2018). The most important feature of Latvia's urban network is the dominant role of Riga – the State capital.

Sample Collection

In Latvia, mapping of atmospheric pollution using moss was started in 1990, and continued every 5 years except in 2010 due to lack of funding. In this study we do not include the data from 1990 due to a different sample site network and a different moss species (*Hylocomium splendens*). Starting from 1995, *Pleurozium schreberi* was sampled in each survey between August and October. In this study, we included 78 plots (Fig. 1) which were sampled continuously in all years with fixed coordinates. Many of the sampling sites from an initial 103 sites in 1995 had been destroyed due to logging intensification. The sites were located in pine forests. Each plot (50 x 50 m) was located at least 300 m from major highways and at least 1 km from stationary pollution sources and large cities. Following the recommendations of the previously developed method (ICP Vegetation 2010), moss samples were taken outside of

tree crown impact area to avoid canopy throughfall deposition. In the field, moss samples consisting of 5–8 subsamples from each site were placed in polyethylene bags and transported to the University of Latvia laboratory.

1. Figure. Location of plots in Latvia.

Analytical Methods

The entire analysis process was conducted in the soil laboratory of the University of Latvia. Debris (needles, leaves) and dead (brown) segments of moss samples were removed, leaving only green segments for further analysis. The moss samples were then dried at 85°C.

The methods used for analysis changed between sampling years due to technological improvements. To control for quality of results, the moss standards M2 and M3, which were first used in the 1993 European moss survey (collected in semi-open coniferous forests in Finland near Harjavalta and Puolanka, respectively) were analyzed every sampling year (Steinnes et al. 1997).

In 1995, 2000 and 2005, about 1.5 g of homogenized moss was mineralized in 15 mL concentrated HNO_3 , heated at 95°C for 2h, and Cd, Cr, Cu, Ni, Pb, V and Zn concentrations were determined using a flame/graphite furnace a Perkin Elmer AAS Analyst 800 or Perkin Elmer AAS 4110 ZI (Nikodemus et al. 2004). In 2015, 100–200 mg moss samples were mineralized in 5 ml HNO_3 + 2 ml H_2O_2 overnight, then 10 ml HNO_3 was added and heated until a volume of 5 ml remained, filtered and made up to 10 ml with deionized water (Tabors et al. 2017). Concentrations of eight metals (Cd, Cr, Cu, Fe, Ni, Pb, V and Zn) were again measured using an atomic absorption spectrophotometer (AAAnalyst 800, Perkin–Elmer). In 2022, an ETHOS UP system was used with microwave acid digestion of moss was used. 8 ml of nitric acid (HNO_3) and 2 ml of hydrogen peroxide (H_2O_2) were added to 500 mg moss. The sample was then heated at 200°C until the organic material was completely dissolved, filtered and the solution brought up to 50 ml in volume with distilled water. Concentrations of Pb, Cu, Ni, V, Cr, and Zn were determined using a "Thermo Scientific" Inc. ICP-OES spectrometer iCAP7000.

Statistical analysis

As Shapiro-Wilk's tests showed departure from a normal distribution and Q-Q plots indicated a log-normal distribution, the Friedman non-parametric repeated measures test with a Conover's post hoc test were used to test for significant differences between years for each metal. These tests were conducted using JASP 0.16. For each sampled year, and for all years, PCA of a log-transformed matrix of concentrations was conducted using PCord 7.0 to visualise associations among metals and sites.

Results

The results of monitoring of metal concentration in moss between 1995 and 2020 (Table 1; Fig. 2) show different trends for the metals. The concentrations of Pb, V and Ni significantly decreased between years of study. An opposite trend was observed for Cu, as the concentration in 1995 was significantly lower, and the concentration in 2020 was significantly higher than in the other years. Zn concentrations significantly increased between 1995 and 2005 and then decreased in the next years. The opposite occurred for Cr – significant decrease between 1995 and 2005, and then an increase in later years.

Table 1
Median, standard deviation, minimum and maximum concentrations
($\mu\text{g/g}$) of heavy metals (Pb, Cu, Ni, V, Cr, Zn) in *Pleurozium schreberi*
moss.

	Year	Median	Std.deviation	Minimum	Maximum
Pb	1995	7.28	3.68	3.00	36.10
	2000	3.61	4.10	1.50	37.00
	2005	4.62	5.29	2.55	49.97
	2015	1.42	1.03	0.41	9.21
	2020	0.74	0.22	0.35	1.47
Cu	1995	3.96	1.04	2.70	8.30
	2000	5.67	2.36	3.10	17.00
	2005	5.09	1.46	3.28	12.10
	2015	5.63	2.17	2.38	12.31
	2020	6.27	1.42	3.33	10.04
Ni	1995	1.42	1.37	0.50	10.57
	2000	1.36	0.95	0.50	5.50
	2005	0.91	0.61	0.10	5.31
	2015	0.57	0.24	0.20	1.64
	2020	0.31	0.24	0.04	1.25
V	1995	4.18	4.23	1.43	29.60
	2000	2.69	3.39	0.60	23.00
	2005	2.11	3.43	0.48	26.75
	2015	0.57	0.35	0.19	2.54
	2020	0.47	0.69	0.16	6.23
Cr	1995	1.26	0.42	0.70	3.23
	2000	1.06	0.43	0.58	3.30
	2005	0.29	0.16	0.13	1.55
	2015	0.37	0.19	0.01	1.04
	2020	0.47	0.15	0.27	1.20
Zn	1995	31.82	10.65	19.05	101.19
	2000	36.01	20.36	20.00	189.00
	2005	44.66	28.30	26.10	279.70
	2015	34.70	9.64	22.40	99.79

Year	Median	Std.deviation	Minimum	Maximum
2020	30.61	5.95	19.58	50.12

Table 1.

Median, standard deviation, minimum and maximum concentrations ($\mu\text{g/g}$) of heavy metals (Pb, Cu, Ni, V, Cr, Zn) in *Pleurozium schreberi* moss.

Figure 2. The median concentration of heavy metals ($\mu\text{g/g}$) with interquartile ranges and outliers, during the period 1995–2020 (a. – Pb; b.- Cu; c.-Ni; d.- V; e.- Cr; f.- Zn. Different letters indicate significant differences (Conover's post hoc test) between years.

The PCA of metal concentrations for all years (Fig. 3a) clearly shows differences between years and grouping of metals –V, Ni, Pb and Cr in one cluster and Zn and Cu in the other. While outlier sampling sites clearly affect the derived PCA gradients, there are also distinct clusters of background sampling sites with a time trend (1995 to 2020) from the left to right side of the ordination (Fig. 3b-f).

PCA of concentrations in each year visually depict the main outliers sampling sites with high concentrations. In all years, Grobiņa (Grob) was the key outlier (Fig. 3). This sampling site is close to a metallurgical industrial complex in Liepāja, which had disruptions in activity and now is closed. The clusters of metals in the ordinations indicate that the main metal deposition in the Liepāja area was contributed by Zn and Pb, but this association breaks down by 2020, when it is associated with Ni, V and Pb. In 1995, sampling sites in Rīga, the largest city of Latvia formed the outliers – TEC-2 (TEC) and Ulbroka (Ulbr), along with other sites in the vicinity of Rīga –. Beberbeķi (Bebe), Ķekava (Ķeka), Jaunciems (Jaun) and Olaine (Olai). These sites were associated with high V and Ni concentrations in 1995 (Fig. 3b). In subsequent years (2005 to 2015) these sites lost their importance for metal deposition and were replaced by sites (Ezere, Ezer; Grieze, Grie; and Kareļi, Kareļi) in the border area of Latvia, north of the Lithuanian Mazeikiai oil refinery and the Naujoji Akmenė cement plant in Lithuania (Fig. 3d, Fig. 3e). This deposition in the border area was associated consistently with V and Ni, and in separate years with Cu or Cr.

Figure 3. PCA of heavy metal concentrations (Pb, Cu, Ni, V, Cr, Zn) in all years (a); 1995 (b); 2000 (c); 2005 (d); 2015 (e) and 2020 (f) in Latvia.

Discussion

Accumulation of heavy metals in moss can be affected by meteorological conditions, size of the particles and their deposition properties can affect the absorption of (Wolterbeek 2002). A review showed that only 40.1% of studies found a significant correlation between the concentrations of pollutants in moss and deposition (Aboal et al. 2010). Sometimes, the small size of moss samples, large distances between moss sampling sites, and differences in the time of collecting moss samples, create problems for the interpretation of the data (Aboal et al. 2010). Also, large uncertainties can be associated with the legacy contribution of metals in soils and therefore the contribution of wind-blown dust to the calculated total deposition of metals (Harmens et al. 2015). While previous studies have shown that heavy metals in moss show mainly the deposits of heavy metals in the atmosphere, each country may also have specific elements emitting into the atmosphere (Schröder et al. 2013).

Despite the limitations of pollutant monitoring using moss, the results clearly reflect the changes in emissions that occurred during the vast economic, industrial and energy sector restructuring that occurred after escape from the

totalitarian Soviet system in 1991. The observed spatial and temporal differences in the main outliers of high metal concentrations is particularly interesting, considering that air pollution levels in Latvia were among the lowest in Europe, for example in 2015 (Frontasyeva et al. 2020). Even with this relatively low level of pollution at the European level, a general decrease of heavy metal concentration in moss was still observed.

The observed changes in the concentration of heavy metals in moss in Latvia showed similar trends as the European average data from 1990 to 2015, where the most rapid fall was reflected in Pb, Cd and V (Frontasyeva et al. 2020). Despite an increased number of vehicles in the Latvia following the recovery of Latvia's independence (Paiders 2018), the reduction of Pb emissions was linked with improved of petrol and vehicle quality in Latvia (Nikodemus et al. 2004), and a reduction in cross-border pollution transfer from Europe (Tabors et al. 2017). The effect of the recent transition from the combustion of petroleum products to wood biomass in many local boiler houses on distribution of heavy metal emissions (Steinnes et al. 2011) is presently not clear, but a decrease would be expected, and likely partly explain the general decrease of metal deposition between 2005 and 2020.

The results of the PCA analysis reflect the impact of specific sites on the concentration of heavy metals in moss and their interrelations. The association of the heavy metal into clusters in the ordination change between years, particularly for Pb, Zn, Cu, and Cr, which might be explained by changes in operation of industries that are regional and local emission sources. There might also be a legacy contribution of metals in soil and roadside dust due to previous atmospheric deposition (Harmens et al. 2015), which tends to be high for metals such as Cd and Pb (Iljin et al. 2007). It is however necessary to take into account secondary contamination accumulated in vegetation and soil, as well as natural sources of heavy metals, which may affect the content of heavy metals in moss. The relatively low concentration of Cu, as in many European countries (Steinnes et al. 2011) indicates lack of a major source of emissions of this element and inconsistent association with the other metals. However, the observed increase in Cu concentration in Latvia is consistent with the general trend in Europe (Harmens et al. 2015), which has not yet been explained.

The Grobina (Grob) site was affected by heavy metal (particularly Zn and Pb) emissions from a long-standing metallurgical company inherited from the Soviet period. The switch in metals associated with this source in 2020 to Pb, Ni and V can be explained by its disruption of operation in 2013 and closure in 2016. (<https://lr1.lsm.lv/lv/raksts/pusdiena/metalurga-darbibas-apturesana-sobrid-rada-mazaku-triecienuekono.a65621/>). However, the decrease in Zn concentration in 2020 in the Liepaja area was not as low as might have been expected after industry closure, which might be due to washout from tree canopies (Nickel et al. 2022; Steinnes 1995). Secondly, the new importance of Ni and V at the Grobina site is likely explained by emissions from industrial sources utilizing combustion of petroleum products (Rühling and Tyler 2004; Steinnes et al. 2011). The high Ni and V concentrations in and around Riga in 1995, but not later years, can be explained reconstruction of the Riga electrical thermal power station (TEC – 2) carried out between 2006 and 2013, resulting in a transition from the use of petroleum products for heating to gas. (http://www.latvenergo.lv/lat/Jaunumi/preses_relizes/5355-rigas-tec-2-rekonstrukcija-moderna-un-efektiva-bazes-jauda-latvijai; Nikodemus et al. 2004; Tabors et al. 2017). The Ezere (Ezer), Grieze (Grie), and Kareļi (Kareļi) sites, which are outliers in 2000, 2005 and 2015 were likely affected by cross-border pollution transfer from the Lithuanian Mazeikiai oil refinery and Naujoji Akmene cement plant. In Lithuania, high concentrations of Ni, Pb, Mn and Cr in moss were found at a 2.5-km and 3.5-km distances in the downwind direction from the Naujoji Akmene cement plant enterprise for Zn, Cu and Cd in both cases (Baltrėnaitė et al. 2014). The loss of these outliers in 2020 seems to be associated with emission abatement.

Conclusions

The study showed that atmospheric air pollution with heavy metals has been decreasing in Latvia due to loss of some major point sources, which has resulted in spatial homogenization of deposition. The loss of point sources has been due to industry closure due to economic reasons, and pollution abatement technology in industry, energy production and transport. While transborder pollution has decreased, the Mazeikiai oil refinery and Naujoji Akmenė cement plant in Lithuania remain sources of heavy metal deposition to Latvia. Future studies need to consider legacy pollution that has accumulated in forest ecosystems and its effect on chemical composition of moss. An important issue Latvia also loss of permanent sampling sites due to intensification of forest cutting, creating a need to choose sites only in protected territories. The study confirmed the efficiency of moss monitoring of atmospheric heavy metal deposition at various spatial levels.

Declarations

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Ethical approval Ethical approval is not required as there is no human data or primary data involved in the manuscript.

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Consent for publication Not applicable, and no human or individual is involved.

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Competing interest

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Author Contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Guntis Tabors, Linda Dobkeviča and Konstantīns Vilgurs. The first draft of the manuscript was written by Guntis Tabors, Guntis Brūmelis and Oļģerts Nikodemus and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Figures

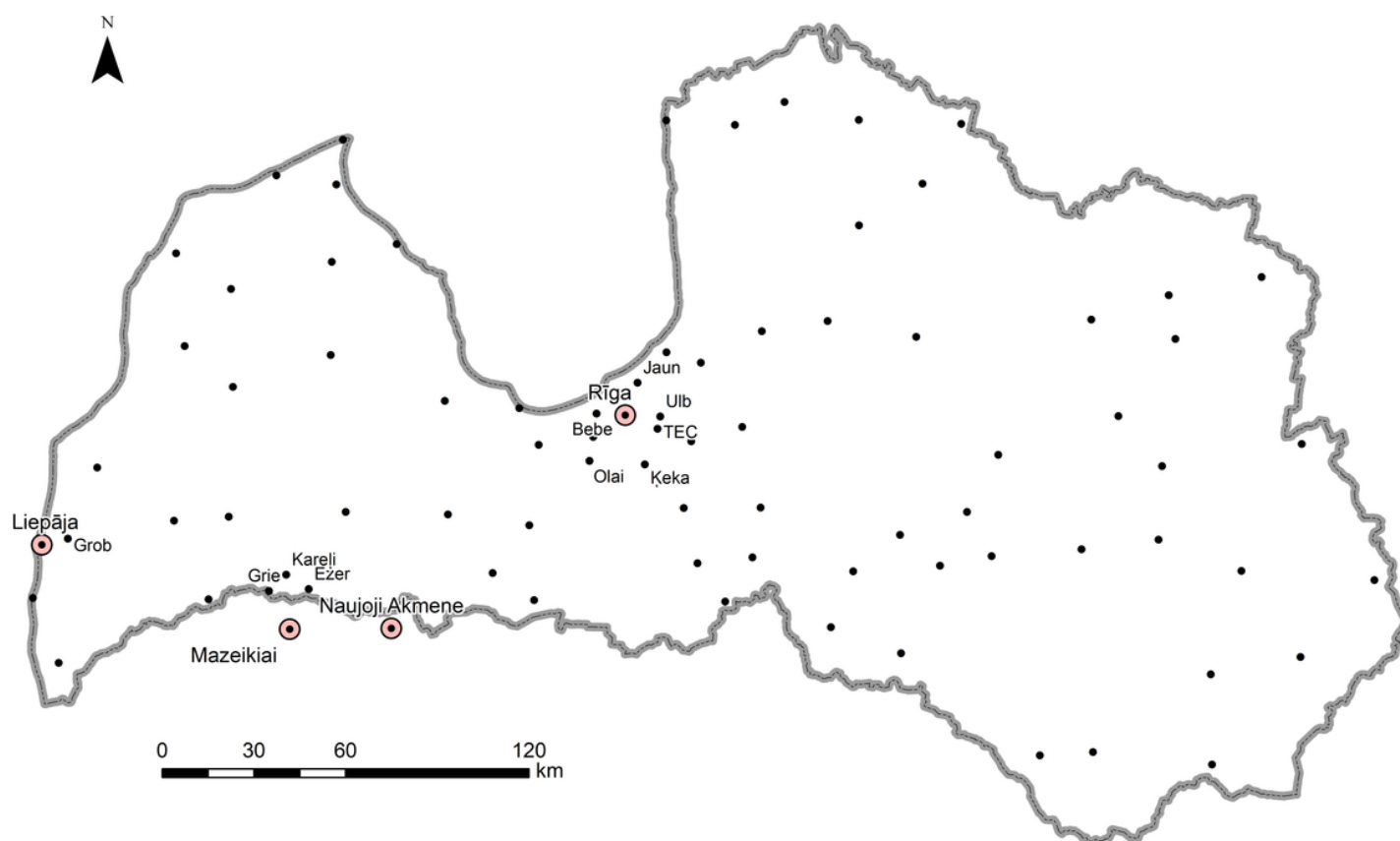


Figure 1

Location of plots in Latvia.

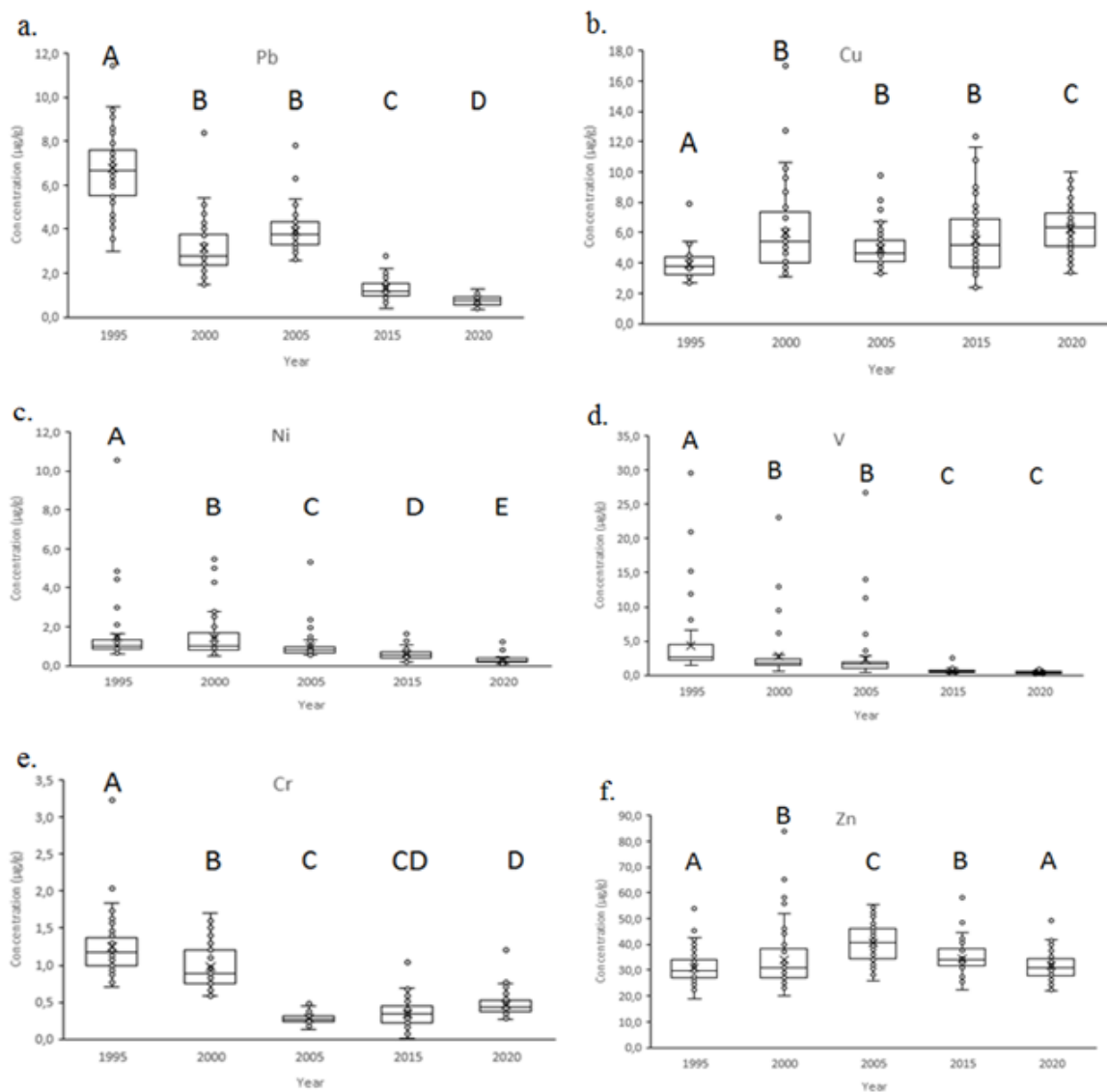


Figure 2

The median concentration of heavy metals (µg/g) with interquartile ranges and outliers, during the period 1995-2020 (a. – Pb; b.- Cu; c.-Ni; d.- V; e.- Cr; f.- Zn. Different letters indicate significant differences (Conover's post hoc test) between years.

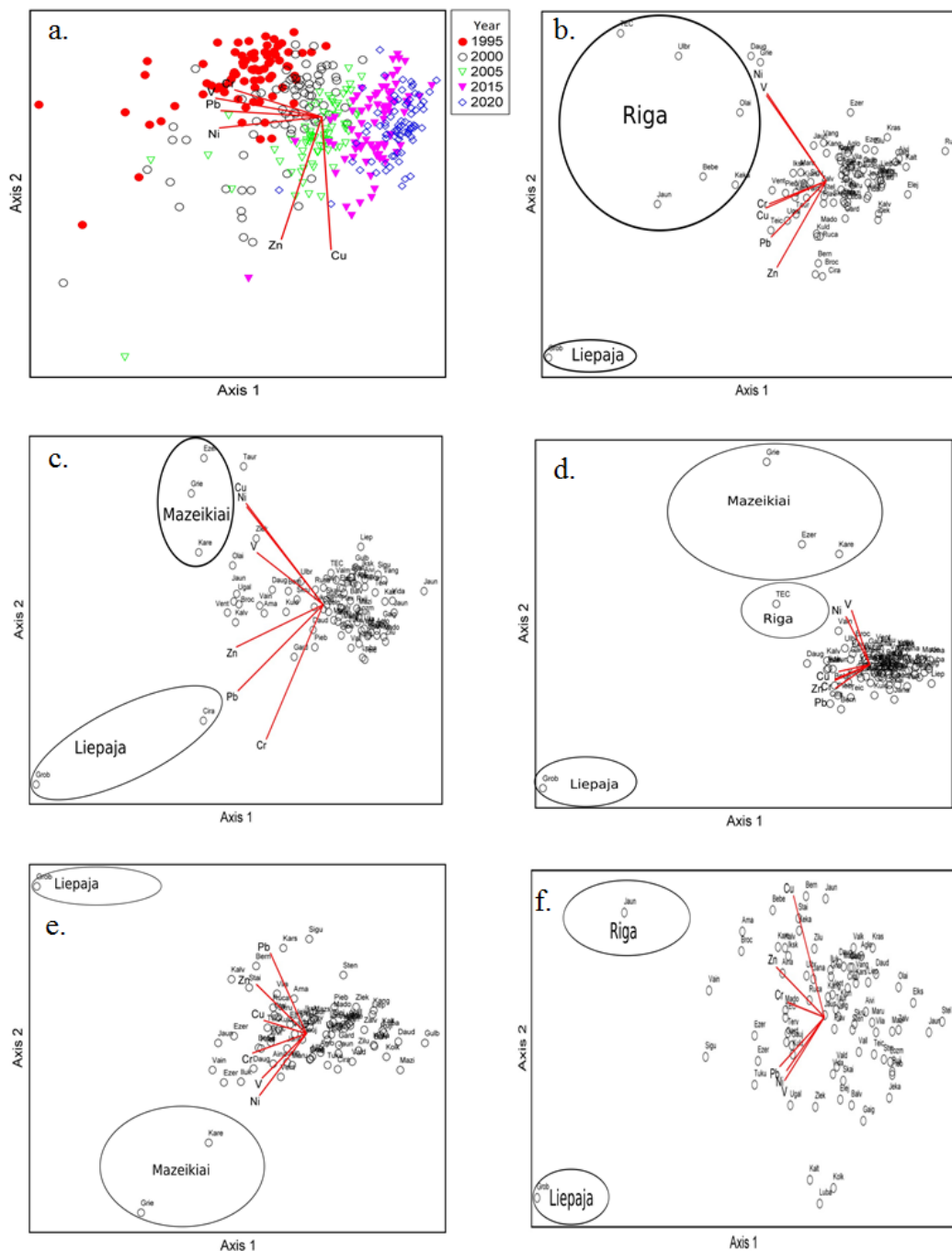


Figure 3

PCA of heavy metal concentrations (Pb, Cu, Ni, V, Cr, Zn) in all years (a); 1995 (b); 2000 (c); 2005 (d); 2015 (e) and 2020 (f) in Latvia.