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Atmospheric Deposition of Lead and Cadmium in a Central European Country over the Last Three Decades

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Abstract: Lead (Pb) and cadmium (Cd) levels in ambient air were explored due to their toxicity and deleterious environmental effects. The aim of this study was to assess the time tendencies and spatial changes in Pb and Cd atmospheric deposition in a Central European country with a long history of ambient air pollution. We used measured data on precipitation chemistry and ambient air pollutant concentrations in the Czech Republic (CR) obtained within a nation-wide monitoring network. Our analysis is based on spatial patterns of annual wet-only and dry deposition fluxes constructed for 1996–2021. The results indicated that both Pb and Cd deposition over the CR during the last three decades decreased substantially, about 10 times, the absolute values for Cd being one order of magnitude lower than those for Pb. The wet-only deposition pathway dominated over the dry deposition pathway. This trend reflects the heavy metal (HM) emission reductions in the CR and neighboring countries and is in line with decreasing trends in ambient air HM concentrations in Europe. The spatial patterns showed that the northern industrial portions of the CR were loaded more as compared to the southern parts, and that the extension of affected regions has recently decreased substantially.

Keywords: heavy metals; Czech Republic; time tendencies; spatial patterns; 1996–2021

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1. Introduction

Lead (Pb) and cadmium (Cd) are listed among the group of heavy metals (HM), a term widely used, though defined diversely in individual science fields and including different elements depending on the context [1–3]. Nevertheless, regardless of some uncertainties in classification, HM are synonymous with pollution and toxicity [4] and have been widely recognized as a major environmental issue for decades [5–7]. HM are of concern for both humans and ecosystems [8]. Some are recognized as human carcinogens, and their persistence and accumulation in food chains are detrimental for both nature and humans [9]. With respect to the above, airborne heavy metals are observed and studied worldwide [10–13], as they represent a considerable risk for our environment [14,15].

Though HM are naturally present in the Earth's crust, uncontrolled human activities have substantially altered their natural biogeochemical cycles [16]. It is generally assumed that HM contamination was the highest in the 1960s and 1970s due to industrial activities peaking in regions of North America and Europe; however, modern measurements of ambient air concentrations of HM only started as late as the 1980s [17]. Emitted predominantly as a result of human industrial activities, HM are often bound to fine particles, $PM_{2.5}$ [18], and can be transported far (thousands of km) from their emission sources, thereby affecting even the most remote regions [19,20]. There is evidence of the effects of HM in Arctic and subarctic regions resulting from coal burning in the mid latitudes [17]. HM enter ecosystems via both dry and wet atmospheric deposition pathways, affecting water, soil, plants and trees [11].

In this paper we focus on two of the range of HM: lead (Pb) and cadmium (Cd), the toxic elements emitted primarily due to anthropogenic activities and demonstrating major peaks in $PM_{2.5}$ [21]. Pb and Cd have multiple effects on human health, including effects on the immune system, which is known to have a key role in the pathophysiology of cancer [22]. The International Agency for Research on Cancer (IARC) has classified Cd and its compounds as group 1 carcinogens, whereas Pb and its compounds have been classified as 'probable' human carcinogens, group 2a [23]. In recognition of their detrimental effects, based on WHO ambient air quality guidelines [24], European legislation sets up the limit value for Pb as a year average of 0.5 $\mu g \cdot m^{-3}$ [25] and target values for ambient air concentrations of Cd set up as an average over a calendar year as 5 $ng \cdot m^{-3}$ [26].

Both Cd and Pb exposures seriously threaten human health through bio-accumulation via food chains [27]. Hence mechanisms of foliar uptake and behavior in plants, including those used as principal components of human food, such as rice, cereals, fruits and vegetables, tea etc. are studied extensively [28–31]. For proper and efficient remediation it is of the utmost importance to correctly identify the pathways of HM inputs to the environment. Ma et al. [32] reported that wheat grain Pb contents originated primarily from atmospheric deposition rather than soil. Feng et al. [30] warned of higher health risks via the consumption of rice due to increased exchangeable Cd and Pb in surface soil due to atmospheric deposition. With respect to their importance, ambient concentrations of heavy metals are observed in many places over the world. Long-term records exist, for example in the United Kingdom [33].

In the Czech Republic, the emissions of HM peaking in the 1970s and 1980s were associated with the burning of fossil fuels in large lignite-burning power plants and industries, such as metallurgy, chemistry and glass and ceramic manufacturing, agriculture (industrial fertilizers and pesticides) and the use of leaded petrol in cars [34]. The aim of this study was to evaluate the long-term time trends and spatial changes in the atmospheric deposition of Pb and Cd over the Czech Republic in the last three decades. To this end, we used the measurements obtained by the Czech Hydrometeorological Institute (CHMI) and stored in a nation-wide ambient air quality database (ISKO) run by the CHMI.

2. Materials and Methods

Our analysis is based on the spatial distribution of atmospheric deposition fluxes of Pb and Cd obtained by observation-based geostatistical modelling, as described in detail below. Maps of total deposition fluxes were constructed as sums of dry and wet deposition maps. The maps were derived in a fine spatial resolution of 1 × 1 km. The input data were measured at sites depicted in Figures 1 and 2. We present the current state of the monitoring network (2019). The monitoring network in the CR has obviously developed over time, though with respect to number of stations measuring Pb and Cd in the period examined in our study, it has not changed substantially.

2.1. Wet-Only Deposition

Maps of wet-only deposition fluxes were created on the basis of fields of concentrations of individual HM in precipitation (annual volume-weighted averages) and fields of precipitation totals created on the basis of data observed at 750 meteorological station precipitation gauges accounting for the effect of altitude on precipitation amounts. The monitoring network for sampling precipitations for HM analyses, presently amounting to almost 30 sites, is presented in Figure 1. Precipitation samples for HM analysis were collected year-round, in rain and snow, using (i) automated wet-only samplers operated on a weekly/daily basis and (ii) bulk collectors operated on a monthly basis. HM concentrations in samples were analyzed using inductively coupled plasma mass spectroscopy (ICP-MS), the standard laboratory method capable of detecting HM at very low concentrations [35] since 2011. In 1996–2010, the graphite furnace atomic absorption spectrophotometry (GF-AAS) was used. According to the CHMI laboratory validation reports, these two methods deliver comparable results.

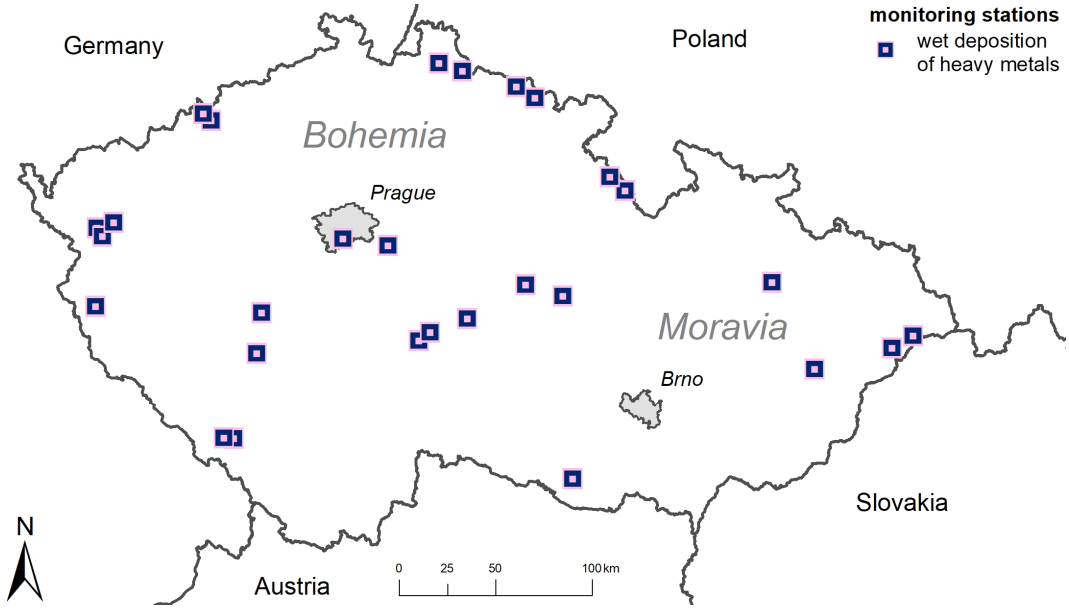

Figure 1. Map showing stations for monitoring heavy metals in precipitations used for creating wet deposition maps, situation in 2019.

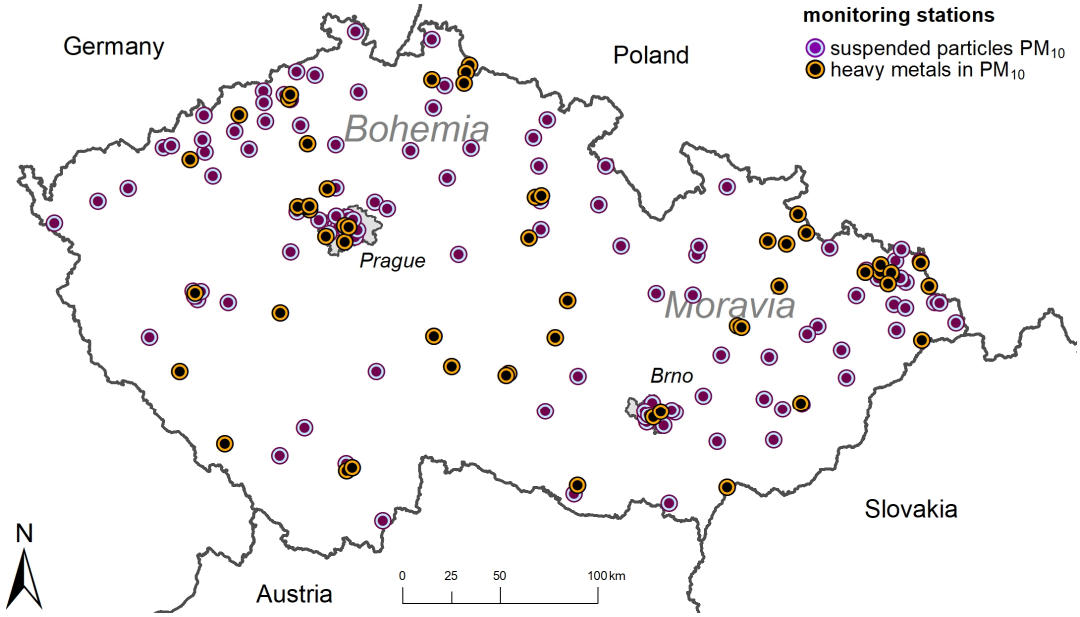

Figure 2. Map showing stations for monitoring heavy metals in PM_{10} used for creating dry deposition maps, situation in 2019.

The wet-only deposition spatial patterns were created from fixed station measurements using the inverse distance-weighted spatial interpolation technique, IDW [36]. The precipitation chemistry sampling network is sparse with respect to mapping (27 stations for the territory of the CR equal to 78,841 km^2); hence, the spatial interpolation was carried out in two stages. Firstly, the values were extracted into a regular 20 × 20 km point network, and secondly, the interpolation was generated in a regular 1 × 1 km grid for smoothing. In contrast, the meteorological network for observing precipitation depths amounting to hundreds of sites is much denser, allowing for the use of a more sophisticated approach of universal linear kriging [37]. The mapping approach for HM wet-only spatial patterns was analogous to that used earlier for sulfur [38,39] and nitrogen [40].

2.2. Dry Deposition

Dry deposition was calculated on the basis of the simplified inferential method [41,42], multiplying measured HM ambient air concentration and relevant mean annual dry deposition velocity. Though HM are closely associated with $PM_{2.5}$, we could not use this fraction, as $PM_{2.5}$ has not been measured in the CR until the mid-2000s. Hence, we used the data available on HM in PM_{10}, considering the clear linkage between the concentrations of HM in both aerosol fractions [43,44]. We used measured concentrations of fixed monitoring stations observing PM_{10} aerosol fraction (Figure 2). Pb and Cd concentrations in PM_{10} samples were analyzed using the inductively coupled plasma mass spectroscopy (ICP-MS) method (Jin et al., 2020) since 2003. In 1996–2002, graphite furnace atomic absorption spectrophotometry (GF-AAS) was used. According to the CHMI laboratory validation reports, these two methods deliver comparable results.

With respect to deposition velocities, we used a very rough approximation for the land-use distribution into forested and unforested areas [45]. Furthermore, we have not considered the seasonal or year-to-year changes in deposition velocity values and used a uniform mean annual deposition velocity identical for the entire period investigated. The deposition velocities used were as follows:

Pb: 0.25 $cm \cdot s^{-1}$ (for forested areas), 0.08 $cm \cdot s^{-1}$ (for unforested areas),
Cd: 0.27 $cm \cdot s^{-1}$ (for forested areas), 0.10 $cm \cdot s^{-1}$ (for unforested areas).

3. Results

3.1. Atmospheric Deposition of Lead

Considering the entire area of the CR (i.e., 78,841 km^2) our results indicated that the total atmospheric deposition of Pb decreased substantially over the period of 1996–2021 (Figure 3). It peaked in 1997 with 366 t, whereas the minimum of 48 t (split into 30 t deposited by wet-only and 18 t by dry deposition pathways) was reached in 2020. According to our estimates, the wet deposition pathway dominated over the dry pathway during the entire period investigated (Figure 4). A slight decrease in wet deposition contribution has been evident since 2002. Wet deposition contribution amounted to 70–90% until 2007. Its proportion then decreased somewhat, ranging from 52% to 70%, after 2008.

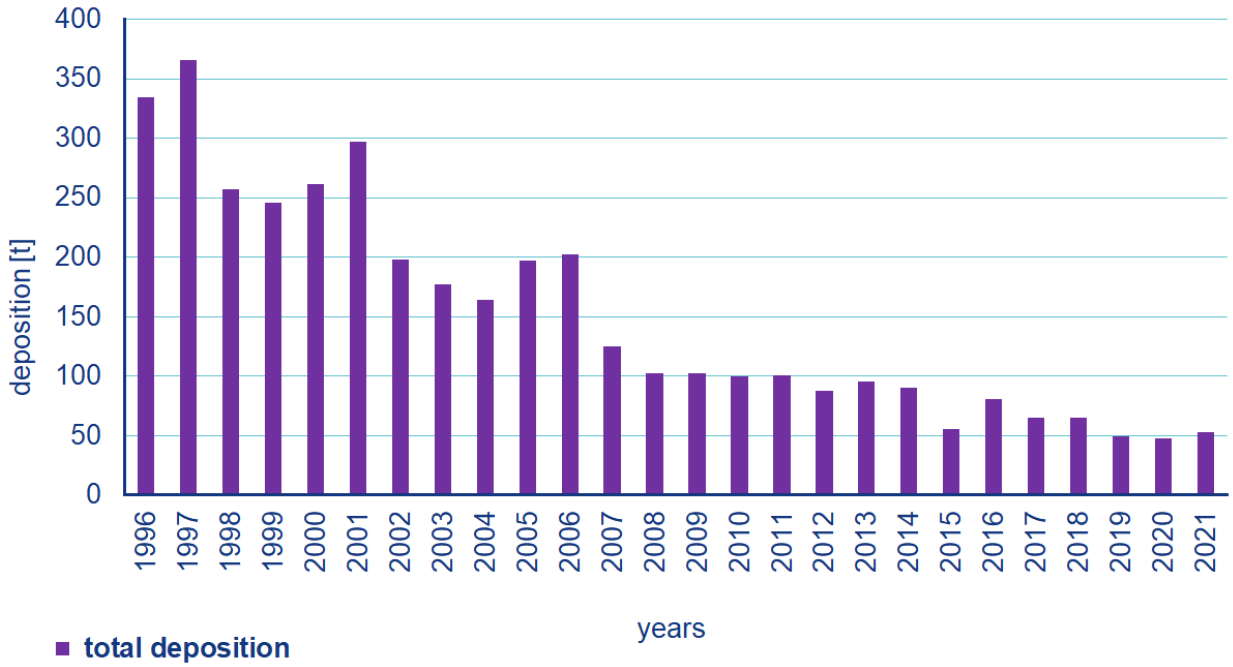

Figure 3. Estimate of annual total deposition of Pb over the entire area of the Czech Republic (78,841 km^2) based on data-driven geostatistic model, 1996–2021.

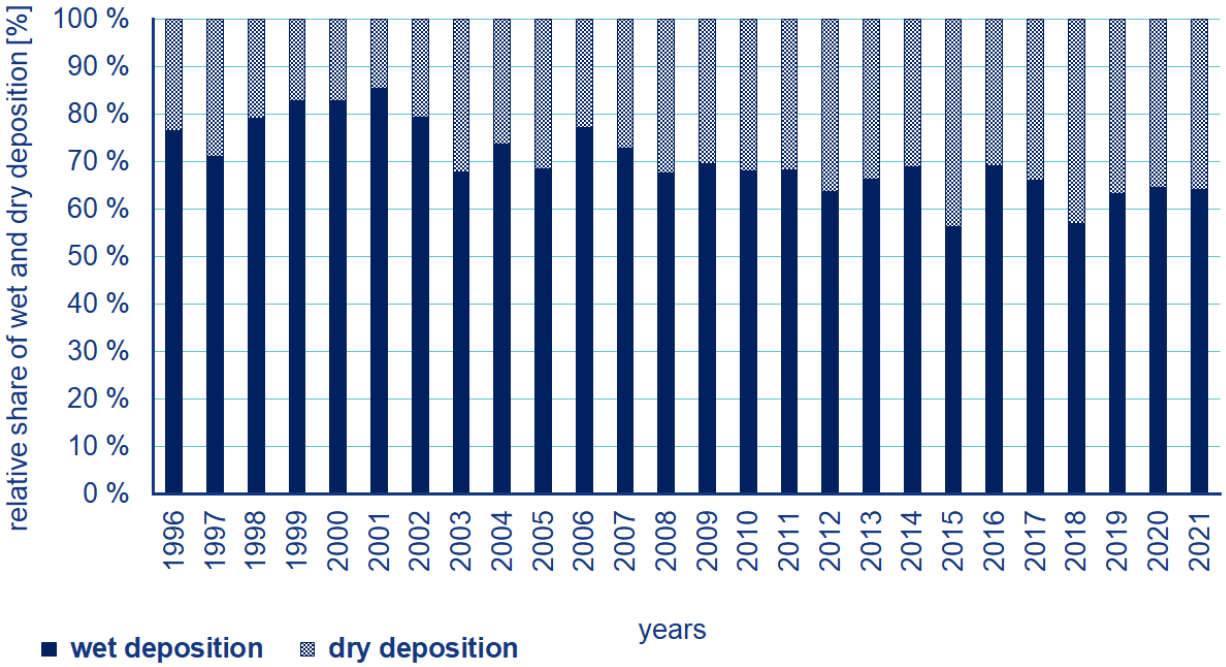

Figure 4. Relative contributions of wet and dry deposition of Pb over the entire area of the Czech Republic (78,841 km^2) based on data-driven geostatistic model, 1996–2021.

To visualize the spatial distribution of HM annual deposition fluxes, we chose two years, 2012 and 2019, as we intended to contrast different meteorology of the respective years. Whereas 2012 can be still considered as the year representing normal conditions, 2019 represents a long-lasting hot and drought spell beginning in 2014. The total Pb deposition decreased from 88 t (over the entire CR area) in 2012 to 49 t in 2019 (Figure 3); the proportions of wet and dry deposition were nearly identical—64% and 63% of wet deposition in 2012 and 2019, respectively (Figure 4). The spatial pattern of the total annual Pb deposition (Figure 5) revealed that the most affected regions in the past (2012) were Northern Moravia and the extended region of the Jizerske hory Mts. in North Bohemia, both being adjacent to industrialized Polish regions. Later, the Pb deposition fluxes decreased over major portions of the CR. The most affected region in Northern Moravia shrunk substantially (Figure 6).

3.2. Atmospheric Deposition of Cadmium

Similarly, a decreasing trend in total atmospheric deposition has been recorded for Cd. The absolute values for Cd are one order of magnitude lower than those for Pb. The highest Cd deposition of 21 t over the entire area of the CR (equal to 78,841 km^2) was recorded in 1996; the lowest deposition of 2.6 t was observed in 2018 (Figure 7). Similarly to Pb, the major deposition pathway for Cd over the entire time period examined was wet deposition as well. Its portion ranged between 80% and 90% until 2003, and decreased somewhat in proportion to 60–80% from 2004 on (Figure 8).

The total deposition of Cd decreased from 7.4 t (over the entire CR area) in 2012 to 2.7 t in 2019 (Figure 7); the proportion of wet deposition decreased from 74% in 2012 to 59% in 2019 (Figure 8). The spatial pattern of annual total deposition of Cd shows a higher load in the northern portion of the country in the past (Figure 9) and a substantial overall current decrease, except for one area, the vicinity of the town of Tanvald adjacent to the Jizerske hory Mts. (Figure 10).

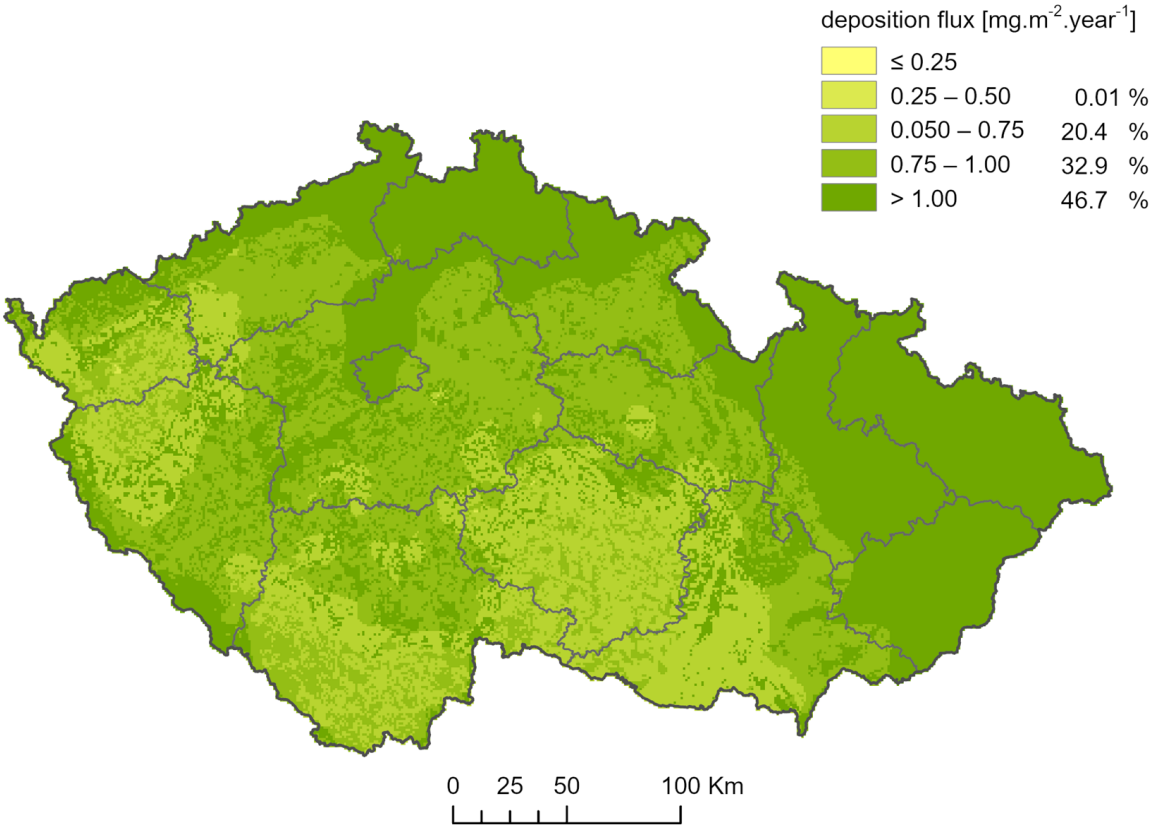

Figure 5. Spatial pattern of total Pb deposition, 2012.

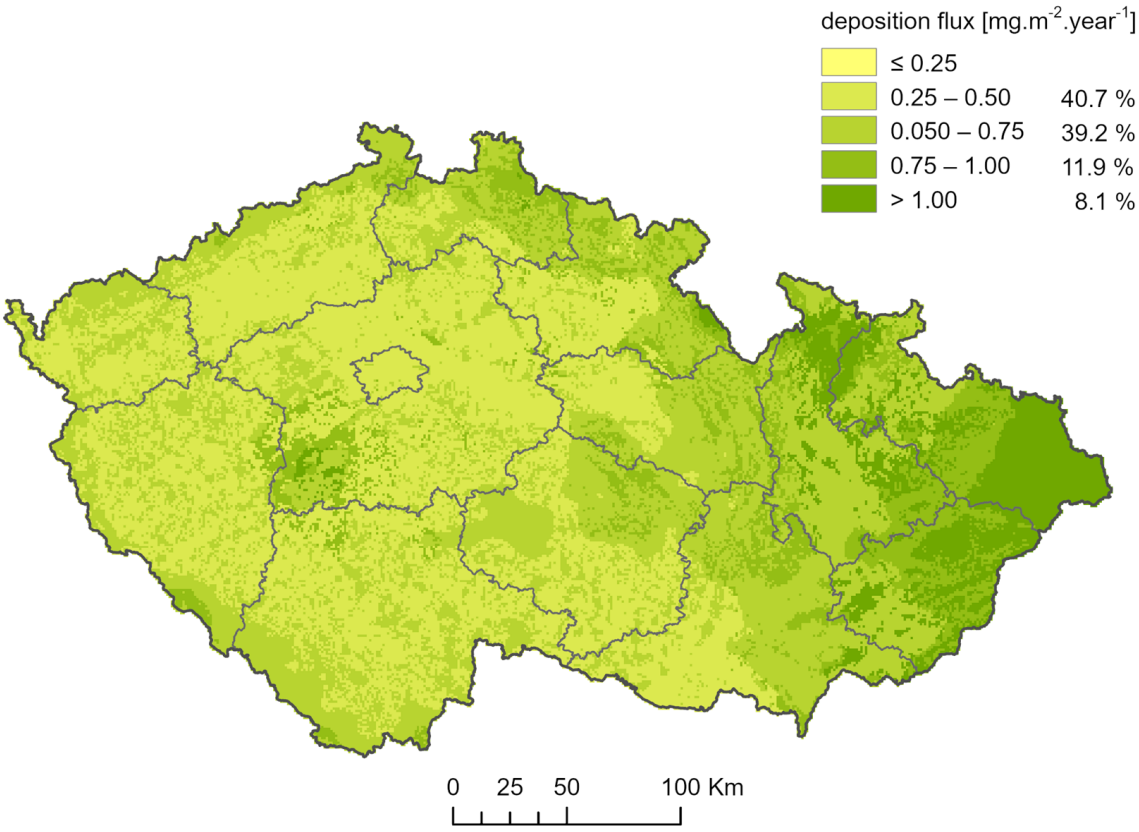

Figure 6. Spatial pattern of total Pb deposition, 2019.

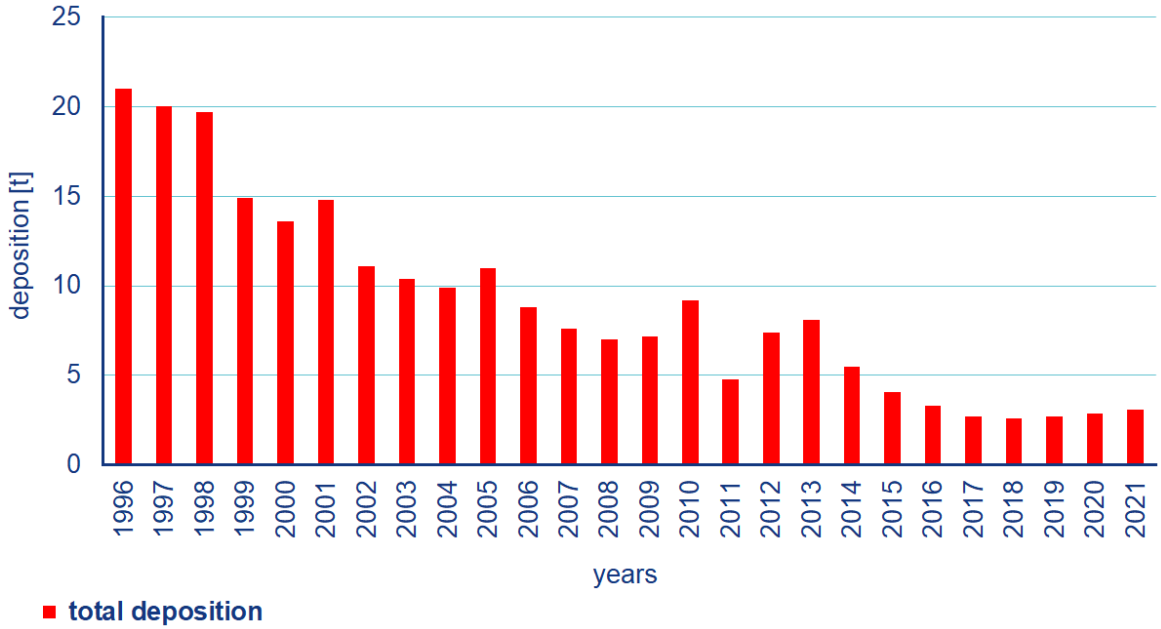

Figure 7. Estimate of annual total deposition of Cd over the entire area of the Czech Republic (78,841 km^2) based on data-driven geostatistic model, 1996–2021.

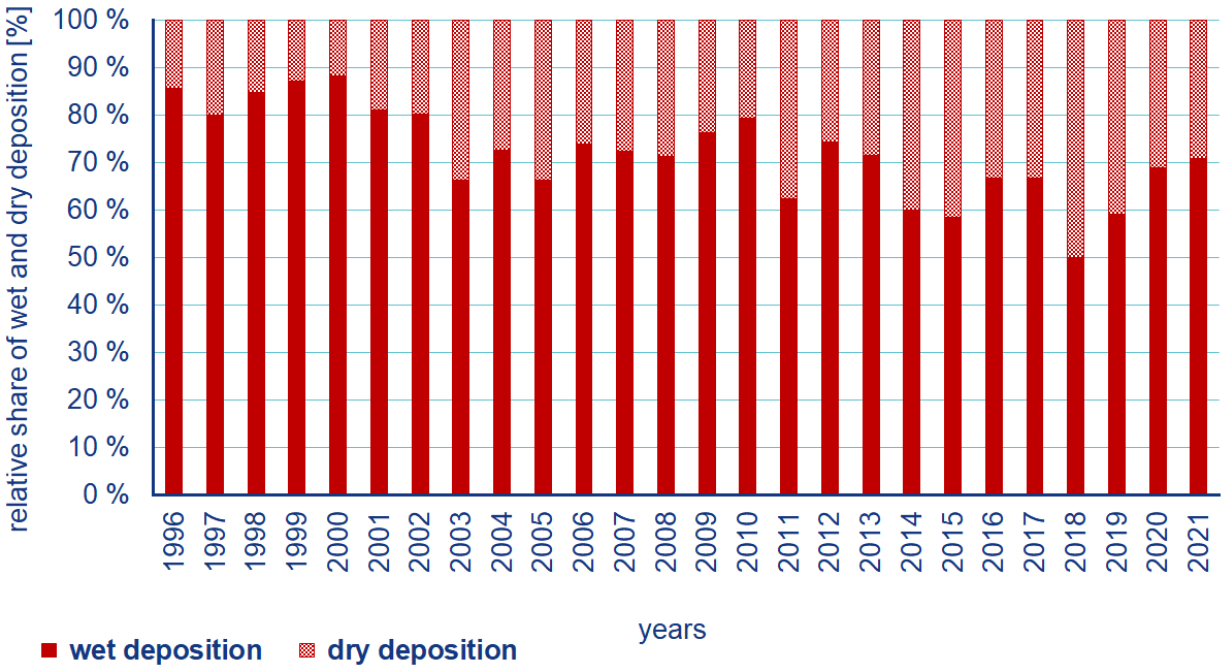

Figure 8. Relative contributions of wet and dry deposition of Cd over the entire area of the Czech Republic (78,841 km^2) based on data-driven geostatistic model, 1996–2021.

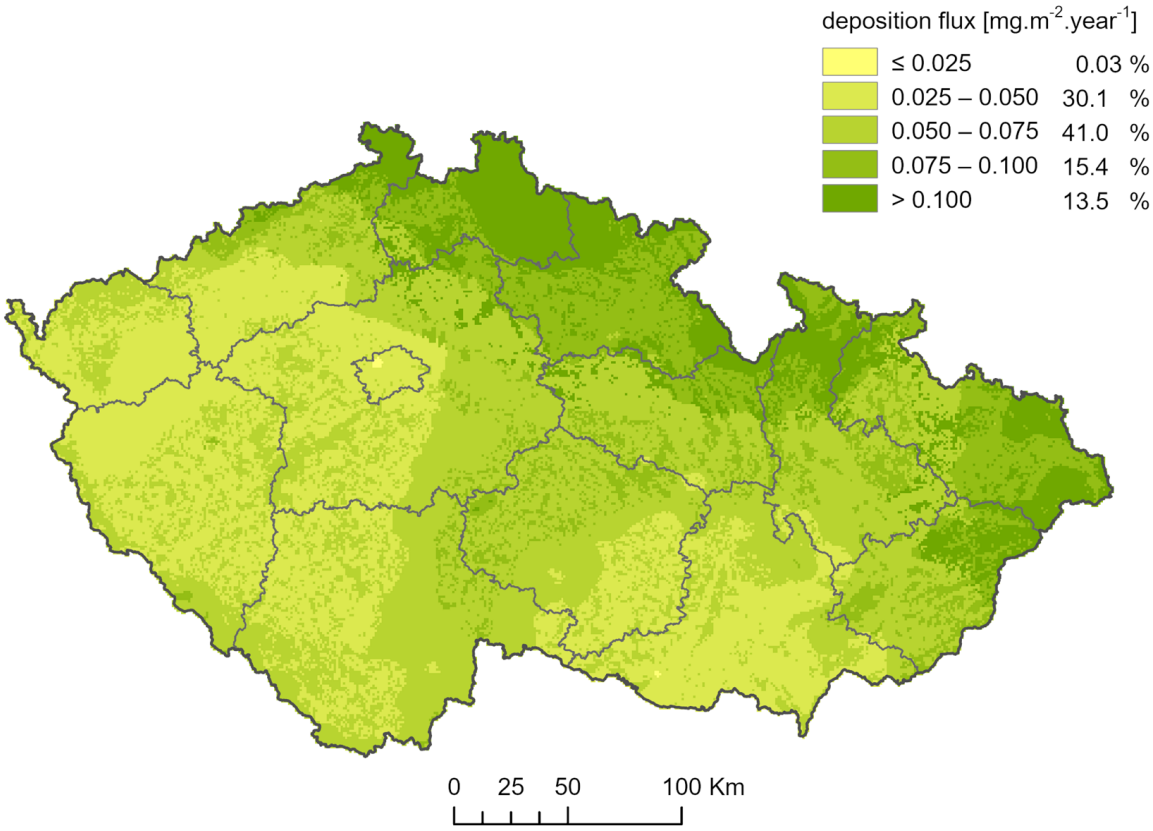

Figure 9. Spatial pattern of total Cd deposition, 2012.

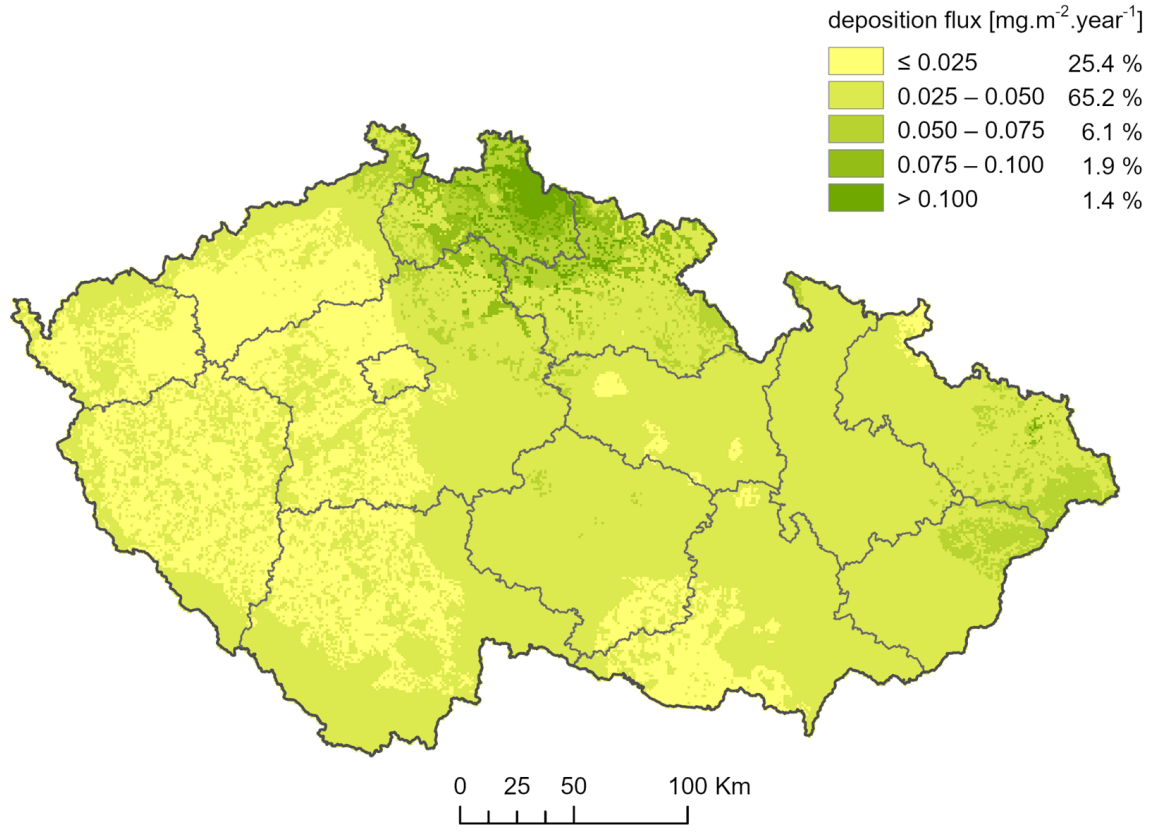

Figure 10. Spatial pattern of total Cd deposition, 2019.

4. Discussion

In this work, we present the time trends of estimated Pb and Cd deposition fluxes (split into wet-only and dry pathways) over the CR in 1996–2021. Our estimates were derived from the Pb and Cd deposition maps with spatial resolution of 1 × 1 km. The beginning of our analysis, i.e., 1996, was not chosen by pure chance. In spite of the fact that both precipitation chemistry and ambient air quality levels were measured earlier at some places in the CR and these data are available through the Ambient Air Quality Information database (ISKO) run by the CHMI [46], it was not until 1996 that the spatial coverage of the data was dense enough to enable us to construct spatial patterns of dry and wet deposition as two substantial parts of total atmospheric deposition. To enable the comparison of annual values over a longer time span, we adhered to the same methods both for measurements and for developing spatial maps of Pb and Cd deposition fluxes.

Considering the overall estimates of wet-only and dry proportions of deposition, we have to keep in mind, however, that the maps were constructed based on the measurements from completely different measuring sites (Figures 1 and 2), using different input data burdened by different and unspecified uncertainties and applying different interpolation approaches (Sections 2.1 and 2.2.). Predominance of the dry deposition over the wet-only pathway can be expected in impacted, air polluted cities and regions, whereas the wet-only fluxes dominate in relatively clean, unpolluted regions, frequently in mountain ranges, in higher altitudes where the deposition flux is modified by precipitation totals rather than by HM concentrations [47–50]. Our approach collating an interpolated map of precipitation chemistry measurements from almost 30 sites with an interpolated map of annual precipitation amounts from 750 precipitation gauges can be considered more reliable than the dry deposition map.

Whereas the estimated wet-only deposition fluxes can be considered reliable, the estimate of dry deposition fluxes is burdened with high uncertainties. With respect to dry deposition flux estimation, the deposition velocities of ambient air pollutants, including aerosol bounding HM, are burdened by major uncertainties and a vast number of values in a broad range, obtained either through experiments or models, are available [51]. The factors influencing deposition velocity are numerous. Among the most important are the land cover of the region under consideration, vegetation, temporal changes (winter and summer months), diurnal variations and micrometeorological conditions (wind direction and velocity, and atmospheric stability). Additionally, experimental uncertainties are to be accounted for [52].

Mohan [53] indicated that an increase in particle size results in increased deposition velocity. The deposition velocities we used in this study (i.e., 0.25/0.08 cm·s^{-1} for Pb and 0.27/0.10 cm·s^{-1} for Cd, for forested/unforested areas) are within the range reported in scientific literature. For example, v_d for anthropogenic elements, including Pb, are reported to be within the vast range of 0.3–23.1 cm·s^{-1} [54]. Actually, our estimates are based on v_d values approaching the lower point of the range indicated in scientific literature. This implies that our estimates of dry deposition fluxes are conservative, and we can reasonably assume that the estimated HM deposition fluxes were rather underestimated than overestimated. We are aware of the fact that the simplification we used here, considering only two values for each HM under review (i.e., deposition velocity for forested and unforested areas), was a very rough approximation. We were not aiming for "accurate values" here; rather, we aimed to examine a spatial pattern over time, define changing proportions of dry and wet pathways and differ and contrast the individual regions due to their atmospheric deposition fluxes. We believe that for the above purposes, the applied simplified approach is acceptable.

Our results suggest that for both Pb and Cd, the atmospheric deposition fluxes in the CR decreased about ten times over 1996–2021, though in absolute values, Pb scored one order of magnitude higher. This development reflects the substantial decrease in HM emissions reported for the CR. Whereas the total annual emission of lead in 1990 was 318.29 t, it decreased to 36.63 t in 2005 and 17.8 t in 2018. Similar development is reported

for Cd, the total annual emission of which was 5.28 t in 1990, 1.75 t in 2005 and 1.33 t in 2018 [46]. This finding is in line with the continuous reduction of heavy metal emissions in Europe during the last four decades [10] and the improving ambient air quality with respect to HM [55]. The changes in Pb and Cd deposition (Figures 3 and 7) have not been simultaneous, however, as these elements originate from different emission sources. The major emission source for Pb was leaded petrol used in cars until its phase out in the CR in 2001 [56]. The major emission sources for Cd are burning of fossil fuels in thermal power plants, burning of refuse and glass manufacturing [57]. These sources were regulated by strict emission limits set up in the 1990s to be met by 1998, which was an impetus to the most pronounced improvement in ambient air quality, including the decrease in Cd deposition [34].

According to our results, the decreases in wet deposition for both Pb and Cd were much faster than in the dry deposition over 1996–2021. This fact can indicate the decreasing air trans-boundary transport of these metals. Additionally, it can reflect on-going climate change with a long lasting drought spell hitting the CR in recent years, since 2014 [58,59].

For mapping spatial patterns of Pb and Cd deposition, we selected two years contrasting in meteorological conditions, 2012 and 2019. Climate factors are known to be closely interlinked with ambient air quality, as they modify the life cycles of atmospheric pollutants, including their removal from the atmosphere via wet and dry processes [41,60]. According to the long-term observations of the CHMI, the on-going climate change manifests itself by gradually increasing temperatures and frequent extreme weather events [61]; this trend is consistent with the WMO analysis [62]. In our mapping, we intended to visualize the deposition in the year, which can be reckoned as a new normal (2012) and the year representing extraordinary weather conditions. The year 2019 represents a long-lasting spell of hot weather and drought beginning in 2014. With respect to the mean annual temperature of 9.5 °C with a deviation of 1.6 °C above the normal of 1981–2010 (and +2.0 °C above the normal of 1961–1990), the year 2019 belonged to the extremely warm years in the CR. Actually, the year 2019 was the second warmest year on record in the CR since 1775 when the temperature measurements started in the Prague Klementinum Observatory [61,63]. Based on significantly different meteorology in 2012 and 2019, we expected changing proportions of wet and dry deposition pathways. This was not true, however, at least with respect to overall estimate indicating about the same relative shares of wet deposition for both years for Pb—64% in 2012 and 63% in 2019 (Figure 4). For Cd, the relative share of wet deposition decreased somewhat from 74% in 2012 to 59% in 2019 (Figure 8).

Considering the changes in total annual deposition fluxes of Pb and Cd between 2012 and 2019 (Figures 3 and 7), in the context of changing emissions, we can see that whereas the Pb emissions changed substantially, the Cd emission remained about the same. According to the EMEP emission inventory, the Pb emission in the CR decreased from ca 24 t in 2012 to ca 19 t in 2019; the Cd emission in the CR decreased from ca 1.4 t in 2012 to ca 1.3 t in 2019 [64].

In spite of the substantial decrease in deposition fluxes, by looking at spatial patterns, we can see that both ambient air and atmospheric deposition in the northern CR remain more loaded with HM than in the past [46,65]. Actually, the northern part of the CR is traditionally more industrial than the southern part. Furthermore, the northern part is also affected by the influence of both large and local emission sources from adjacent, highly industrialized regions in Poland [66,67]. According to EMEP inventories, the total Polish emissions of Pb decreased from some 300 t in 2012 to 260 t in 2019, whereas emissions of Cd remained about 10 t for the same years [64]. However, the detailed spatiotemporal information on changes in Pb and Cd air concentrations or deposition fluxes in Poland in the period examined in our study is not available.

That the north CR is generally more contaminated with respect to ambient air pollution than the south is also permanently reported by a nation-wide assessment published yearly by the CHMI [46]. The above statement also fits well if only HM loads are considered, which is documented by the extensive long-term biondication studies targeted on HM

contamination [68]. As a proxy for Pb and Cd loads, sampling mosses appears to be a valuable tool for determining and mapping the spatial variability of these HM in atmospheric deposition, as was shown in a study at a high spatial resolution for Europe [69]. Whereas the instrumentation used for deposition fluxes measurements is costly, measuring pollutant concentration in bioindicators, such as mosses, enables the collection of a large number of samples useful for spatial analysis [70]. Averaged across Europe, since 1990, the median concentration in mosses has been reported to decline the most for lead (77%), followed by cadmium (51%), [71].

Occult deposition of heavy metals was neglected in this study due to the lack of data, though it was indicated that both fog and rime are likely to contribute substantially both in elevated and industrial areas due to (i) duration and frequency of fog and rime events and (ii) much higher mineralization of occult deposition [39,72–74].

5. Conclusions

In this study, we evaluated time trends and spatial changes in the atmospheric deposition fluxes of Pb and Cd over the CR in the last three decades based on data measured by the CHMI in a nation-wide monitoring network. Our estimates are based on a time series of annual wet-only and dry deposition maps created by data-driven geostatistic models. Our results suggest that both Pb and Cd deposition fluxes over the CR over 1996–2021 decreased substantially, by about 10 times. The wet-only deposition decreased much faster than the dry deposition and was responsible for a major decrease in total deposition over 1996–2021. The absolute values for Cd were one order of magnitude lower than those for Pb. For both HM examined, the wet deposition pathway dominated the dry deposition pathway over the entire time period. With respect to spatial distribution, the northern portions of the CR were more loaded compared to the southern parts; the size of these affected regions has shrunk substantially recently, however. Our long-term time trends fit well within the developments reported for other EU countries.

Author Contributions: Conceptualization, I.H.; methodology, I.H., P.K., M.S. and L.V.; formal analysis, P.K., M.S., L.V. and H.Š.; investigation, I.H.; data curation, H.Š.; writing—original draft preparation, I.H.; writing—review and editing, I.H., M.S., L.V. and H.Š.; visualization, P.K. and M.S.; project administration, I.H. All authors have read and agreed to the published version of the manuscript.

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References

1. Hawkes, S.J. What Is a "Heavy Metal"? *Chem. Educ.* **1997**, *74*, 11. [CrossRef]
2. Duffus, J.H. "Heavy metals" a meaningless term? (IUPAC Technical Report). *Pure Appl. Chem.* **2002**, *74*, 793–807. [CrossRef]
3. Ali, H.; Khan, E. What are heavy metals? Long-standing controversy over the scientific use of the term 'heavy metals'–proposal of a comprehensive definition. *Toxicol. Environ. Chem.* **2018**, *100*, 6–19. [CrossRef]
4. Hodson, M.E. Heavy metals-Geochemical bogey men? *Environ. Pollut.* **2004**, *129*, 341–343. [CrossRef]

5. Rodríguez Martín, J.A.; de Arana, C.; Ramos-Miras, J.J.; Gil, C.; Boluda, R. Impact of 70 years urban growth associated with heavy metal pollution. *Environ. Pollut.* **2015**, *196*, 156–163. [CrossRef]
6. Popoola, L.T.; Adebanjo, S.A.; Adeoye, B.K. Assessment of atmospheric particulate matter and heavy metals: A critical review. *Int. J. Environ. Sci. Technol.* **2018**, *15*, 935–948. [CrossRef]
7. Han, R.; Zhou, B.; Huang, Y.; Lu, X.; Li, S.; Li, N. Bibliometric overview of research trends on heavy metal health risks and impacts in 1989–2018. *J. Clean. Prod.* **2020**, *276*, 123249. [CrossRef]
8. Rahman, Z.; Singh, V.P. The relative impact of toxic heavy metals (THMs) (arsenic (As), cadmium (Cd), chromium (Cr)(VI), mercury (Hg), and lead (Pb)) on the total environment: An overview. *Environ. Monit. Assess.* **2019**, *191*, 419. [CrossRef]
9. Squadrone, S.; Prearo, M.; Brizio, P.; Gavinelli, S.; Pellegrino, M.; Scanzio, T.; Guarise, S.; Benedetto, A.; Abete, M.C. Heavy metals distribution in muscle, liver, kidney and gill of European catfish (Silurus glanis) from Italian Rivers. *Chemosphere* **2013**, *90*, 358–365. [CrossRef]
10. Pacyna, E.G.; Pacyna, J.M.; Fudala, J.; Strzelecka-Jastrzab, E.; Hlawiczka, S.; Panasiuk, D.; Nitter, S.; Pregger, T.; Pfeiffer, H.; Friedrich, R. Current and future emissions of selected heavy metals to the atmosphere from anthropogenic sources in Europe. *Atmos. Environ.* **2007**, *41*, 8557–8566. [CrossRef]
11. Shahid, M.; Dumat, C.; Khalid, S.; Schreck, E.; Xiong, T.; Niazi, N.K. Foliar heavy metal uptake, toxicity and detoxification in plants: A comparison of foliar and root metal uptake. *J. Hazard. Mater.* **2017**, *325*, 36–58. [CrossRef]
12. Suvarapu, L.N.; Baek, S.-O. Determination of heavy metals in the ambient atmosphere: A review. *Toxicol. Ind. Health* **2017**, *33*, 79–96. [CrossRef]
13. Penezic, A.; Milinkovic, A.; Alempijvic, S.B.; Zuzul, S.; Frka, S. Atmospheric deposition of biologically relevant trace metals in the eastern Adriatic costal area. *Chemosphere* **2021**, *283*, 131178. [CrossRef]
14. Sawidis, T.; Breuste, J.; Mitrovic, M.; Pavlovic, P.; Tsigaridas, K. Trees as bioindicator of heavy metal pollution in three European cities. *Environ. Pollut.* **2011**, *159*, 3560–3570. [CrossRef]
15. Dimitriou, K.; Kassomenos, P. Airborne heavy metals in two cities of North Rhine Westphalia–Performing inhalation cancer risk assessment in terms of atmospheric circulation. *Chemosphere* **2017**, *186*, 78–87. [CrossRef]
16. Vitousek, P.M.; Mooney, H.A.; Lubchenko, J.; Melilo, J.M. Human Domination of Earth's Ecosystems. *Science* **1997**, *277*, 494–499. [CrossRef]
17. McConell, J.R.; Edwards, R. Coal burning leaves toxic heavy metal legacy in the Arctic. *Proc. Natl. Acad. Sci. USA* **2008**, *105*, 12140–12144. [CrossRef]
18. EC. Ambient Air Pollution by As, Cd and Ni Compounds, Position Paper. 2001. Available online: https://ec.europa.eu/environment/air/pdf/pp_as_cd_ni.pdf (accessed on 11 November 2021).
19. WHO. Regional Office for Europe & Joint WHO/Convention Task Force on the Health Aspects of Air Pollution. Health Risks of Heavy Metals from Long-Range Transboundary Air Pollution. World Health Organization. Regional Office for Europe. 2007. Available online: https://apps.who.int/iris/handle/10665/107872 (accessed on 20 March 2022).
20. Ilyin, I.; Rozovskaya, O.; Sokovykh, V.; Travnikov, O.; Varygina, M.; Aas, W.; Uggerud, H.T. Heavy Metals: Transboundary Pollution of the Environment. EMEP Status Report 2/2010, Kjeller, Moscow. 2010. Available online: https://www.msceast.org/reports/2_2010.pdf (accessed on 16 November 2022).
21. Al Mamun, A.; Cheng, I.; Zhag, L.; Dabek-Zlotorzynska, E.; Charland, J.-P. Overview of size distribution, concentration, and dry deposition of airborne particulate elements measured worldwide. *Environ. Rev.* **2020**, *28*, 77–88. [CrossRef]
22. Ebrahimi, M.; Khalili, N.; Razi, S.; Keshavarz-Fathi, M.; Khalili, N.; Rezaei, N. Effects of lead and cadmium on the immune system and cancer progression. *J. Environ. Health Sci. Eng.* **2020**, *18*, 335–343. [CrossRef]
23. IARC. *Working Group on the Evaluation of Carcinogenic Risks to Humans: Inorganic and Organic Lead Compounds*; IARC mono-graphs on the evaluation of carcinogenic risks to humans; International Agency for Research on Cancer: Lyon, France, 2006.
24. WHO. *Air Quality Guidelines*, 2nd ed.; World Health Organization: Copenhagen, Denmark, 2000.
25. EC. Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe. *Off. J. Eur. Union* **2008**, L 152/1–152/44.
26. EC. Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air. *Off. J. Eur. Union* **2004**, L 23/3–23/16.
27. Ouyang, X.; Ma, J.; Zhang, R.; Li, P.; Gao, M.; Sun, C.; Weng, L.; Chen, Y.; Yan, S.; Li, Y. Uptake of atmospherically deposited cadmium by leaves of vegetables: Subcellular localization by NanoSIMS and potential risks. *J. Hazard. Mater.* **2022**, *431*, 128624. [CrossRef] [PubMed]
28. Cao, X.; Tan, C.; Wu, L.; Luo, Y.; He, Q.; Liang, Y.; Peng, B.; Christie, P. Atmospheric deposition of cadmium in an urbanized region and the effect of simulated wet precipitation on the uptake performance of rice. *Sci. Total Environ.* **2020**, *700*, 134513. [CrossRef] [PubMed]
29. Dala-Paula, B.M.; Custódio, F.B.; Knupp, E.A.N.; Palmieri, H.E.L.; Silva, J.B.B.; Glória, M.B.A. Cadmium, copper and lead levels in different cultivars of lettuce and soil from urban agriculture. *Environ. Pollut.* **2019**, *242*, 383–389. [CrossRef] [PubMed]
30. Feng, W.; Guo, Z.; Xiao, X.; Peng, C.; Shi, L.; Ran, H.; Xu, W. Atmospheric deposition as a source of cadmium and lead to soil-rice system and associated risk assessment. *Ecotoxicol. Environ. Saf.* **2019**, *180*, 160–167. [CrossRef] [PubMed]
31. Sanaeifar, A.; Zhu, F.; Sha, J.; Li, X.; He, Y.; Zhan, Z. Rapid quantitative characterization of tea seedlings under lead-containing aerosol particles stress using Vis-NIR spectra. *Sci. Total Environ.* **2022**, *802*, 149824. [CrossRef] [PubMed]

32. Ma, C.; Xie, P.; Yang, J.; Liu, F.; Hu, H.; Du, J.; Zhang, K.; Lin, L.; Zhang, H. Relative contribution of environmental medium and internal organs to lead accumulation of wheat grain. *Sci. Total Environ.* **2022**, *818*, 151832. [CrossRef]
33. Brown, R.J.C.; Yardley, R.E.; Mukunthan, D.; Butterfield, D.M.; Williams, M.; Woods, P.T.; Brown, A.S.; Goddard, S.-L. Twenty-five years of nationwide ambient metals measurement in the United Kingdom: Concentration levels and trends. *Environ. Monit. Assess.* **2008**, *142*, 127–140. [CrossRef]
34. Hůnová, I. Ambient Air Quality in the Czech Republic: Past and Present. *Atmosphere* **2020**, *11*, 214. [CrossRef]
35. Jin, M.; Yuan, H.; Liu, B.; Peng, J.; Xu, L.; Yang, D. Review of the distribution and detection methods of heavy metals in the environment. *Anal. Methods* **2020**, *12*, 5747–5766. [CrossRef]
36. Isaaks, E.H.; Srivastava, R.M. *An Introduction to Applied Geostatistics*; Oxford University Press: Oxford, UK, 1989; p. 561. ISBN 0-19-505013-4.
37. Tolasz, R.; Míková, T.; Valeriánová, A.; Voženílek, V. *Climate Atlas of Czechia*; Český hydrometeorologický ústav; Palacký University Olomouc: Olomouc, Czech Republic, 2007; p. 255, ISBN 978-80-86690-26-1.
38. Hůnová, I.; Kurfürst, P.; Maznová, J.; Coňková, M. Contribution of occult precipitation to sulphur deposition in the Czech Republic. *Erdkunde* **2011**, *65*, 247–259. [CrossRef]
39. Hůnová, I.; Novák, M.; Kurfürst, P.; Škáchová, H.; Štěpánová, M.; Přechová, E.; Komárek, A.; Čuřík, J.; Veselovský, F.; Bohdálková, L. Contribution of rime to atmospheric sulphur deposition in Central Europe: A combined empirical and modelling approach. *Atmos. Environ.* **2020**, *270*, 118877. [CrossRef]
40. Hůnová, I.; Kurfürst, P.; Vlček, O.; Stráník, V.; Stoklasová, P.; Schovánková, J.; Srbová, D. Towards a better spatial quantification of nitrogen deposition: A case study for Czech forests. *Environ. Pollut.* **2016**, *213*, 1028–1041. [CrossRef]
41. Seinfeld, J.H.; Pandis, S.N. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, 3rd ed.; John Wiley: New York, NY, USA, 2016; p. 1152, ISBN 978-1-118-94740-1.
42. Wesely, M.L.; Hicks, B.B. A review of the current status of knowledge on dry deposition. *Atmos. Environ.* **2000**, *34*, 2261–2282. [CrossRef]
43. He, H.; Lu, W. Comparison of three prediction strategies within $PM_{2.5}$ and PM_{10} monitoring networks. *Atmos. Pollut. Res.* **2020**, *11*, 590–597. [CrossRef]
44. Pastuszka, J.S.; Rogula-Kozłowska, W.; Zajusz-Zubek, E. Characterization of PM_{10} and $PM_{2.5}$ and associated heavy metals at the crossroads and urban background site in Zabrze, Upper Silesia, Poland, during the smog episodes. *Environ. Monit. Assess.* **2010**, *168*, 613–627. [CrossRef] [PubMed]
45. Dvořáková, M.; Fiala, J.; Livorová, H.; Srněnský, R. *Vypracování Postupů Pro Zohlednění Druhů Pokryvu Terénu Při Odhadu Rychlosti Suché Depozice SO2 a Prašného Aerosol*; Zdokonalení metod územního a časového hodnocení kvality ovzduší; CHMI: Praha, Czech Republic, 1995.
46. CHMI. Air pollution in the Czech Republic in 2019. Czech Hydrometeorological Institute, Prague. 2021. Available online: https://www.chmi.cz/files/portal/docs/uoco/isko/grafroc/grafroc_CZ.html (accessed on 20 November 2022).
47. Connan, O.; Maro, D.; Hébert, D.; Roupsard, P.; Goujan, R.; Letelier, B.; Le Cavalier, S. Wet and dry deposition of particles associated metals (Cd, Pb, Zn, Ni, Hg) in a rural wetland site, Marais Vernier, France. *Atmos. Environ.* **2013**, *67*, 394–403. [CrossRef]
48. Lynam, M.M.; Dvonch, J.T.; Hall, N.L.; Morishita, M.; Barres, J.A. Trace elements and major ions in atmospheric wet and dry deposition across central Illinois, USA. *Air Qual. Atmos. Health* **2015**, *8*, 135–147. [CrossRef]
49. Morselli, L.; Olivieri, P.; Brusori, B.; Passarini, F. Soluble and insoluble fractions of heavy metals in wet and dry atmospheric depositions in Bologna, Italy. *Environ. Pollut.* **2003**, *124*, 457–469. [CrossRef] [PubMed]
50. Sakata, M.; Maramuto, K.; Narukawa, M.; Asakura, K. Regional variations in wet and dry deposition fluxes of trace elements in Japan. *Atmos. Environ.* **2006**, *40*, 521–531. [CrossRef]
51. Petroff, A.; Maillat, A.; Amielh, M.; Anselmet, F. Aerosol dry deposition on vegetative canopies. Part I: Review of present knowledge. *Atmos. Environ.* **2008**, *42*, 3625–3653. [CrossRef]
52. Finlayson-Pitts, B.J.; Pitts, J.N., Jr. *Chemistry of the Upper and Lower Atmosphere*; John Wiley: New York, NY, USA, 1986; ISBN 10: 0471882275.
53. Mohan, S.M. An overview of particulate dry deposition: Measuring methods, deposition velocity and controlling factors. *Int. J. Environ. Sci. Technol.* **2016**, *13*, 387–402. [CrossRef]
54. Yi, S.-M.; Shahin, U.; Sivadechathep, J.; Sofuoglu, S.C.; Holsen, T.M. Overall elemental dry deposition velocities measured around Lake Michigan. *Atmos. Environ.* **2001**, *35*, 1133–1140. [CrossRef]
55. EEA. Air Quality in Europe-2020 Report. EEA Report 09/2020. European Environment Agency, Luxembourg. 2020. Available online: https://www.actu-environnement.com/media/pdf/36559.pdf (accessed on 15 November 2022).
56. Von Storch, H.; Costa-Cabral, M.; Hagner, C.; Feser, F.; Pacyna, J.; Pacyna, E.; Kolb, S. Four decades of gasoline lead emissions and control policies in Europe: A retrospective assessment. *Sci. Total Environ.* **2003**, *311*, 151–176. [CrossRef] [PubMed]
57. CHMI. Czech Informative Inventory Report 2021. Submission under the UNECE Convention on Long-Range Transboundary Air Pollution. Czech Hydrometeorological Institute, Prague. 2021. Available online: https://www.chmi.cz/files/portal/docs/uoco/oez/embil/CZ-informativni-zprava-emisni-inventury-2021.pdf (accessed on 10 November 2022).
58. Trnka, M.; Možný, M.; Jurečka, F.; Balek, J.; Semerádová, D.; Hlavinka, P.; Štěpánek, P.; Farda, A.; Skalák, P.; Cienciala, E.; et al. Observed and estimated consequences of climate change for the fire weather regime in the moist-temperate climate of the Czech Republic. *Agric. For. Meteorol.* **2021**, *310*, 108583. [CrossRef]

59. Buntgen, U.; Urban, O.; Krusic, P.J.; Rybníček, M.; Kolář, T.; Kyncl, T.; Ač, A.; Koňasová, E.; Čáslavský, J.; Esper, J.; et al. Recent European drought extremes beyond Common Era background variability. *Nat. Geosci.* **2021**, *14*, 190–196. [CrossRef]
60. Giorgi, F.; Meleux, F. Modelling the regional effects of climate change on air quality. *C. R. Geosci.* **2007**, *339*, 721–733. [CrossRef]
61. Tolasz, R.; Čekal, R.; Škáchová, H.; Vlasáková, L. The year 2019 in Czechia. *Meteorol. Zprávy* **2020**, *73*, 1–11.
62. IPCC. *Climate Change 2022: Impacts, Adaptation and Vulnerability*; Pörtner, H.-O., Roberts, D.C., Tignor, M., Poloczanska, E.S., Mintenbeck, K., Alegría, A., Craig, M., Langsdorf, S., Löschke, S., Möller, V., et al., Eds.; Contribution of Working Group II to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change; Cambridge University Press: Cambridge, UK, 2022; p. 3056. [CrossRef]
63. Brázdil, R.; Zahradníček, P.; Pišoft, P.; Štěpánek, P.; Bělínová, M.; Dobrovolný, P. Temperature and precipitation fluctuations in the Czech Republic during the period of instrumental measurements. *Theor. Appl. Climatol.* **2012**, *110*, 17–34. [CrossRef]
64. EMEP; The Emission Datrabase. EMEP Centre on Emission Inventories and Projections. 2022. Available online: https://www.ceip.at/webdab-emission-database (accessed on 1 December 2022).
65. Hůnová, I. Ambient air quality for the territory of the Czech Republic in 1996–1999 expressed by three essential factors. *Sci. Total Environ.* **2003**, *303*, 245–251. [CrossRef]
66. Kozáková, J.; Pokorná, P.; Vodička, P.; Ondráčková, L.; Ondráček, J.; Křůmal, K.; Mikuška, P.; Hovorka, J.; Moravec, P.; Schwarz, J. The influence of local emissions and regional air pollution transport on a European air pollution hot spot. *Environ. Sci. Pollut. Res.* **2019**, *26*, 1675–1692. [CrossRef]
67. Volná, V.; Hladký, D.; Seibert, R.; Krejčí, B. Transboundary Air Pollution Transport of PM_{10} and Benzo[a]pyrene in the Czech–Polish Border Region. *Atmosphere* **2022**, *13*, 341. [CrossRef]
68. Suchara, I.; Sucharova, J.; Hola, M.; Reimann, C.; Boyd, R.; Filzmoser, P.; Englmaier, P. The performance of moss, grass, and 1- and 2-year old spruce needles as bioindicators of contamination: A comparative study at the scale of the Czech Republic. *Sci. Total Environ.* **2011**, *409*, 2281–2297. [CrossRef] [PubMed]
69. Schröder, W.; Holy, M.; Pesch, R.; Harmens, H.; Ilyin, I.; Steinnes, E.; Alber, L.; Aleksiayenak, Y.; Blum, O.; Coskun, M.; et al. Are cadmium, lead and mercury concentrations in mosses across Europe primarily determined by atmospheric deposition of these metals? *J. Soils Sediments* **2010**, *10*, 1572–1584. [CrossRef]
70. Zhou, X.; Chen, Q.; Liu, C.; Fang, Y. Using Moss to Assess Airborne Heavy Metal Pollution in Taizhou, China. *Int. J. Environ. Res. Public Health* **2017**, *14*, 430. [CrossRef] [PubMed]
71. Harmens, H.; Norris, D.A.; Sharps, K.; Mills, G.; Alber, R.; Aleksiayenak, Y.; Blum, O.; Cucu-Man, S.M.; Dam, M.; de Temmerman, L.; et al. Heavy metal and nitrogen concentrations in mosses are declining across Europe whilst some "hotspots" remain in 2010. *Environ. Pollut.* **2015**, *200*, 93–104. [CrossRef]
72. Cimova, N.; Novak, M.; Chrastny, V.; Curik, J.; Veselovsky, F.; Blaha, V.; Prechova, E.; Pasava, J.; Houskova, M.; Bohdalkova, L. Lead fluxes and 206Pb/207Pb isotope ratios in rime and snow collected at remote mountain-top locations (Czech Republic, Central Europe): Patterns and sources. *Atmos. Environ.* **2016**, *143*, 51–59. [CrossRef]
73. Hůnová, I.; Brabec, M.; Geletič, J.; Malý, M.; Dumitrescu, A. Statistical analysis of the effects of forests on fog. *Sci. Total Environ.* **2021**, *781*, 146675. [CrossRef]
74. Hůnová, I.; Brabec, M.; Malý, M.; Dumitrescu, A.; Geletič, J. Terrain and its effects on fog occurrence. *Sci. Total Environ.* **2021**, *768*, 144359. [CrossRef]

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