Chapter 7 Heavy Metal Stocks and Concentrations in Forest Soils



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7.1 Introduction

From a scientific perspective, heavy metals are metals with a density >5 g cm⁻³. In this section, the term "heavy metals" includes the elements arsenic (As), lead (Pb), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), mercury (Hg) and zinc (Zn); chemically, arsenic is considered a semimetal.

Heavy metals occur naturally in the geosphere at highly variable concentrations. Concentrations vary primarily as a function of the mineral composition of the parent rock. Elements with geogenically elevated concentrations are principally found where there is solid bedrock. In Germany, geogenically elevated element concentrations are present in particular where soils are found on periglacial sites over basic magmatic and metamorphic rock (Cr, Ni, Cu, Zn), clay (especially Liassic clay) (As, Cd, Cr, Cu, Ni, Pb, Zn), acidic metamorphic rock (Cu, Ni) and mica slate (Cr, Cu, Ni, Zn), as well as carbonate rocks as a result of accumulation of residual clay in terra fusca-type soils. The subsoil and bedrock layers that have little loess concentration contain higher concentrations of the elements compared to the topsoil; in particular for Cr and Ni in areas with basic magmatic and metamorphic bedrock, these elements then significantly trace into the topsoil (Utermann et al. 2006).

Due to the action of trees in filtering out airborne pollutants (the "Auskämmeffekt"), heavy metal loading from the atmosphere is especially high in the soils under forest. On both regional and national scales, this effect can lead to a significant change of the natural heavy metal concentrations in soils. Regionally high concentrations of heavy metals are found in particular in areas leeward of large centres of heavy industry, such as in North Rhine-Westphalia, due to long-term emissions from industry (Gehrmann 2013). Although pollutant emissions from factories and steel processing plants have now been reduced considerably, the resulting loads in the soils will persist for many decades because heavy metals are not biodegradable and migrate relatively slowly through soil. Patterns of topsoil loading across the country are apparent especially for lead, as this element was released diffusely and ubiquitously through burning of leaded fuels for decades up until 1988. As a result, there are elevated levels of lead in the soils under forests of the low mountain ranges throughout Germany (BGR 2016).

In addition to inputs of heavy metals from industrial emissions and traffic exhaust, mining of metal ores and the associated metallurgy have also deposited significant loads in the soils of regions such as the Harz Mountains, Mansfeld Land, the Rhenish Slate Mountains or the Erzgebirge (Wippermann 2000). In many cases, former waste and slag heaps in these regions are protected, as heavy metal sites are listed in Annex 1 of the FFH Directive (Habitats Directive) (habitat type 6130, metallophyte grasslands of the Violetalia calaminariae) and represent a federally protected biotype according to § 30 BNatSchG (Nature Protection Act). If these sites had no metallophytes and were left to themselves, over time and through processes of natural succession, they would develop into forested sites with substantial heavy metal contamination (Knolle et al. 2011).

At low concentrations, some of the heavy metals (e.g. Cu, Zn) can be essential nutrients and therefore have nutritional value. At higher concentrations, the metals have toxic effects for both ecosystems and humans (Ohnesorge and Wilhelm 1991; Wilke et al. 2003). Other heavy metals (e.g. Cd, Pb, Hg) are only known to have toxic effects (Litz et al. 2015). In the geosphere, the ecotoxicological effects of the heavy metals are present only when the metal is in a bioavailable form, either dissolved in soil solution or bound to the solid phase of the soil. The heavy metal concentrations discussed in this section have been extracted from soil using a strong acid ("aqua regia") and hence represent the total heavy metal concentration. This includes the fraction that is not bioavailable or cannot be displaced; consequently, conclusions based on this database are limited with respected statements about effects. In general, with the exception of the elements that are more likely present in the soil in anionic form (e.g. As), the heavy metals tend to be more mobile/ bioavailable at lower pH values in the soil. Hence, higher heavy metal concentrations in forest soils, where pH is typically significantly lower compared to agricultural sites, present a higher risk for both the biosphere and in terms of displacement into groundwater. Different heavy metals are absorbed to different extents by mineral surfaces and, depending on pH, can also precipitate as low solubility oxides, hydroxides or carbonates or in other forms. The degree of absorption tends to follow the sequence Cd, Zn < Cu < Ni, Cr < Pb. The ability of heavy metals to form complexes with humic substances is also variable: Cd and Zn form only weak complexes, while Pb, Cr, Ni and Cu form stable complexes, with Cu binding more strongly to low molecular weight humic substances and Pb to higher molecular weight substances (König et al. 1986). Thus, both absorption and the tendency to form complexes depend on pH, and both factors affect the rate of displacement of heavy metals into groundwater.

The datasets from the NFSI I are limited nationally to analyses of heavy metal concentrations in the organic layer. In the NFSI II, heavy metal concentration was measured in the first two depth levels (0-5, 5-10 cm) of the mineral soil at all sample plots and over the entire depth profile at selected sites. Comparative analyses between the NFSI I and NFSI II are thus possible at a national level only for the organic layer. For this reason, data from North Rhine-Westphalia are used by way of example for the mineral soil, because in this state heavy metal concentrations were measured in the first two depth increments of the mineral soil in both inventories.

7.2 Heavy Metal Stocks in the Organic Layer and Mineral Soil

7.2.1 Status and Depth Gradients

Figures 7.1 and 7.2 present boxplots illustrating the depth gradients (organic layer, 0-5, 5-10 cm) for the stocks of all heavy metals analysed for NFSI II as well as in



Fig. 7.1 Depth gradients of stocks for the elements (a) copper (Cu) and arsenic (As), (b) lead (Pb) and zinc (Zn) for the organic layer and the first two mineral soil increments (0-5, 5-10 cm)



Fig. 7.2 Depth gradients of stocks for the elements (**a**) cadmium (Cd) and mercury (Hg), (**b**) nickel (Ni) and chromium (Cr) for the organic layer and the first two mineral soil increments (0-5, 5-10 cm)

case of organic layer the stocks of NFSI I for the elements Pb, Cd, Cu, Cr, Ni and Zn. Unless otherwise specified, means or comparisons of middle values are in relation to the median. The elements with data from the NFSI II encompassed all depth levels. In the NFSI I, only the data for the organic layer can be considered as this inventory did not measure heavy metals for the mineral soil layer throughout Germany. Two heavy metals are shown in each figure; the pairings are based on comparable stocks for the elements.

In terms of stocks, all the heavy metals studied have a right-skewed distribution since all elements have a few very high measurements. The upper quartile and upper whisker are therefore considerably farther from the median than are the lower quartile and lower whisker. For the same reason, the arithmetic mean for all heavy metals is greater than the median (Figs. 7.1 and 7.2). The magnitudes of the values and the depth profiles differ for each element; usually, the stocks in the organic layer are lower than that in the mineral soils because the organic layer is lacking the geogenic components. The lowest stocks both in the organic layer and in the mineral soil layers were found for Hg and Cd (NFSI II; organic layer; median; Cd, 0.02 kg ha^{-1} ; Hg, 0.01 kg ha^{-1}) (Fig. 7.2), followed by As and Cu (NFSI II; organic layer; median; As, 0.14 kg ha⁻¹; Cu, 0.63 kg ha⁻¹) (Fig. 7.1) and Ni and Cr (NFSI II; organic layer; median; Ni, 0.34 kg ha⁻¹; Cr, 0.43 kg ha⁻¹) (Fig. 7.2). The highest stocks were documented for Pb and Zn (NFSI II; organic layer; median; Pb, 2.58 kg ha⁻¹; Zn, 2.86 kg ha⁻¹) (Fig. 7.1). The elements Ni, Cr and As have significantly lower stocks in the organic layer compared to the mineral soil, which points to a source that is primarily geogenic. For As, it is important to note that this element is present in an anionic form and therefore is only weakly bound in the organic layer, and rapid deposition into the mineral subsoil is possible. The elements Ni, Cr, As and Zn have the highest stocks at 5-10 cm, which (except in the case of As) is further evidence in support of an origin that is primarily geogenic. In contrast, the elements Pb and Hg have the highest stocks at 0-5 cm and decrease at the 5-10 cm depth, which suggests a significant anthropogenic impact (atmospheric sources) on the heavy metal stocks arising from geogenic processes. This trend is less obvious for Cd and Cu, which on average have similar inventories in the 0-5 cm and 5–10 cm layers.

In general, the stocks in the organic layer decreased for all heavy metals between NFSI I and NFSI II; there was particularly clear decline for Pb. The mean (arithmetic mean) decrease is significant for all the heavy metals analysed (Pb, Cd, Cu, Cr, Ni, Zn) (see Sect. 7.2.3).

In the following sections, the results for Pb and Ni are used by way of example to highlight and elucidate one element that is characterised by a more anthropogenic influence (Pb) and one that is more geogenic (Ni). Nevertheless, all heavy metals are discussed in the analyses. If an element features a deviation from the typical pattern exemplified by Pb or Ni, this case is explained in more detail.



Fig. 7.3 Distribution of specific heavy metal stocks in the organic layer into six percentile classes for the forest soils of Germany using lead as an example

7.2.2 Spatial Distributions

7.2.2.1 The Organic Layer

The spatial distribution of heavy metal stocks in the organic layer is shown in Fig. 7.3 using Pb as an example. In the map, specific stock values are classified into one of six percentile groups. The difference between the stocks for the individual elements is comparatively low, as the levels of heavy metals are determined to a large extent by the stock levels of organic matter in the organic layer. Section 7.3



therefore addresses the differences in heavy metal concentrations in the organic layer.

The relationship between the amount of humus and heavy metal stock also becomes apparent in comparing with humus stocks (see Chap. 5). Hence, the thick organic layer of the acidic soils in the low mountainous regions (e.g. the Harz, Hunsrück, Thuringian and Bavarian forests) has significantly higher heavy metal stocks than do the calcareous regions with relatively thin organic layers (e.g. the Swabian and Franconian mountains and the hills of Lower Saxony). The soils of the lowlands of northern Germany have a greater small-scale variability of heavy metal stocks in the organic layer compared to sites in the low mountainous regions. Figure 7.4 shows the relationship between heavy metal stocks in the organic layer and the humus stocks using Pb as an example. The figure highlights the difference between regions with thinner organic layers and lower heavy metal levels in contrast to regions with thicker layers of humus and higher heavy metals stocks. For all heavy metals, the increase in the stocks thus follows the sequence MU < MOM < MOT < MR < RO.

7.2.2.2 Mineral Soil Layers

Compared to the levels in the organic layer, the heavy metal stocks in the mineral topsoil are much more strongly characterised by the heavy metal concentrations. This is understandable since the dry bulk density, with the exception of the organic soils, varies within a much narrower range compared to the concentrations of heavy metals. This can be clearly seen by comparing Figs. 7.5 and 7.17 with Ni as the example element.

The Ni stocks in the upper mineral soil layer (0-5 cm), like the stocks for Cr and Zn, which show a very similar distribution, feature a distinct dichotomy across Germany. While the lowlands of northern Germany have a clear predominance of



Fig. 7.5 Distribution of specific heavy metal stocks in the first layer of the mineral soil into six percentile classes (map volume Table II-6-50) for the forest soils of Germany using nickel as an example

sites with distribution of the element in the "lower" classes (0-10%, 10-25%) and 25–50%), locations in southern Germany (low mountain ranges, alpine foothills, mountains) are mostly in the higher classes (50-75%, 75-90%) and 90-100%). The mineral soils of forested areas in the Palatinate Forest, in Odenwald/Spessart and in the northern regions of the Black Forest have lower stocks (and also concentrations) than other low mountain forests (Fig. 7.17). This is consistent with the distribution of background values of Ni in the topsoil documented in the Soil Atlas of

Germany (BGR 2016), although with higher classes for locations in the Erzgebirge, in the Süderbergland and in places in the hills of Schleswig-Holstein.

7.2.3 Changes in Heavy Metal Stocks

The differences in heavy metal stocks in the organic layer between NFSI I and NFSI II are calculated based on the collective of paired samples. Because no paired measurements are available for As and Hg, differences cannot be determined for these elements. The time span between NFSI I and NFSI II varies between the respective sites. Whereas in most cases the time span accounts for about 17 years, it is less than 10 years for 94 sites.

Table 7.1 shows the change in heavy metal stocks in the organic layer between NFSI I and NFSI II for the entire country. It is apparent that the stocks of all the heavy metals measured (Pb, Cd, Cr, Cu, Ni, Zn) and the humus stock have declined. The largest decrease was documented for Pb, at -33%, while Cd, Cr, Cu and Ni are all at about -20%. Relative to the other heavy metals, the decline for Zn is lowest (-11%). Overall, the declines of the heavy metals exceed the decrease in the humus stock, which on average is only -2%.

Figure 7.6 illustrates the change in heavy metal stocks between NFSI I and NFSI II in g ha⁻¹ year⁻¹ differentiated by humus type, using lead as the example. The pattern shown is similar for all the heavy metals (Cd, Cr, Cu, Ni, Zn). The scatter of absolute differences in heavy metal stocks between NFSI I and NFSI II diminishes with decreasing thickness of the humus type (MU < MOM < MOT < MR < RO). This result is based on the fact that heavy metal stocks are generally higher in thicker humus types. On average, the heavy metal stocks in the organic layer decreased most strikingly from NFSI I to NFSI II in the humus type MOM (Pb: -96.3 g ha⁻¹ year⁻¹). In general, thinner sections of the organic layer (MU, MOM) showed decreases in heavy metals, while thicker organic layers (RO) instead showed an increase in heavy metals.

The difference in heavy metal stocks and the organic layer per year relative to the total stock for each humus type is shown in Fig. 7.6 using Pb as the example. This

	Pb	Cd	Cr	Cu	Ni	Zn	Organic layer
Median NFSI I	4.49	0.024	0.67	0.83	0.48	3.22	47,909
Median NFSI II	3.01	0.019	0.52	0.68	0.39	2.86	47,024
NFSI II – NFSI I	-1.47	-0.005	-0.14	-0.15	-0.09	-0.36	-885
Change (%)	-33	-20	-22	-18	-20	-11	-2
n	1183	1091	520	1183	551	1183	1224

Table 7.1 Average stocks (kg ha⁻¹) of the heavy metals in the organic layer and the humus stocks in the paired sample collective dataset for NFSI I and NFSI II as well as differences and changes (%)



figure clearly illustrates that separation according to humus type makes the scatter of the differences comparable. The differences in stocks correlated with humus type, with greater declines in stock in thinner humus types (Pb, MU -5.0%, MOM -4.2%) and slight increases in stock in thicker humus types (Pb, RO 0.9%). The decrease in heavy metal stocks in the humus types MU and MOM indicates a decline of atmospheric inputs of heavy metals in the period between NFSI I and NFSI II, since these humus types (as a result of their rapid mineralisation) have been completely reconditioned and accordingly reveal the current (at the time just prior to NFSI II) status of heavy metal input. As a whole, the decrease in heavy metal stock is more marked than the decrease in humus stock, and the increase in heavy metal stocks is less than the increase in humus stock. This result is further evidence to support the observation that the change in heavy metal stocks cannot be attributed solely to the change in humus stock; instead, an additional translocation of heavy metals into the mineral soil and/or a reduction of atmospheric deposition have taken place. This is most apparent for Pb (Fig. 7.7), Cr and Ni and to a lesser extent for Cu and Zn. This result is weakest for Cd (Fig. 7.8).

The decrease in atmospheric deposition of heavy metals in the period between NFSI I and NFSI II apparent in the change in heavy metal stocks in the organic layer is confirmed in Figs. 7.9 and 7.10 for Pb and Cd. These figures illustrate the clear decrease in inputs of Pb and Cd, differentiated by tree species and area, in 20 sample sites in Lower Saxony and Hessen between 1982 and 2014. The total inputs (canopy drip + litterfall + stemflow) are between 30 and 50% higher than inputs from canopy drip alone (Keuffel-Türk et al. 2012).



7.2.3.1 Impacts of Liming on Changes in Heavy Metal Stocks in the Organic Layer

Figures 7.11 and 7.12 illustrate the effect of liming on the heavy metal stocks in the organic layer. Depending on the humus type, liming the organic layer causes the humus stocks to decompose or negatively impacts the formation of humus by moving the organic substances into the upper layers of the mineral soil (see Chap. 6). The effect of heavy metal depletions is somewhat enhanced by liming. Hence, liming tends to reduce the heavy metal stocks in the organic layer. This applies to almost all the elements to the same extent but is somewhat more pronounced in thicker humus types such as mor humus. For lead, the effect of liming is weakest in mor humus, which may be related to the strong affinity of lead to form complexes and the simultaneous increase in pH.



Fig. 7.9 Lead input with canopy drip for 20 sites in Lower Saxony and Hessen: red, beech stands (BU); blue, spruce stands (FI); grey, pine stands (KI); yellow, oak stands (EI); locations: AU Augustendorf, FOD Fürth/Odw, GW Göttingen Forest, HRI Hessian Ried, LB Lange Bramke (KA, ridge; NH, northern slope), WIZ Witzenhausen, EH Ehrhorn, SPE Spessart, ZIE Zierenberg, KR Krofdorf, KST Königstein



Fig. 7.10 Cadmium input with canopy drip for 20 sites in Lower Saxony and Hessen: red, beech stands (BU); blue, spruce stands (FI); grey, pine stands (KI); yellow, oak stands (EI); locations: *AU* Augustendorf, *FOD* Fürth/Odw, *GW* Göttingen Forest, *HRI* Hessian Ried, *LB* Lange Bramke (KA, ridge; NH, northern slope), *WIZ* Witzenhausen, *EH* Ehrhorn, *SPE* Spessart, *ZIE* Zierenberg, *KR* Krofdorf, *KST* Königstein



Fig. 7.11 Change in stock between NFSI I and NFSI II per year [% of the NFSI I stock] for the humus content and lead in relation to humus type and separated by sites that were limed or not. Nine sites with a change in lead stock per year > 100% were removed as outliers. *MU* mull, *MOM* mull-like moder, *MOT* typical moder, *MR* raw humus-like moder, *RO* raw humus



Fig. 7.12 Change in stock between NFSI I and NFSI II per year [% of the NFSI I stock] for the humus content and cadmium in relation to humus type and separated by sites that were limed or not. Three sites with a change in cadmium stock per year > 100% were removed as outliers. *MU* mull, *MOM* mull-like moder, *MOT* typical moder, *MR* mor humus-like moder, *RO* mor humus

7.2.3.2 Inventory Changes in the Soil (Organic Layer and Topsoil) Using the NFSI Plots in North Rhine-Westphalia

Interpretation of the changes in heavy metal stocks between NFSI I and NFSI II must also consider the changes in the mineral soil layers. Although data on heavy metal stocks in the mineral soil for the entire country are available only for NFSI II, in North Rhine-Westphalia, these analyses were conducted for both NFSI I and NFSI II. Therefore changes in the heavy metal stocks between NFSI I and NFSI II can be explored for the mineral soil in this state.

Sampling for NFSI II in North Rhine-Westphalia consisted of a nationwide 8×8 km grid consolidated to 4×4 km squares in the lowland forests and in the Egge forested hills. Oriented on the middle inventory year of NFSI I and NFSI II, the comparisons below relate to a span of 17 years.

The humus stocks in the organic layer and in the mineral soil layers that had been measured directly in NFSI I and NFSI II were used as the basis for stock calculations. However, the quantity of fine soil in the mineral soil was determined only once for each inventory plot (NFSI I) and was then assumed as a constant in the comparisons of stocks.

Heavy metal stocks in the organic layer declined in the period between inventories for all elements (Table 7.2). The most distinct changes were observed for Pb and Hg. Mean stocks compared to NFSI I dropped by 59% for Pb and 51% for Hg. Stocks of the remaining heavy metals dropped over the same period by 33% for Cd and 46% for Cr, while the humus stock decreased by only 17% over this period.

Statistically, the changes in heavy metal stocks (arithmetic mean) were compared in two-way Gauss's test for stratified samples to better assess the signal strength of the changes after the first repeat of the inventory. With this test, the decrease in heavy metal stocks in the organic layer can be confirmed with a significance level of 1% as can the dry substance quantity in the organic layer.

In the mineral soil depth of 0–10 cm (Table 7.2), the stocks of a few of the heavy metals have changed in patterns deviating from the trend in the organic layer. In some cases, depletion in the organic layer is tied to an accumulation in the upper layers of the mineral soil. This type of shift in concentration to the mineral soil is seen for As, Pb, Cu, Hg and Zn. For some, the mean stocks in the 0–10 cm depth have increased only slightly by 8% (Cu) and 9% (Pb), whereas Hg increased significantly by 41%. At the same time, the decrease seen for Cd and Cr in the organic layers was continued in the upper layer of the mineral soil, with decreases of -16% and -14%, respectively, while the mean stocks of As, Ni and Zn showed only negligible change in the mineral soil compared to the first inventory.

The changes in stocks for the mineral soil (arithmetic mean) were not statistically significant for As, Cu and Ni. This result is most likely explained by the relatively high geogenic components in North Rhine-Westphalia, especially for Ni and As. In contrast are the highly significant changes for Cd and Cr that have taken place as a result of the decreased atmospheric inputs of these elements into the upper layers of the mineral soil. The overall increase in the quantity of humus in the mineral soil has had not caused an increase in the stocks of these heavy metals. In contrast, the highly significant increase in Pb and Hg in the mineral soil is due to both the influence of humus dynamics and the close correlation between the stocks of these heavy metals and organic matter. This relationship is further strengthened by inputs of Hg that are presumably increasing. The significance level for the slight increase in concentration or stocks of Zn in the mineral soil is at 90%.

	\mathbf{As}	Pb	Cd	Cr	Cu	Ż	Hg	Zn	Organic layer
Organic layer									
Median NFSI I	0.29	8.12	0.032	0.77	1.09	0.58	0.018	4.95	43,084
Median NFSI II	0.16	3.34	0.021	0.41	0.61	0.37	0.009	2.93	35,672
NFSI II – NFSI I	-0.13	-4.78	-0.010	-0.35	-0.48	-0.21	-0.009	-2.02	-7412
Change (%)	-45	-59	-33	-46	-44	-37	-51	-41	-17
Mineral soil									
Median NFSI I	8.58	62.7	0.177	23.25	10.00	10.80	0.086	41.68	
Median NFSI II	8.90	68.3	0.148	20.05	10.76	11.16	0.121	42.53	
NFSI II – NFSI I	0.33	5.62	-0.029	-3.19	0.76	0.36	0.035	0.84	
Change (%)	4	6	-16	-14	8	e	41	2	
Total stocks									
Median NFSI I	9.00	75.41	0.221	24.33	11.35	11.56	0.115	49.18	
Median NFSI II	9.11	74.63	0.176	21.06	11.79	11.80	0.136	48.56	
NFSI II – NFSI I	0.11	-0.79	-0.045	-3.28	0.44	0.24	0.021	-0.63	
Change (%)	1		-20	-13	4	2	18		

Table 7.2 Average stocks [kg ha⁻¹] for heavy metals and humus and changes between NFSI I and NFSI II in the organic layer, the mineral soil (0–10 cm) and

Because of the relatively low quantities of dry matter in the organic layer, the total of the stocks in the mineral soil plus the organic layer (Table 7.2) are determined primarily by the stocks in the mineral soil. Considering the entire layer from topsoil to a depth of 10 cm, based on NFSI II (median), the quantities of heavy metals bound in the organic layer make up a maximum of 12% of the total stocks.

As the comparison of the average total stocks shows, stocks of Pb, Cu, Zn, Ni and As in the topsoil have not changed significantly. The quantities of heavy metals that have been released from the organic layer are mirrored in the mineral soil to a depth of 10 cm, with the exception of Hg, Cd and Cr. While the Cr stock decreased by 13%, the amount of Cd declined by as much as 20%. The change in Hg is most striking; for this heavy metal, the increase by 18% is opposite to the general trend. This increase in Hg in the mineral soils clearly exceeds the reduction that was documented for the organic layer.

While the change in the total stocks of Cd, Cr and Hg in the topsoil was significant at a 1% level, the changes in Pb, Cu, Zn, Ni and As were not significant. For these elements the changes in the organic layer and the mineral soil cancel each other out. Thus, most heavy metals have no significant shift within the depth profile into deeper mineral soil layers. A slight translocation to the deeper mineral soil layers was observed only for Cd, which is a relatively mobile heavy metal. According to the data from the NFSI, at this plots an increase in the atmospheric inputs of Hg is assumed; however, this conclusion needs to be verified with more data.

7.3 Heavy Metal Concentrations in the Organic Layer and Mineral Soil

7.3.1 Spatial Distribution

7.3.1.1 Organic Layer

The spatial distribution of heavy metals concentrations in organic layer apparently differs throughout Germany. In order to help elucidate these differences, the maps for Pb and Zn concentrations are compared exemplarily for the total set of heavy metals investigated. Unlike the heavy metal stocks in the mineral topsoil (0–5 cm), for which there is a clear division in the mapping of the data across Germany (see Sect. 7.2.2), the distribution of heavy metal concentrations in the organic layer features a smaller-scale variability and hence suggests smaller-scale input pathways. For example, for Pb both atmospheric input and direct input from mining activities are evident (Fig. 7.13). The Süderbergland located in the leeward side of the industrial centres of North Rhine-Westphalia and sites in the higher elevations of the central German lowlands (e.g. the Thuringian Forest) are examples of sites with the highest Pb concentrations. Considerable impact from mining is evident in the Harz region and for As also in the Erzgebirge. The distribution of Cu is similar to that of Pb but with a few locations in Hessen and the Nuremburg/Fürth region in higher



Fig. 7.13 Distribution of heavy metal content measured in the organic layer into six percentile classes for the forest soils of Germany using lead as an example

percentile classes. Figure 7.14 depicts the distribution of Zn concentrations in the organic layer. Elevated Zn concentrations are found in the regions around Nuremburg/Fürth and eastwards as far as the Upper Palatinate Forest. Similarly in the higher percentile classes are the Zn and also the Cd concentrations in the Alps; in contrast, the Cr, Ni and Pb concentrations in the organic layer of the Alps are below average. Conspicuously low Zn concentrations were documented in the organic layers in sites in north-eastern Germany. The heavy metal concentrations in the Black Forest organic layer are also relatively low.



Fig. 7.14 Distribution of heavy metal content measured in the organic layer into six percentile classes for the forest soils of Germany using zinc as an example

Heavy Metal Concentrations Differentiated by Organic Horizon

Figure 7.15 differentiates the heavy metals in the organic layer according to the concentration in the organic horizons using principal component analysis. It appears that the variance in heavy metal concentrations can be represented well with just two components. Component 1 (PC1) and component 2 (PC2) alone explain 66.5% of the total variance: PC1 explains 49.0%, and PC2 explains 17.5% of the variance.

There is clear differentiation by organic layer horizon. From bottom left to top right, there is a gradient in the sequence $L - L + Of \approx Of \approx L + Of + Oh \approx Of + Oh$ – Oh, with a clear distinction between the L- and Oh-horizons and between the mixed and Of-horizons. The vectors for As and Pb and somewhat less so for Cu, Cr



Fig. 7.15 Principal component analysis (PCA) for heavy metal contents $[mg kg^{-1}]$ in the organic layer. The element mercury is not shown due to the low number of count sites in the organic layer. Organic layer horizons are distinguished by colour. Left: All measurements and the 95% confidence regions. Right: Vectors for the heavy metals and 95% confidence regions

and Ni correlate with these gradients, whereas the vectors for the elements Cd and Zn are orthogonal to the gradients along the organic layer horizons. This means that unlike the other elements, Cd and Zn are not differentiated by organic layer horizon. The direction of the vectors also indicates that the highest concentrations of the elements analysed, other than Cd and Zn, are found in Oh-horizons. This pattern can be explained based on the significantly weaker binding of Cd and Zn to organic substances in the organic layer.

Differentiation of the concentrations of Cd and Pb by organic layer horizon is shown in Fig. 7.16. As highlighted by the principal components analysis, no differentiation is apparent for Cd – the concentrations are all comparably low in all horizons; in contrast, Pb concentration is significantly higher in the Oh-horizon.

7.3.1.2 Mineral Soil

The distribution of concentrations in the uppermost layer of the mineral soil largely corresponds with the stocks distribution (see Sect. 7.2.2). For example, Fig. 7.17 shows the spatial distribution of concentrations for the element Ni in 0–5 cm of the mineral soil. As explained in Sect. 7.2.2, the observed distribution of Ni concentrations in the topsoil corresponds closely with the distribution of background values for Ni in the topsoil (BGR 2016). This result is clear evidence of the influence of the parent rock on Ni concentration in the mineral soil; this topic will be discussed in more detail in the next section.



Fig. 7.16 Differentiation of the contents $[mg kg^{-1}]$ of (**a**) cadmium and (**b**) lead by horizon of the organic layer. N = 81 per boxplot

7.3.2 Influence of the Parent Rock on Heavy Metal Concentrations in the Mineral Soil

One of the most important factors influencing heavy metal concentrations in the mineral soil is the parent rock (see Chap. 2). Heavy metal concentrations in the mineral soil vary depending on the geogenic base concentration of the parent rock. Heavy metal concentrations elevated as a result of geogenic processes occur in particular in soils derived from periglacial layers over basic magmatic and meta-morphic rock (Cr, Ni, Cu, Zn), clay rock (especially Liassic clay) (As, Cd, Cr, Cu, Ni, Pb, Zn), acidic metamorphic rock (Cu, Ni) and mica slate (Cr, Cu, Ni, Zn), as well as carbonate rocks as a result of accumulation of residual clay.

Figures 7.18 and 7.19 depict the differentiation of concentrations by parent rock using Pb and Ni as examples. Differentiation of concentrations by parent rock was based on the classifications of parent rocks throughout Germany into 16 classes by the Federal Institute for Geosciences and Natural Resources (Bundesanstalt für Geowissenschaften und Rohstoffe, BGR). Sediments in littoral zones (Unit 1), sandy loess (Unit 8) and tephra (Unit 13) are three classes not shown here as they have little relevance on a nationwide basis for forested sites. Sediments and alluvial soils (Unit 2) are not listed as the heavy metal concentrations of these substrates differ considerably depending on region and the source area of the watercourses; hence, general conclusions are not valid. Because only the topsoil is considered, till and boulder clay with sandy surface layers (Unit 5) are combined with sand and thick sandy surface layers (Unit 4) for this analysis.

In general, when differentiated by parent rock type, concentrations of heavy metals that are significantly characterised by anthropogenic processes, such as Pb, are strongly overlaid by inputs from emissions. This pattern is also apparent in the result that concentrations in the 0-5 cm depth layer always exceed those in the 5-10 cm depth. This result is particularly obvious for clay soils (Unit 10), where Pb



Fig. 7.17 Classification of the measured heavy metal contents in the first layer (0–5 cm) of the mineral soil into six percentile classes for the forest soils of Germany using nickel as an example

as well as As feature the highest concentrations. The explanation lies both in a high binding capacity in soils rich in clay as well as the spatial distribution of clay stones across Germany. Clay stones are particularly predominant in the Rhenish Slate Mountains leeward of the Ruhr district known as an industrial and steel production centre, and hence emissions of heavy metals are high. Concentrations that are above average on clay soils also include the elements Cu, Cr, Ni and Zn. Cd and Zn are highest on carbonate rocks (Unit 9), as these elements are naturally present in this rock type and the high soil pH due to the carbonate which favours binding of heavy



Fig. 7.18 Lead content [mg Pb kg⁻¹] differentiated by parent rock for the depth increments 0–5 cm and 5–10 cm. Numbering units: (3) terrace and gravel sediments, (4) sand and thick sandy surface layers plus till and boulder clay with sandy surface layers, (6) till and boulder clay, (7) loess and loess derivatives, (9) carbonate rock, (10) clay, (11) sandstone and other silicate rocks, (12) basic and intermediate magmatic and metamorphic rock, (14) acidic magmatic and metamorphic rock, (15) peat bog, (16) anthropogenic soil



Fig. 7.19 Nickel content [mg Ni kg⁻¹] differentiated by parent rock for the depth increments 0–5 cm and 5–10 cm. An explanation of the numbering system for parent rock type is given in the caption for Fig. 7.18

	Parent rock type					
Heavy metal	R^2 adj	F-value	<i>p</i> -value			
Arsenic	0.34	126.8	< 0.001			
Lead	0.25	81.7	< 0.001			
Cadmium	0.29	100.9	< 0.001			
Chromium	0.47	211.0	< 0.001			
Copper	0.33	117.7	< 0.001			
Nickel	0.43	182.0	< 0.001			
Zinc	0.41	167.2	< 0.001			

Table 7.3 Proportion of the variance in heavy metal concentrations explained by the stratum parent rock type $[R^2adj]$ and *F*-values and *p*-values. Mercury is not included in the analysis since data was available only for North Rhine-Westphalia, Rhineland Palatinate, Hessen and Saarland

metals. The elements As, Cr, Cu, Ni and Pb also have above average concentrations on carbonate rocks (Unit 9).

A different pattern emerges in the differentiation by parent rock type for the elements Ni and Cr, which are primarily geogenic in origin (Ni, Fig. 7.19). This figure indicates that the concentrations in 5-10 cm are higher than those in the 0-5 cm layer. Because of this high basic geogenic concentration, the highest concentrations of Cr and Ni, as well as Cu, are on basic and intermediate magmatic and metamorphic rocks (BAG 12). The elements Cd, Zn and Pb also have higher than average concentrations for this rock category. Consistently low heavy metal concentrations are found for terrace and gravel sediments (Unit 3), sandy and thick sandy surface layers (Unit 4), as well as till and boulder clay (Unit 6). Mid-range concentrations for all elements are found for loess and loess derivatives (Unit 7). Sandstone and other silicate rocks (Unit 11) feature low (Cd, Cr, Ni) to moderate (As, Cu, Pb, Zn) heavy metal concentrations, while the class of acidic magmatic and metamorphic rocks (Unit 14) have moderate (Cd, Cu, Zn) to high (As, Cr, Ni, Pb) concentrations. The pattern for peat bog (Unit 15) is relatively heterogeneous: there are elements with concentrations that are low (Cr, Ni), moderate (As, Cu, Zn) as well as high (Cd and Pb). Because moors are not likely to have high underlying geogenic concentrations of heavy metals, it is apparent that in particular Pb and Cd are deposited from anthropogenic sources via air pathways. Anthropogenic soils (Unit 16) have low (Cr, Cu, Ni) to mid-range (As, Pb, Cd, Zn) heavy metal concentrations.

Table 7.3 indicates the strength of the relationship between heavy metal concentrations and the parent rock type based on explained variance (R^2_{adj}) and the *F*-value. All 16 classes of parent rock were included in this analysis. The element Hg was not included due to the low sample size. The elements Pb and Cd show the lowest R^2_{adj} and *F*-values, presumably as a result of the considerable impact of anthropogenic factors for the concentrations of these elements in the topsoil. As and Cu have mid-range R^2_{adj} and *F*-values, whereas the values for Cr, Ni and Zn indicate the strongest relationship with parent rock type. The latter result is evidence of the importance of the geogenic origin of these three elements.



The ratio between heavy metal concentrations in the organic layer and the mineral soil (1-10 cm) is shown in Fig. 7.20. With equal stocks, the heavy metal concentrations differ due to their mass reference between the organic layer and the mineral soil based on the significantly lower dry bulk density of the organic layer, by up to a factor of 5–7; hence the heavy metal concentration in the organic layer should be five to seven times greater as the concentration in the mineral soil. In fact, the heavy metal stock in the organic layer accounts for only 12% of the stock in the mineral soil (see Sect. 7.2.3), such that the effect of the different dry bulk densities on the heavy metal concentrations in the organic layer and the mineral soil approximately cancel out. The relationship between heavy metal concentrations in the organic layer and the mineral soil depicted in Fig. 7.20 is therefore best evaluated on a comparative basis. For elements with inputs that are primarily from anthropogenic (atmospheric) processes, a significantly higher proportion (>>1) of the concentrations are expected in the organic layer compared to the mineral soil. However, other factors that affect this ratio must be considered, including the ionic charge of the heavy metal compounds present in the soil and uptake of the element by plants and thus the amount of the metal deposited through litterfall. Hence, elements that are present in the soil principally in anionic form, such as As, are less bound in the organic layer and are therefore transferred quickly into the mineral soil. In contrast, elements such as Cu and Zn are sometimes taken up from the mineral soil by plants and returned to the organic layer in litterfall ("vegetation pump"). The ratio for As is relatively low, which can be attributed to its more geogenic origin and anionic binding. Chromium and Ni also have moderate ratios < 1, confirming the predominantly geogenic origin of these elements. Cadmium, Cu, Zn and Pb have ratios considerably > 1; the "vegetation pump" may play a role for Cu and Zn as well. However, the high ratios for Pb and Cd must be attributed to input pathways that are mostly anthropogenic (atmospheric).

In Fig. 7.21, the depth profile for the concentrations of a heavy metal with a more anthropogenic influence (Pb) is contrasted with an element with a more geogenic

Fig. 7.20 Ratio of heavy metal content in the organic layer to the mineral soil (0-10 cm) for seven heavy metals. N = 806 for each element



Fig. 7.21 Depth profile for contents $[mg kg^{-1}]$ of (**a**) lead and (**b**) nickel for the parent rock class basic and intermediate magmatic and metamorphic rock (Unit 12)

origin for the entire profile on basic and intermediate magmatic and metamorphic rock (Unit 12). For Pb, concentrations are higher in the topsoil (0–5 cm) and rapidly decrease with increasing depth, whereas the opposite is true for Ni. This contrast clearly reveals the anthropogenic (atmospheric) overprinting of Pb within this parent rock class and confirms the primarily geogenic origin of the element Ni for soils on basic and intermediate magmatic and metamorphic rock.

7.3.3 Evaluation of Heavy Metal Concentrations in the Mineral Soil

The precautionary values listed in Annex 2 No. 4.1 of the Federal Soil Protection and Contaminated Sites Ordinance (Bundes-Bodenschutz- und Altlastenverordnung; (BBodSchV 1999)) can be used to evaluate the heavy metal concentrations in the mineral soil. In accordance with § 8 (2) of the Federal Soil Protection Act (Bundes-Bodenschutzgesetz; BBodSchG (1998)), exceedance of precautionary values for soil, when taking into account the harmful substance concentration from sources that are geogenic or due to extensive settlement, generally raises concern that harmful changes to the soil have taken place pursuant to § 9 BBodSchV. The precautionary values thus do not represent a danger threshold but instead indicate a threshold for concern, which, if exceeded, demands that precautionary measures such as avoiding or reducing further inputs should be taken.

So far, the BBodSchV (1999) regulates the precautionary values for seven heavy metals (Cd, Pb, Cr, Cu, Hg, Ni, Zn). An amended edition of the BBodSchV will also include precautionary values for As and thallium (Tl). The present evaluation of

Heavy metal	Sand	Loam/silt	Clay
Arsenic	10	20	20
Lead	40	70	100
Cadmium	0.4	1	1.5
Chromium	30	60	100
Copper	20	40	60
Nickel	15	50	70
Mercury	0.2	0.3	0.3
Zinc	60	150	200

Table 7.4 Precautionary values for inorganic substances (in mg kg^{-1} dry mass, fine soil aqua regia digestion)

Table 7.5 Proportion [%] of seven heavy metals in relation to class in terms of the extent to which they exceed or fall short of their precautionary value. "Other" includes missing values as well as peat bogs and sites with humus concentrations > 30 mass-%, for which no precautionary value has been defined

	Proportion [%]						
	As	Pb	Cd	Cr	Cu	Ni	Zn
\leq 50% of the precautionary value	54.9	32.0	82.0	65.6	77.0	70.1	68.2
$>50\% \leq 100\%$ of the precautionary value	26.8	38.9	8.6	21.8	12.4	16.8	20.3
$>100\% \le 150\%$ of the precautionary value	6.7	11.3	1.8	3.5	2.4	3.7	3.0
$>150\% \leq 200\%$ of the precautionary value	2.0	4.8	0.4	0.8	0.4	1.1	1.1
>200% of the precautionary value	2.5	6.0	0.2	1.4	0.8	1.4	0.4
Others	7.0	6.9	6.9	6.9	6.9	6.9	6.9

heavy metal concentrations in the mineral soil references the precautionary values proposed in the third working draft of the revision of the BBodSchV (2015); hence, the same reference scale is used for all the heavy metal concentrations analysed. In addition, this reference scale allows all mineral soils to be included, whereas the BBodSchV (1999) is officially valid only for soils with humus concentration up to 8 mass-%. Table 7.4 lists the precautionary values from the third working draft of the BBodSchV (2015). The values are differentiated for the heavy metals according to the main soil types: sand, loam/silt and clay.

The heavy metal concentrations were then correlated with their precautionary values to evaluate the concentrations in the mineral soil. Six classes were identified, and the proportion of each element in these six classes was calculated as a percentage. Table 7.5 shows the results of this process.

The results of this analysis indicate that in the majority of forest soils in Germany, the heavy metal concentrations are below the precautionary values. For the elements As, Cd, Cr, Cu, Ni and Zn, the majority of concentrations are even below or equal to 50% of the precautionary values. This is a positive result, in that it makes clear that the forest soils are mostly in good condition in terms of heavy metal concentrations. In the country as a whole, the elements As and Pb exceed the precautionary levels by



Fig. 7.22 Spatial distribution of arsenic in terms of the extent to which they exceed or fall short of their precautionary values in mineral soil (0-5 cm) for forest soils in Germany. Precautionary values are not defined for peat bogs or for sites with humus contents > 30 mass-%, so these sites are not mapped here

11.2% for As and 22.1% for Pb. Figures 7.22 and 7.23 show the spatial distribution of As and Pb in terms of this class of exceedance of the precautionary values. The most obvious results here are the loading of As in the Erzgebirge region that was described already in Sect. 7.2.2, as well as the elevated As concentrations in several locations in the Harz region, the Süder uplands and parts of the Black Forest. Although the cause for these elevated levels can be primarily attributed to mining in the Harz and Erzgebirge regions, the source of As in the Süderbergland is largely geogenic plus atmospheric inputs from the Ruhr district. In the southern Black



Fig. 7.23 Spatial distribution of lead in terms of the extent to which they exceed or fall short of their precautionary values in mineral soil (0–5 cm) for forest soils in Germany. Precautionary values are not defined for peat bogs or for sites with humus contents > 30 mass-%, so these sites are not mapped here

Forest, the occurrence of hydrothermal precipitates and the use of calcium arsenate for combating bark beetles have been cited as potential causes.

Lead concentrations that exceed the precautionary value are found in particular in sites in the Harz region, the Rhenish Slate Mountains, the Erzgebirge region and parts of the Thuringian Forest. In these cases too, the former mining activity can be named among the causes for the high concentrations in the Harz and Erzgebirge regions, while atmospheric inputs dominate in the Thuringian Forest and Rhenish Slate Mountains.

For Cd, 82% of sites included in the NFSI II are below or at 50% of the precautionary value, and only 2.4% of sites exceed the value (Table 7.5). Only isolated sites in the Harz region, the Westphalian Bay and the Rhenish Slate Mountains have Cd concentrations that are well above the precautionary values.

For Ni and Cr, 6.2% and 5.7% of sites, respectively, have concentrations above the precautionary values. In places, the explanation lies in geogenic inputs (basic magmatic and metamorphic rocks in Vogelsberg, limestones in the Swabian Alb), and in other sites anthropogenic causes are the source (Rhenish Slate Mountains). For Zn and Cu, <5% of sites have concentrations above the precautionary value. These sites are distributed heterogeneously throughout the country.

7.4 Conclusions/Recommendations for Action

The results of the NFSI on heavy metal burdens in forest soils suggest a need for further reduction of anthropogenic (atmospheric) input of heavy metals. This need is justified on the basis of the inability of heavy metals to biodegrade. Forest soils play an essential role in the balance of ecosystems; they must ensure that heavy metals entering the soils cannot reach the ground and surface waters unchecked but instead these substances permanently and extensively remain below levels that are harmful to plants, animals and other organisms. Thus, the nationwide NFSI is further justified by the risks that are posed by pollution of ground, spring and surface waters. In addition to the calculated heavy metal concentrations and stocks, forest management demands concrete evidence from the NFSI regarding the appropriate actions to maintain the filtering and regulatory function of forest soils. Key parameters that can favourably influence the natural retention capacity of forest soils include the humus concentration, pH and base saturation levels. These variables that describe soils can also be positively affected by forest management practices.

From the perspective of conserving soils and water systems, forest management practices must seek to counter forms of humus in the organic layer and promote the formation of humus in the mineral soil. In addition to increased cultivation and targeted maintenance of deciduous trees in mixed growth forests, forest liming is an option that creates favourable conditions for enriching the humus in the mineral soil layers. Forest liming has also proven useful for increasing the base saturation level of soils while decreasing acidity. If these measures are well coordinated, there is the potential to considerably increase stable, ecologically compatible compounds between the heavy metals and humus particles in mineral soil.

These measures can be concentrated on a regional basis, taking into account the calculated heavy metal concentrations and stocks, as well as the acidification of forest soils. Regions where forest soils have particularly high heavy metal burdens and significant soil acidification should be the focus of forest management practices that place a higher value on soil and water conservation than in regions with relatively lower heavy metal concentrations in the topsoil.

7.5 Summary

The heavy metal concentrations of forest soils in Germany are the result of both the geogenic basic concentration in the parent rock and the atmospheric inputs that can overprint this basic geogenic concentration especially in the topsoil layers. Evidence of significant atmospheric overprinting can be found for Pb, Cd and Hg, while As and Cu are less distinctly overprinted. Concentrations of the elements Ni, Cr and Zn are primarily determined by the basic geogenic concentration. The highest heavy metal concentrations are found on clay, carbonate rocks and basic and intermediate magmatic and metamorphic rocks, whereas relatively lower concentrations are documented on terrace and gravel sediments, sand and thick sandy surface layers as well as till and boulder clay.

Especially for elements with a high affinity for binding to organic substances such as Pb, Cu, Cr, Ni and Hg, heavy metal concentrations in the organic layer are clearly differentiated by humus horizon with increasing concentrations from the L- through Of- to the Oh-horizons. In contrast, Cd and Zn concentrations are not differentiated by horizon.

Over the period between the NFSI I and NFSI II, atmospheric inputs of heavy metals decreased, which, together with relocation/incorporation of the metals into the upper increments of the mineral soil, has resulted in decreased concentrations in the organic layer. Forest liming, which causes a shift of the humus from the organic layer to the upper mineral soil, has also tended to enhance this effect. Using the data from North Rhine-Westphalia by way of example, an analysis of the change in heavy metal stocks in the organic layer and the first two depth layers of the mineral soil was carried out; the results indicated that while heavy metal stocks shift from the organic layer to the mineral topsoil, the total stock of heavy metals remains largely unchanged. Special attention should be paid to Hg, as this element is the only one that has increased in soil, due to various elevated inputs through deposition.

Precautionary values based on the BBodSchV were used to assess the heavy metal concentrations in the mineral soil. For most heavy metals, concentrations in the majority of forest soils in Germany appear to be below the precautionary value; thus, in terms of heavy metal burden, forest soils can be said to be in relatively good condition in most areas. Only the elements As and Pb exceed the precautionary values in many regions, with 11.2% for As and 22.1% for Pb significantly exceeding the precautionary values.

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