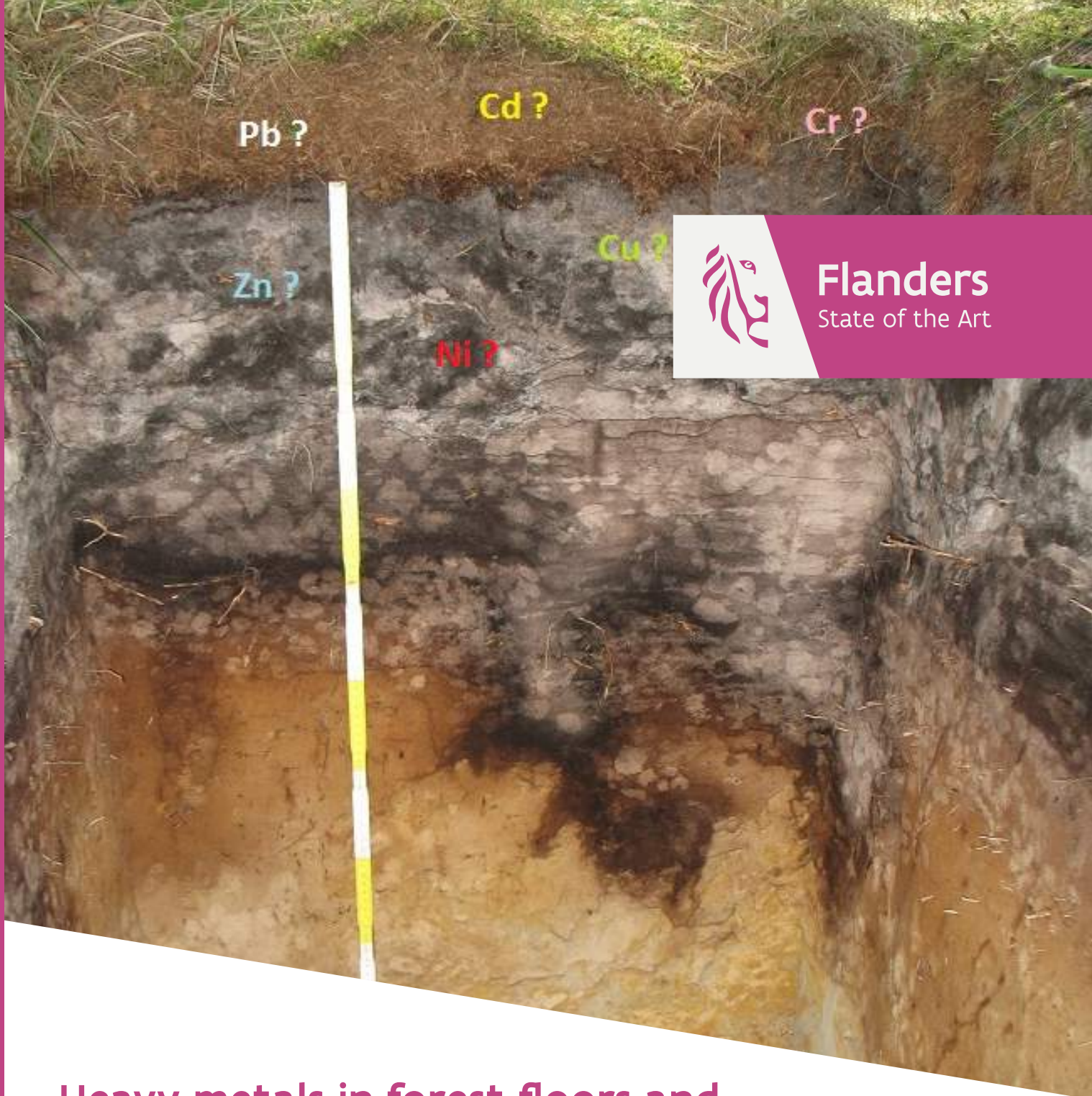




Heavy metals in forest floors and topsoils of ICP Forests Level I plots

Based on the combined Forest Soil Condition Database – Level I (FSCDB.LI)

Tine Bommarez, Nathalie Cools, Bruno De Vos

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Way of quoting:

Bommarez, T., Cools, N. and De Vos, B. (2021). Heavy metals in forest floors and topsoils of ICP Forests Level I plots. Forest Soil Coordinating Centre of ICP Forests. Report of the Research Institute for Nature and Forest 2021 (5). Research Institute for Nature and Forest, Brussels.
DOI: doi.org/10.21436/inbor.29316481

D/2021/3241/005

Report of the Research Institute for Nature and Forest 2021 (5)

ISSN: 1782-9054

Responsible publisher:

Maurice Hoffmann

Cover photograph:

Podzol profile © INBO

HEAVY METALS IN FOREST FLOORS AND TOPSOILS OF ICP FORESTS LEVEL I PLOTS

BASED ON THE COMBINED FOREST SOIL CONDITION
DATABASE - LEVEL I (FSCDB.LI)

Contract for Work and Services ordered by Johann Heinrich von Thünen Institute and executed by Research Institute for Nature and Forest (INBO) hosting the Forest Soil Coordinating Centre (FSCC)

Tine Bommarez, Nathalie Cools and Bruno De Vos

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ACRONYMS AND ABBREVIATIONS

AAS	Atomic Absorption Spectrometry
BD	Bulk density of the fine earth
BL	Baseline level (concentration)
CLRTAP	Convention on Long-Range Transboundary Air Pollution
CI _{95%}	Confidence interval at the P = 0.05 level (95% confidence)
CL	Critical level
EF	Enrichment factor
EMEP	European Monitoring and Evaluation Programme
ESDAC	European Soil Data Centre of the Joint Research Centre (JRC)
ETRS89	European Terrestrial Reference System (1989)
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
FF	Forest floor (ectorganic layer)
FSCC	Forest Soil Coordinating Centre of ICP Forests
FSCR	Forest Soil Condition Report
GM	Geometric mean
HM	Heavy metal
ICP Forests	International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests
I _{geo}	Geo-accumulation Index
INBO	Research Institute for Nature and Forest
LOD	Limit of detection
LOQ	Limit of quantification
MAC	Maximum allowable concentration
PCC	Programme Coordinating Centre of ICP Forests
UNECE	United Nations Economic Commission for Europe
UNEP	United Nations Environment Programme
ROS	Regression on Order Statistics
S1	First forest soil condition survey (1985 - 2000)
S2	Second forest soil condition survey (2000 - 2015)
SPIs	Soil pollution indices
TL	Trigger Level (concentration)
WGE	Working Group on Effects
WGS84	World Geodetic System (1984)

SUMMARY

Objectives The aim of this exploratory study is to investigate total heavy metal (HM) concentrations in European forest soils. The objectives are to: (1) explore the spatial variation (patterns and hotspots) of heavy metal concentrations and stocks in forest floors (FF) and topsoils throughout Europe; (2) investigate if there is a significant temporal change between the data observed during the first (S1) and second (S2) soil survey; (3) evaluate whether the HM concentrations and stocks exceed contamination or pollution levels and (4) compare the observed forest soil concentration levels with reference databases and maps of HM in soils or in mosses at the European scale.

Methods The study is based on data from the Combined Forest Soil Condition Database (FSCDB.LI) of ICP Forests holding descriptive and analytical information of soil samples obtained from two soil surveys on the ICP Forests' Level I systematic grid, a 16 x 16 km grid covering over 5000 forested sampling locations within Europe. The soil samples were analyzed for their Cd, Cr, Cu, Hg, Ni, Pb and Zn aqua-regia extractable concentrations in FFs and mineral topsoils (0-10 cm). The left-censored data are explored with appropriate statistical techniques in order to take concentrations below quantification limits (LOQ) into account. Sample geometric means are used as distribution metric and the bootstrapping technique to estimate 95% confidence intervals for evaluation of factor differences (e.g soil group) and temporal changes. For each HM, maps are produced and the average HM concentration and stocks by country, biogeographical region, soil group and humus form are calculated and presented.

Results and conclusions Heavy metal specific variation patterns in forest floors and topsoils are found within countries, biogeographical regions and Europe. Regional hotspots where elevated metal concentrations compared to baseline levels occurred are clearly visible on maps, and could be linked to local pollution sources and well-known contaminated areas. Geochemically related metals (e.g. Ni and Cr) show similar spatial distribution patterns. Soil group and humus form help explaining large-scale differences in HM concentrations. The HM concentrations of Cd, Cu, Pb, Zn and Hg in FFs are generally higher than in the underlying mineral topsoil indicating that FF concentrations are interesting indicators for HM contamination. Substantial enrichment of Cd, Pb and Hg in FF compared to mineral soils was found.

Generally the HM concentrations in forest soils have declined from 1990 onwards, although rates of change differ by heavy metal and between countries. Undoubtedly a methodological country effect can be seen. The decline between surveys could be evidenced better for FFs than in mineral soils because more temporally paired data is available for FFs. Except

for Cr a significant decrease is found in more than half of all paired Level I plots with 62% of plots showing a significant decrease in Pb concentration. About a quarter of plots still show increasing HM concentrations in FFs.

In this study two approaches were tested for evaluation of contamination levels in forest soils. Commonly used indicators as the Geo-accumulation Index and the Nemorow Pollution Index were applied. They indicated polluted areas especially for Pb, Hg and Cd, but almost no pollution for Cr and Ni and only regional hotspots for Cu and Zn. The Nemorow index indicated more than 55% of the LI sites as slightly polluted and 7% as heavily polluted, but could only be computed for 10 countries. Another approach was to apply national screening values, for which we calculated median baseline and critical levels and compared these with estimated baselines and critical levels. The estimated baselines, computed as geometric means of the distribution including values below LOQ, are generally lower than the median of national baselines. Significant differences were found among estimated baseline values of biogeographical regions indicating that an evaluation scheme should be developed for each biogeographical region separately. This approach demonstrated that only few percent of the level I plots exceeded the critical levels and is classified as polluted, 5-10% is classified as enriched and for all metals more than 50% of the level I plots is well below the baseline concentration level.

An evaluation scheme for HM concentrations in FFs was tested and a FF contamination index (FFMCI) calculated. Pb, Cd and Zn exceeded more the baseline levels than Ni, Cr and Cu. The FFMCI decreased from S1 to S2, also when considering paired plots only. However, 56% (S1) and 70% (S2) of the observed plots show background concentrations for all HM metals in their FFs.

When comparing the observed forest soil HM concentration levels with the LUCAS HM topsoil database and maps, no significant differences for Ni and Cu concentrations were found, but higher levels for Cd, Cr, Pb and Hg in the Level I forest topsoils compared to the interpolated LUCAS topsoil maps. Cd and Hg concentrations are a factor 3.5 higher than the predicted LUCAS concentrations at LI plots, Pb about double as high and Cr a factor 1.23. These results support the hypothesis that forest soils accumulate more metals than agricultural land, especially for Cd, Hg and Pb. When qualitatively comparing both maps, regional hotspots of all metals from LUCAS maps are clearly correlated with increased levels at the Level I sites, as expected. Similarly, increased levels indicated by the maps of HM concentrations in mosses, produced by ICP Vegetation, are also related to the concentration in forest floors and topsoil, albeit less strongly than with LUCAS data. The European-wide significant decline of HM concentrations in mosses between 1990 and 2015 was also found in the forest floor for all metals but less pronounced. These temporal changes seem to suggest that Cd and Pb concentrations are indeed decreasing but much slower than observed in mosses or by deposition time-series. Comparison with other datasets learns that heavy metals clearly accumulate and reside in forest soils and that their concentration levels are slightly higher than in mosses and agricultural soils.

Finally this study provides suggestions for future surveys and more profound heavy metal data explorations in forest ecosystems.

CHAPTER 1

INTRODUCTION

The International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests¹) acts since 1985 under the Convention on Long-Range Trans-boundary Air Pollution (CLRTAP) of the United Nations Economic Commission for Europe (UNECE) (Sanders et al., 2016).

This convention is an international instrument aimed at reducing and preventing air pollution in order to decrease the pressure of air pollutants on the environment and human health. The heavy metals cadmium (Cd), lead (Pb) and mercury (Hg) are common air pollutants, being emitted mainly as a result of various industrial activities. Atmospheric deposition of pollutants contributes to the build-up of these elements in soils across the globe (World Health Organization, 2007). Other trace metals like nickel (Ni), zinc (Zn), chromium (Cr) and copper (Cu) have natural background concentrations in soils related to the soil parent material. Human activity and resulting products (e.g. fertilisers, waste) or short-range air pollution from industry (e.g. smelters) can lead to local soil contamination.

The 1998 Aarhus Protocol on Heavy Metals came into force in 2003 and was amended to the CLRTAP in 2012. Its objective is to introduce measures for the reduction of the emissions of the three particularly harmful metals Cd, Pb and Hg into the atmosphere, aiming to prevent adverse effects. The Protocol describes measures and best practices for controlling emissions and initiates programmes, strategies and policies for achieving the heavy metal limit values as specified in the Protocol.

In 2013 the Minamata Convention on Mercury was adopted, a treaty negotiated under the auspices of the United Nations Environment Programme (UNEP). Building on the 1998 Protocol on Heavy Metals, the Minamata Convention raised global awareness on the hazards of Hg pollution. While Hg occurs naturally, its use in everyday objects has led to accumulation of this metal in the atmosphere, soil and water bodies. Controlling the anthropogenic releases of Hg throughout its lifecycle has been a key factor in shaping the obligations under the Convention. The Minamata Convention entered into force on 16 August 2017.

Referring to both conventions the Working Group on Effects (WGE) stimulated ICPs for actions. In the 2020–2021 workplan² for the implementation of the LRTAP Convention, scientific activities to develop or improve tools to assess air pollution and its effects in the ECE region were listed. This report fits under workplan item 1.1.1.12: *Status and trends of heavy metals in forest ecosystems* with expected deliverable for 2020: maps of heavy metal concentrations and stocks across Europe for two different survey periods.

¹www.icp-forests.net

²https://www.unece.org/fileadmin/DAM/env/documents/2019/AIR/EB/ECE_EB.AIR_144_Add.2__Advance_version_.pdf

1.1 MONITORING HEAVY METALS IN EUROPEAN SOILS

Heavy metals (HMs) is the term applied to a large group of trace elements which are both industrially and biologically important (Alloway, 2012). In the absence of a unanimous definition for 'heavy metals' a common approach is to use density as a criterion by selecting all metals with a density of more than 5 g/cm³. In this study we consider the heavy metals Cd, Zn, Ni, Cr, Cu, Pb and Hg, which are the most extensively studied elements in ecotoxicology. All of these metals are toxic to living organisms when present in excess (Nagajyoti et al., 2010), but some (e.g. Cr, Cu, Mn, Zn) are essential in small but critical concentrations for the normal development and health of either plants, animals or both (Alloway, 2012).

It is important to realise that soils can act both as a (geogenic) **source** of metals and as a **sink** for metal contaminants. The latter may originate from anthropogenic activity or natural processes, such as volcanic activity. All soils and ecosystems on the planet are affected to some extent by HM pollution. This is the result of global atmospheric deposition of these elements.

Heavy metal loading from the atmosphere is especially high in forest soils, due to the role of trees in filtering out airborne pollutants, a phenomenon called "the Auskämmeffekt" in German (Wellbrock and Bolte, 2019). Especially the non-essential metals Cd, Hg and Pb are recognised as important pollutants entering forest soils through deposition. Therefore efforts have been made to model the spatial deposition patterns of these elements at a pan-European scale by the European Monitoring and Evaluation Programme (EMEP). HM concentrations in mosses, which can be regarded as a proxy for atmospheric deposition, are also being monitored at five-yearly intervals by ICP Vegetation.

For Europe, the FOREGS Geochemical database contains heavy metal concentrations of 1588 georeferenced topsoil samples taken from all land-uses. Lado et al. (2008) mapped the concentrations of As, Cd, Cr, Hg, Ni, Pb and Zn using block regression-kriging over the 26 European countries that contributed to this database. Another HM reference dataset for European soils is provided by ESDAC and based on LUCAS 2009 and 2012 surveys. The topsoil data of all land-uses were mapped by Tóth et al. (2016) and compared to the heavy metal data of forest soils in this study.

1.2 HEAVY METAL MONITORING BY ICP FORESTS

Since the very beginning of ICP Forests' soil surveys in 1985 (S1), soil scientists recognised the important role heavy metals could play in the process of soil acidification as a result of 'Acid Rains'. However, in the early years of forest soil monitoring by ICP Forests it was optional and not mandatory to measure HM concentrations (Figure 1.1).

Moreover, for soil sampling on the systematic level I grid, sampling was only mandatory in the organic layer (O) and in mineral layers 0-10 cm (M01) and 10-20 cm (M12), but optional in deeper soil layers. Participating countries were allowed to choose whether M01 samples were split up into a layer of 0 - 5 cm (M05) and 5 - 10 cm (M51) or not. Conversely, at level II plots it was mandatory to sample mandatory parameters in M01, M12, M24 (20 - 40 cm) and M48 (40 - 80 cm).

Mandatory set of parameters				Optional set of parameters
Parameter	Reference Analytical Method	Units (1)	Reference literature	Parameter
1. pH(CaCl ₂)	Extractant: 0.01 M CaCl ₂ Measurement: pH-electrode		LABEX 8703-01-1-1 ISO-TC190/SC3/GT8	1. CaCO ₃ if pH(CaCl ₂) > 6
2. C _{org}	dry combustion	g/kg		2. Na
3. Total N	dry combustion	g/kg		3. Al
4. P	digestion: aqua regia (2)	mg/kg		4. Fe
5. K	digestion: aqua regia (2)	mg/kg		5. Cr
6. Ca	digestion: aqua regia (2)	mg/kg		6. Ni
7. Mg	digestion: aqua regia (2)	mg/kg		7. Mn
8. Amount of organic layer	Volume (cylindric)-dry weight	kg/m ²		8. Zn
				9. Cu
				10. Pb
				11. Cd

Figure 1.1: Mandatory and optional parameters for the first level I forest soil survey, extract of S1 soil manual of 1998

Important mandatory parameters in S1 for predicting heavy metal bio-availability were pH_{CaCl₂}, organic carbon content and organic layer dry weight to estimate the HM stock in the organic layer. Note that bulk density was not a mandatory parameter, although it was advised to determine dry bulk density on undisturbed samples or to provide a reasonable estimation. The heavy metals Cr, Ni, Zn, Cu, Pb and Cd were included in the list of optional parameters. Hg was not included in the first level I forest soil study, so no data was collected for this metal during S1. More parameters were included in level II surveys, such as Hg which was listed as an optional parameter.

For the second forest soil survey (S2), as taken from the Manual III published in 2006, more parameters were included (Figure 1.2). Here the aqua-regia extractable metals were split in two groups: (1) Cu, Pb, Cd, Zn and (2) Al, Fe, Cr, Ni and Hg. Analysis of the second group of elements was optional, resulting in a lower data-availability of the elements in this group. Analysing the first group of elements was mandatory in the layers OF (fermented organic layer), OH (humified organic layer), H01 (0 - 10 cm in peat soils) and M01 (0 - 10 cm in mineral soils). The focus in S2 was on collecting topsoil data and not on studying deeper soil layers, although countries were free to sample and report deeper layers as well. The same mandatory sampling scheme for heavy metals was used in Level I and in Level II.

However, during the BioSoil demonstration project, conducting the second survey (S2), the ICPF sampling scheme was overruled and the analysis of all parameters (mandatory and optional) for the soil layers 0-10 cm, 10-20 cm, 20-40 cm and 40-80 cm was financed and had to be reported (De Vos and Cools, 2011). This resulted in much more heavy metal data for S2 than required on the basis of the soil manual of 2006. Since forest soils are often limited in depth by lithic contact or coarse fragments, data from deeper soil layers is often missing for large areas. Important to mention is that measured bulk density and

Parameter	Unit	Decimals	Level I				
			Organic Layer		Mineral Layer		
			OL	OF+OH, H-layers ⁽²⁾	0-10 cm	10-20 cm	20-40 cm 40-80 cm
<i>Physical soil parameter</i>							
Organic layer weight	kg/m ³	2	O	M	-	-	-
Coarse fragments	%	0	-	-	M ^{(3), (4)}	O ^{(3), (4)}	O
Bulk density of the fine earth	kg/m ³	0	-	-	M ^{(3), (5), (8)}	O ⁽⁸⁾	O
Particle size distribution (FAO, 1990a)	-	-	-	-	M ^{(3), (7)}	M ^{(3), (7)}	O
Clay content	%	0	-	-	M ⁽⁷⁾	M ⁽⁷⁾	O
Silt Content	%	0	-	-	O	O	O
Sand Content	%	0	-	-	O	O	O
<i>Chemical soil parameter</i>							
pH(CaCl ₂)	-	1	-	M	M	M	O
Organic carbon	g/kg	1	-	M	M	M	O
Total nitrogen	g/kg	1	-	M	M	M	O
Carbonates	g/kg	0	-	M ⁽⁸⁾	M ⁽⁹⁾	M ⁽⁹⁾	O
Aqua Regia extracted P, Ca, K, Mg, Mn	mg/kg	1	O	M	O	O	O
Aqua Regia extracted Cu, Pb, Cd, Zn	mg/kg	1	O	M	M	-	-
Aqua Regia extracted Al, Fe, Cr, Ni, S, Hg, Na	mg/kg	1	O	O	O	-	-
Exchangeable Acidity	cmol(+)/ kg	2	-	M ⁽¹⁰⁾	M	M	O
Exchangeable Cations: Ca, Mg, K, Na, Al, Fe, Mn, H	cmol(+)/ kg	2	-	M ⁽¹⁰⁾	M	M	O
pH(H ₂ O)	-	2	-	O	O	O	O
Total Elements: Ca, Mg, Na, K, Al, Fe, Mn	mg/kg	1	-	-	-	-	-
Oxalate extractable Fe, Al	mg/kg	1	-	O	O	O	O

Figure 1.2: Mandatory and optional parameters for the second LI soil survey, extract of S2 soil manual of 2006

volumetric coarse fragment content was mandatory as well so that stocks of heavy metals can be calculated.

The current soil manual of ICP Forests sticks to mandatory reporting of Cu, Pb, Cd and Zn in the OF, OH, M01 and H01 layers. Analysis of all other metals is optional (Cools and De Vos, 2016).

Heavy metals are subject of study in the other ICP Forests' surveys and datasets as well. Table 1.1 provides an overview of heavy metals studied in the 2020 manuals of various ICP Forests' surveys. As is clear from this table, the analysis of heavy metals is only mandatory in soils and just 4 metals, i.e. Cd, Zn, Cu and Pb can be traced throughout the forest ecosystem from deposition, foliage and litterfall to the soil. Hg is measured in soil and deposition only, whereas Co and Mo are assessed in deposition but not in soil solution nor solid soil.

Table 1.1: Mandatory (M) and optional (O) heavy metal analyses in ICP Forests' surveys.

Survey	Plots	Cd	Zn	Ni	Cr	Cu	Pb	Hg	Co	Mo
Soil (incl. FF)	LI and LII	M	M	O	O	M	M	O		
Soil solution	LII	O	O	O	O	O	O			
Foliage	LII	O	O			O	O			
Litterfall	LII	O	O			O	O			
Deposition	LII	O	O	O		O	O	O	O	O

1.3 AIM OF THIS STUDY

The heavy metal data collected in the ICP Forests' soil surveys has never been thoroughly examined at the European level. Only some countries analyzed their data on a national level. Therefore, under the lead of the Programme Coordinating Centre (PCC), the Forest Soil Coordinating Centre (FSCC) explores with this study the heavy metal data in forest

floors and mineral topsoils of the two pan-European LI forest soil surveys. This report entails the scientific approach, an evaluation of the available data on heavy metal concentrations and stocks and a discussion on the results.

The research is executed during the contract period 01/09/2020 until 30/11/2020, and shortly extended till 24/12/2020 on INBO budget. For this project the FSCC hired Tine Bom-marez (MSc) to conduct the study under scientific supervision of Dr. Nathalie Cools and Dr. Bruno De Vos. All work is performed at the Environment and Climate Unit of the Research Institute for Nature and Forest (INBO) in Belgium. In this document, we will analyse and report on the spatial patterns observed in the data of the second forest soil condition survey mainly as well as the temporal change of concentrations from the first (S1) to the second survey (S2).

The objectives of this research are to: (1) explore the spatial variation (patterns and hotspots) of heavy metal concentrations and stocks in forest floors and topsoils throughout Europe (2) investigate if there is a significant temporal change between the data observed during the first and second soil survey (3) evaluate whether the HM concentrations and stocks exceed contamination or pollution levels and (4) compare the observed forest soil concentration levels with reference databases and maps of HM in soils or in mosses at the European scale. The tasks and deliverables of this project are described in Table 1.2.

Table 1.2: Overview of tasks and deliverables of this study

Task	Task Description	Deliverable
1	Map HM concentrations of Zn, Pb, Ni, Cu, Cr and Cd in European forest floors and topsoils for the first survey period (S1: 1985 – 1999)	GIS layers in ESRI shape format Report chapter per metal
2	Map HM concentrations and pools of Zn, Pb, Ni, Cu, Cr, Cd and Hg in forest floors and topsoils across Europe for the second survey period (S2: 2000 - 2015)	GIS layers in ESRI shape format Report chapter per metal
3	Map the difference in HM concentrations between S1 and S2 for plots included in both surveys to detect changes	GIS layers in ESRI shape format Report chapter per metal
4	Estimate natural background concentrations and anthropogenic input (deposition) for all level I plots	Report chapter on background
5	Develop an evaluation scheme (critical levels) at the EU level based ecotoxicological risk assessment by testing existing national evaluation schemes	Report chapter on pollution indices and evaluation schemes
6	Compare the HM maps in forest soils with maps based on HM concentration in soils and mosses to detect common regional hot spots	GIS layers in ESRI shape format Report Chapter on contamination patterns in mosses versus forest floors

This report consists of seven chapters. Chapter 2 provides a concise overview of data availability and how the working database was compiled. In Chapter 3 a detailed explanation of the materials and methods, including the statistical approach can be found. Chapter 4 summarizes the obtained results, which are being discussed further referring to external material in Chapter 5. In Chapter 6, the main conclusions of this study are given and in Chapter 7 some brief suggestions for further investigations and pan-European soil surveys are provided.

CHAPTER 2

DATA HANDLING AND

VALIDATION

In this chapter we will explain how the original European Forest Soil Condition Database (FSCDB.LI) was improved to enable the evaluation of heavy metal concentrations and stocks in forest soils (Figure 2.1).

2.1 DEVELOPMENT OF WORKING DATABASE

The ICP Forests database holds comprehensive datasets structured according to type of survey on the level I or Level II network. For soil related data, five survey datasets exist:

- S1** Solid soil data of 1st survey (1985 - 1999) on Level I plots
- S2** Solid soil data of 2nd survey (2000 - 2015) on Level I plots
- SO** Solid soil data on Level II plots
- SS** Soil solution data on Level II plots
- SW** Soil water content and water retention characteristics of Level II plots

The Forest Soil Condition Database (FSCDB.LI) combines all soil data from S1 and S2 surveys, whereas FSCDB.LII stores all data of the Level II soil surveys conducted every 10 years (SO survey). The structure and field names of both FSCDBs is identical and consists of following data-modules which are linked to data submission forms. Through these forms the countries submit their national data to the PCC data center.

- PLS** Georeferenced plot information
- PRF** Soil profile description
- PFH** Soil physicochemical data of profile horizons
- SOM** Soil physicochemical data of fixed depth layers
- LQA** Laboratory QA/QC information

More information can be found in the [online documentation of ICP Forests](#).

This study is based mainly on the FSCDB.LI data stored in **PLS** and **SOM** modules, since no heavy metal data of soil horizons is present in the PFH module. If information on bulk density (BD) was missing in SOM, measured BD for a specific depth was retrieved from the corresponding horizon in PFH. For level I, virtually no LQA information is present.

The **PLS** module from FSCDB.LI contains 10447 records and 16 columns (i.e. attributes, further denoted in *italic*). Exactly 5289 unique plots belong to survey 1 (S1) and 5158 plots to

survey 2 (S2). For this study the attributes used from **PLS** are: country (*code_country*) and plot (*code_plot*) we usually concatenate to the attribute *PLOTID* (*=code_country_code_plot*, e.g: 2_101), plot LAT-LONG coordinates in WGS84 (*latitude*, *longitude*), survey year (*survey_year*) and date of sampling (*date_sampling*).

The **SOM** module from FSCDB.LI contains 45571 records and 78 columns (attributes). The following attributes were retrieved from the original **SOM** file: *survey*, *survey_year*, *code_country*, *code_plot*, *code_layer*, *layer_limit_superior*, *layer_limit_inferior*, *bulk_density*, *coarse_fragment_vol*, *organic_layer_weight*, *extrac_cd*, *extrac_cr*, *extrac_cu*, *extrac_hg*, *extrac_ni*, *extrac_pb*, and *extrac_zn*.

In addition we added extra attributes from the working database setup developed for the 2nd Forest Soil Condition Report (De Vos and Cools, 2011): *BIOSOILCOUNTRY*, *PLOTID*, *BPLOTID*, *BDEST* and *CFMASS*.

During S2, German Bundesländer acted as separate countries and *code_plot* was only unique within these countries. Same holds true for Belgium (Flanders and Walloon region). Therefore *BIOSOILCOUNTRY* was defined instead of *code_country* and *BPLOTID* was applied as most unique level I plot identifier for the whole FSCDB.LI, which was simply the concatenation of *BIOSOILCOUNTRY* and *code_plot*.

Two other help variables were added: *BDEST*, being estimated bulk density by pedo-transferfunctions or expert judgement when measured *bulk_density* was missing and *CFMASS* when coarse fragment information was available by mass instead of by volume (*coarse_fragment_vol*).

The quality and comparability of data from the first survey was insufficient to conduct an extensive study on heavy metal pollution in European forest soils. This was mainly due to differing sampling strategies and analytical procedures used by national laboratories. Hence, several attributes obtained from the second survey were taken to ensure higher quality and comparability of the S1 data.

2.2 DATA AVAILABILITY

The geographic extent of the available data is different for each heavy metal. GIS layers were created in the metric European Terrestrial Reference System of 1989 (ETRS89) to display the amount of available data per sampling location. In these layers the sampling depth for the heavy metal can be verified, as well as whether or not the heavy metal concentration of the organic layer was analyzed. The geographic coverage of the second forest soil condition survey (S2) is better than the first one (S1). This indicates the importance of the engagement of each individual country to participate in the European forest soil condition surveys.

Especially in S1, sampling depths varied on a national or regional level. To meet the need of a harmonized protocol for soil sampling and analysis, a manual with good practices has

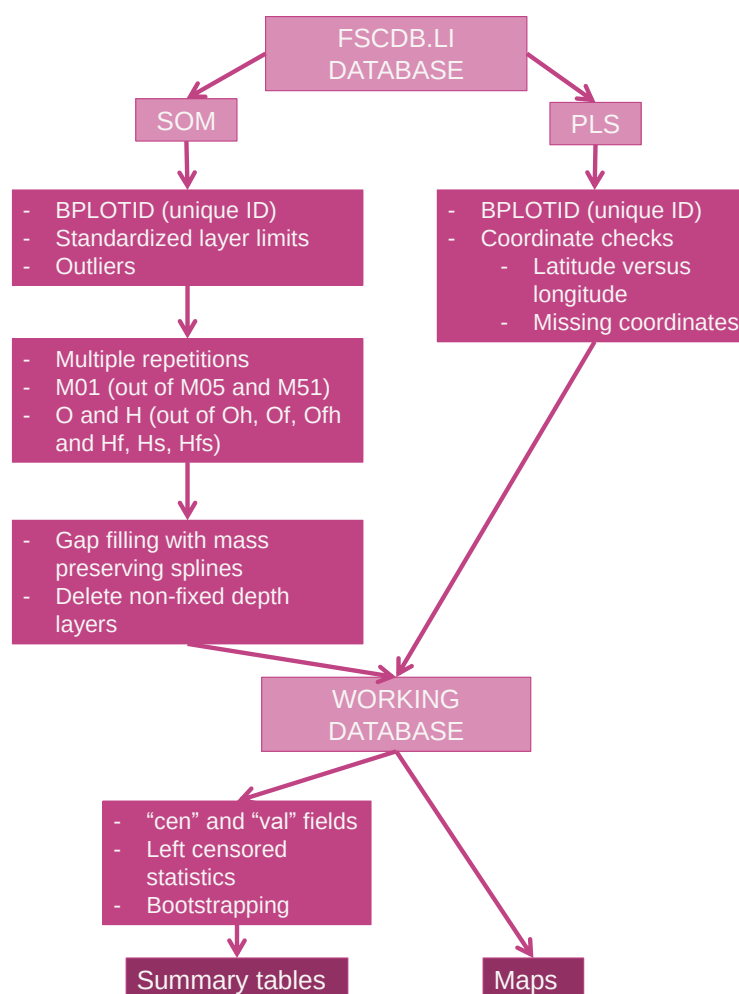


Figure 2.1: Scheme of different steps taken during the development of a working database from the original FSCDB.LI database.

been developed and improved over the years (Ferretti and Fisher, 2013; Cools and De Vos, 2016). This manual is kept up-to-date so its latest version includes the latest standard practices and methods, agreed by the Task Force of all participating countries.

2.3 DATA ACCURACY

According to the ICPF manuals, all aqua regia extractable heavy metals have to be reported in mg/kg. The required precision for reporting in this unit is 1 decimal place for Zn, Ni, Cr, Cu and Pb and 2 decimals for Cd and Hg for which the concentration ranges are usually smallest.

If laboratories reported values below limit of quantification (see Chapter 3), as for example <0.5 mg/kg, this was stored in the database as '-1' because the field needed to be numerical. This allows appropriate statistical handling of these left censored values that indicate very low concentrations that are not accurately quantifiable with the standard methods, but still have great ecological relevance for the data evaluation. Note that quantification limits

are country, laboratory, instrument, method and element dependent and may also vary over time along with laboratory experience. Limited information on these limits is available from the first survey, more details from the second and these limits could also be retrieved from the interlaboratory ringtests where the laboratories participated in (De Vos, 2008).

The analytical error, both within labs (repeatability error) as between labs (reproducibility) was estimated for each laboratory during various ringtest events organised by ICP Forests. Labs were evaluated if their analyses of real-life forest soil samples were accurate enough for ICPF monitoring and could take measures to improve their analytical proficiency. Undoubtedly, competence and hence accuracy of the labs increased over time. Moreover, also the technological evolution towards high performance analytical instruments, more specifically from (Flame) Atomic Absorption Spectroscopy (AAS) to Inductive-Coupled Plasma Atomic Emission Spectroscopy (ICP-AES or OES) increased precision and trueness of results, lower detection and quantification limits and high throughput of samples by multi-element determination. Most labs worked with AAS during the first survey, but changed to ICP-AES or even ICP-MS (Mass Spectrometry) instruments during the second.

During the second survey, FSCC distributed reference soil material with known concentrations of heavy metals to the labs to support optimisation of their analytical methods using control charts.

At least during the second survey, many institutes stored their soil samples in their national soil archive. Since heavy metals do not disappear from well-stored soil samples, they can be analysed again during a next survey together with the new samples, enabling elimination of errors due to instrumental and/or methodological changes over time. Unfortunately, heavy metal data of resampled historical samples was not available for this study in order to assess the magnitude of methodological errors for each metal.

2.4 VALIDATION OF WORKING DATABASE

Three main types of validation checks have subsequently been carried out: compliance, conformity and uniformity checks. As the data validation progresses the degree of automation decreases and the need for expert knowledge increases.

2.4.1 COMPLIANCE CHECKS

These checks verify if the format (syntax) of the submitted information is according to the required specifications. These checks do not test if the content (value) of a parameter is valid. Data ranges are not verified, only syntactic checks are applied.

SPECIAL VALUES

Concentrations below limit of quantification (LOQ) consistently needs to be indicated by "-1". Some records of HM concentrations still contained "<0.1" like for Cd concentrations

reported by Estonia. All left-censored data in the *extrac_xx* fields were therefore replaced by "-1", and associated fields were added as *cen_xx* = *TRUE* (logical) to indicate these were censored values and *val_xx* = *LOQ* to indicate the LOQ with *xx* the heavy metal (e.g. *cd*). So, for each heavy metal with field *extrac_xx*, the fields *cen_xx* and *val_xx* = *LOQ* are associated in the working database, required for statistical treatment.

Missing values were indicated as 'NA' or 'NULL'. In the working database NA's were systematically deleted because empty (NULL) values become automatically 'NA' when processed with R, so that missing values can be handled in a statistically sound way.

SYNTACTIC INCONSISTENCIES

Some concentration levels were expressed with decimal comma instead of decimal point, which was corrected in the working database.

For some records the *code_country* character field had prefix 0 (e.g. 01 for France) and were recoded to the numerical value ('01' => '1'). For part of the Swedish dataset, country codes were missing for 54 records. These were added.

In the FSCDB.LI some *code_layer* designations were not following the right syntax for depth layers, for example "Mxx" or "Hxx" with *xx* referring to unstandardized depths. These codes were harmonised using the layer depth info or depths of neighbouring layers into standard layers (e.g. M01, M12, M24, ...).

2.4.2 CONFORMITY CHECKS

Conformity checks evaluate if the data (value or observation) in the database is realistic. It includes plausible range tests of quantitative variables, evaluations of attributed classes and qualitative descriptions. Typically, single observations are checked individually, not compared with observations within the profile or the plot, nor with observations of other plots.

COORDINATE CHECKING

The PLS file of the combined FSCDB.LI contains 10447 plot coordinates. The ICPF format of latitude-longitude coordinates in degrees-minutes-second (DMS) were transformed to decimal degrees (DD) according to the WGS84 system and further into the ETRS89 LAEA metric system. Using the latter georeference, the LI plots were situated on GIS maps in order to find inconsistent georeferencing and locations. In total 38 inconsistencies of erroneous coordinates were found. Obvious errors were found for UK plots 6_9, 6_41, 6_410 and 6_420 situated in the North sea (Fig 2.2). The plots of the first survey (6_410 and 6_420) were corrected using the plot file (PL1) from the System Instalment survey (Y1) of the ICPF database. Conversely, plots 6_9 and 6_141 were missing in PL1 (needs to be added) but were found in the GPL file of the Biodiversity survey (BD). The error for these 4 plots was mainly in the longitude coordinates, which need to be negative instead of positive.

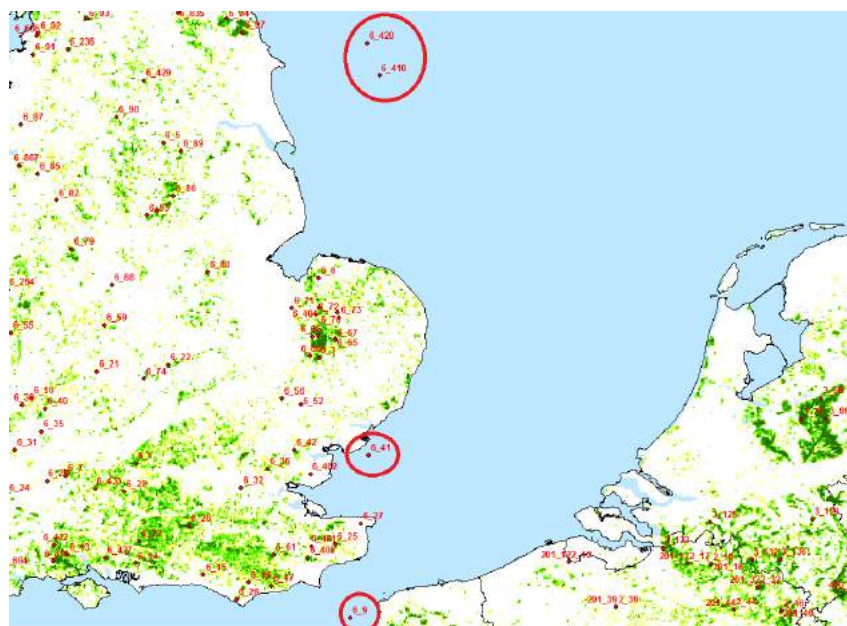


Figure 2.2: Level I plots falling in the North-sea: obvious errors in the red circles

Other plots falling in the Mediterranean sea were 22 Spanish plots. Other plots are situated next to islands but into the sea (4 Swedish and 5 Croatian sites). Some plot coordinates were completely wrong, like for plot 13_11022 or for the Serbian plot 67_69 where Latitude and Longitude were switched. No other plots of the PLS file were found to fall outside the EU borders. Next step was to check if plots belonging to a specific country according to their *code_country* were effectively situated in that country based on their plot coordinates. This was not the case for the Slovenian plot 60_2574, which was in the first survey located in Austria. Coordinates of the second soil survey were copied to that specific *PLOTID* for S1. The Lithuanian plot 56_647 had S1 coordinates in Belarus, but was situated in S2 inside Lithuania (just crossing the border), so the latter coordinates were applied. This indicated also a general shift for the plots in that country (see next section). The Croatian plot 57_2725 was based on its coordinates situated in Bosnia and Herzegovina, but just about 64 m crossing the border. We left the coordinates unchanged. Both in S1 and S2 the Slovenian plot 60_1148 is situated on Croatian territory, about 360 m across the border. Since we had no more precise coordinates, these were left unchanged. The German Plot 4_677, was mapped in Czech Republic, about 80 m from the border. Since the coordinates were identical as in the Installment file, they were left unchanged. The Spanish plot 11_400 was during S1 located in France, but in S2 in Spain, 56 km to the East. Considering the 16x16 km grid the S2 coordinates were judged most correct and copied to the S1 coordinates. The Spanish plot 11_534 was mapped about 100 m from the border in France. We left the coordinates unchanged. The Lithuanian plot 56_96 was in S1 situated in Latvia, but in S2 correctly in Lithuania (3.5 km SW), so the S2 coordinates were copied to S1. The Spanish Plot 11_1544 was just over the border with Portugal (70 m), so coordinates were left unchanged since identical for S1 and S2. Since missing minus signs were recurrently detected for the Spanish plots, we specifically compared the sign between S1 and S2 surveys. Indeed, we could further resolve this problem for another 10 Spanish plots by changing the S1 coordinates with the correct S2 coordinates. All these examples illustrate that coordinate checking is

absolutely necessary prior to overlaying the plots with other geodata (soil maps, forest and climate data, etc.)

FOREST FLOOR NEGATIVE DEPTHS

BY convention in ICP Forests counting depth is starting from the top of the mineral soil (= 0cm) with positive values for increasing depth and negative values for the thickness of the forest floor layers. Not all forest floor (O, OL, OF, OH, OFH layers) had negative depths which was corrected in the working database.

Another conformity check was testing if depth of the superior layer limit > inferior layer limit and that the depths of juxtapositioned organic layers (OL, OF, OH) were matching. Corrections were made accordingly. Layers with 0 cm thickness were not allowed but got a minimum thickness of 0.5 cm).

PLAUSIBLE RANGE TESTS

Based on ICP Forests data, plausible ranges are defined for all soil parameters including heavy metals (see Table 3.1).

For specific countries and plots HM concentrations were outside the plausible range, and therefore thoroughly checked. For instance for Serbia, the reported Pb values of year 2014 were a factor 10 higher than the average Pb values of all other countries, and the value of 430 mg/kg Pb exceeded both maxima of the plausible ranges for forest floor (245 mg/kg) and mineral soil (110 mg/kg). After contacting the NFC and Serbian Soil experts they found out that erroneously Pb and P concentrations were swapped and we corrected the data accordingly.

For other specific plots, plausible ranges were exceeded for several metals simultaneously. For instance on plot 66_9 of Cyprus, plausible ranges were exceeded for Ni (426 > 80 mg/kg), Cu (982 > 55 mg/kg) and Cr (1067 > 80 mg/kg), presumably caused by asbestos minerals. Obviously this plot was strongly polluted and the data were judged realistic and left unchanged. Similarly, 18 other extreme values in different countries were verified.

2.4.3 UNIFORMITY CHECKS

Uniformity checks are comparative in nature. Data values or qualitative observations (e.g. horizon designations) are compared with spatially or temporally related values or observations. This way, data of adjacent layers are compared, samples within and between plots, etc. Expert judgment is crucial for these checks. Mapping of classified variables is used to detect lack of spatial uniformity. Data are also compared between surveys (S1 vs. S2) to detect unrealistic temporal changes.

DUPLICATES

Checking if data are unique is essential in any dataset. We found duplicate PLOTIDs within the same survey. When identical data was associated with the PLOTIDs the duplicated record was deleted.

NON-STANDARD SOIL DEPTHS

Legacy soil data during S1 was collected according to national standards, often coinciding with national sampling schemes or pedogenetic horizons. Hence, the reported layer limits in S1 often deviated from the fixed depth ranges prescribed by De Vos and Cools (2011). In order to be able to compare soil data between countries and between periods (surveys), it was necessary to standardize the values of soil attributes at fixed depth ranges as illustrated in Figure 2.3.

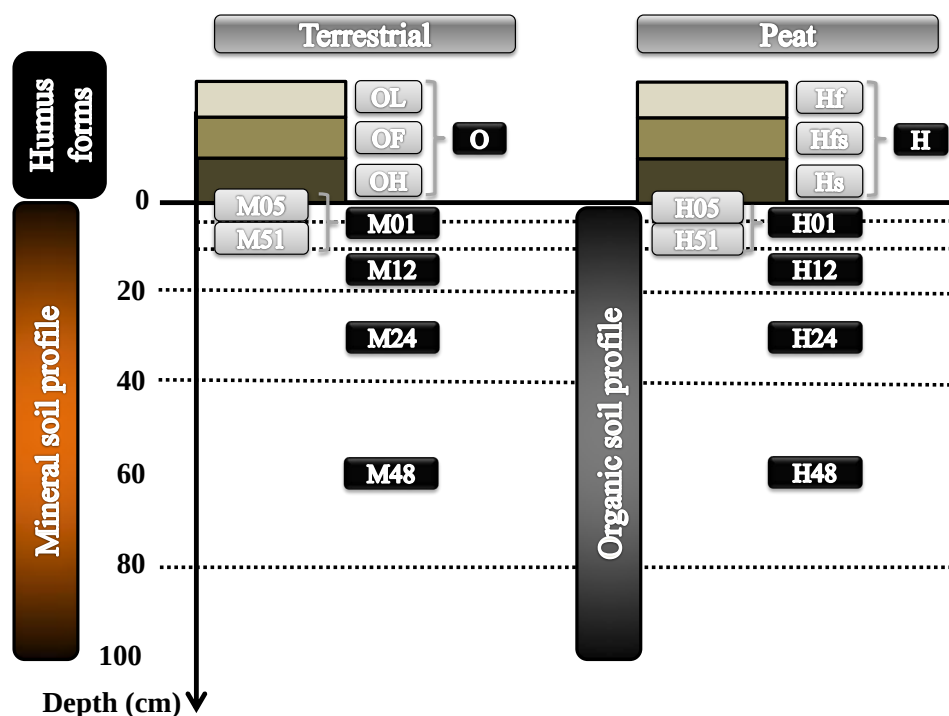


Figure 2.3: Fixed depth layer stratification scheme of the forest floor and fixed depth layers. Figure edited from De Vos et al. (2015).

In case the soil profile layers of 0 to 5 cm (M05) and 5 to 10 cm (M51) were reported separately, the mean of the soil attribute values in both layers was taken in order to create a standardized layer with depth 0 to 10 cm (M01).

In the second forest soil condition survey (S2), the soil attributes for litter (OL), the fragmentation horizon (OF) and humus (OH) were reported separately. In S1 on the other hand, this subdivision was not made and only one sample was taken to represent the entire organic layer (O). To facilitate the comparison of heavy metal concentrations between S1 and S2, the mean for soil attributes in OL, OF and OH was taken weighted by the mass of each individual organic layer to obtain soil attribute values for the O layer.

The values of soil attributes at standard depth increments were estimated using equal-area quadratic smoothing splines (Figure 2.4). The procedure of using splines to model soil attribute depth functions is widely accepted by the soil science community (Malone et al., 2009; Odgers et al., 2012). The lambda (λ) parameter was set to 0.1 as suggested by Bishop et al. (1999).

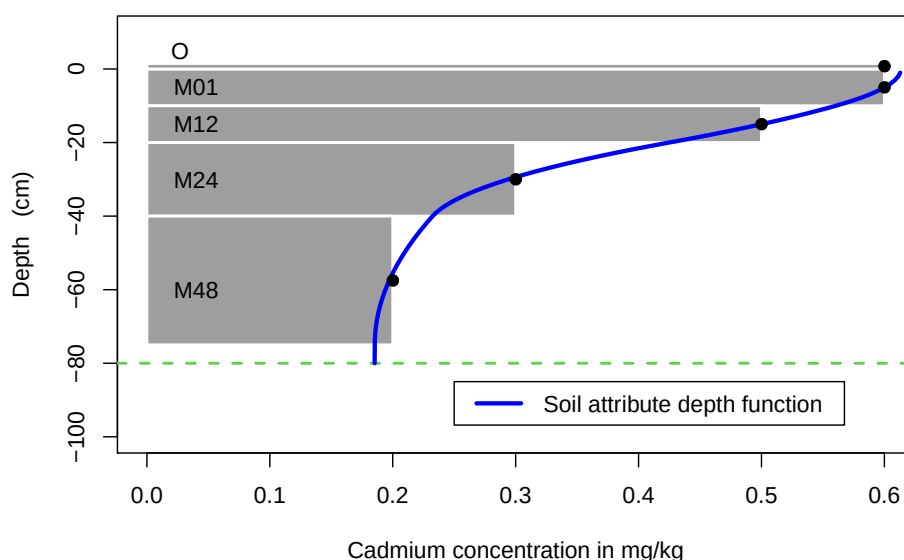


Figure 2.4: Example of the vertical distribution of layer specific cadmium concentrations with a fitted depth function. An equal-area quadratic smoothing spline was used to estimate the cadmium concentration at standard depth intervals of 1 cm.

Standardising depths and interpolating concentrations was an important step in the creation of the working database (Figure 2.1) and essential for the calculation of summary statistics for each metal and layer (Annex B.2).

COMPARABILITY CHECKS BETWEEN SURVEYS

Comparing the HM concentrations for the same plots between the surveys S1 and S2 enabled identification of unrealistic temporal changes and possible reporting errors.

Figure 2.5 plots all Pb concentrations of the same layers and plots analysed during both surveys. Note that many paired observations are below the 1:1 line, suggesting a significant decline in Pb concentration from S1 to S2. In contrast three plots within blue oval are outliers with high Pb concentration in S2 compared to S1. Concentrations in these plots were checked and compared with concentrations in other layers and of other metals. If elevated concentrations levels are found for other heavy metals as well, the plot was considered polluted. When no indications of pollution or reporting errors were found, outliers were set to NA in the working dataset.

By comparing the paired observations, errors were corrected for Cd concentrations in plot 58_26 (factor 100 to high), Zn in plots 13_366 and 13_774 (also factor 100 too high), Zn in

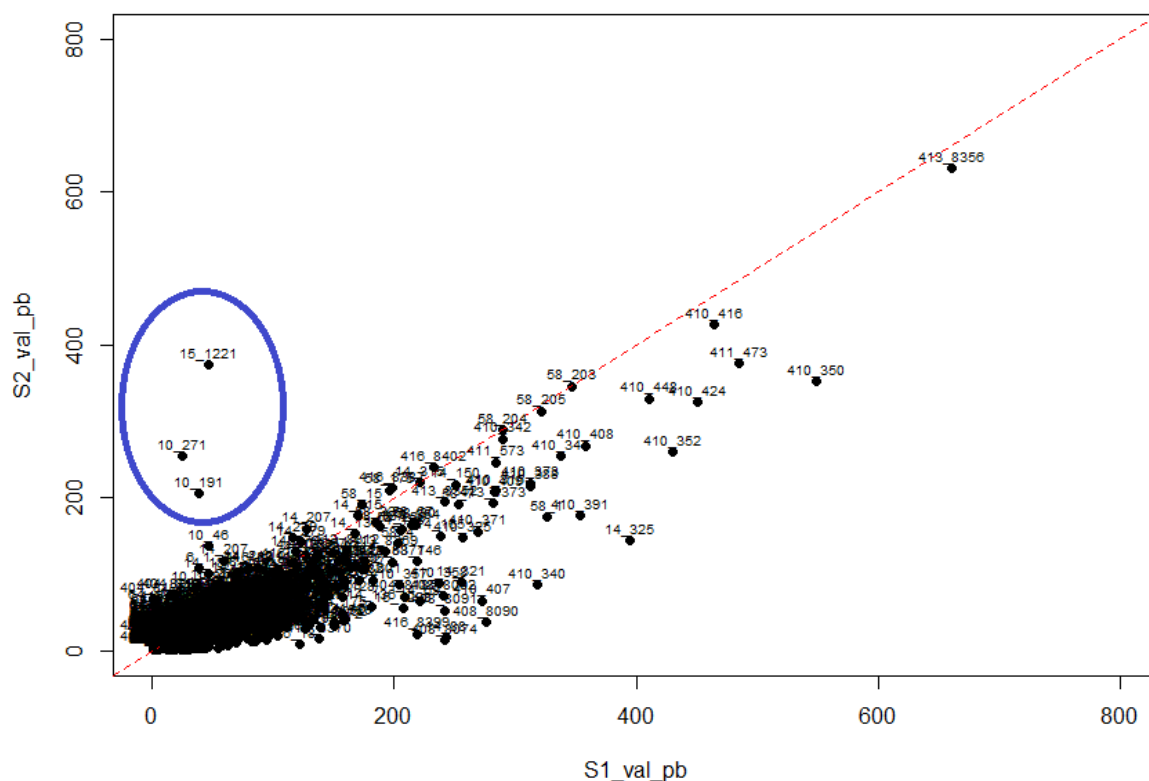


Figure 2.5: Uniformity check by comparing lead concentrations in soil layers of the first survey (S1, X-axis) vs. second survey (S2, Y-axis). Dashed line is 1:1 line (no change). PlotIDs are printed above dots. Plots in blue oval are clear outliers: high Pb concentrations observed during S2 compared to S1

plot 54_1 (factor 10 too high). Most probably these were typo's or unit conversion errors. Similar cases were also found for Cr and Cu on specific plots. In total 10 concentration values were effectively corrected in the working database.

It is important to note that the current dataset will never be completely free of errors, unless all suspicious data are thoroughly checked by national soil experts and labs.

2.4.4 DATA GAP FILLING

In order to calculate stocks in mineral soils, heavy metal concentration levels need to be multiplied by the bulk density (BD, *bulk_density*) of the fine earth, the thickness of the soil layer (*TOP*–*BOT*) and the volume proportion of coarse fragments (*coarse_fragment_vol*). For forest floors (O layers) and peat layers (H) the organic layer mass (*organic_layer_weight*) is required.

BULK DENSITY

During the first survey, BD has been determined and reported by few countries (Vanmechelen et al., 1997).

If BD data was reported we stored this data in the help variable BD0. If BD data was missing from S1, but BD was measured for the same plot and layer during S2, we attributed the BD value to S1 in the variable BD1.

If no value was measured in both S1 and S2, we applied a pedotransfer function (PTF) calibrated on the S2 dataset, using the methodology developed by De Vos et al. (2005).

PTFs for bulk density (kg/m^3) were calibrated for each fixed depth layer separately with the square root of *organic_carbon_total* (TOC, mg/kg) as single predictor:

M01 layer	$\text{BD} = 1523.689 - (81.107 * \sqrt{\text{TOC}})$	$n = 5553$	$R^2 = 0.39$	$\text{RMSPE} = 244$
M12 layer	$\text{BD} = 1562.394 - (91.546 * \sqrt{\text{TOC}})$	$n = 4152$	$R^2 = 0.35$	$\text{RMSPE} = 242$
M24 layer	$\text{BD} = 1604.850 - (111.26 * \sqrt{\text{TOC}})$	$n = 3150$	$R^2 = 0.40$	$\text{RMSPE} = 227$
M48 layer	$\text{BD} = 1608.029 - (120.709 * \sqrt{\text{TOC}})$	$n = 2568$	$R^2 = 0.38$	$\text{RMSPE} = 211$

The datapairs for the BD prediction are quite high, from 5553 pairs for M01 to 2568 in the deepest layer (40-80 cm, M48). The calibrated PTFs explain about 35 to 40% of the observed BD variation, and the overall prediction error is maximal 244 kg/m^3 .

THICKNESS OF THE SOIL LAYER

The thickness of the soil layer is simply derived from upper minus lower depth of each layer, so 10 cm for M01, 20 cm for M24, ...

VOLUME PROPORTION OF COARSE FRAGMENTS

The stoniness is expressed as volume percentage of stones and available from the attribute *coarse_fragment_vol* in FSCDB.LI. We assumed stoniness as invariant for the LI plots. If stoniness was assessed during S1 and not known in S2, it was copied and vice versa. Volume proportion of coarse fragments was set to 0 if no stones were observed during profile description. The percentage was divided by 100 to yield the proportion.

ORGANIC LAYER MASS

The dry mass of the forest floor is stored directly in FSCDB.LI as *organic_layer_weight*, expressed in kg/m^2 . Heavy metal concentration (mg/kg) multiplied by *organic_layer_weight* yields the heavy metal stock (mg/m^2) of the forest floor.

CHAPTER 3

MATERIALS AND METHODS

3.1 LEVEL I MONITORING NETWORK

This study is based on samples collected from forest patches in the ICP Forests systematic Level I grid established in 1985 (Figure 3.1). The network contains about 6000 forested plots on a transnational 16 x 16 km grid (32 x 32 km in Nordic countries). The level I monitoring network is dedicated to generating periodic overviews of the spatial and temporal variation of forest condition in relation to anthropogenic (in particular air pollution) and natural stress factors. The Level I grid is complemented by the Level II intensive monitoring network. This network consists out of 300 to 500 permanent plots that are being more intensely monitored to gain an in-depth understanding of the cause–effect relationships between the condition of forest ecosystems and stress factors.

Both monitoring networks complement each other and serve their own purpose. ICP Forests conducts an annual evaluation on tree crown condition and forest vitality on the large-scale Level I network. Additional parameters that require more intensive survey efforts such as tree growth, ground vegetation and foliar chemistry are being monitored on the Level II intensive monitoring network only. For the respective methods see ICP Forests Manual¹ Parts V, VII and XII.

Since the foundation of ICP Forests, two Europe-wide forest soil condition surveys have been carried out on the plots of the Level I grid. The first forest soil condition survey (S1) took place between 1985 and 1996, the second one between 2006 and 2008. The aim is to revisit the sampling locations every ten to twenty years to assess the state of European forest soils.

Soil surveys should be carried out temporally synchronized in all participating countries. This was not the case for S1 conducted between 1985-1996. Sweden and Finland were the first countries that started surveying soils and by the end of 1996, 23 countries had finalised the surveying Level I plots on their territory, resulting in a total of 5289 plots visited. The findings of this first survey have been reported by Vanmechelen et al. (1997) in the first European Forest Soil Condition reported. The report of Vanmechelen et al. (1997) made clear that there was a need of increased harmonisation and standardisation of national soil survey methods. This process took roughly ten years and entailed the publication of manuals with descriptions of standardized sampling and sample analysis techniques.

The BioSoil demonstration project took off in 2006. During this project 21 countries were involved in conducting the second pan-European soil survey (S2). The set of soil parame-

¹<http://icp-forests.net/page/icp-forests-manual>

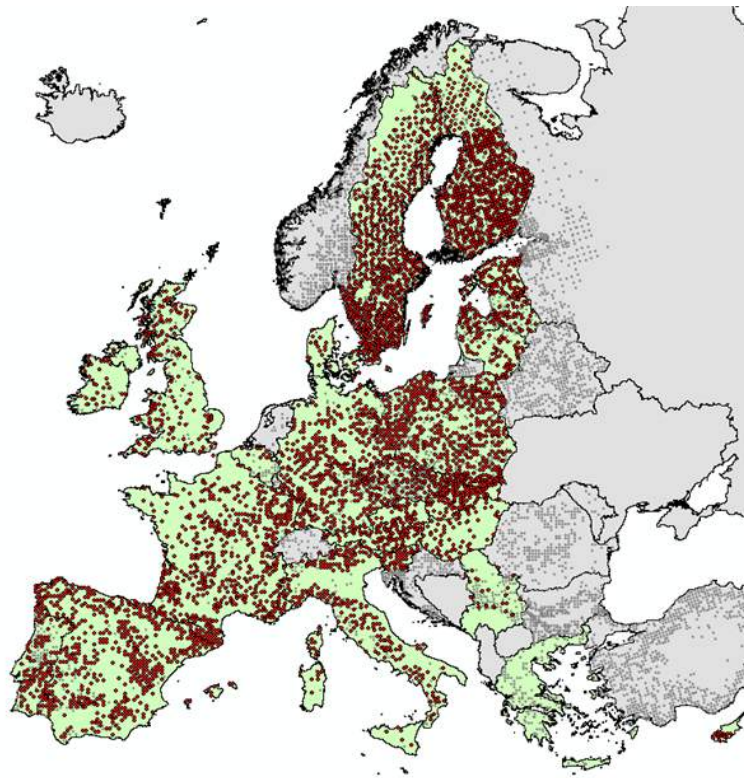


Figure 3.1: Level I systematic 16x16 km monitoring grid (grey dots) with second survey plots indicated in red. Countries participating in second survey are indicated in green.

ters to collect data on during S2 was drastically increased compared to S1. This resulted in an extensive database containing soil data on 4928 plots, soil profile descriptions and classifications included (Figure 3.1). The results of S2 were reported in the second Forest Soil Condition Report by De Vos and Cools (2011). Soil data of the Russian Federation (2009) and Serbia (2014) were later added to the level I forest soil condition database.

The FSCC is currently preparing a third pan-European LI soil survey initiative and looking for (co)funding by the EC or other international bodies, which seems a prerequisite for a harmonised approach.

3.2 SOIL SAMPLING, ANALYSIS AND QUALITY ASSURANCE

As previously described, survey methods are applied according to the guidelines of the ICP Forests soil manuals. During S1, the 1992 submanual on methods and criteria for monitoring of forest soils was used. This was a first attempt to harmonize sampling schemes among national methods and approaches and was synthesised in the ICPF Manual² of 1994. During S2, the Manual IIIa was used (Cools and De Vos, 2016), with mandatory and optional parameters as described in Chapter 1.

²http://www.icp-forests.org/pdf/manual/1994/ICPFforests_Manual_1994.pdf

Sampling of the soil profile was performed according to fixed depths. During S1 these depths were not entirely harmonised among countries. Some countries chose to sample according to their national sampling schemes over the approach of the transnational programme. For example, Germany reported results on the 10 to 30 cm layer. These differences were overcome and during S2 all countries sampled according to standard depths (Figure 2.3).

For both surveys, one representative composite sample per plot and per depth layer was collected from augerings at different locations in or near the plot area, or from one or more profile pits. During S1, it was recommended to collect 12 to 15 subsamples (Vanmechelen et al., 1997). During S2, the required number of subsamples was lowered to a minimum of 5 to increase the feasibility (De Vos and Cools, 2011). The collected samples were homogenised and a subsample of this mixture was taken for further laboratory analysis.

HM analysis was always performed following aqua-regia digestion and concentrations were expressed on an oven-dried basis (105°C). During S1, the most frequently used analytical technique was Atomic Absorption Spectrometry (AAS), whereas most countries had switched to Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) by the beginning of S2. This resulted in higher throughput and more accurate multi-element analysis of metals (Manning and Grow, 1997). Only few laboratories use ICP Mass Spectrometry (ICP-MS). This technique enables the detection of very low concentrations, which is especially beneficial for measuring Cd and Hg concentrations. For the latter element, dedicated Hg-elemental analysers were found to perform better than Hg analysis through ICP-AES.

To ensure the quality of analytical results, national laboratories were asked to participate in a Quality Control Programme. The methods used to obtain a harmonized, well-defined and well-documented physico-chemical analysis of soils are available in König et al. (2013). A table with plausible concentration ranges for each heavy metal was added to assist in evaluating analytical results (Table 3.1). The ranges are based on results from S2 and include the 95% interval, determined by the 2.5 to 97.5 percentile limits of all observations. This interval encompasses the most likely range for analytical results of a specific soil variable for a specific matrix (mineral soil, organic matter) and analytical method (e.g aqua regia extraction). Note the differences between plausible ranges for organic versus mineral matrices.

Table 3.1: Plausible ranges for heavy metal concentrations (mg/kg) in forest soils based on S2 results.

Parameter	Organic matrix		Mineral soil	
	Min	Max	Min	Max
Extractable Cd	< 0.01	2.2	< 0.01	2.5
Extractable Zn	0.8	300	2.5	165
Extractable Ni	0.06	45	0.5	80
Extractable Cr	0.1	95	1	80
Extractable Cu	0.2	75	0.3	55
Extractable Pb	0.03	245	1	110
Extractable Hg	< 0.01	1.65	0.02	2.25

For the statistical data-analysis, it was crucial that each national laboratory reported the limit of detection (LOD) and limit of quantification (LOQ) of each heavy metal analysed. The

LOQ is the minimal concentration above which HM concentration in a sample can be quantified with relative certainty. The LOD is smaller than the LOQ, and is equal to the minimal concentration above which the presence of a HM in a sample can be detected. If a HM concentration is between LOD and LOQ, the HM can be detected but the HM concentration cannot be accurately quantified.

During S1, unfortunately most national laboratories did not report their LOQ. However, a rough estimation was made based on the concentrations that were marked as 'below LOQ'. During S2, most laboratories did report their LOQ during their participation in interlaboratory ringtests. Based on data of the second and fifth soil ringtest, average tolerable limits (TL) and quantification limits were computed (De Vos, 2008). The intra-laboratory TL is the maximum percentage deviance of the mean that is regarded as acceptable when re-analysing an identical soil sample, a so-called *repeatability error*.

Table 3.2 illustrates that most labs were able to quantify heavy metals with repeatability error lower than 10%. However, the variability sores when taking into account between-lab variability, the so-called *reproducibility error*. The reproducibility error ranges between 15% and 100% and is the largest for measuring low Cd and Hg concentrations. Although Cd can generally be detected from 0.04 mg/kg onwards, it can only be quantified reliably by most labs from 0.5 mg/kg onwards and Hg from 0.34 mg/kg onwards.

The average LOQs per heavy metal used in the statistical data processing are listed in Subsection 3.3.1. These values are realistic for the results of S2 and the results of future research, but might be too optimistic for data collected during S1.

Table 3.2: The limit of detection (LOD), limit of quantification (LOQ) and tolerable limits (TL) for national laboratories per heavy metal.

Metal	Range	Level (mg/kg)	LOD (mg/kg)	LOQ (mg/kg)	Ringtest TL (% of mean)	Intra-lab TL (% of mean)
Cd	low	≤ 0.25	0.04	0.52	± 100	± 5
	high	< 0.25	-	-	± 55	± 6
Zn	low	≤ 20	0.58	2.1	± 40	± 7
	high	< 20	-	-	± 20	± 3
Ni	low	≤ 10	0.6	1.6	± 40	± 6
	high	< 10	-	-	± 15	± 4
Cr	low	≤ 10	0.01	0.64	± 40	± 7
	high	< 10	-	-	± 25	± 4
Cu	low	≤ 5	0.09	1.36	± 40	± 8
	high	< 5	-	-	± 15	± 4
Pb	full	3 - 70	1	2.4	± 30	± 4
Hg	full	0 - 0.16	0.01	0.34	± 75	± 6

3.3 STATISTICAL TECHNIQUES

The data obtained from analysing the heavy metal concentrations in soil samples has some characteristics which are typical for environmental data. First, concentrations are always positive numerical values and the marginal distribution of heavy metal concentrations is usually positively skewed (Manchuk et al., 2009). Hence, traditional statistical techniques based on the underlying assumption of normality are inadequate. One could argue that log-transforming positively skewed data fixes this problem, but only true for distributions that are clearly log-normal.

Another common problem in the analysis of environmental heavy metal data is the occurrence of so-called *left-censored values* or *nondetects*. These are data points of which the value is below a certain value (often the LOQ), but it is unknown by how much (Helsel et al., 2005). In fact, analytical concentration levels can never be zero, but they can be too small to detect ($< LOD$) or quantify ($< LOQ$) depending on the instrument and analytical method applied.

These two characteristics combined require the use of alternative statistical techniques, such as left-censored statistics and the bootstrapping technique. These statistical techniques will be discussed in the next sections.

3.3.1 LEFT CENSORED STATISTICS

Excluding or substituting left-censored data leads to incorrect conclusions, therefore appropriate statistical techniques for censored data should be used to take these data points into account in any statistical analysis (Helsel, 2010). Helsel et al. (2005) recommends estimating values below LOQ with the Kaplan-Meier (KM) method or Regression on Order Statistics (ROS). The summary statistics on HM concentrations available in Tables B.3 to B.15 were computed using these functions, implemented in the R package NADA (Lee, 2020).

The percentiles ($P_{2.5}$, P_{25} , P_{50} , P_{75} , $P_{97.5}$) were estimated using ROS, while the mean and its 95% confidence interval were estimated using the KM method. The LOQs used in this routine are: $LOQ_{Cd} = 0.1$ mg/kg; $LOQ_{Cr} = 0.5$ mg/kg; $LOQ_{Cu} = 1$ mg/kg; $LOQ_{Ni} = 0.5$ mg/kg; $LOQ_{Pb} = 1$ mg/kg; $LOQ_{Zn} = 2$ mg/kg and $LOQ_{Hg} = 0.03$ mg/kg.

Note that for Cd, Ni, Pb and Hg these LOQs are lower than the empirically determined LOQs in Table 3.2 taken from the interlaboratory ringtests.

Tóth et al. (2016) reported the detection limits (LODs) for HM analyses from the LUCAS 2009 and 2012 surveys. These limits are generally lower (except for Pb) than the ones we used in our study: $LOD_{Cd} = 0.07$ mg/kg; $LOD_{Cr} = 0.32$ mg/kg; $LOD_{Cu} = 0.26$ mg/kg; $LOQ_{Ni} = 0.27$ mg/kg; $LOD_{Pb} = 1.16$ mg/kg and $LOD_{Hg} = 0.00005$ mg/kg. We applied these LODs when comparing our S2 data with the LUCAS data.

3.3.2 BOOTSTRAPPING

Figure 3.2 shows the distribution of Zn concentrations measured in the mineral topsoil (0 - 10 cm). This distribution is representative for all HM distributions in the forest soil database. As is clear from the figure, the distribution is strongly skewed to the right. Statistical handling of these data can be performed by classical log transformation of the data followed by parametrical statistical methods including p-values calculation, or directly on the original data by a non-parametric approach using testing by confidence intervals. A frequently used statistical method used in the latter case is *bootstrapping*.

Bootstrapping is a statistical method for estimating the sampling distribution of an estimator by *random resampling with replacement* from the original sample, most often with the purpose of deriving robust estimates of standard errors or confidence intervals of population parameters. We used the bootstrapping resampling technique to obtain 95% confidence intervals ($CI_{95\%}$) for parameters of interest, in this study mainly the geometric mean (GM) value or specific indices (Tibshirani and Leish, 2019). Bootstrapping assumes that observed sample data are representative for the underlying population, and therefore we set the minimum number of observations to 30. The default number of resamples (B) is 5000, which is recommended for estimating robust confidence intervals of any metric.

CONFIDENCE INTERVALS OF SKEWED DISTRIBUTIONS

Confidence intervals at the 95% level are calculated based on bias-corrected and accelerated (BCa) percentiles at 2.5 and 97.5%, respectively, using the function `bcanon` (Nonparametric BCa Confidence Limits) from the R package `bootstrap` (Tibshirani and Leish, 2019). BCa intervals are a substantial improvement over empirical percentiles in both theory and practice (Tibshirani and Efron, 1993). They have two important theoretical advantages: (1) they are transformation respecting if data are transformed (the BCa endpoints transform correctly according to the function of the parameter of interest) and (2) BCa intervals can be shown to be second order accurate while standard and percentile methods are only first-order accurate. The BCa method leads to much better approximations of exact endpoints, when exact endpoints exist.

Half of the $CI_{95\%}$ is conventionally called the margin of error (ME) and in case distributions are Gaussian (normal distribution), the margins of error of the mean are symmetric around this bias-corrected mean. However, for distributions skewed to the right, the BCa endpoints of the CI yield asymmetric margins of error and unequal tails of the bootstrap distribution. If the geometric mean is bootstrapped, then the tails of the $CI_{95\%}$ are equal when the population distribution is log-normal, but unequal when deviating from log-normality. Hence, some extra parameters can be derived from BCa means and $CI_{95\%}$:

- Total range of the $CI_{95\%}$ (CIR): $CIR = P_{97.5\%} - P_{2.5\%}$
- Lower margin of error (LME): $LME = Mean - P_{2.5\%}$
- Upper margin of error (UME): $UME = P_{97.5\%} - Mean$

- Relative margin of error (RME): $RME = 100 \frac{ME}{Mean}$

These parameters can be applied to the Zn distribution in Figure 3.2. It is clear from the density distribution that the distribution is skewed to the right. This implicates that the median (32.8 mg/kg) and sample geometric mean (28.4 mg/kg) are lower than arithmetic mean (48 mg/kg). The bootstrapped geometric mean yields a BCa CI_{95%} with a lower limit of 27.5 mg/kg and an upper limit of 29.4 mg/kg. The range is small because of the high number of observations ($n = 4212$) used in the bootstrapping procedure. The upper margin of error (UME) is slightly larger than the lower one (LME). This is the case for distributions that are even stronger right-skewed than perfect log-normal distributions.

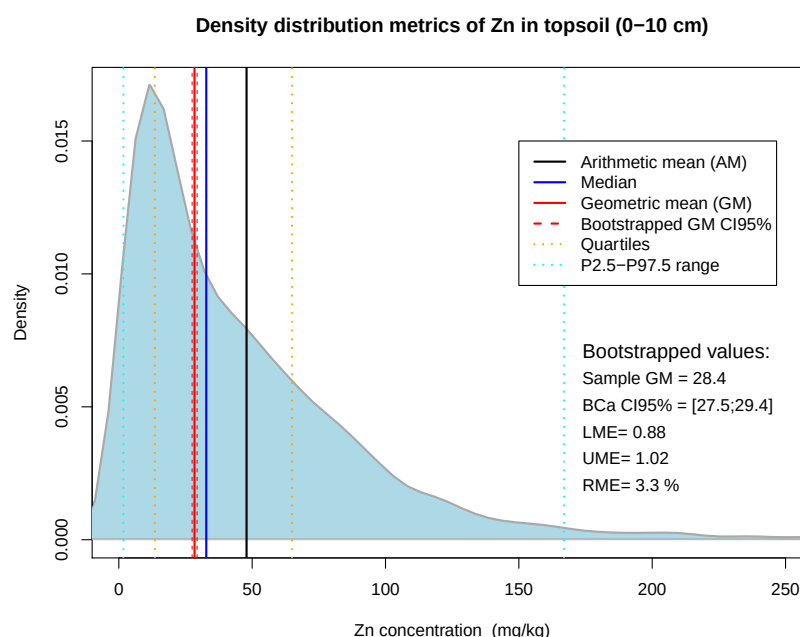


Figure 3.2: Example of geometric mean with 95% confidence interval versus other metrics of the Zn concentration distribution

It can be shown that, when sample numbers are high ($n > 30$), bootstrapped ME and precision converge, standard error of the mean (SEM) may be estimated reliably as $ME/1.96$ and standard deviation of the population may be estimated as $(\frac{ME}{1.96})\sqrt{n}$. This way standard deviations reported in literature may be compared with our bootstrapped data. Coefficient of variation (CV) may be estimated as half the RME.

GEOMETRIC MEAN AS KEY PARAMETER

The sample geometric mean (SGM) introduced by Cauchy in 1821, is a measure of central tendency with many applications in the natural and social sciences including environmental monitoring, ecology and geoscience. Numerous studies on heavy metals applied geometric mean (GM) instead of arithmetic mean (AM) (Kabata-Pendias and Pendias, 2011; Gałuszka, 2007), because metal concentrations and stocks are usually log-normally distributed for which GM performs better and GM accounts for the spread of the concentration data. The

more data-values are spread apart, the smaller the GM while the AM remains constant. The GM is always smaller than AM unless all values in the dataset are equal.

Vogel (2020) points out that for lognormal population distributions the SGM is the maximum likelihood estimator of the median, and that GM is equal to the median for perfect log-normal distributions. In contrast to the median, the GM lacks a clear intuitive interpretation and makes this metric more difficult to interpret. However, GM is a sensible choice as a summary metric for lognormal and strongly skewed distributions, and appropriate for summarizing normalized results like relative errors, ratios, indices . . . where AM can lead to grossly incorrect conclusions.

In his critical review on geometric mean, Vogel (2020) suggests that under lognormal or skewed sampling distributions, investigators are encouraged to report both SGM and the non-parametric rank based median, along with their associated confidence intervals. Our example in Figure 3.2) shows that SGM and median are lie close to each other.

SIGNIFICANT CHANGE IN CONCENTRATION OVER TIME

In order to detect temporal changes of HM concentrations or stocks between surveys, the difference of paired plots ($S_2 - S_1$) was bootstrapped yielding a bias corrected mean difference along with a BCa 95% confidence interval. When this $CI_{95\%}$ range encompasses zero, the change in HM concentration between S_1 and S_2 is not statistically significant. A positive $CI_{95\%}$ excluding 0 implicates a statistically significant increase in HM concentration, whereas a negative $CI_{95\%}$ excluding 0 implicates a statistically significant decrease in HM concentration.

A similar approach was used when deciding for each observation from S_2 if there was a significant change compared to S_1 . First the BCa $CI_{95\%}$ range ($CIR = 2 \text{ times ME}$) was derived from the bootstrapped S_2-S_1 differences of all plots. When for an individual observation the S_2-S_1 difference is positive and larger then CIR, the change is marked as an increase. If the S_2-S_1 difference is negative and larger than CIR, than the change is considered a decrease, while in all other cases the (small) change is judged non-significant.

3.4 SOIL POLLUTION ASSESSMENT

It is not straightforward to distinguish areas with naturally elevated heavy metal concentration from areas where high HM concentrations are caused by anthropogenic factors. Some concepts of heavy metal sciences are essential to clarify this matter.

The total heavy metal concentration in a sample results from multiple sources. The *pedo-geochemical concentration* is the concentration originating exclusively from natural geological and pedological processes (ISO 19258:2018(E), 2018; Baize and Sterckeman, 2001). The *geochemical baseline concentration* is made up of the pedo-geochemical concentration and *diffuse contamination*. Because diffuse contamination has reached even the most remote corners of the world through long-distance airborne transport of pollutants, it is

difficult to distinguish pedo-geochemical concentration from diffuse source input in top-soils (Salminen and Tarvainen, 1997). Scientific studies aimed at quantifying background concentrations are therefore generally interested in quantifying the geochemical baseline concentration.

The geochemical baseline may not be confused with *geochemical background*, which refers to a natural value not impacted by anthropogenic activities (Gough et al., 1993). However, in relatively pristine ecosystems such as forests geochemical baseline concentrations are often close to background concentrations (Gałuszka, 2007).

Evaluation schemes for HM concentrations require the definition of a reference concentration, also called a *reference level* (RL). In this study the reference level is set to the upper limit of the bootstrapped 95% confidence interval of the sample geometric mean. Throughout the study this reference level will be regarded as the geochemical baseline concentration. All concentrations below the reference level are considered as background concentrations (including ubiquitous pollution (Figure 3.3). For the example Zn distribution in Figure 3.2) the upper limit of the $CI_{95\%}$ is equal to 29.4 mg/kg.

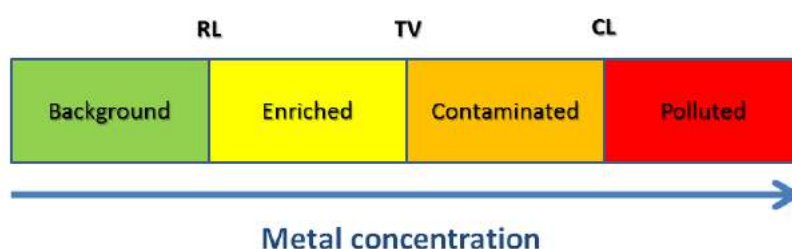


Figure 3.3: Concept of a heavy metal evaluation scheme with four levels. The levels are distinguished from one another by the reference level (LV), the trigger value (TV) and the critical level (CL).

For higher concentration ranges, a *critical level* (CL) must be defined. The critical level is the concentration above which the soil sample is considered as polluted. Various approaches exist to define CL, these will be discussed further in Chapter 5. In between the reference level and critical level many evaluation schemes discern a *trigger value* (TV) as a warning level. Above this warning concentration soils are regarded as contaminated, but not polluted. Below the trigger value, HM enrichment is found in comparison to the baseline, but this is not at an alarming level.

3.4.1 SOIL POLLUTION INDICES

A second approach to assess the degree of soil pollution entails the quantification of so-called *soil pollution indices*. Soil pollution indices (SPIs) facilitate the differentiation between high concentration levels of geogenic versus anthropogenic origin, which is key to environmental impact assessments. Underlying assumptions of most indices are that the heavy metal concentration in deeper soil layers can be considered as the local natural pedo-geochemical background (i.e reference level) and that HM contamination remains mostly restricted to surface horizons (Baize and Sterckeman, 2001).

On the one hand, a disadvantage of this approach is that it requires a more intensive sampling strategy, since heavy metal concentrations of deeper soil layers must also be determined. On the other hand, an advantage of SPIs is that there is no need to quantify critical levels. Some authors prefer soil pollution indices over the critical level approach, because it takes into account the background concentration of every point and does not make use of a single generalized background concentration for the entire area (Baize and Sterckeman, 2001).

A first straightforward index is the Enrichment Factor (EF). This is the relative abundance of a heavy metal in a top soil layer compared to the concentration in deeper soil layers, standardized by the concentration of a "conservative" reference element in both layers (Hernandez et al., 2003).

$$EF = \frac{\left[\frac{C_{metal}}{C_{reference}} \right]_{topsoil}}{\left[\frac{C_{metal}}{C_{reference}} \right]_{subsoil}} \quad (3.1)$$

with C_{metal} the heavy metal concentration in the upper and deeper soil layer and $C_{reference}$ the concentration of the reference metal. Fe is often used as $C_{reference}$ because its concentration is not markedly disturbed by anthropogenic activity. The higher a soil's Fe content, the more likely it is to have a naturally high Cu, Cr, Ni, Pb and Zn content. Therefore Fe concentration can help to reveal anomalous versus natural heavy metal contents (Baize and Sterckeman, 2001).

Another widely-used soil pollution index is the Geo-accumulation Index (I_{geo}) (Muller, 1969). Soil contamination is assessed based on the ratio between the content of heavy metals in the topsoil versus the content of heavy metals in natural horizons (subsoils). Hence, the underlying assumption is that anthropogenic contamination is mainly restricted to upper soil layers. This index can be calculated using the following formula:

$$I_{geo} = \log_2 \left[\frac{C}{1.5B} \right] \quad (3.2)$$

with C the heavy metal content in topsoil, B the heavy metal content in natural horizons and 1.5 a constant allowing fluctuations as a result of natural processes. The index is classified as follows: $I_{geo} < 0$ unpolluted; $0 \leq I_{geo} < 1$: unpolluted to moderately polluted; $1 \leq I_{geo} < 2$: moderately polluted; $2 \leq I_{geo} < 3$: moderately to strongly polluted; $3 \leq I_{geo} < 4$ strongly polluted; $4 \leq I_{geo} < 5$ strongly to very strongly polluted; $5 \leq I_{geo}$ very strongly polluted.

The previously discussed pollution indices in formulas 3.1 and 3.2 assess the degree of contamination caused by a single heavy metal. To get an idea of the overall combined contamination caused by multiple heavy metals the Nemorow Pollution Index ($PI_{Nemorow}$)

can be used. $PI_{Nemorow}$ is an integrated index to assess the overall degree of contamination in a soil by evaluating single pollution indices (Hong-gui et al., 2012; Dung et al., 2013).

$$PI_{Nemorow} = \frac{\sqrt{(P_{j,ave}^2 + P_{j,max}^2)}}{2} \quad (3.3)$$

$$\text{with } P_{ij} = \frac{C_{ij}}{S_{ij}}$$

P_{ij} is a single factor pollution index with C_{ij} equal to the heavy metal concentration in the soil sample and S_{ij} being the background value of the heavy metal. $P_{j,ave}$ is the arrhythmic average of all P_{ij} for different heavy metals at a particular site and $P_{j,max}$ the maximum of all P_{ij} . A $PI_{Nemorow} < 0.7$ is evaluated as clean; $0.7 \leq PI_{Nemorow} < 1$ warning limit; $1 \leq PI_{Nemorow} < 2$ slight pollution; $2 \leq PI_{Nemorow} < 3$ moderate pollution; $PI_{Nemorow} > 3$ heavy pollution.

3.5 CORRELATIONS AND PREDICTION ERRORS

The Spearman's rank correlation coefficient (Spearman's ρ) is a non-parametric correlation coefficient that is often used to detect trends in environmental data (Gautheir, 2001). Spearman's ρ can be used when the assumptions of the Pearson correlation coefficient are violated. For instance, a prerequisite to use Pearson's correlations is that each variable should be continuous. If at least one of the variables is ordinal, Spearman's correlation is better suited. The technique operates on the ranks of data and therefore it is unaffected by the distribution of the population and relatively insensitive to outliers (Gautheir, 2001). If the data has tied ranks, the formula to use to calculate ρ is

$$\rho = \frac{\sum_i (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_i (x_i - \bar{x})^2 \sum_i (y_i - \bar{y})^2}} \quad (3.4)$$

To investigate temporal trends in HM concentrations, we take a closer look to paired observations (e.g. sampling sites that were included in both S1 and S2). Since heavy metals are persistent in soils, it is reasonable to think that the concentration found in S1 will be a good predictor for the observed concentration in S2. The prediction quality can be determined by complementary indices: the mean predicted error (MPE), the root mean squared prediction error (RMSPE) and the prediction coefficient of determination (R^2). These are defined as:

$$MPE = \frac{1}{n} \sum_{i=1}^n (\hat{P}_i - O_i) \quad (3.5)$$

$$RMSPE = \sqrt{\frac{1}{n} \sum_{i=1}^n (\hat{P}_i - O_i)^2} \quad (3.6)$$

$$R_p^2 = \frac{[cov(\hat{P}_i, O_i)]^2}{var(O_i) \cdot var(\hat{P}_i)} \quad (3.7)$$

with O_i and $\hat{P}_i$ the observed and predicted values. The MPE allows the evaluation of a positive or negative change between surveys. The RMSPE is a measure of the overall error of the prediction, or how accurate the predictor is able to predict concentrations from S2. The prediction coefficient of determination (R^2) is a measure of the strength of the linear relationship between measurements and predictions, and indicates the fraction of the variation that is shared between them.

$$d = 1 - \frac{\sum_{i=1}^n (P_i - O_i)^2}{\sum_{i=1}^n (|P_i - \bar{O}| + |O_i - \bar{O}|)^2} \quad (3.8)$$

Finally d is defined, the index of agreement developed by Willmott (1981) as a standardized measure of the degree of model prediction error and d varies between 0 and 1. A value of 1 indicates a perfect match (values are on 1:1 line and S1 concentrations equal S2 concentrations), and $d=0$ would indicate no agreement at all.

3.6 SOFTWARE AND GEODATASETS

3.6.1 SOFTWARE

Statistical analysis was performed using R v4.0.3 R Core Team (2020) in RStudio v.1.3.1073, and scripts were developed for almost every data handling, processing and statistical evaluation. An overview of the packages used can be found in Table 3.3.

Table 3.3: R packages used for this study.

R Package	Application purpose	Author(s)
<i>ggplot2</i>	Graphical representation of data	Wickham (2016)
<i>dplyr</i>	Data manipulation	Wickham et al. (2020)
<i>bootstrap</i>	Bootstrap statistics	Tibshirani and Leish (2019)
<i>NADA</i>	Left-censored statistics	Lee (2020)
<i>Hmisc</i>	Empirical cumulative distribution functions	Harrell Jr et al. (2020)
<i>sp</i>	Spatial data analysis	Bivand et al. (2013)

3.6.2 GIS AND GEODATA

Maps were created in QGIS, a free and open source geographic information system (QGIS Development Team, 2020). ArcMap v10.4.1 was used for coordinate transformations and overlays with auxiliary georeferenced data. The sampling sites in this database were linked with other variables such as soil type, biogeographical region, elevation, mean annual precipitation, mean annual temperature . . .

The following geodata were used in this study:

- Geographical borders of EU countries
- European Soils database v2.0 (ESDAC, JRC)
- Biogeographical regions (2005)

All shapefiles were projected in ETRS89-LAEA metric XY coordinates.

CHAPTER 4

RESULTS

4.1 HEAVY METALS IN ORGANIC AND MINERAL SOIL LAYERS

Forest ecosystems contain pools of heavy metals in virtually all forest compartments: forest floor, vegetation (trees, shrubs, ground vegetation), fauna, micro-organisms, soil and soil solution. Fluxes of these trace metals cycle along with carbon and nutrients (e.g. litterfall) and water (e.g. leaching). This study focuses on heavy metal concentrations and stocks in the forest soil compartment, i.e. the mineral or organic (peat) soil including the ecto-organic layer (forest floor), without considering heavy metals in the soil solution.

Hg generally shows the lowest concentration and Zn the highest in all soil compartments. The common order from low to high concentration ranges is $\text{Hg} < \text{Cd} \ll \text{Ni} \approx \text{Cr} \approx \text{Cu} < \text{Pb} < \text{Zn}$. Depending on the heavy metal, the concentration within a soil profile can be higher in the forest floor than in the mineral or organic soil, or vice versa. This depends on the nature and behaviour of the heavy metal, its source (geogenic or anthropogenic), environmental soil conditions (pH, electrical conductivity, redox conditions) and presence of clay-humus complexes, sesquioxides and organic acids.

A statistical summary of the heavy metal concentrations in the forest floor (O), in the mineral soil layers (M01, M12, M24, M48) and in the organic soil layers (H01, H12, H24, and H48) is listed in **Annex B2.1**.

The concentrations summarized in **Annex B2.1** are aqua-regia extractable concentrations which may be considered as semi-total concentrations. "Semi-total" because aqua-regia does not bring silicates into solution and the metals bound to these. However, it is commonly assumed that biota are unable to extract this specific fraction and that aqua-regia extractions provide a reliable measure of the maximal available fraction to biota. Hence, the actual bioavailable fraction of heavy metals will always be less than the semi-total concentration by aqua-regia extraction, strongly determined by the local soil conditions. So, in this study, no assessments are made to predict bioavailability of the metals.

Apart from concentration, we determined the stocks of each of the heavy metals in the forest floor and in the upper 10 cm of the mineral soil for both surveys. Summary statistics are given in **Annex B2.2**. These stocks reflect the volumetric content of heavy metals for a given area and are expressed in mg/m^2 ($=0.01 \text{ kg/ha}$). This is important to link the present heavy metal pool to the critical load and target load approach (de Vries et al., 2013), expressed in mg/m^2 per year of a specific metal entering the ecosystem.

4.2 SPATIAL PATTERNS

The spatial pattern of the heavy metal concentration or stock in forest floors and topsoils is metal-specific. Therefore the spatial pattern of each trace element will be discussed separately. Maps of both heavy metal concentration and stocks, as well as the geometric mean concentration per country and biogeographical region are presented. The legend of concentration maps consists of five concentration classes whose under and upper limits were chosen as suggested by Vanmechelen et al. (1997) in the first Forest Soil Condition Report, except for Hg where concentration limits were derived from Kuusinen (2010). Evaluation of heavy metal stocks in forest floors was done according to De Vos (2003).

Locations or wider geographic zones with elevated HM concentration or stock are appointed. Subsequently, the influence of soil- and humustype on heavy metal concentrations is discussed, as well as the potential of defining background concentrations per biogeographical region.

4.2.1 CADMIUM

Cadmium is a relatively rare metal, has no essential biological function and can be highly toxic to plants and animals. Two major anthropogenic sources of Cd in soils are rock phosphate fertilizer and atmospheric deposition (Alloway, 2012). Assuming phosphate fertilizer usage is absent in forests, atmospheric deposition of Cd is the root cause of elevated levels of this element in forest soils. It is often associated with Zn, because both metals have a similar geochemistry and Cd is a by-product of the smelting of Zn and other base metals. Depending on local emission sources (e.g. smelters),

The summary statistics of Cd concentrations in Appendix B (Tables B.3 and B.3) show average Cd concentrations ranging from 0.35 to 0.62 mg/kg in mineral soil, 0.40-0.65 mg/kg in forest floors and 0.26 - 0.60 mg/kg in peat soils. Cd in forest floor and upper soil layer varies among countries (Figure 4.1).

In most countries, Cd concentration in the forest floor is higher than in the forest topsoil, suggesting deposition as main input (Figure 4.5). Exceptions are United Kingdom (UK) and Serbia (RS) where geometric mean of the Cd concentration in the topsoil is significantly higher than in the forest floor (Figure 4.1). This may be linked to specific parent materials like sedimentary rocks or black shales containing high natural Cd content. When comparing the Cd concentration in the forest floor of different countries, the geometric means in this soil layer vary apparently less than in the forest topsoil.

Industrial and mining areas are associated with elevated heavy metal topsoil concentrations (Tóth et al., 2016). A hotspot of elevated Cd concentration is clearly visible in the Upper Silesian mining district in south-central Poland. High Cd concentrations in the area are known to be the consequence of historical Zn-Pb mining (Pan et al., 2010). Other regions with elevated Cd concentration in forest floors are the Ruhr region (Germany), Campine region in Flanders (Belgium), northern Slovenia and eastern Slovakia. High topsoil concentrations are observed in UK, Austria, Slovenia and Serbia.

The forest topsoils in the Boreal region generally show lower concentrations of Cd in the mineral topsoil, whereas the opposite is true for Alpine forest topsoils (Figure 4.2). Note however that their geometric mean topsoil concentrations are lower than the LOQ, while their forest floor concentrations are above LOQ and therefore reliably quantifiable. Podzols are typical soils of boreal forests and Mor-humus is their dominant humus type. Both Podzols and Mor are associated with low Cd concentrations (Figure 4.3, Figure 4.4). Other sandy soils like Arenosols, also show low Cd concentrations, well below LOQ.

On calcareous soils like Calcisols and Regosols, Cd concentrations are generally low. Moreover, Cd bio-availability in these soils is also low due to adsorption on calcite or precipitation as Cd-carbonates.

Histosols (peat soils) and Phaeozems are soils rich in organic matter. These soil types show the highest Cd concentrations, illustrating the affinity of this metal for organic matter. Their Cd concentration levels in forest floors and topsoils is not significantly different from each other.

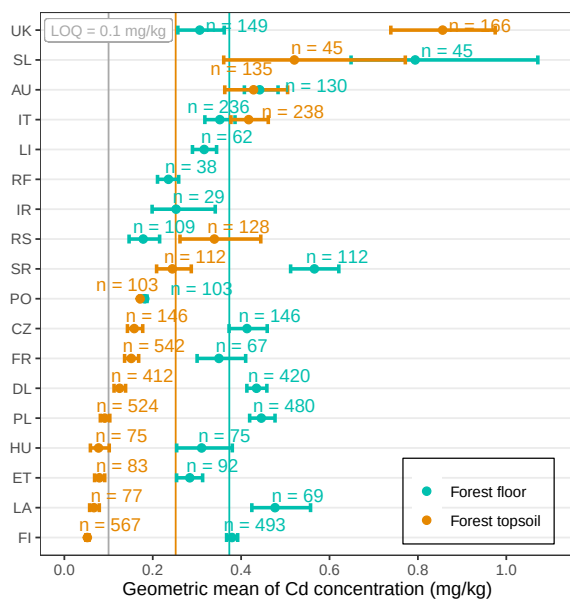


Figure 4.1: Bootstrapped geometric mean and CI95% range of Cd per country.

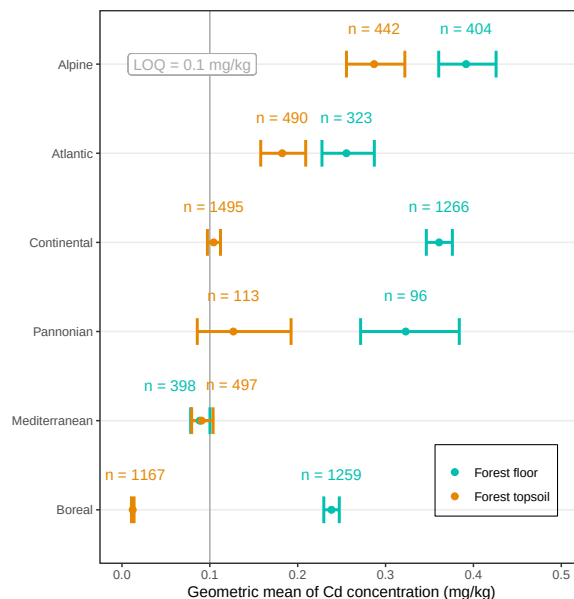


Figure 4.2: Bootstrapped geometric mean of Cd per biogeographical region.

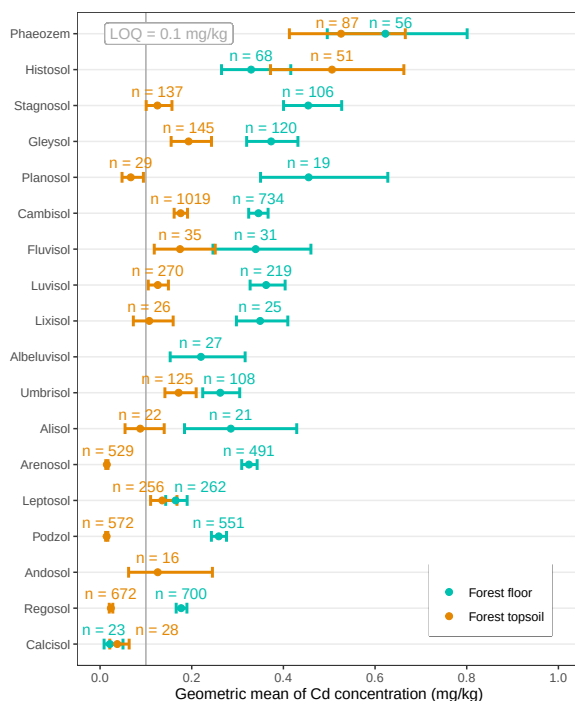


Figure 4.3: Bootstrapped geometric mean of Cd per soil group.

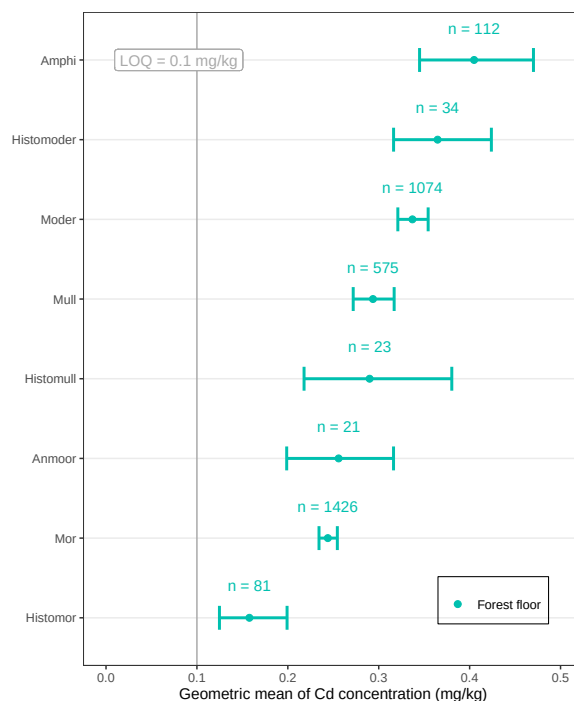
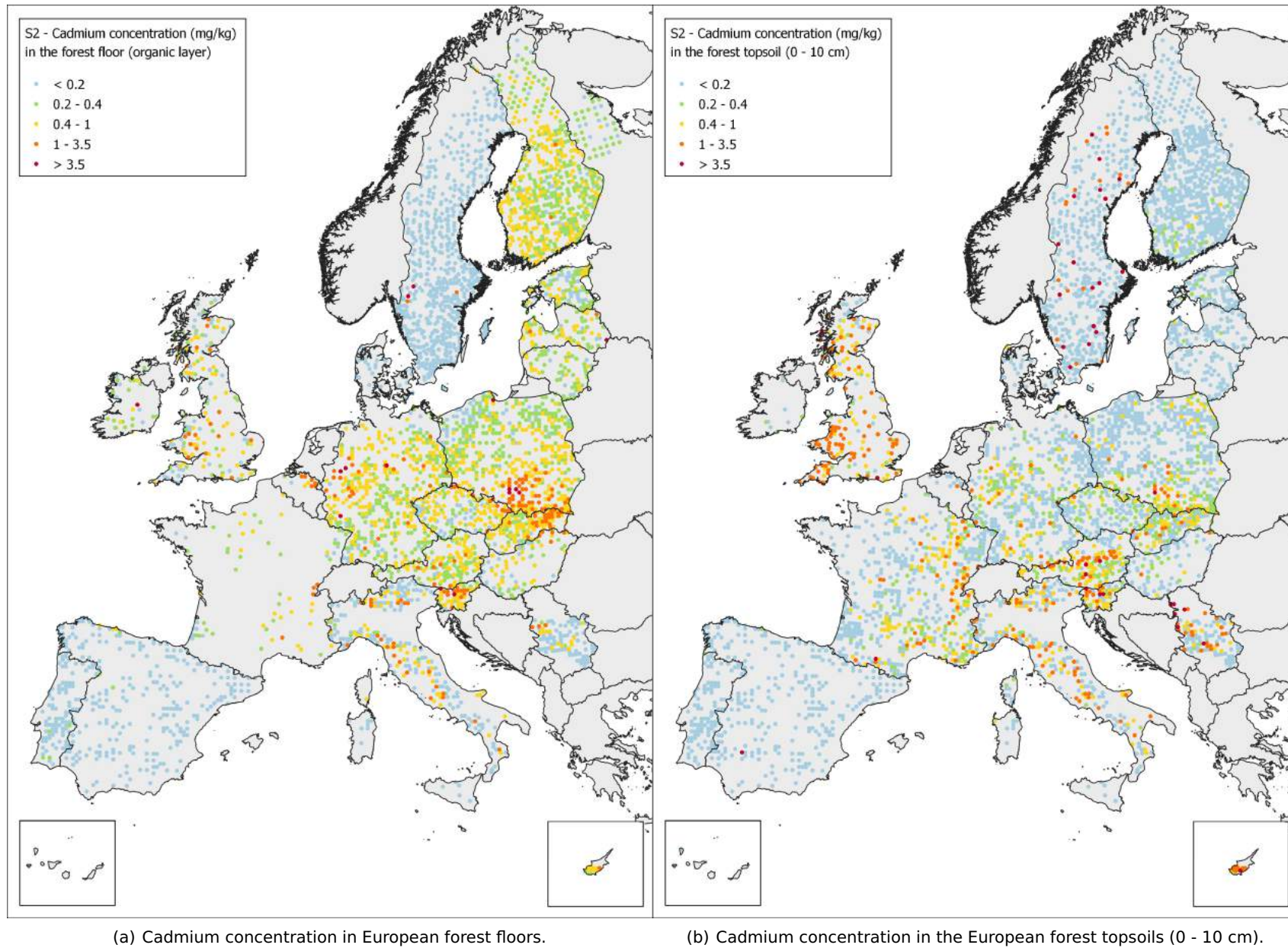


Figure 4.4: Bootstrapped geometric mean of Cd per humustype.



(a) Cadmium concentration in European forest floors.

(b) Cadmium concentration in the European forest topsoils (0 - 10 cm).

Figure 4.5: Maps of the cadmium concentration in European forest floors and topsoils for the second forest soil condition survey (S2).

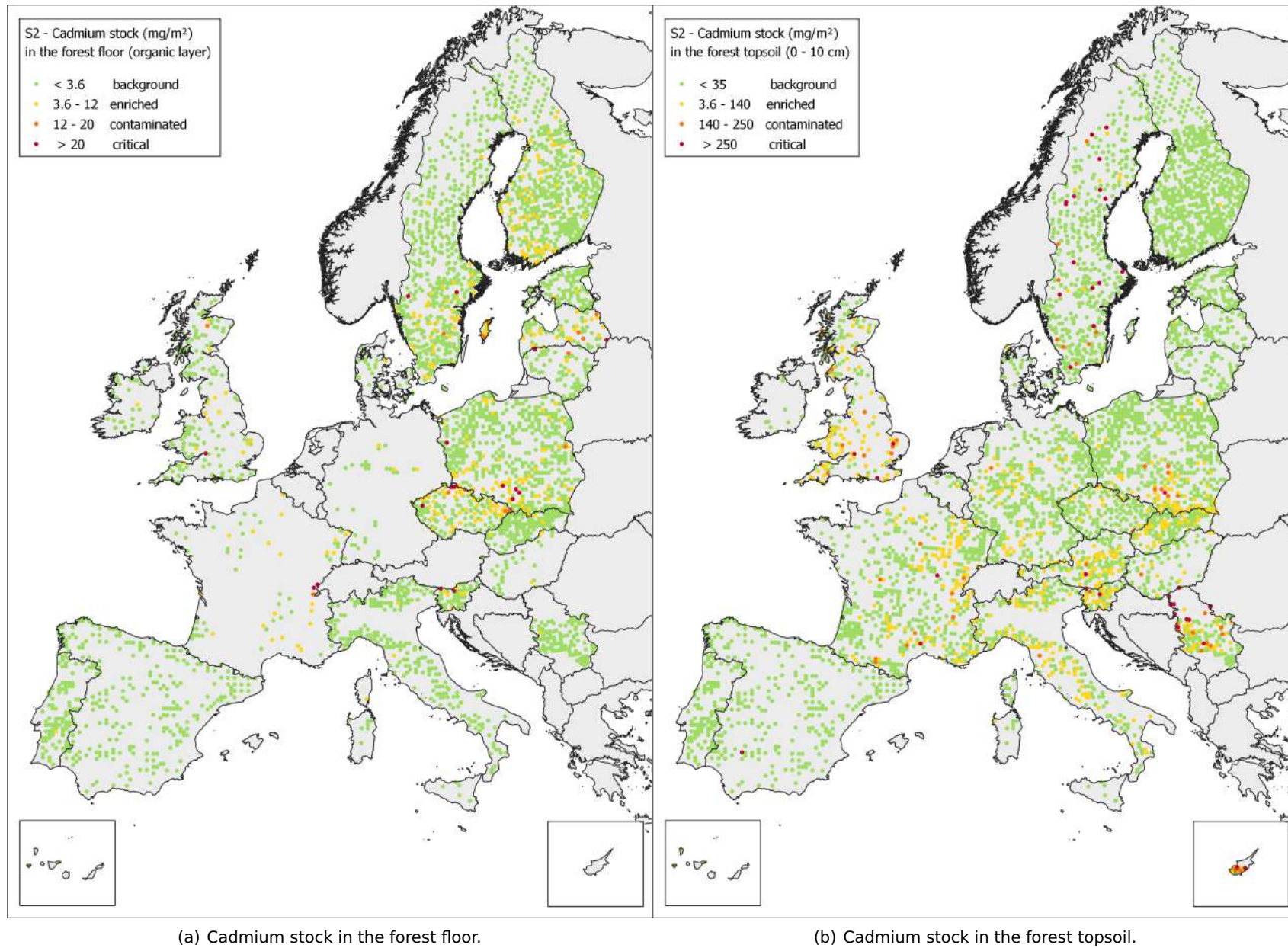


Figure 4.6: Maps of the cadmium stock in European forest floors and topsoils for the second forest soil condition survey (S2).

4.2.2 CHROMIUM

Chromium concentrations are generally well above LOQ. The summary statistics in Tables B.6 and B.7 reveal average Cr concentrations of 21-33 mg/kg in mineral soils, around 18 mg/kg in forest floors and 4-13 mg/kg in peat soils.

For most countries, Cr concentration in the forest floor is lower than in the forest topsoil (Figure 4.7). If the geometric mean concentrations are investigated per biogeographical region, it is clear that the Boreal region hosts the lowest Cr concentrations, while the opposite is true for the Alpine region (Figure 4.8). The differences between concentrations in the forest floor versus mineral soil are mostly non-significant in the Mediterranean, Pannonian, Continental and Boreal zone, while on country level Cr concentration in the forest floor is often significantly lower than in the mineral topsoil. This shows that Cr concentrations are spatially very variable.

Hence, the majority of the Cr content in soils is believed to be of lithogenic origin. Moreover, Cr is hardly taken up aboveground by plants so no enrichment via plant litter is taking place. The boundary of the most recent glaciation is clearly visible in the Cr concentration of the forest topsoil, with lower Cr content north of this boundary (Figure 4.11). Another area with naturally low Cr concentration is the region of Landes (France), which leads us to suspect that the local parent material is also an important parameter influencing Cr concentration. In some regions the contribution from wind-blown dust plays a significant role (Frontasyeva et al., 2020). This is for example the case for sandy soils in Poland showing elevated Cr concentrations.

When Cr stocks are evaluated most plots show background or enriched levels and only few plots have contaminated or critical stocks (Figure 4.12). Critical zones derived from topsoil stocks are not reflected in forest floor stocks and vice versa.

Cr concentration is lowest in Podzols and Histosols, and highest in Calcisols (Figure 4.9). Likewise, in histic humusforms the concentration is significantly lower than in well-aerated terrestrial forms with still concentration differences between Mor and the Moder/Mull forms (Figure 4.10). Since concentrations are higher in mineral soil, enhanced bioturbation in mull and moder types increases the concentration through mixing (contaminating) with mineral soil particles.

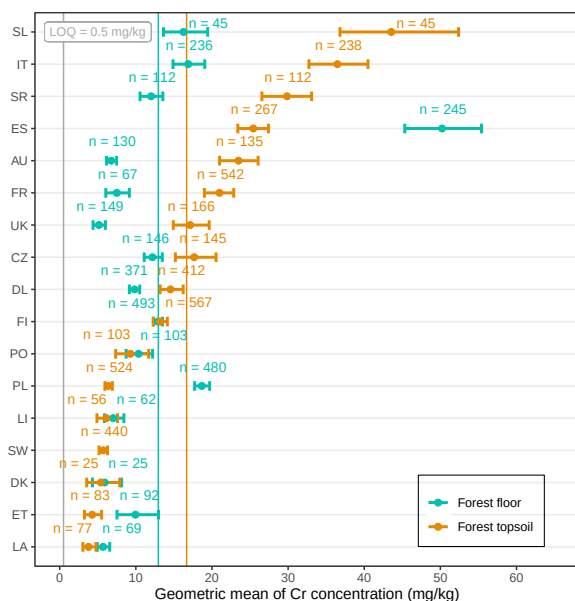


Figure 4.7: Bootstrapped geometric mean and 95% CI range of Cr per country.

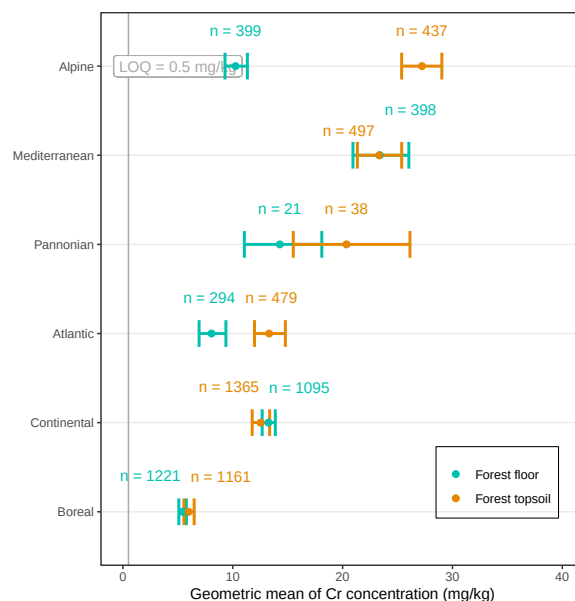


Figure 4.8: Bootstrapped geometric mean of Cr per biogeographical region.

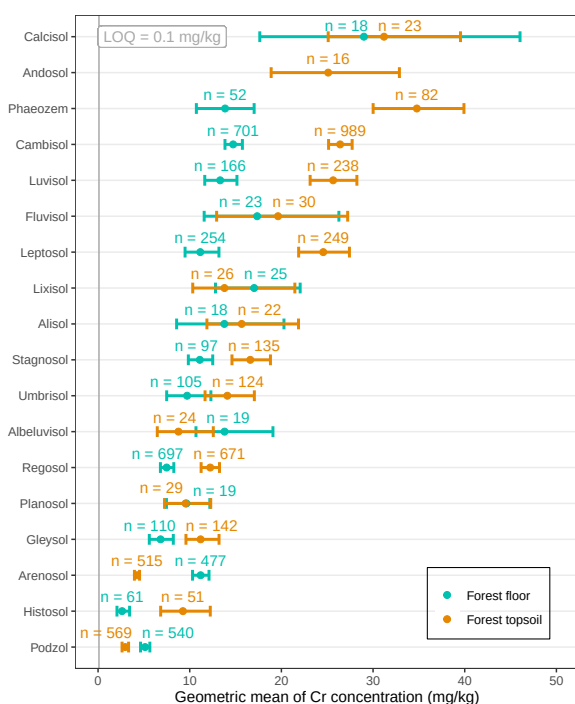


Figure 4.9: Bootstrapped geometric mean of Cr per soil group.

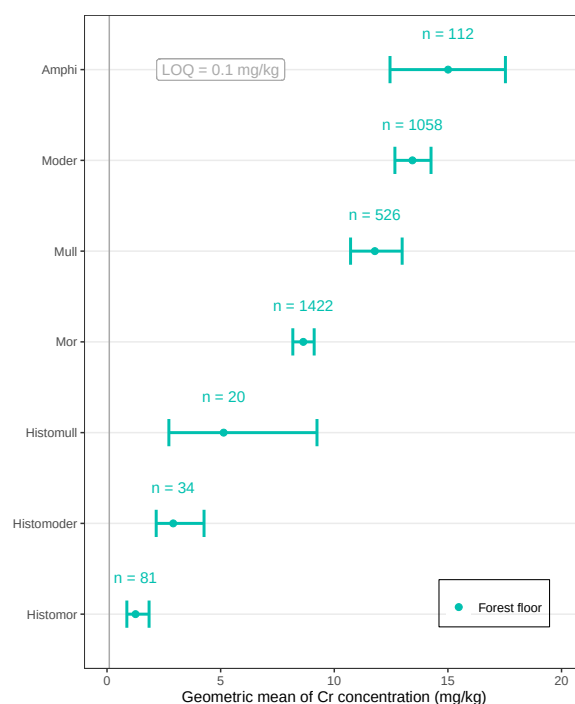


Figure 4.10: Bootstrapped geometric mean of Cr per humustype.

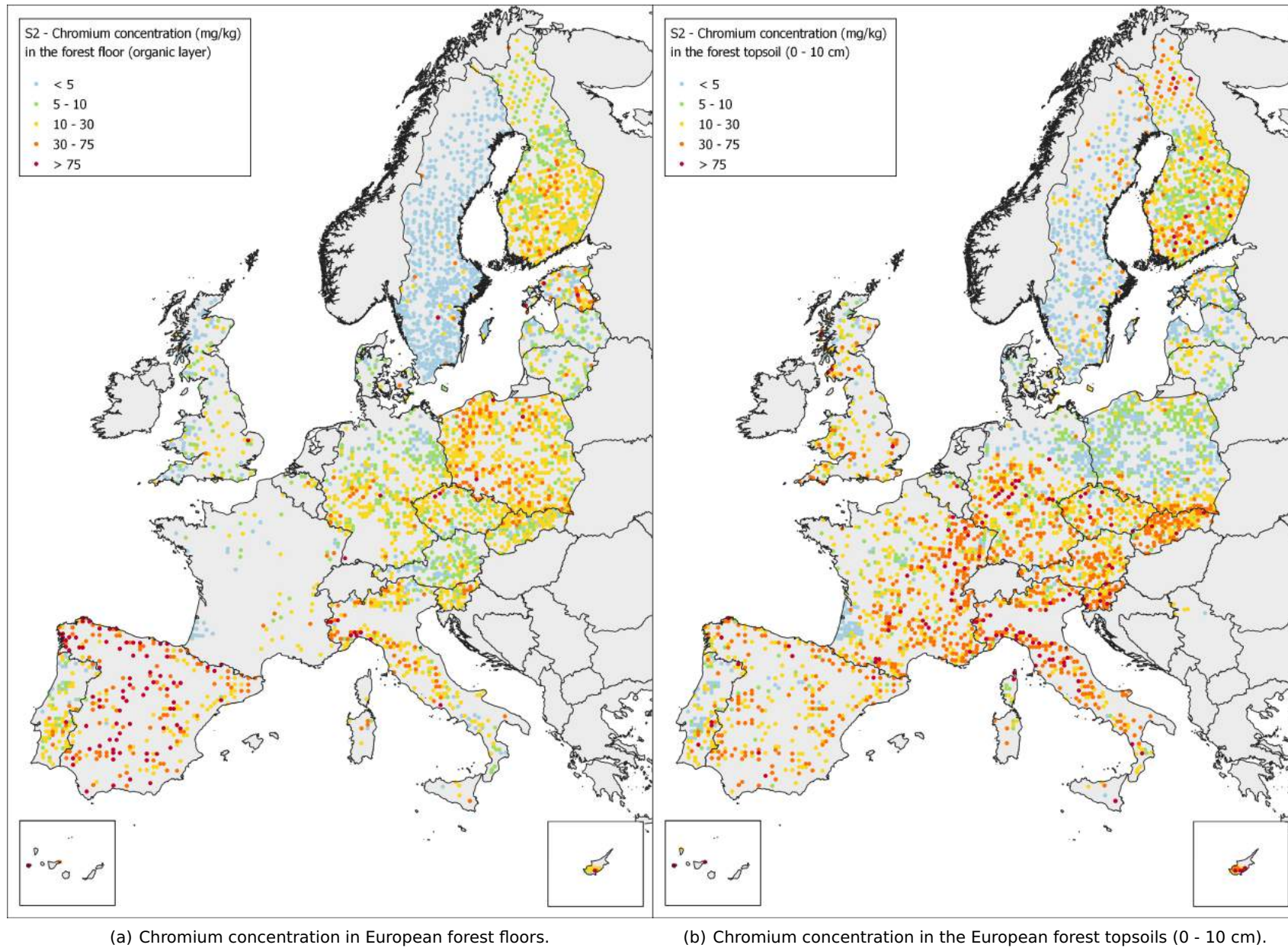


Figure 4.11: Maps of the chromium concentration in European forest floors and topsoils for the second forest soil condition survey (S2).

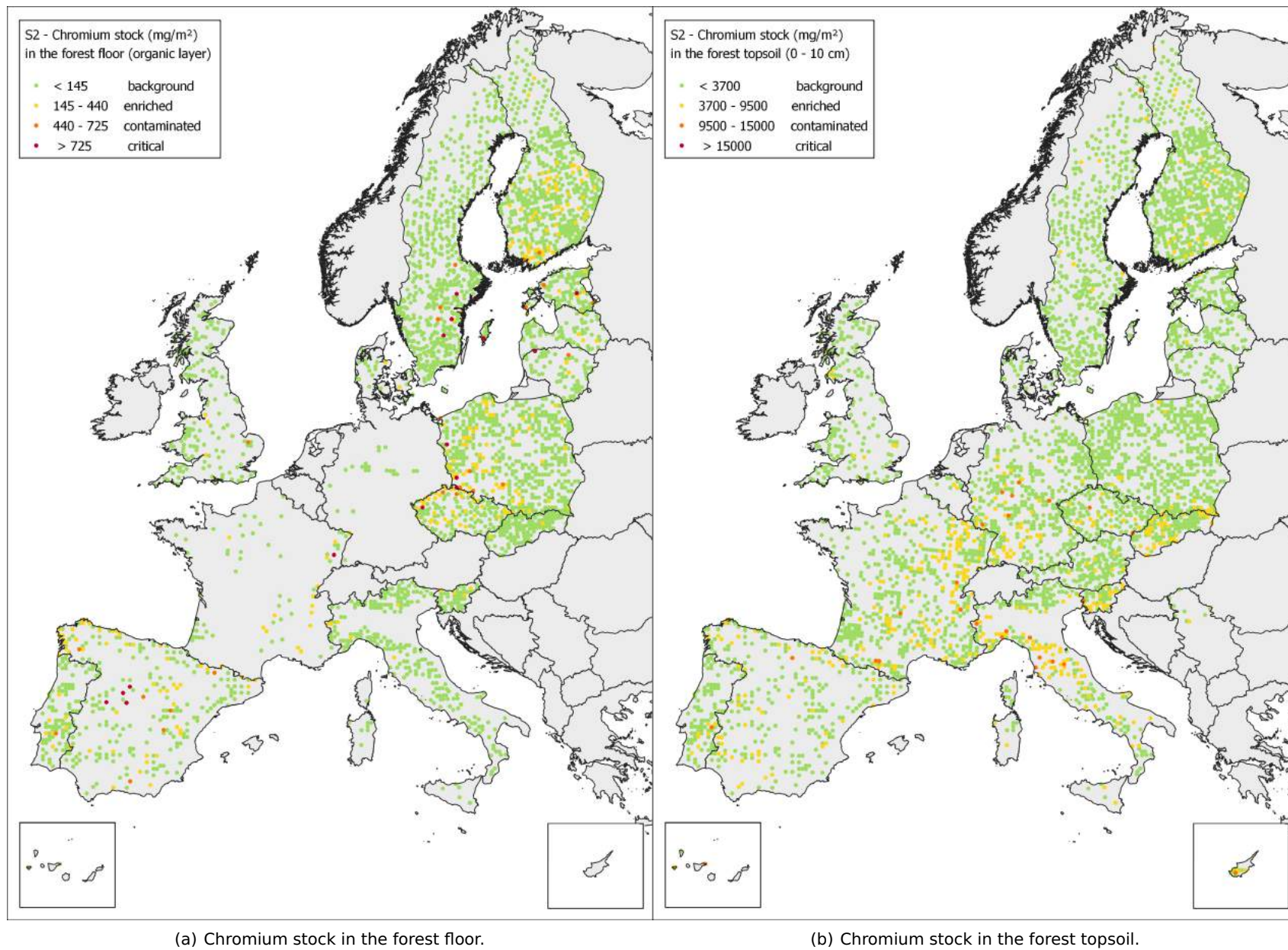


Figure 4.12: Maps of the chromium stock in European forest floors and topsoils for the second forest soil condition survey (S2).

4.2.3 COPPER

Average Cu concentrations in our dataset range from 10 to 22 mg/kg in mineral soils, from 11 to 16 mg/kg in forest floors and from 6 to 17 mg/kg in peat soils (Tables B.8 and B.9)

In most countries, the Cu concentration in the forest floor is higher than in the forest topsoil (Figure 4.13). Exceptions are Italy, Slovenia and Austria, and this is also reflected in the Alpine and partly Mediterranean bioregion (Figure 4.14). Yet unexplained is the high concentration of Cu in Danish forest floors, compared to their very low mineral soil concentrations near the LOQ.

The higher concentration in forest floors might reflect the importance of the contribution of atmospheric deposition to the total Cu content in the forest soil. The Boreal region hosts on average lower Cu concentrations in the forest soil than other biogeographical regions (Figure 4.14). This is presumably linked with the dominance of Podzols and Mor-humus (Figure 4.15, Figure 4.16) and the tendency of Cu to be stabilized by organic matter through adsorption.

Geographically, high Cu concentrations in the forest topsoil can be found in the Mediterranean as the Apennine peninsula hosts high natural concentrations of Cu (Ballabio et al., 2018), as well as Trodos mountain range in Cyprus and southwestern Spain (Figure 4.17).

Important anthropogenic sources of Cu are mining and Cu-Ni melting. For example, the hotspot around the urban industrial centres of Krompachy in Slovakia is due to metallurgic activities (Bobro et al., 2000). The load of Cu is also critical in the Black Triangle region along the Czech-Polish-German border (Figure 4.18). Note that critical stocks for Cu are reached in the forest floor, but apparently not in the mineral topsoil. So the forest floor compartment seems a better indicator for Cu contamination than the mineral topsoil.

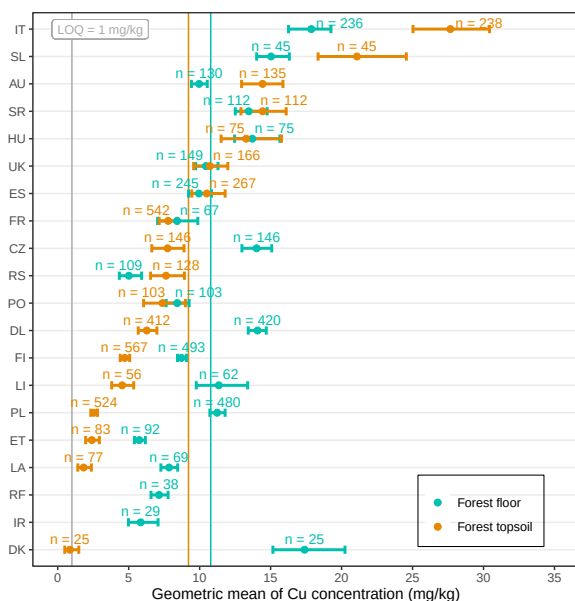


Figure 4.13: Bootstrapped geometric mean of Cu per country.

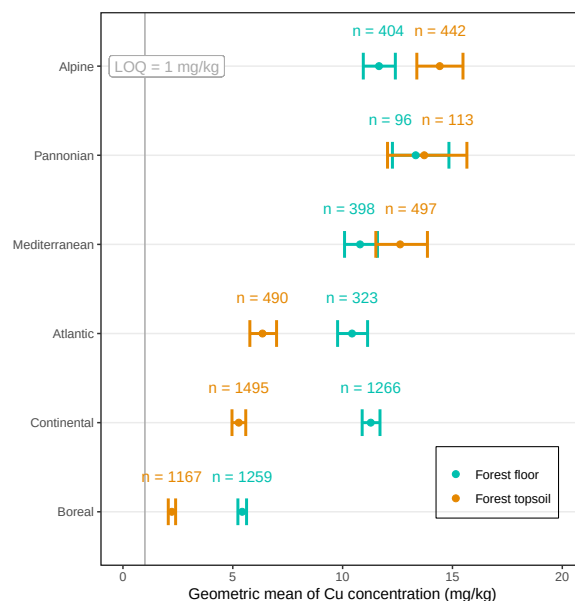


Figure 4.14: Bootstrapped geometric mean of Cu per biogeographical region.

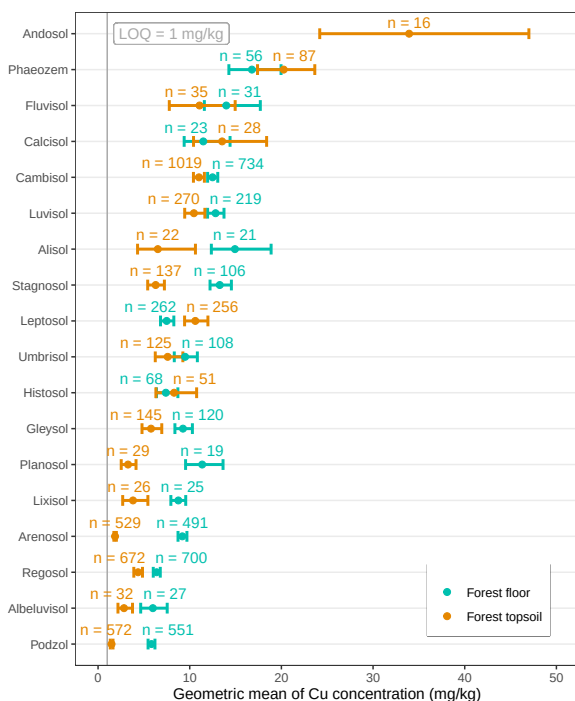


Figure 4.15: Bootstrapped geometric mean of Cu per soil group.

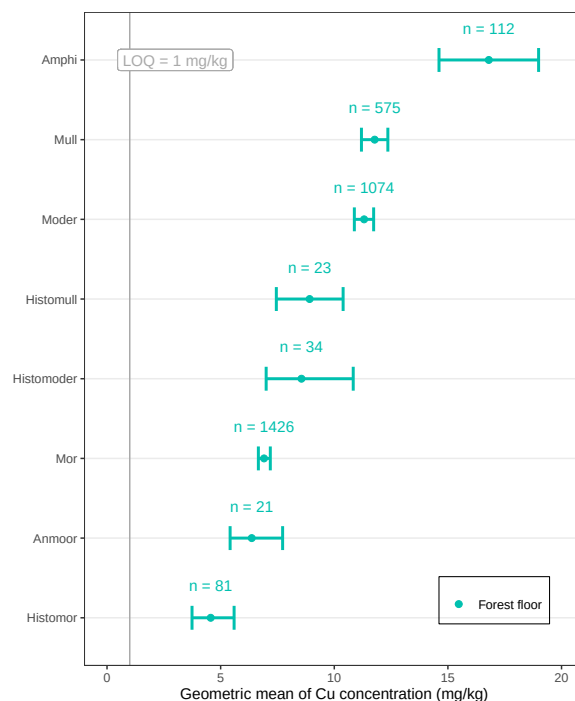


Figure 4.16: Bootstrapped geometric mean of Cu per humustype.

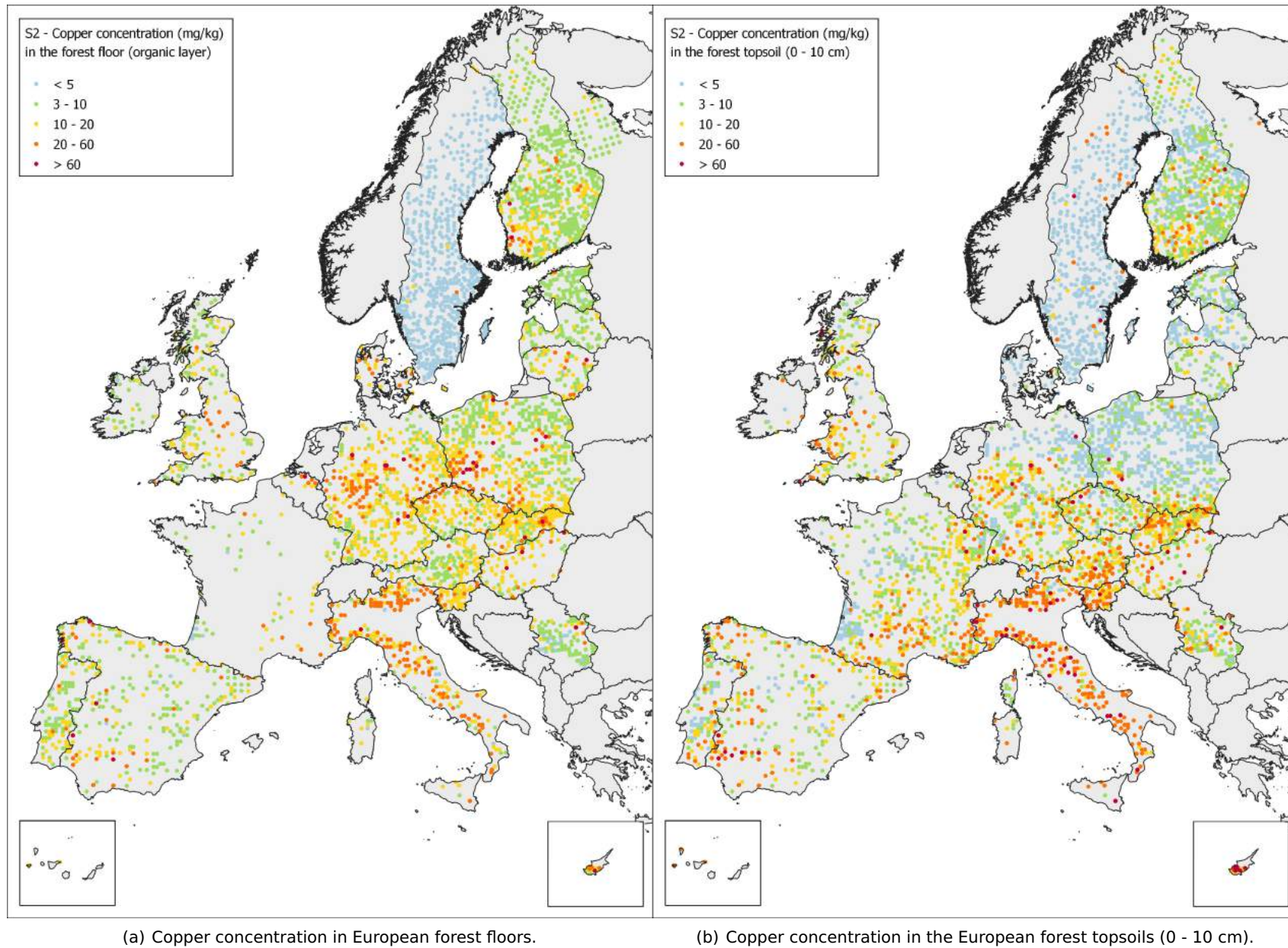


Figure 4.17: Maps of the copper concentration in European forest floors and topsoils for the second forest soil condition survey (S2).

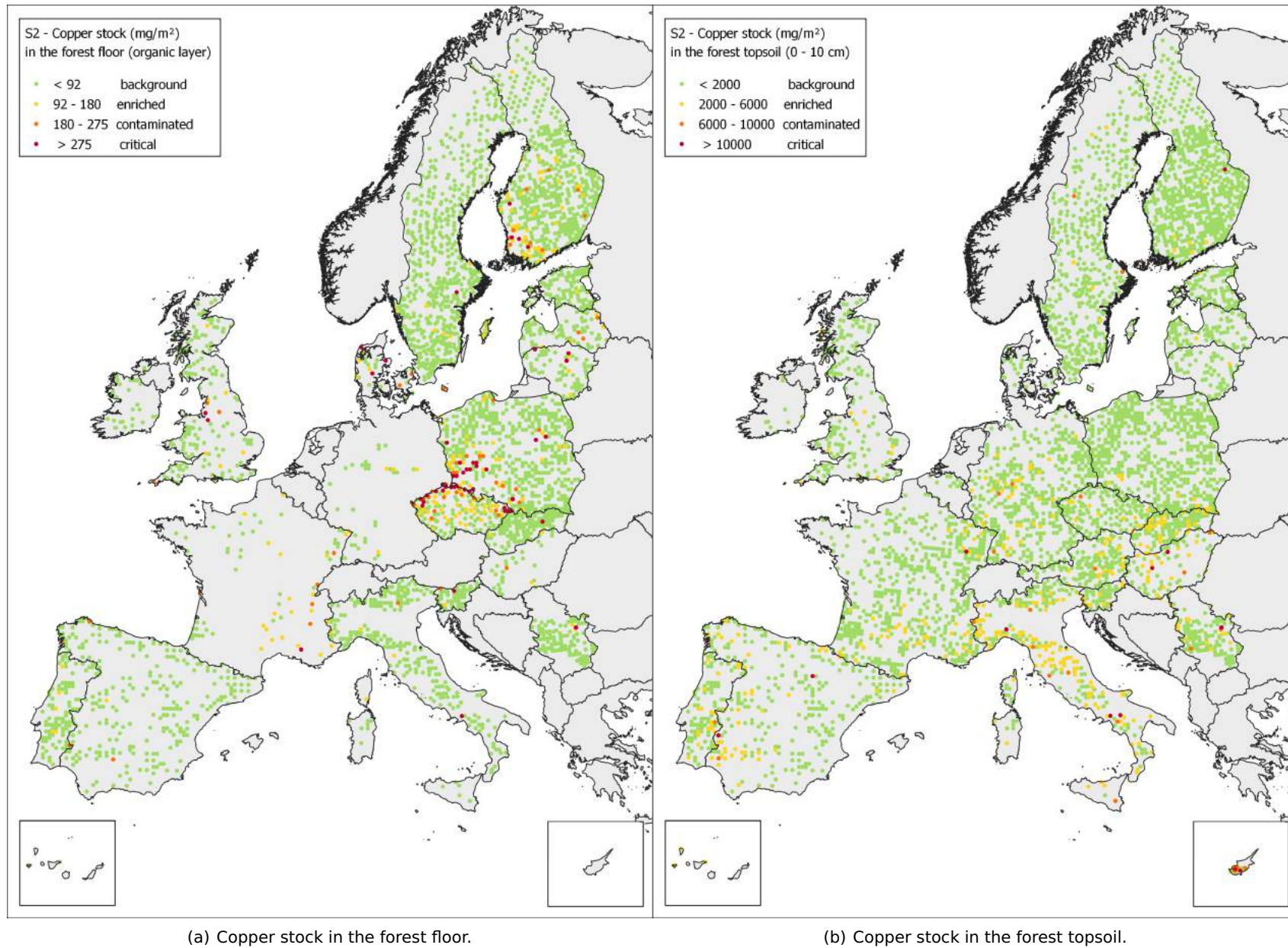


Figure 4.18: Maps of the copper stock in European forest floors and topsoils for the second forest soil condition survey (S2).

4.2.4 NICKEL

The average concentration of Ni in world soils is probably around 20 mg/kg (Alloway, 2012). In the summary of Appendix B Tables B.10 and B.11, concentrations in mineral soil range indeed from 15 to 32.7 mg/kg, but are much smaller in peat soils: 3-11 mg/kg and around 10 mg/kg in forest floors.

Stratified by countries, Ni concentrations of forest floors can be smaller or greater than their mineral topsoils (Figure 4.19). In Boreal and Continental bioregions forest floor concentrations are usually higher than in mineral soil, whereas the inverse is true for the Alpine region (Figure 4.20).

Ni and Cr concentrations are generally smaller in coarse textured and peaty soils, and greater in clayey soils (Alloway, 2012). This is in line with the ranking by soil type in Figure 4.21. Low concentrations Ni concentrations are found in Histosols and sandy soil groups (Arenosols, Podzols, Regosols) and higher concentrations in Luvisols and Fluvisols.

Stratification by humus type gives exactly the same order as for Cr, with smaller Ni concentrations in semi-terrestrial humus forms (histomor, -moder and -mull), medium Ni concentrations in mor and greatest Ni concentrations in moder and mull forms (Figure 4.22). This is expected because Cr and Ni have similar geochemistry.

As for Cr, the Ni content in soils is clearly divided by the last glaciation, with higher concentrations in postglacial southern areas (Figure 4.23). Ni load is classified as critical in certain areas like northern Slovakia, central Germany and northern Italy (Figure 4.24). As was the case for Cr stocks, critical zones derived from topsoil Ni stocks are not reflected in forest floor Ni stocks and vice versa.

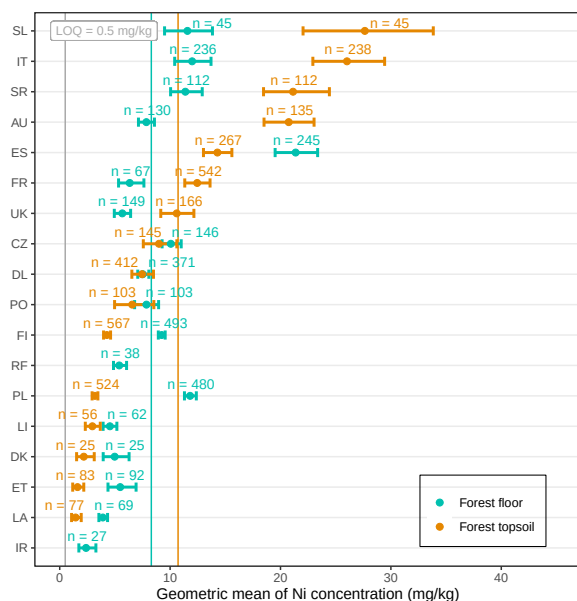


Figure 4.19: Bootstrapped geometric mean of Ni per country.

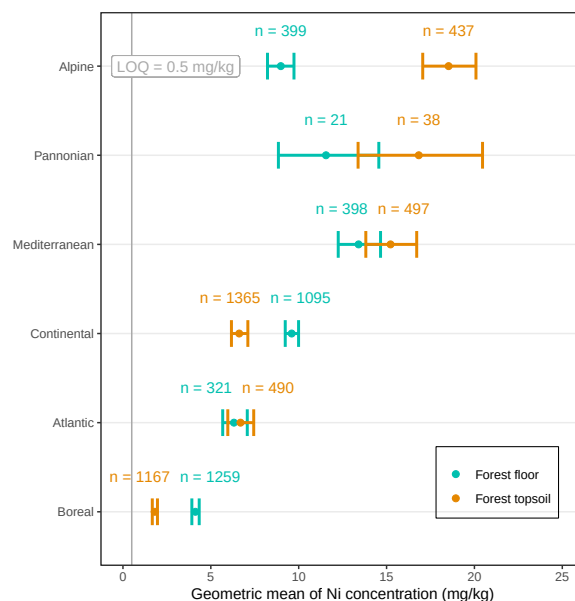


Figure 4.20: Bootstrapped geometric mean of Ni per biogeographical region.

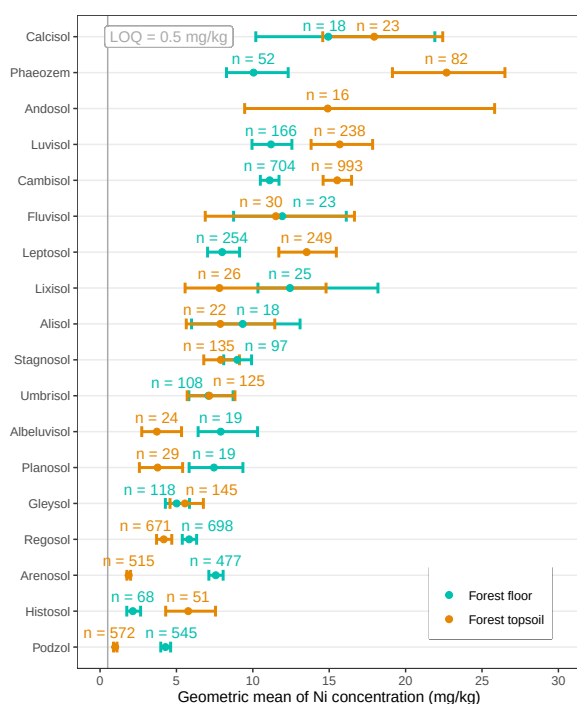


Figure 4.21: Bootstrapped geometric mean of Ni per soil group.

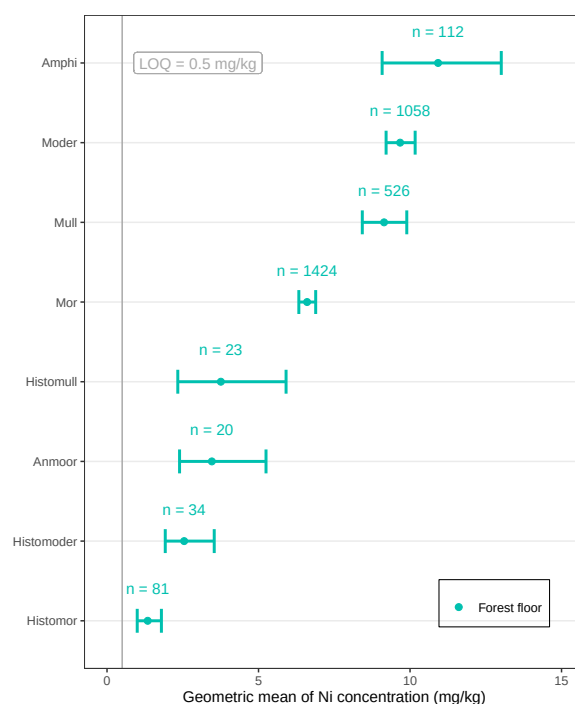


Figure 4.22: Bootstrapped geometric mean of Ni per humustype.

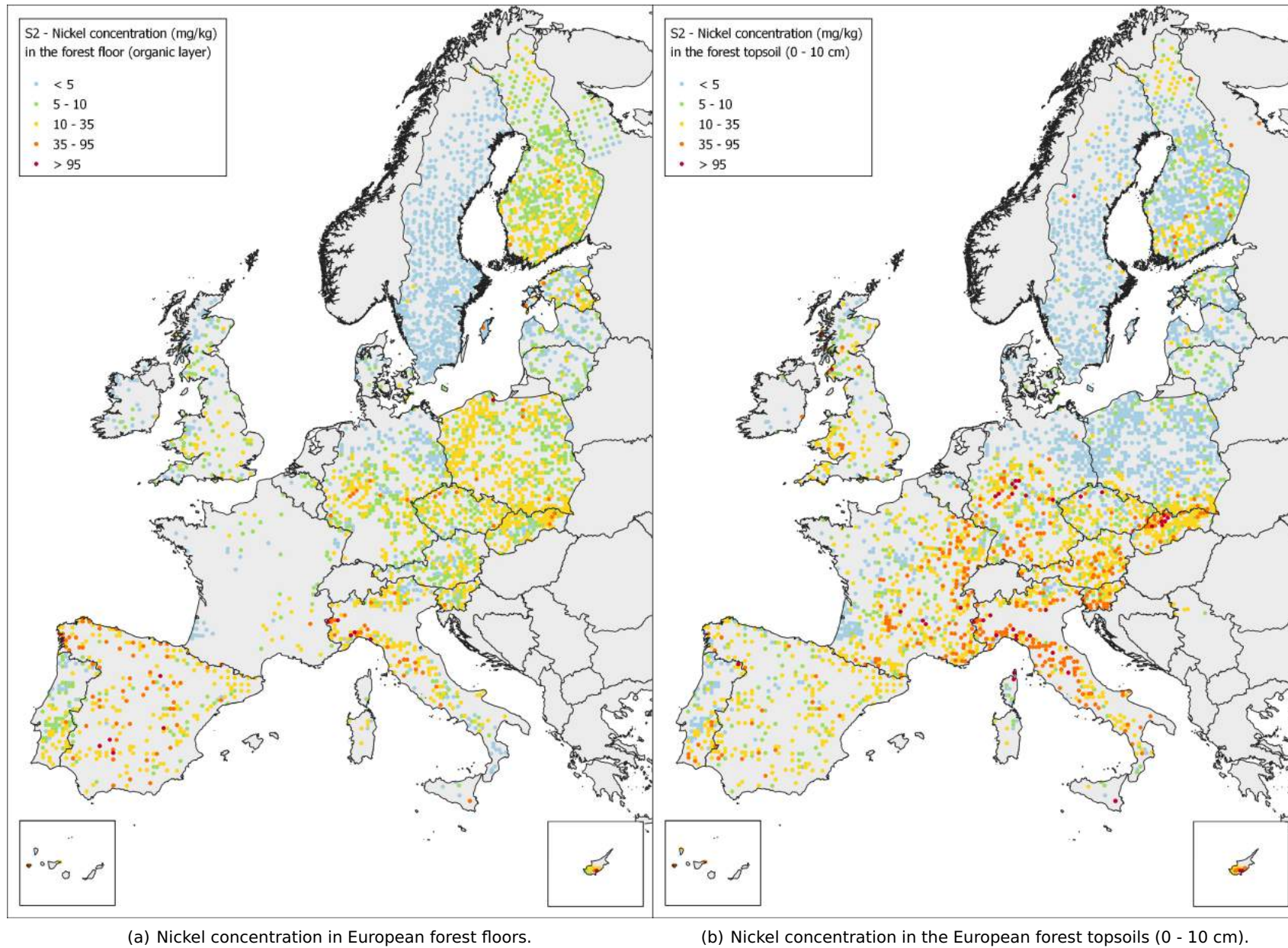


Figure 4.23: Maps of the nickel concentration in European forest floors and topsoils for the second forest soil condition survey (S2).

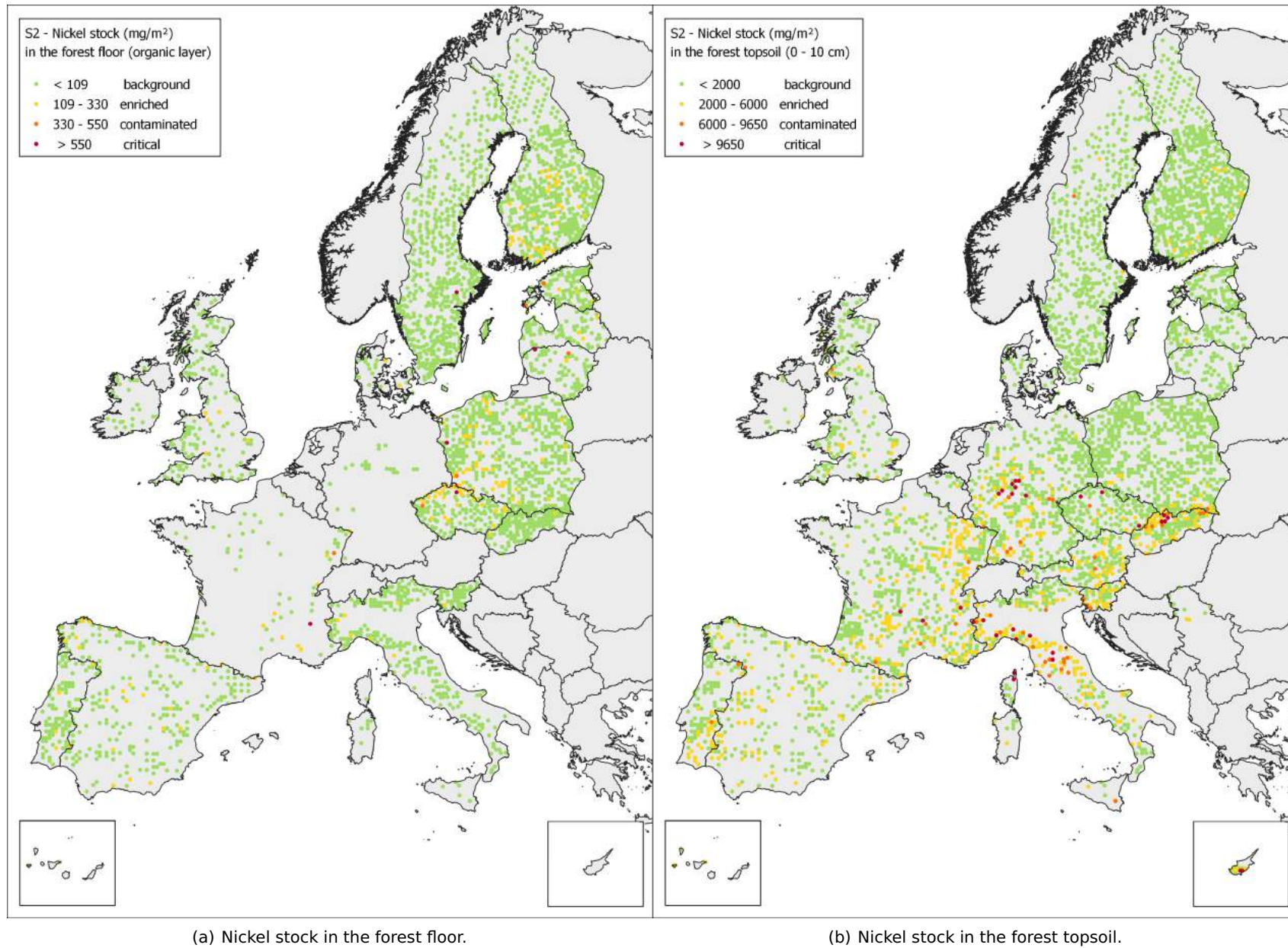


Figure 4.24: Maps of the nickel stock in European forest floors and topsoils for the second forest soil condition survey (S2).

4.2.5 LEAD

Soil is a sink for anthropogenic Pb and there are several well-known major Pb sources like mining and melting activities, contamination from vehicle exhausts and application of sludges. Alloway (2012) stated that most soil datasets support the hypothesis that much of the observed Pb in soil in many areas has originated from anthropogenic emissions, leading to low-level contamination of about 30-100 mg/kg. The summary statistics in Tables B.12 and B.13 reveal that in mineral topsoil average concentrations are around 30-40 mg/kg whereas 10-15 mg/kg in subsoil (M24, M48). This finding points towards significant deposition effects. Concentrations in the forest floors are generally greater (40-65 mg/kg) and greatest (30-340 mg/kg) in peat soils. This illustrates the strong affinity of Pb for organic matter.

At national level, no clear pattern is observed whether forest floors contain more Pb than mineral topsoils (Figure 4.25) or the inverse. Stratified according to biogeographical region shows the lowest Pb concentrations in Boreal zone (in forest floor higher than in mineral soil) and also in the Mediterranean region (but then in mineral soil higher than in forest floor) (Figure 4.26).

No clear patterns are found on preferential accumulation of Pb in specific soil groups (Figure 4.27) since most concentration levels are not significantly different from each other. Stratified according to humus type (Figure 4.28) semi-terrestrial forms (histo-mor, -moder, -mull and anmoor) show lower concentrations than terrestrial forms but mulls.

High levels of lead in forest floors can be found in North Rhine-Westphalia, southern Poland and along the border of the Czech Republic with Germany and Poland. The Harz Mountains of Germany are important for the extraction of ore (mainly Cu, Pb and Zn) (Pan et al., 2010). This location is clearly marked on the maps as polluted with Pb.

Contamination patterns are better indicated by forest floor than topsoil concentrations (Figure 4.29). Critical Pb stocks in forest floors do not always correlate well with stocks in topsoils and vice versa (Figure 4.30). For France and Germany data on Pb stocks in forest floors is limited.

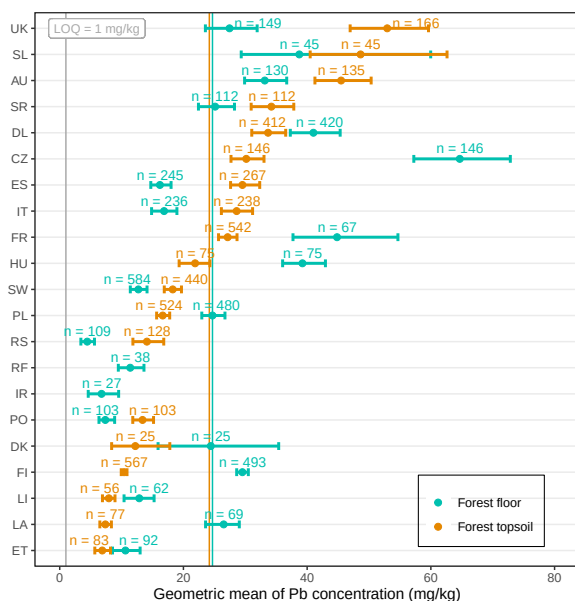


Figure 4.25: Bootstrapped geometric mean of Pb per country.

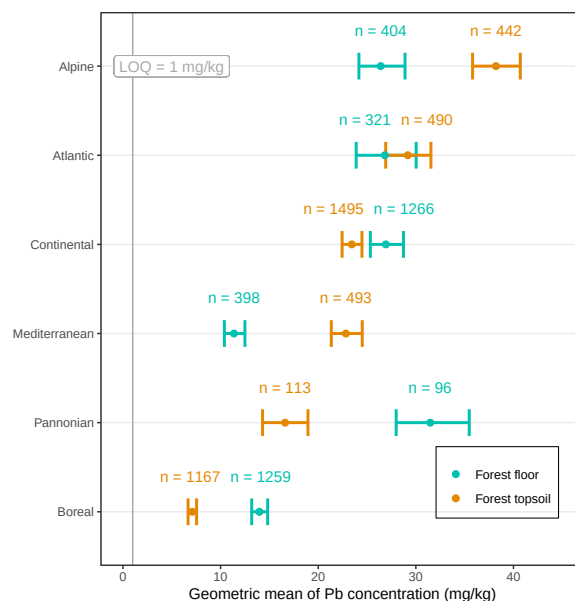


Figure 4.26: Bootstrapped geometric mean of Pb per biogeographical region.

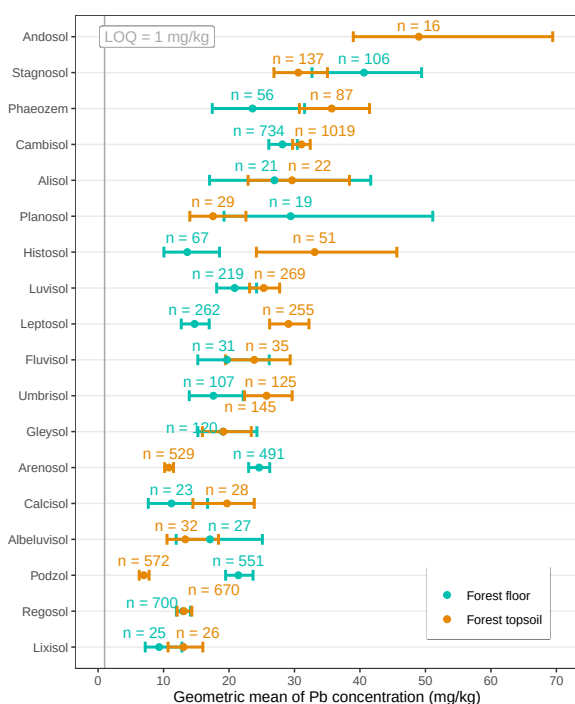


Figure 4.27: Bootstrapped geometric mean of Pb per soil group.

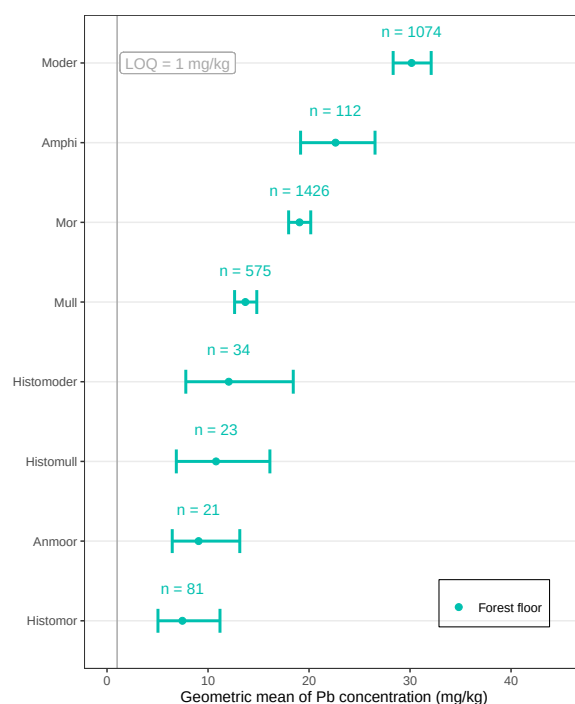


Figure 4.28: Bootstrapped geometric mean of Pb per humustype.

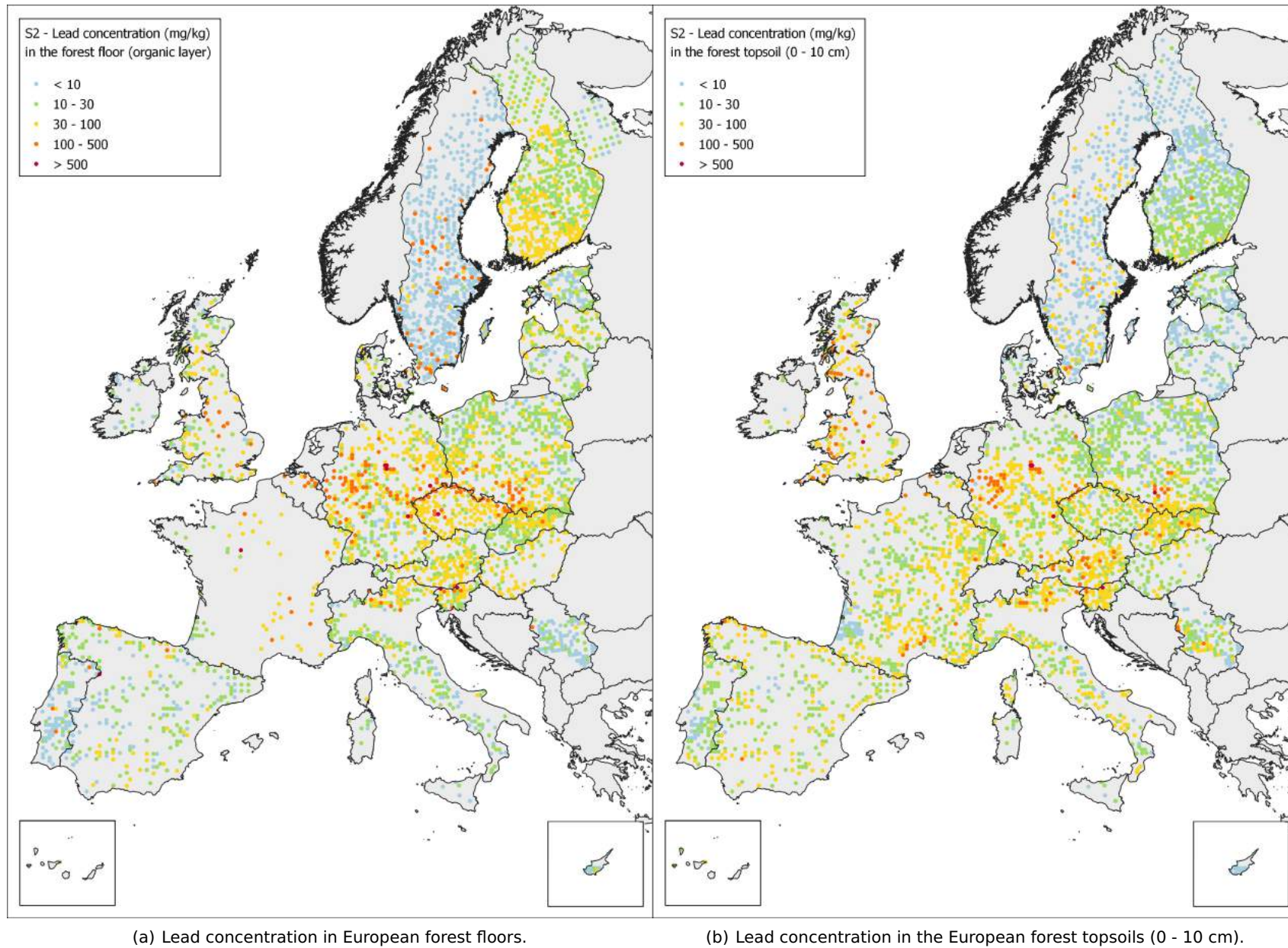


Figure 4.29: Maps of the lead concentration in European forest floors and topsoils for the second forest soil condition survey (S2).

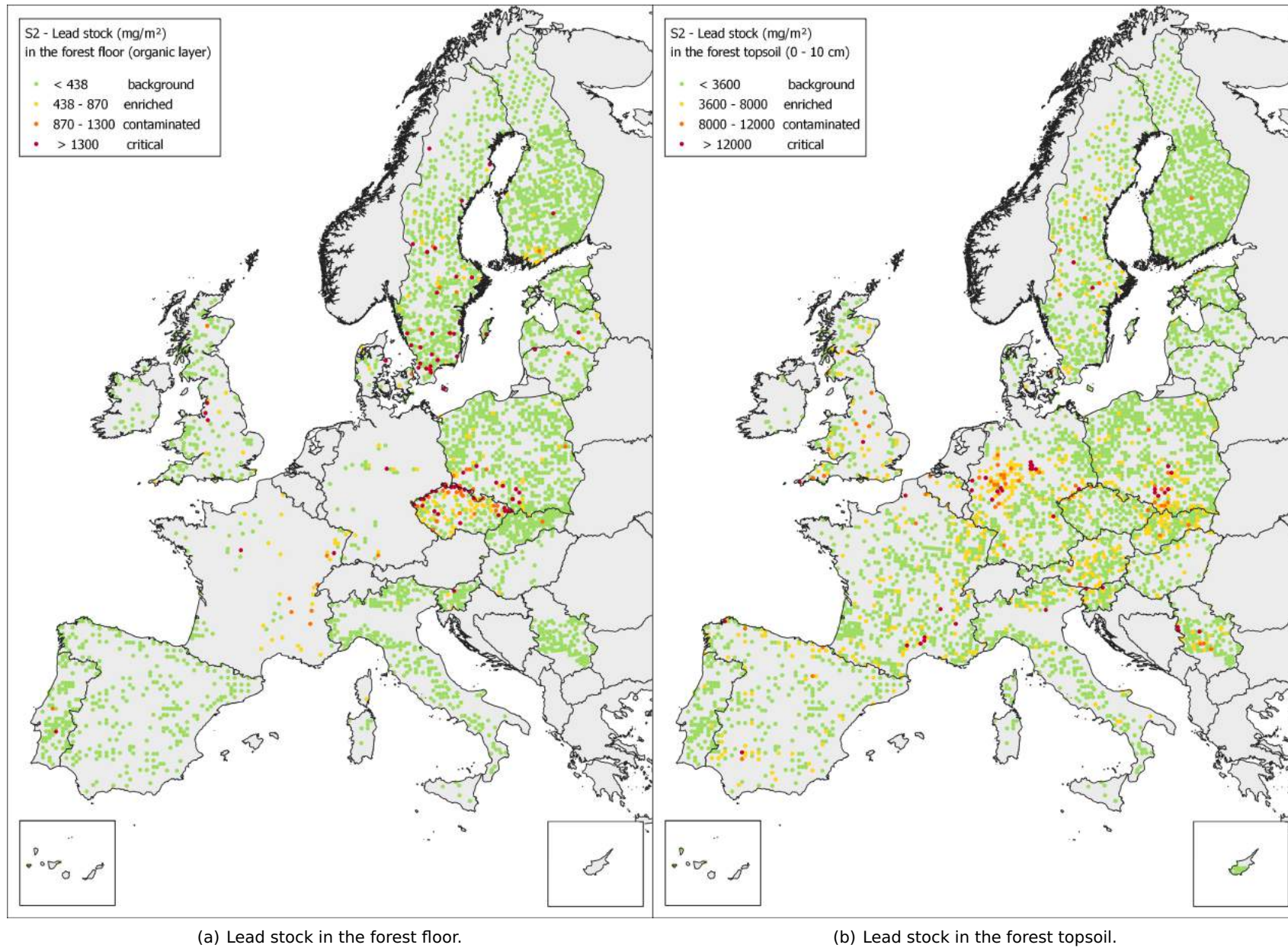


Figure 4.30: Maps of the lead stock in European forest floors and topsoils for the second forest soil condition survey (S2).

4.2.6 ZINC

Zinc is the metal with the highest concentration level of the seven metals included in this study. Together with Cd these heavy metals are the most mobile and potentially bio-available. It is an essential trace element for humans, animals and plants, although it can be toxic in higher concentrations. The average total Zn content in the lithosphere is approximately 80 mg/kg. In sedimentary rocks the highest concentrations are found in shales and clayey sediments (80 - 120 mg/kg), while sandstones, limestones and dolomites hold lower concentrations (10 - 30 mg/kg) (Alloway, 2012).

The summary statistics in Appendix B (Tables B.14 and B.15) list mean concentrations in mineral soil between 40 - 70 mg/kg, with a mean around 70 mg/kg in forest floors but lower concentrations in peat soils (20 - 60 mg/kg).

Concentrations of Zn in forest floors are generally higher than in mineral topsoils when stratified by country (Figure 4.31). Except for the Mediterranean, Zn concentrations per biogeographical region in the forest floor are higher than in mineral soils (Figure 4.32) and also remarkable, the difference between forest floor and upper soil concentrations is often quite large suggesting Zn cycling by trees.

In fact, the variation in forest floor Zn concentration is low (Figure 4.33) compared to soil groups. Andosols show highest Zn levels (around 100 mg/kg) while Podzols, Arensols and Albeluvisols have lowest concentrations (< 20 mg/kg). Mor, Histomors and Anmoors show slightly smaller concentrations than other humus forms, but differences are mostly non-significant.

Zones with elevated concentrations are found in Slovakia and southern Poland, the Campine region in Belgium close to the (former) Znelters, the Ruhr area in Germany, Northern Italy and Slovenia (Figure 4.35). Contaminated and critical levels are exceeded in forest floors in southern Sweden (Figure 4.36) but this is not reflected in topsoil stocks.

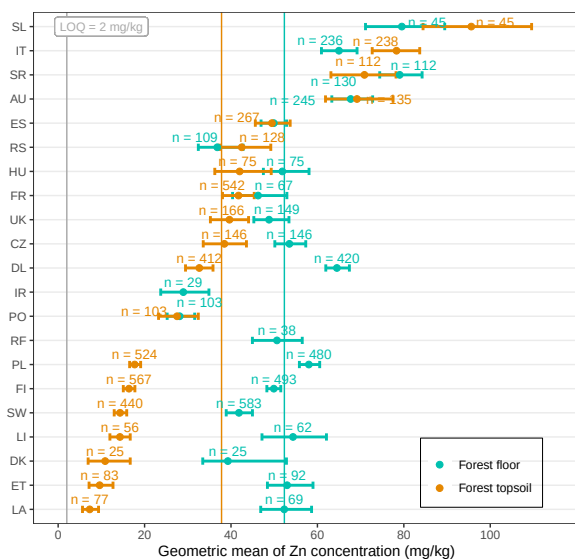


Figure 4.31: Bootstrapped geometric mean of Zn per country.

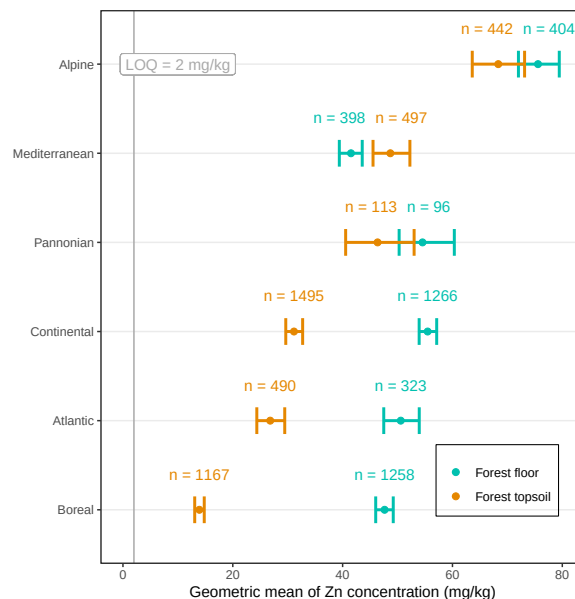


Figure 4.32: Bootstrapped geometric mean of Zn per biogeographical region.

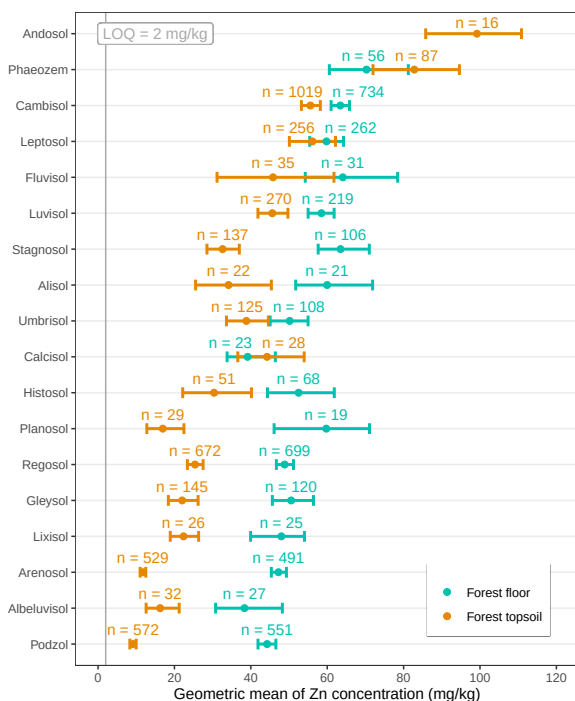


Figure 4.33: Bootstrapped geometric mean of Zn per soil group.

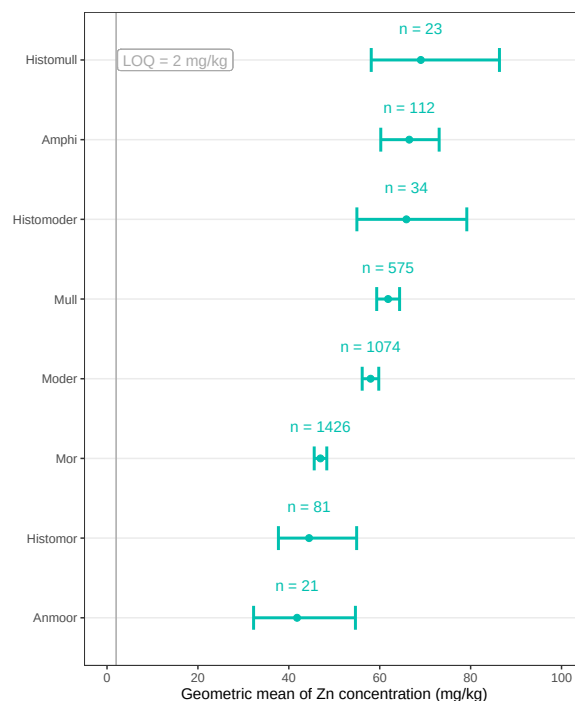


Figure 4.34: Bootstrapped geometric mean of Zn per humustype.

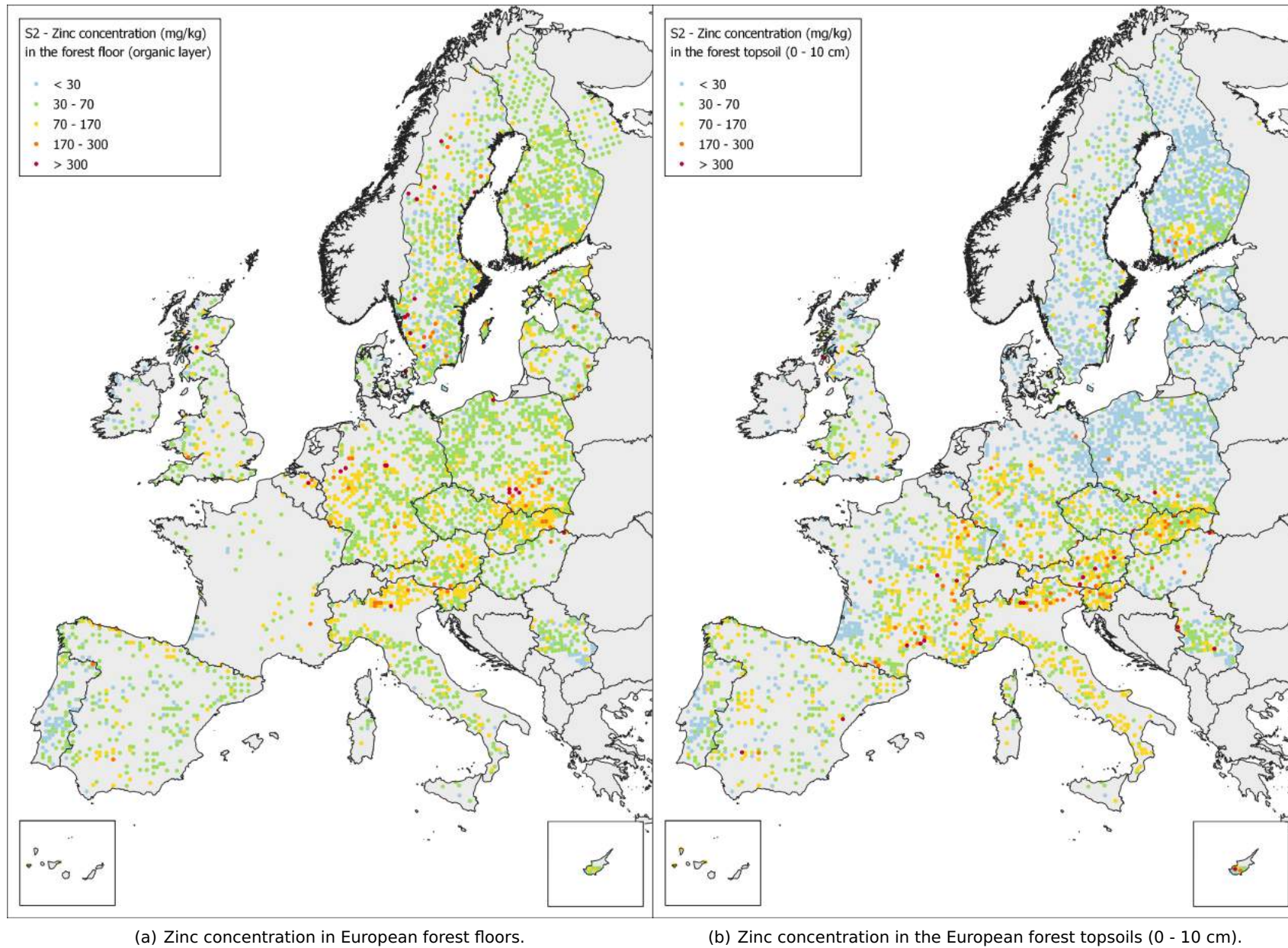


Figure 4.35: Maps of the zinc concentration in European forest floors and topsoils for the second forest soil condition survey (S2).

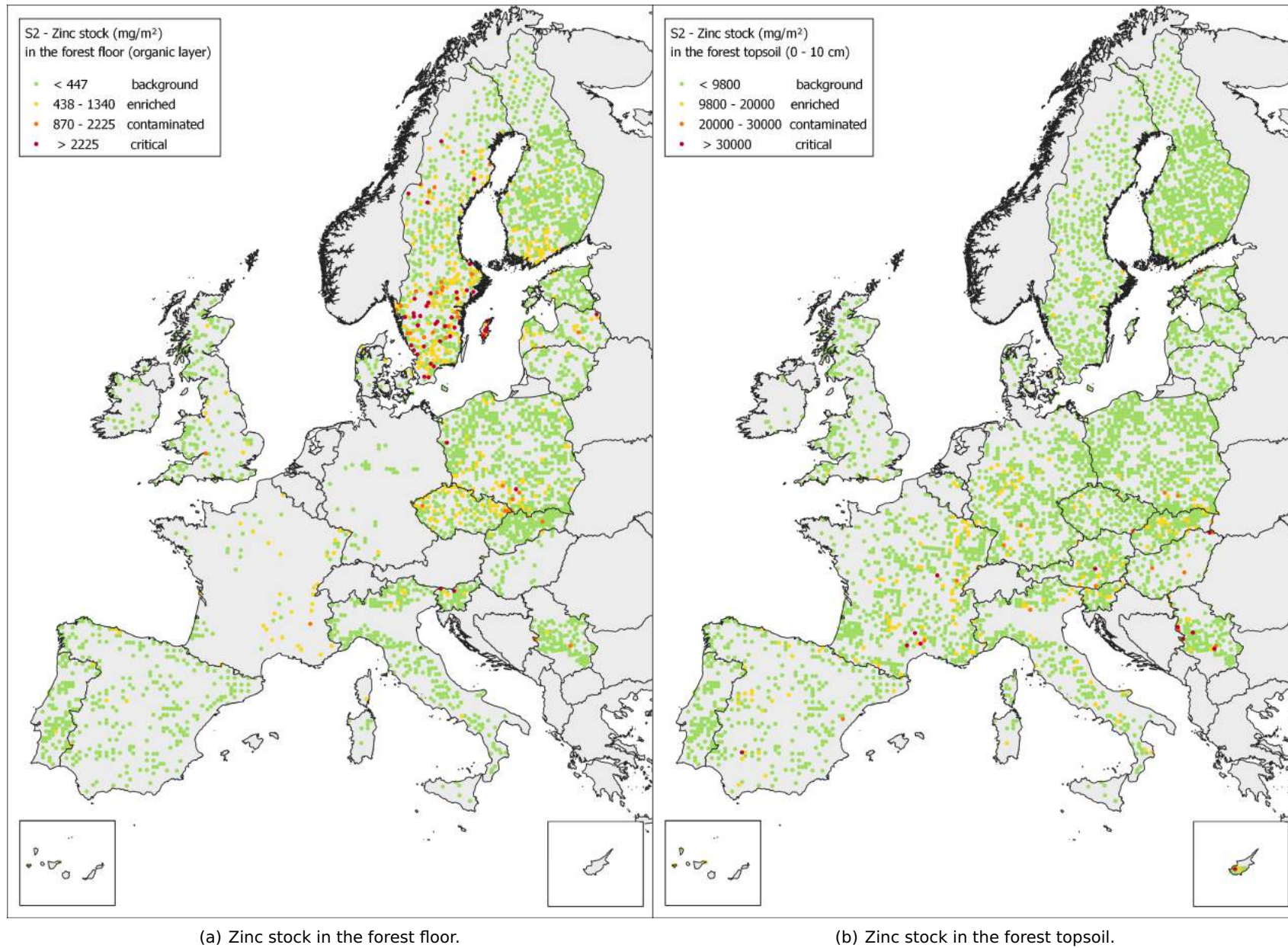


Figure 4.36: Maps of the zinc stock in European forest floors and topsoils for the second forest soil condition survey (S2).

4.2.7 MERCURY

Mercury is of special concern because it is highly toxic to humans and animals and has no biological function nor role in ecosystems. While deposition of most metals is decreasing in Europe, this is not the case for Hg. Hg is released in the environment by mining and smelting of ores, burning of fossil fuels (mainly coal), industrial production processes, and waste incineration (Alloway, 2012). Låg and Steinnes (1978) found a highly significant correlation between Hg and organic matter content in the top layer of forest soils.

Our summary statistics of Hg concentrations (Table B.5) lists mean levels ranging from 0.16 to 0.46 mg/kg in mineral soils, around 0.2 mg/kg in forest floors and 0.14-0.23 mg/kg in peat soils.

Only 8 countries reported Hg data on Level I plots (Fig. 4.37). For most countries, levels in forest floors were higher than in mineral soils. UK showed mean concentrations around 0.3 mg/kg while most other countries have topsoil concentrations below 0.1 mg/kg. Forest floor concentrations are about 0.2 mg/kg.

Stratification by biogeographical region (Fig. 4.38) reveals another pattern: smallest concentrations in the Atlantic zone' topsoils (<0.05 mg/kg) while over 0.15 mg/kg in the other bioregions, whereas concentrations in forest floors are comparable.

Looking at soil groups (Fig. 4.39), Podzols, Arenosols and Histosols have sample geometric means below LOQ. This is surprising for Histosols, because some authors found high Hg levels in these, but maybe they were located in high deposition areas. No significantly different levels were found among other soil groups.

Figure 4.40 shows lowest Hg levels in Histomors and greatest in Moders but no divergence in other humus forms.

The geographical scope of mercury analysis was limited in comparison with the analysis of other heavy metal concentrations. Nevertheless, some hotspots of human release are clearly visible. In the Baltic states, Germany and France mercury concentrations in forest floors are generally higher than in forest topsoils (Figure 4.41), suggesting forest floors to be better indicators than topsoils. However, this is not the case for UK where concentration levels and stocks are greater in topsoils than in forest floors. Hotspots are also found in Slovakia and Lithuania.

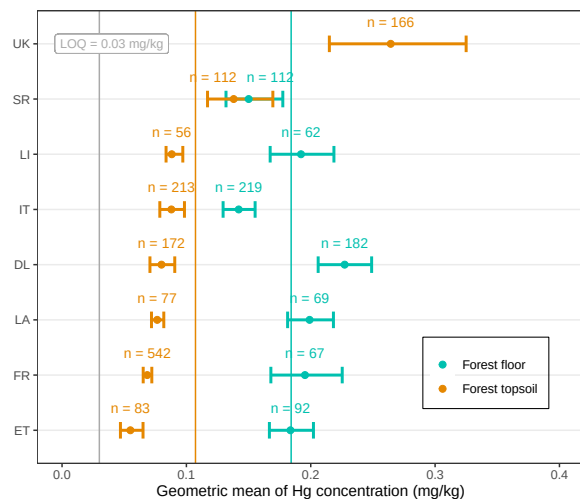


Figure 4.37: Bootstrapped geometric mean of Hg per country.

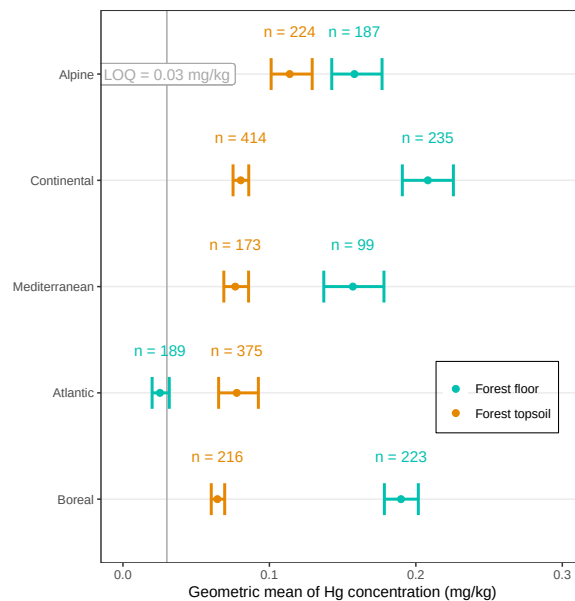


Figure 4.38: Bootstrapped geometric mean of Hg per biogeographical region.

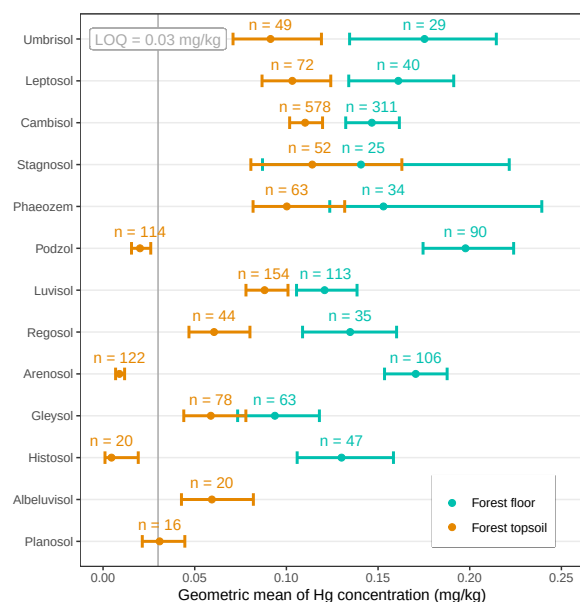


Figure 4.39: Bootstrapped geometric mean of Hg per soil group.

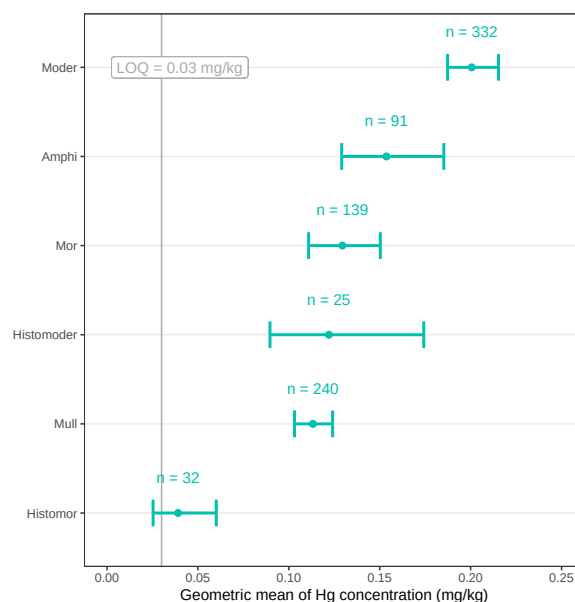


Figure 4.40: Bootstrapped geometric mean of Hg per humustype.

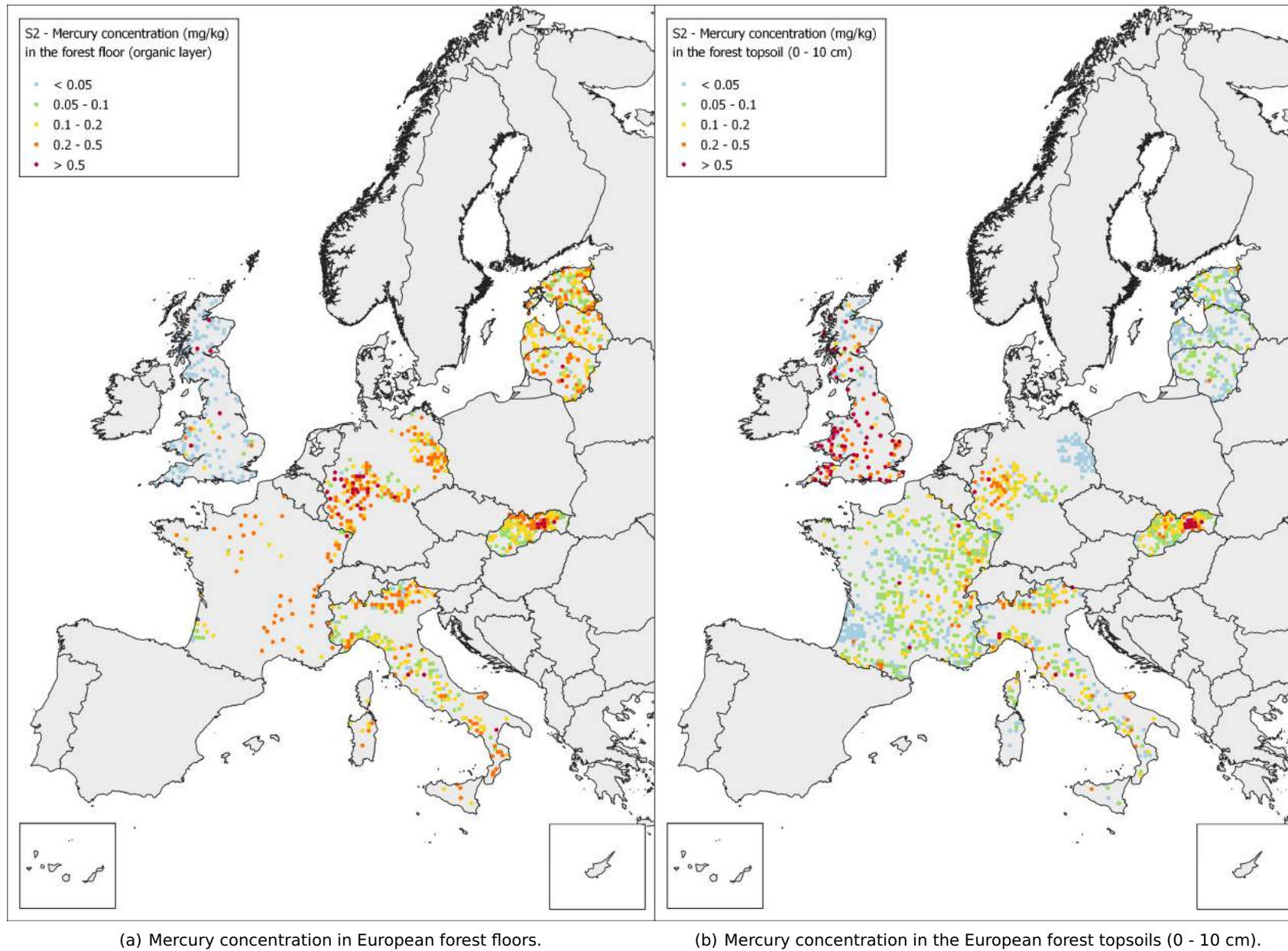


Figure 4.41: Maps of the mercury concentration in European forest floors and topsoils for the second forest soil condition survey (S2).

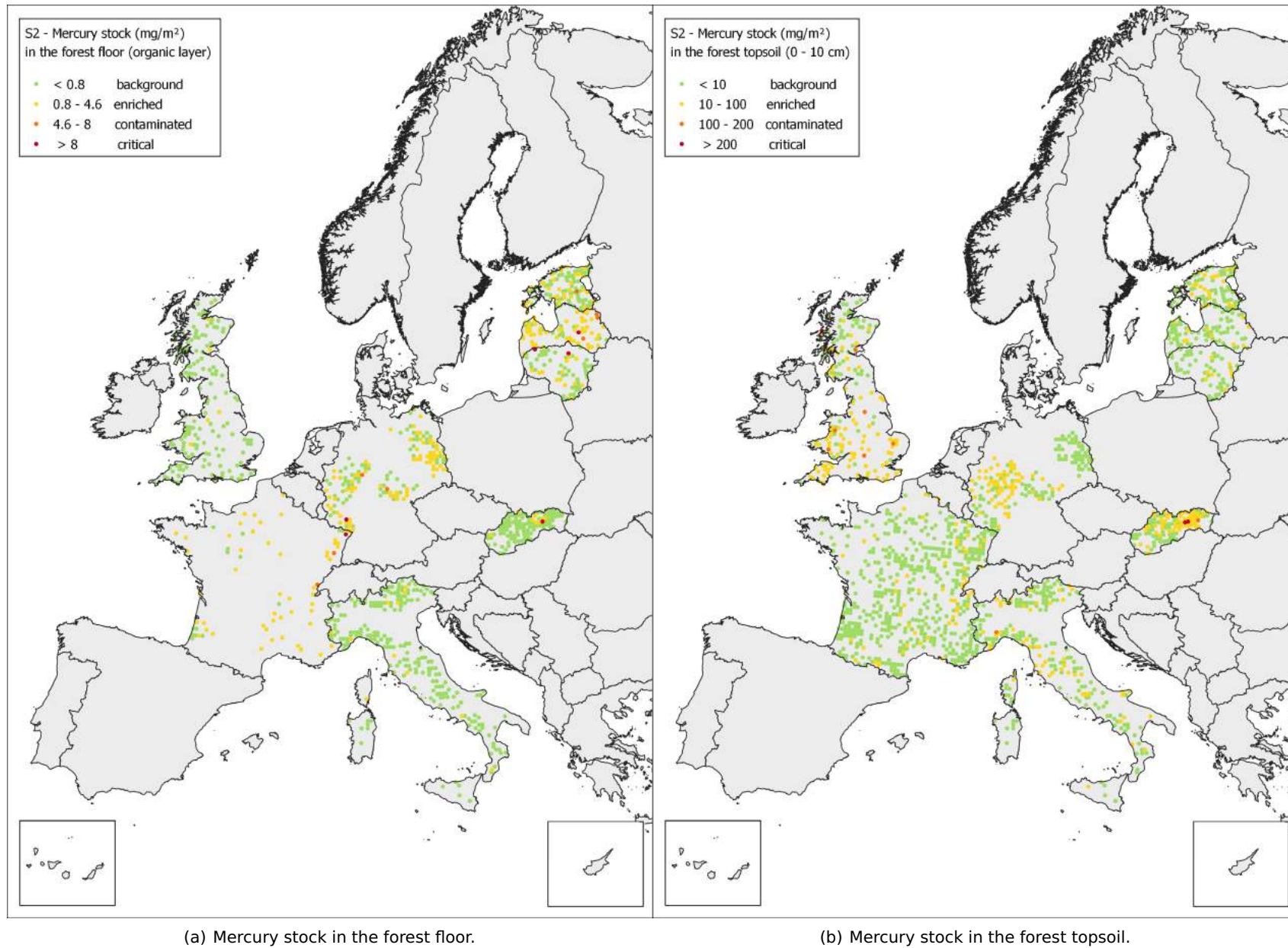


Figure 4.42: Maps of the mercury stock in European forest floors and topsoils for the second forest soil condition survey (S2).

4.3 TEMPORAL CHANGES

For a limited set of countries time series of heavy metal concentrations are available. Germany, Portugal, Finland, Lithuania, the Czech Republic, Estonia, Austria, Slovakia and Latvia reported heavy metal concentrations in both the first and the second forest soil condition survey. Based on paired observations, the change in heavy metal concentration over time was investigated. Countries that moved sampling locations between S1 and S2 were excluded from this analysis. Moreover, no paired measurements are available for Hg, hence no temporal patterns could be determined for this element.

More paired data is available for the organic layer (FF) than for mineral soil.

4.3.1 TEMPORAL CHANGE IN FOREST FLOOR

Concentration change between surveys for six heavy metals is shown in the scatterplot of Figure 4.43. For Cd, the high concentrations found on many plots during S1 were not found anymore during S2, as indicated by the horizontal blue lowess curve. Only 3% of the Variance of S2 data are explained by S1 data. This pattern could have several explanations: (1) analytical overshoot of Cd analysis during S1 and corrected in S2, (2) since Cd is the most mobile metal and deposition decreased, it leached out of forest floors between surveys, or the combination of both. Based on these data (956 paired plots) an average decrease was found of -0.24 mg/kg. When this change is bootstrapped (Table 4.1), the change is clearly significant taking into account the lognormal distribution of the mean changes (lower (LME) and upper (UME) are similar).

Another pattern is seen for Zn, where the S1 concentration explains about 50% of the variance of S2 concentrations, and both concentrations share a high index of agreement ($d=0.8$) (see Equation 3.8). As for all metals, the lowess curve lies well below the 1:1 line and the higher the concentration, the larger the decrease in absolute concentration between surveys. Again this decrease is highly significant (Table 4.1),

Nickel and chromium temporal changes show a similar pattern. Ni concentration in forest floors decreases on average with 2.96 mg/kg and Cr with 3.81 mg/kg, whereas Ni is better correlated among surveys than Cr.

Higher correlations are found for Cu and Pb, metals strongly bound to organic materials in forest floors. S1 concentrations explain 61 and 73% of the variance of S2 concentrations respectively. Cu concentration decreased on average with 2.91 mg/kg and with Pb 18.6 mg/kg. The agreement between S1 and S2 survey data for the metals of interest decreased in the order: Zn = Pb > Cu > Ni > Cd > Cr.

Overall, for all metals the bias corrected mean (BCmean) is negative indicating a decrease in concentration and this decrease is significant since the $CI_{95\%}$ does not encompass zero (Table 4.1), taking into account the outlying samples. The distribution of differences approaches normality for Cd, unlike for the other metals where lower and upper margin of errors are different, indicating right-skewed and sometimes lognormal distributions. For

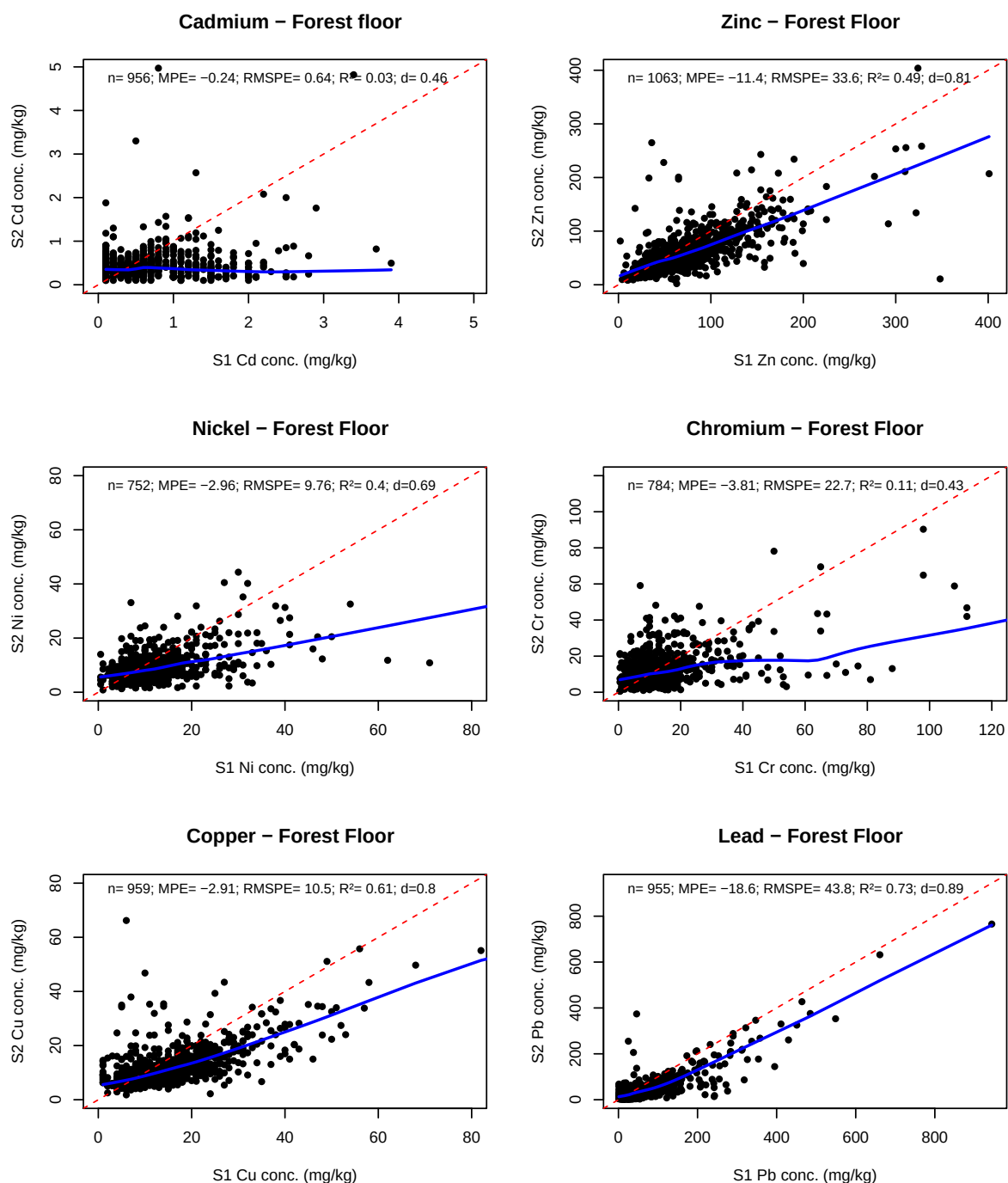


Figure 4.43: Write caption here.

Cd, Pb and Zn the coefficient of variation (CV) is small, so most LI plots (countries) show a similar pattern of change. In contrast, CV of Cr is high indicating large differences among plots and/or countries and since the index of agreement is also lowest, variable changes between paired plots as well.

When using the range of the $CI_{95\%}$ (CIR) each observation can be classified as a decrease, increase or no significant change (see M&M section).

Table 4.1: Bootstrapped mean concentration (mg/kg) temporal change between surveys and its margin of error of heavy metals the forest floor.

Metal	BCmean	P _{2.5}	P _{97.5}	LME	UME	CIR	CV
Cd	-0.24	-0.282	-0.207	0.038	0.036	0.075	7.7
Zn	-11.38	-13.35	-9.56	1.97	1.82	3.79	8.33
Ni	-2.96	-3.79	-2.41	0.83	0.55	1.38	11.6
Cr	-2.81	-4.94	-1.57	2.13	1.23	3.37	29.9
Cu	-2.91	-3.66	-2.34	0.75	0.57	1.32	11.4
Pb	-18.6	-21.23	-16.02	2.63	2.58	5.21	7.0

Table 4.2: Direction of changed number of plots for organic layer concentrations between surveys

Metal	Nb pairs	Decrease	NS change	Increase	Decrease	NS change	Increase
					%	%	%
Cd	956	567	143	237	60.2	15	24.8
Zn	1063	639	168	256	60.1	15.8	24.1
Ni	752	401	175	176	53.3	23.3	23.4
Cr	784	277	290	217	35.3	37.0	27.7
Cu	959	494	253	212	51.5	26.4	22.1
Pb	955	596	229	130	62.4	24.0	13.6

Except for Cr a significant decrease is found in more than half of all paired plots. For Pb 62% of the plots show a decrease. No significant change is found for 15 to 37% of the plots depending on the heavy metal. About a quarter of plots still show increasing concentrations in the forest floor except for Pb.

4.3.2 TEMPORAL CHANGE IN MINERAL TOPSOIL

There are only a few hundreds of LI plots with paired survey observations of heavy metal concentrations in the mineral topsoil. Figure 4.44 shows for 6 heavy metals (no paired data for Hg) how well S1 concentrations are related to S2 concentrations, as indicated by the prediction quality indices in the topline. Cadmium and Chromium concentrations of S1 are poor predictors of their concentration in S2. For Cd, only 32% of the variation in S2 is explained by S1 concentrations, for Cr this is even less (26%). The blue lowess curves indicate a substantial number of sites where high concentrations in S1 are paired with low concentrations in S2. These sites are predominantly Portuguese plots which might indicate an analytical or reporting anomaly. For the 359 Cd pairs, there is an average decrease (MPE) of 0.21 mg/kg over time and for Cr 10.6 mg/kg. For Cr this decrease is mainly found for concentrations greater than 30 mg/kg. Table 4.3 lists the bootstrapped mean difference for all metals, showing that decreases of Cd and Cr are clearly significant, in contrast to Zn where no significant temporal change is found.

Zn concentration from S1 explains the concentration from S2 for 83% (i.e. both observations are highly correlated). The lowess curve is close to the 1:1 line and in the lower range (< 150 mg/kg) the concentrations in S2 are slightly higher than in S1, indicated by a positive MPE. Similarly Pb is very well correlated between surveys explaining 82% of the variance, and an overall significant decrease of 4.21 mg/kg, mainly in the higher range.

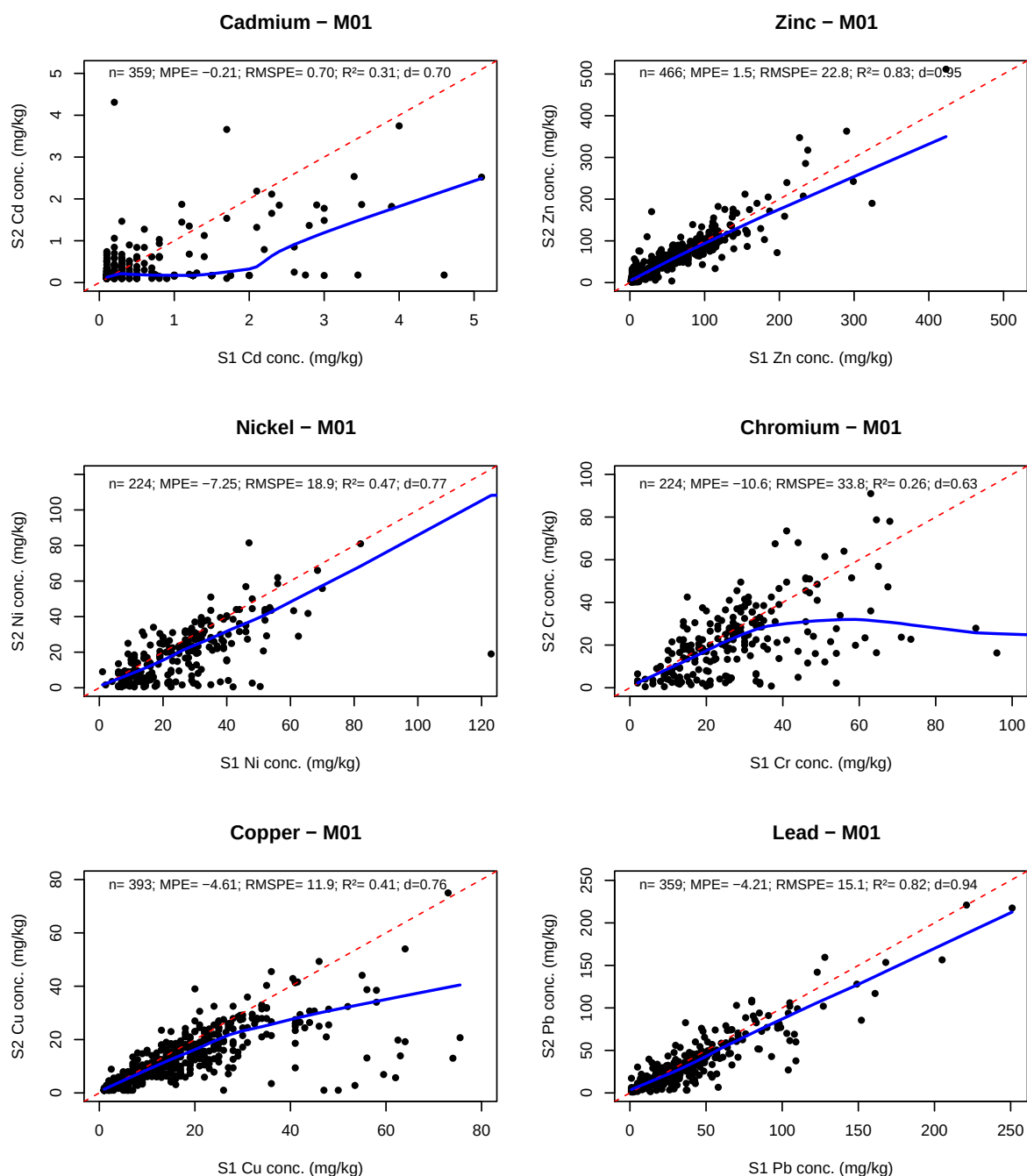


Figure 4.44: Scatterplot of paired observations of heavy metals in the mineral topsoil (0-10 cm) in the first ($x=S1$) and second survey ($y=S2$). Dashed red line indicates 1:1 line, blue line is locally weighted regression line (lowess curve)

Ni and Cu concentrations in S1 explain respectively 41 and 47% of the variance in S2 and lowess curves show a decrease for both which is significantly different from zero (Table 4.3). For Cu the same pattern is found for Portuguese sites, with high levels in S1 but low in S2. Note these sites are representing just 4% of all observed sites and that the bulk of the plots are below the 1:1 line indicating an overall decrease in copper concentrations supported the bootstrapping.

Table 4.3: Bootstrapped mean concentration (mg/kg) temporal change between surveys and its margin of error of heavy metals in the 0-10 cm mineral topsoil.

Metal	Bmean	P _{2.5}	P _{97.5}	LME	UME	TE	ME	CV
Cd	-0.21	-0.284	-0.145	0.074	0.065	0.139	0.069	16.523
Zn	1.49	-0.49	3.64	1.98	2.15	4.13	2.07	69.56
Ni	-7.25	-10.39	-5.43	3.14	1.82	4.96	2.48	17.1
Cr	-10.61	-16	-7.11	5.39	3.5	8.89	4.45	20.95
Cu	-4.61	-5.74	-3.54	1.14	1.06	2.2	1.1	11.94
Pb	-4.21	-5.8	-2.72	1.6	1.49	3.09	1.54	18.36

The index of 'temporal' agreement (d) decreases from very high for Zn and Pb, to medium agreement for Cu, Ni and Cd and lowest for Cr. This is the same order as found for forest floors. It evidences the persistence of heavy metals in mineral soil and forest floors, and is especially important for Pb, Cu and Zn.

4.4 MAPS OF SOIL POLLUTION INDICES

4.4.1 GEO-ACCUMULATION INDEX

The Geo-accumulation Index (I_{geo}) provides an assessment of soil contamination based on the ratio between the content of heavy metals in topsoils versus subsoils (Formula 3.2). An I_{geo} higher than 1 indicates moderate to strong pollution. The most common heavy metal occurring in high levels in polluted forest soils is Pb (53% of plots with I_{geo} higher than 1), followed by Hg (20%), Cd (8%), Cu (6%) and Zn (5%). Cr (2%) and Ni (1.6%) were least frequently encountered.

Soils enriched with Pb are found throughout the European continent (Figure 4.45). Out of all heavy metals, Pb pollution is most widespread.

Although data-availability on Hg pollution is limited, 20% of the sampling sites were classified as polluted with Hg (Figure 4.46). Areas with strong Hg pollution include North Rhine-Westphalia and eastern Slovakia.

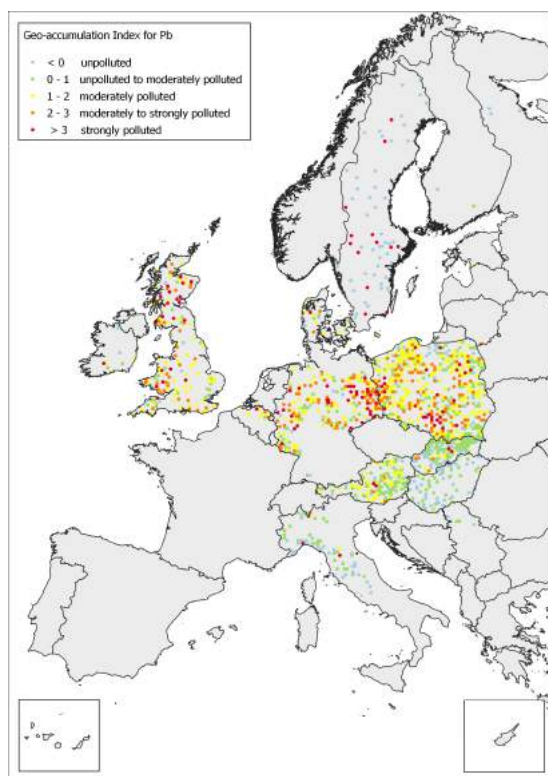


Figure 4.45: Geo-accumulation index for lead.

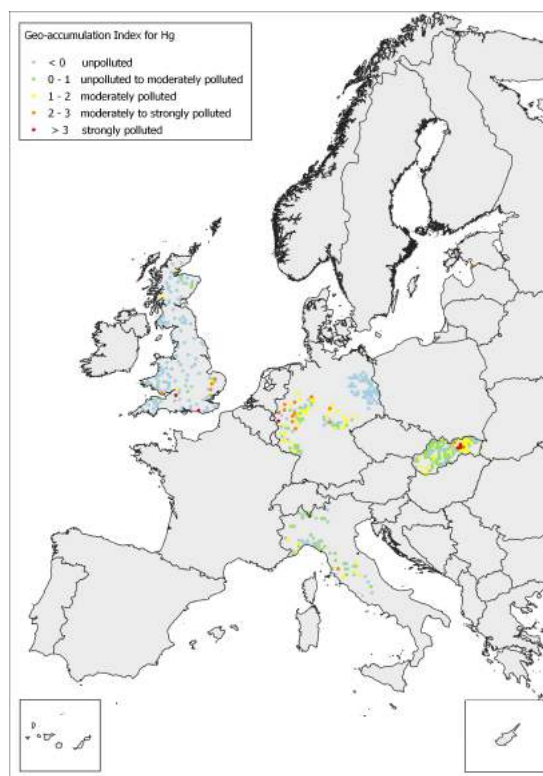


Figure 4.46: Geo-accumulation index for mercury.

For Cd, 8% of the sampling sites are classified as polluted. Pollution hotspots can be found in southern Poland (Figure 4.47). Pollution with Cu arises in 6% of the sampling locations, with elevated Cu levels scattered across the map (Figure 4.48). Zn pollution is encountered in 5% of the sampling sites (Figure 4.49).

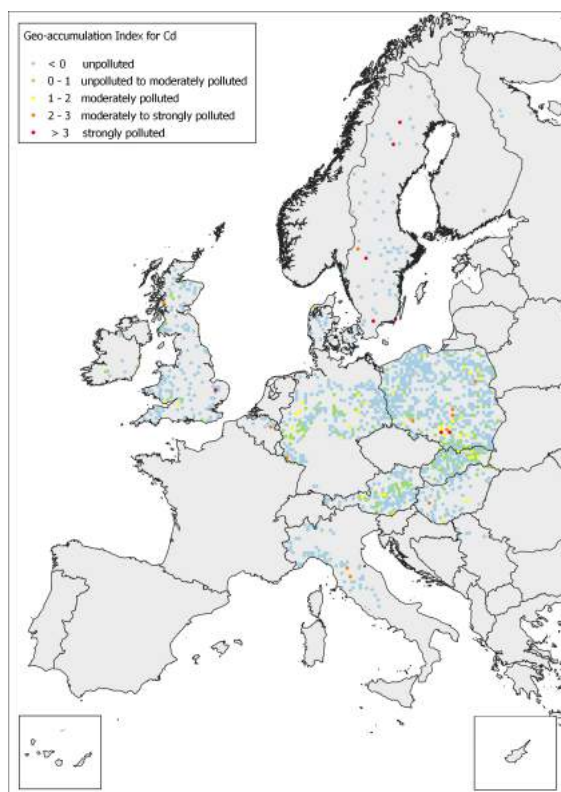


Figure 4.47: Geo-accumulation index for cadmium.

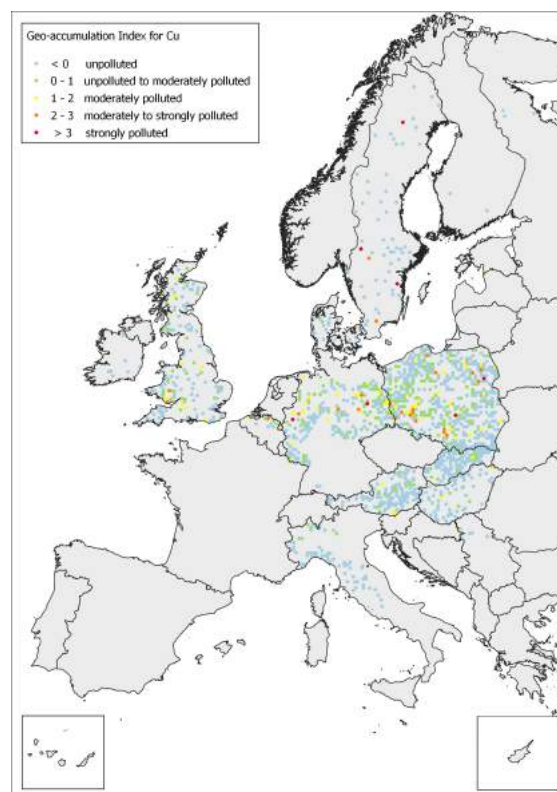


Figure 4.48: Geo-accumulation index for copper.

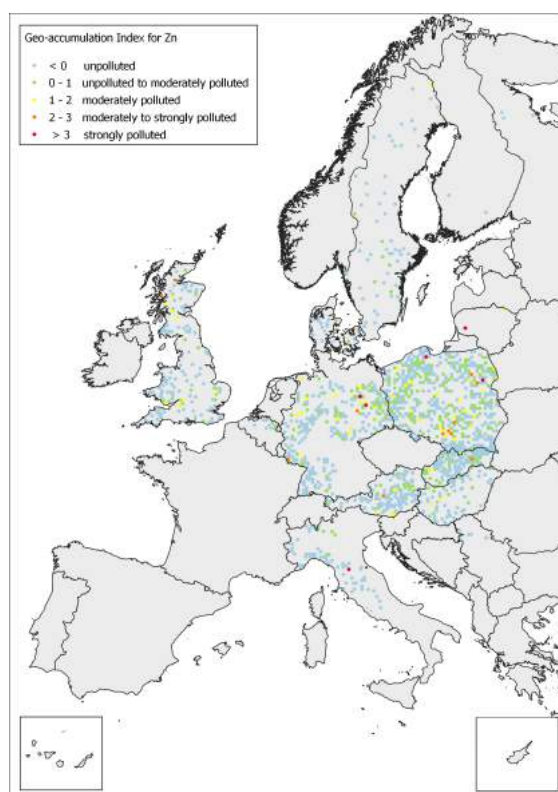


Figure 4.49: Geo-accumulation index for zinc.

Relatively few sampling sites are contaminated with Cr and Ni, 2% and 1.6% respectively. Some strongly polluted sites are located in southern Sweden (Figure 4.50, Figure 4.51) .

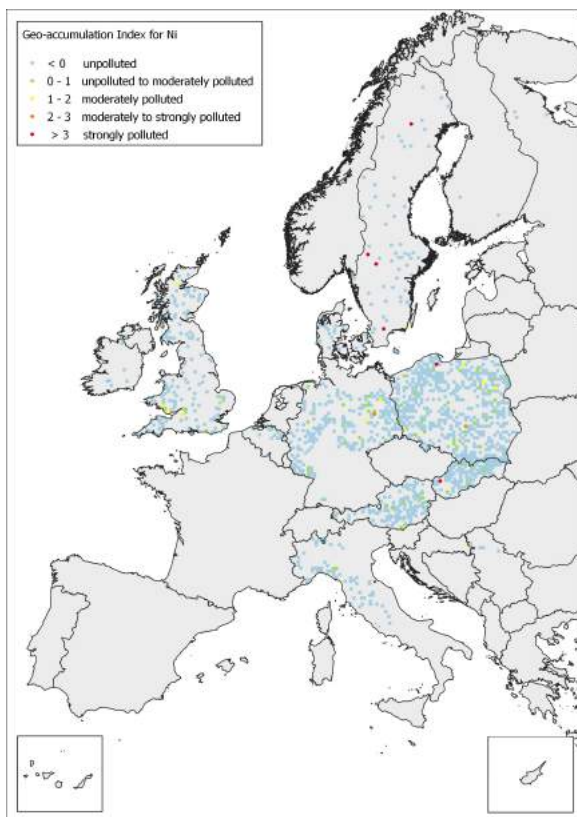


Figure 4.50: Geo-accumulation index for nickel.

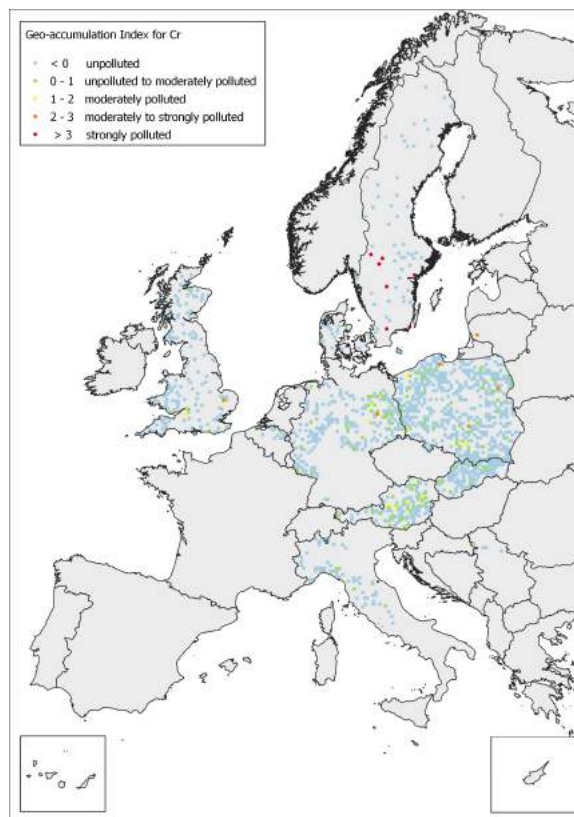


Figure 4.51: Geo-accumulation index for chromium.

4.4.2 NEMOROW POLLUTION INDEX

The Nemorow Pollution Index assesses the overall degree of soil contamination through the combined evaluation of the soil contamination caused by each individual heavy metal (Formula 3.3). For the calculation of the single pollution indices (P_{ij} in Formula 3.3) the same mechanism was used as for I_{geo} : comparing the topsoil concentration and subsoil concentration. Preferably, subsoil concentrations of the fixed layer M48 (40 - 80 cm depth) were used. In case these were not available, the heavy metal concentration in the M24 layer (20 - 40 cm depth) were used to compare to topsoil concentrations in the M01 layer (0 - 10 cm).

The limited geographic extent of $PI_{Nemorow}$ is due to the lack of data on heavy metals in deeper soil layers. Only 6% of the sampling sites is classified as clean or "pristine" and 26 % of the sites are on the verge of being classified as polluted (Figure 4.52). A relatively high share of sites (55%) is classified as "slightly polluted". The categories of moderate and heavy pollution make up 7% and 6% of the sampled sites respectively.

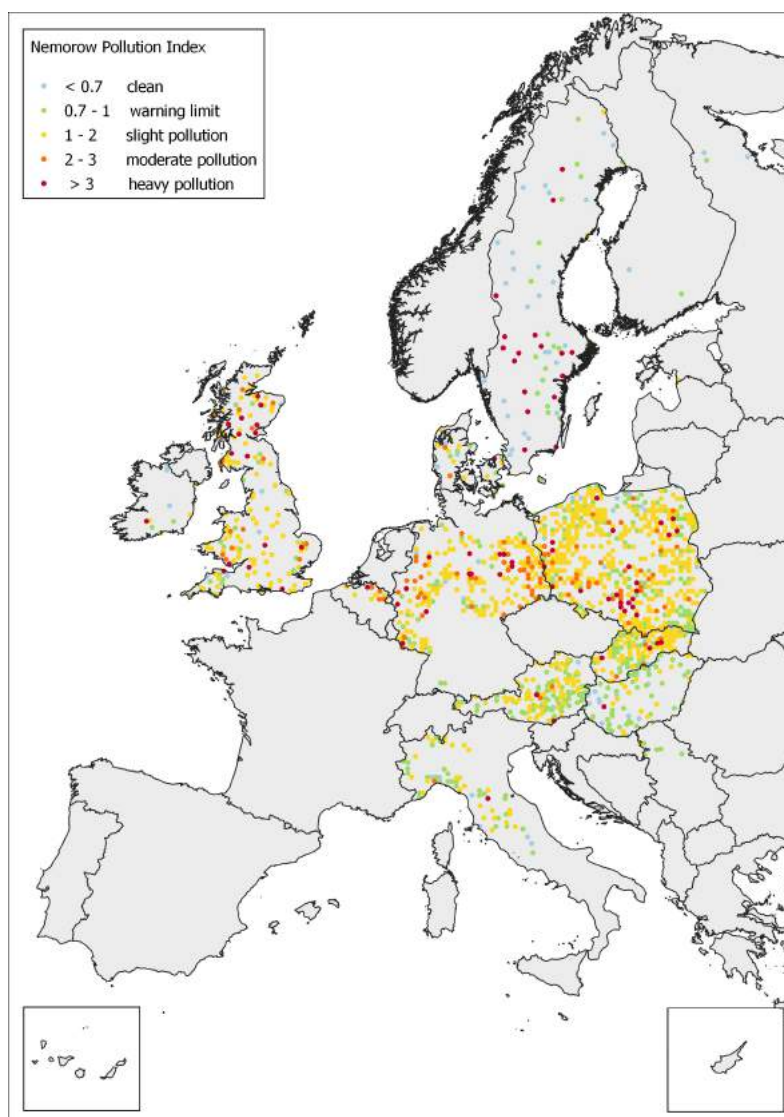


Figure 4.52: Nemorow Pollution index

4.5 CORRELATION BETWEEN HEAVY METALS

Spearman's rank correlation coefficients were used to investigate the correlations between heavy metals in forest soils (Formula 3.4). Both in the forest floor and forest topsoil, all correlations were significant with all p-values < 0.005. The correlation between heavy metals is generally stronger in the forest mineral topsoil than in the forest floor (Figure 4.53).

Ni and Cr have the strongest correlation, with a ρ of 0.85 and 0.89 in the forest floor and forest topsoil respectively. The couple Ni-Cr correlates badly with other metals, except for Cu. Correlations are weakest for Hg, especially in the forest floor. This could be due to the diverging nature and chemistry of this metal.

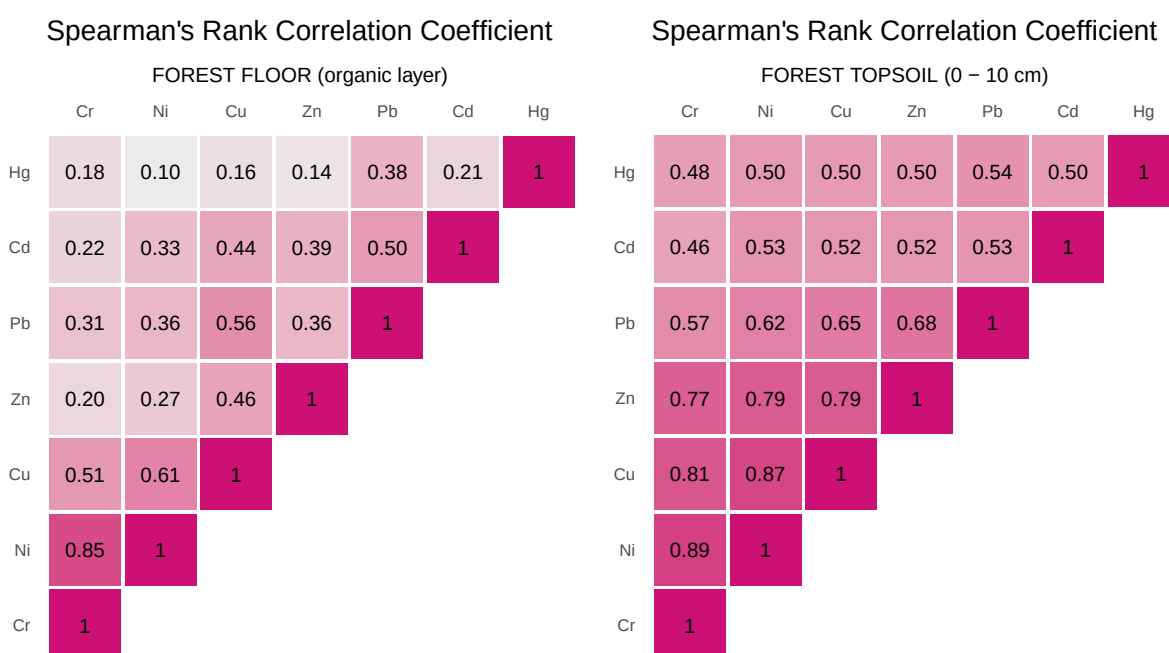


Figure 4.53: Spearman's rank correlation coefficient between heavy metals in the forest floor (left) and the forest topsoil (right).

CHAPTER 5

DISCUSSION

5.1 BASELINE AND CRITICAL LEVELS

Most European countries have developed screening values for inorganic soil contaminants as part of their legislation for soil quality assessment and possible sanitation or remedial actions (Carlon, 2007).

Although screening values have various denominations and meanings among countries, like guidance values, target and intervention values, maximum acceptable concentrations, cut off values, trigger values, environmental quality objectives, etc, similar types of screening values could be discerned: 1) reference values (referring to background or baseline values), 2) trigger values (warnings for starting investigation) and 3) intervention values (initiating actions like clean-up or sanitation).

Another common practice is differentiating screening values among land-uses or 'sensitive or in-sensitive soils'. Obviously heavy metal contamination should be kept as low as possible in agricultural soils while in industrial areas this is less critical. Exceeding a trigger value could for example prohibit a specific sensitive' landuse.

In this study we compiled from the review of Carlon (2007) and national studies specific heavy metal concentration levels applicable to forest soils regarding their a) reference levels (RL), b) trigger values (TV) and c) critical levels (CL). Trigger values are often linked with maximum allowable concentrations (MAC) and are in between RL and CL as suggested by Tyler (1992). Basically, below the TV, there is a negligible ecotoxicological risk, between TV and CL there is contamination (risk for sensitive species), and above CL an unacceptable ecotoxicological risk for various organisms exist (e.g. indicated by effect or lethal concentrations EC50, LC50) and the soil can be classified as polluted.

These levels are readily compared with the observed S1 and S2 data and their derived baseline and critical levels based on S2 data.

5.1.1 REFERENCE LEVELS FOR MINERAL SOILS

We found reference values from 9 countries for the trace metals of interest and included As for completeness (Table 5.1). For Cr only total or trivalent Cr is reported, Levels for Cr(VI) species are lacking in many national regulatory frameworks.

Reference levels of Germany and Lithuania were ranging according to texture class of the soils, so we reported the full range. The average of this range was used when computing the overall median value.

For **cadmium**, reference levels are below 1 mg/kg, except for the German precautionary values for heavy soils. Median value is 0.35 mg/kg which may be accepted as common baseline for Europe.

This baseline value may be compared with our estimated values by biogeographical region (Table 5.2). Estimated average Cd baseline for mineral topsoil ranges from less than 0.1 (Mediterranean zone) to 0.32 mg/kg in Alpine region, with European average of 0.17 mg/kg.

Zinc reference levels in mineral soils range from 26 mg/kg in Lithuania up to 200 mg/kg in German clayey soils, and median value is around 100 mg/kg. Zinc is by far the heavy metal present in the highest concentration under unpolluted conditions.

Our estimated BL concentration ranges from 14.8 mg/kg in Boreal zone to 72.9 mg/kg in Alpine region. The European average is 42.4 mg/kg which is less than half the median reference of national regulatory frameworks.

Nickel concentrations range from 10 to 70 mg/kg (again from German max range) and median value yields 20 mg/kg, but the double is reported in Great Britain and Czech Republic.

Our estimated BL is just 12.3 mg/kg and around 20 mg/kg in Alpine and Pannonian biogeographical regions (Table 5.2).

Table 5.1: Reference levels for heavy metals (mg/kg) applicable to forest soils from national legislative screening guidelines

Metal	DE [1]	BE-F [2]	BE-W [3]	UK [4]	CZ [5]	DK [6]	LT [7]	SR [8]	RO [9]	FR [10]	MEDIAN
Cd	0.4-1.5	0.7	0.2	1	0.4	0.3	0.15-0.2	0.3	1	0.21	0.35
Zn	60-200	77	67	-	105	100	26-36	40	100	98	98
Ni	15-70	16	24	42	45	10	12-18	10	20	-	20
Cr(III)*	30-100	62	34	-	55	-	30-44	10	30	-	37
Cu	20-60	20	14	62	45	30	8.1-11	20	20	14.5	20
Pb	40-100	31	25	180	55	50	15	30	20	40.7	35.9
Hg	0.2-0.3	0.1	0.05	1	0.3	0.1	0.075-0.1	0.3	0.1	-	0.1
As	10-20	16	12	32	15	10	2.5-3.6	5	-	-	13.5

* Cr(VI) is considered more toxic and other levels apply

[1] German precautionary values valid for soils with < 8% organic matter by mass (Wellbrock and Bolte, 2019).

[2] Flemish soil sanitation standards for landuse type I (Nature and Forest areas (OVAM, 2009).

[3] Wallonian Reference value for natural areas (Carlton, 2007)

[4] Normal background concentrations for the principal domain (Ander et al., 2013)

[5] Czech Republic - Decree No. 13/1994 Sb. of Ministry of Environment- agricultural soil protection. Precautionary values for normal soils (Carlton, 2007)

[6] Danish ecotoxicological soil quality criteria for selected organic and inorganic compounds (Carlton, 2007)

[7] Lithuanian background concentrations for sandy to clayey soils (Carlton, 2007)

[8] Slovakian reference levels (uncorrected for clay or organic matter) (Carlton, 2007)

[9] Romanian guideline values for total contents of heavy metals (normal baseline values) (Pope et al., 2005)

[10] French pedo-geochemical background reference values. Median values North of France. (Baize and Sterckeman, 2001)

For trivalent **chromium** a median value of 37 mg/kg is computed as reference level, whereas the BL estimated in this study is half of that value and in all biogeographical regions the BL is less than 30 mg/kg.

Median value of national reference levels for **copper** is 20 mg/kg, whereas the estimated European BL is exactly half (Table 5.2).

For **lead** the median reference level is 36 mg/kg, again higher than the European BL of 24.6 mg/kg but close to the BL in Alpine and Atlantic regions.

Table 5.2: Estimated baseline concentrations (mg/kg) for forest floors (FF) and mineral topsoils (0-10 cm, M01) by biogeographical region

Biogeographical region	Cd		Zn		Ni		Cr		Cu		Pb		Hg	
	FF	M01	FF	M01	FF	M01	FF	M01	FF	M01	FF	M01	FF	M01
Boreal	0.25	<0.1	49.3	14.8	4.33	1.96	5.77	6.47	5.64	2.39	14.8	7.6	0.2	0.07
Atlantic	0.29	0.21	54.1	29.3	7.03	7.43	9.38	14.7	11.1	7	30.1	31.6	0.03	0.09
Continental	0.38	0.11	57.1	32.6	9.98	7.1	13.9	13.3	11.7	5.61	28.7	24.5	0.23	0.09
Alpine	0.43	0.32	79.1	72.9	9.75	20.1	11.3	29.1	12.4	15.5	28.8	40.7	0.18	0.13
Pannonian	0.39	0.19	60.3	52.6	14.5	20.5	17.9	26.4	14.8	15.6	35.2	18.9	-	-
Mediterranean	0.1	0.1	43.6	52	14.7	16.7	26.1	25.4	11.6	13.9	12.5	24.5	0.18	0.09
European average	0.31	0.17	57.3	42.4	10.0	12.3	14.1	19.2	11.2	10.0	25.0	24.6	0.16	0.09

Finally for **mercury** a median value may be inferred of 0.1 mg/kg, which is very close to the average European BL of 0.09 mg/kg. In Alpine region this BL is slightly higher (i.e. 0.13 mg/kg).

From this comparison one can conclude that the estimated baselines in Table 5.2 are always less than (and often half) the median values of national legislative reference values, indicating that the estimated baselines are on the safe side compared to most national standards. Presumably our estimated BL indicate indeed pristine conditions which may be expected from the majority of forest soils.

5.1.2 REFERENCE LEVELS FOR FOREST FLOORS AND ORGANIC SOILS

According to Table 5.2, the BL values for forest floors are greater than for mineral soils for Cd, Zn and Hg, similar for Cu and Pb but smaller for Ni and Cr. The same pattern holds true for most biogeographical regions.

We did not find any review on national legislative screening values for forest floors or organic soils. However, national reference values for specific metals are published (predominantly in technical reports) and making a critical review of these would be beneficial, but this could not be performed in this short study.

Tyler (1992) published a report on critical concentrations of heavy metals in the Mor horizons of Swedish forests. His baseline values for Mor humusforms are presented in Table 5.3.

De Vos (1997) determined baseline values for 50 soil fauna plots in Flanders and computed critical levels with the Tyler method. Later in 2003, baseline values for Flanders were computed for 270 forest sites, as listed in Table 5.3. In Belgium, heavy metal pollution is much more elevated as in Sweden, as can be observed for Zn, Cr, Cu and Pb.

Estimates for baseline values in forest floors for **cadmium** range from 0.1 to 0.43 mg/kg. The 0.71 mg/kg Cd Tyler (1992) reported is about 3 times higher than our estimated baseline for Boreal zone (0.25 mg/kg) and double the European average of 0.31 mg/kg. Same factor holds true for the Belgian baseline value.

The European average BL of 57.3 mg/kg for **zinc** conforms with the baseline of Tyler (1992) but is lower than the baseline of De Vos (2003) for Belgium, exceeding BLs of all bioge-

Table 5.3: References for baseline values of forest floors from literature

Country	Type	Cd	Zn	Ni	Cr	Cu	Pb	Hg	Reference
Sweden	Mor	0.71	58.2	-	2.94	7.1	47.8	0.245	Tyler (1992)
Belgium	all forest floors	0.8	95	22	31	17	88	-	De Vos (2003)

graphical regions. Hence, the Belgian baseline may be too high due to the known historical pollution by Zn and Cd. A European reference, at biogeographical level, would be better justified.

For **nickel**, the Belgian baseline of 20 mg/kg for forest floors is double the European average, same as for **chromium** 31 mg/kg (Belgium) versus 14.1 mg/kg (Europe). Interestingly, Tyler (1992) computed a Cr baseline of 2.9 mg/kg, being a factor 10 lower than the Belgian one, but half the estimated BL for the Boreal zone (5.77 mg/kg).

Copper baseline in Sweden was set to 7.1 mg/kg compared to the estimated BL for Boreal zone of 5.6 mg/kg, whereas the Belgian BL is 17 mg/kg compared to an Atlantic zone BL of 11.1 mg/kg.

Also for **lead**, the European baseline of 25 mg/kg is about half of the BL values applied by Tyler (1992) and one-third of the Belgian one. Note that the estimated BL for Pb is double in the Atlantic region compared to the Boreal zone, so a similar ratio as found in Table 5.3.

For **mercury**, Tyler (1992) calculated a BL of 0.245 mg/kg, which is higher than the Boreal baseline (0.2 mg/kg) and European average (0.16 mg/kg). Note the very low estimated baseline for the Atlantic zone compared to the other zones, which may be an artefact because of limited Hg measurements for the Atlantic region in our dataset.

Also for forest floors, one can conclude that the estimated baselines are generally lower than the national baselines. The use of biogeographically based reference baselines is generally supported.

5.1.3 CRITICAL LEVELS FOR MINERAL SOILS

Critical levels (CL) can be inferred from human- toxicological or ecotoxicological studies, by empirical studies on dose-effect concentrations or soil toxicological modelling. For the selection of CL we preferred data from effect concentrations by ecotoxicological and empirical studies, but this was not always clear from the source data,

Table 5.4 lists legislative critical levels from 12 countries, the median value derived for each heavy metal and the critical levels reported from the first Soil Condition Report (Vanmechelen et al., 1997).

National critical levels for **cadmium** in mineral soils range from 1 mg/kg (Austria, Czech Republic and Sweden) up to 10 mg/kg (Finland and Belgium-Wallonia). The median value at EU level is 2.5 mg/kg. This is lower than the critical level of 3.5 mg/kg set in the first FSCR, taken from Tyler (1992). Kabata-Pendias and Pendias (1984) reported that a cadmium amount of 3 mg/kg in the mineral soil may cause toxic effects in plants.

Table 5.4: Heavy metal critical levels (mg/kg) and maximum allowable concentrations applicable to forest areas for selected EU countries

Metal	BE-F [1]	BE-W [2]	AU [3]	CZ [4]	FI [5]	DL [6]	IT [7]	LT [8]	PL [9]	SR [10]	SW [11]	RO [12]	MEDIAN	ICPF [13]
Cd	2	10	1	1	10	2	2	3	4	5	1	3	2.5	3.5
Zn	333	215	300	200	250	-	150	300	300	500	700	300	300	300
Ni	93	100	60	80	100	70	120	75	100	100	150	75	96.5	95
Cr	130	95	100	200	200	200	150	100	150	250	250	100	150	75
Cu	120	80	100	100	150	-	120	100	150	100	200	100	100	60
Pb	200	80	100	140	200	200	100	100	100	150	300	50	120	500
Hg	2.9	5	1	0.8	2	10	1	1.5	2	2	5	1	2	-
As	58	120	20	30	50	25	20	10	20	30	15	-	25	-

[1] Belgium-Flanders - Clean up levels for standard soil with 10% clay, 2% organic matter and pH-KCl=5 (OVAM, 2009)

[2] Belgium-Wallonia - Intervention value for natural areas (Carlton, 2007)

[3] Austrian Standard S 2088-2 (2000-06-01) Trigger values for pollutant concentrations in topsoil used for agricultural or gardening purposes, as well as non agrarian ecosystems as well as non-agrarian ecosystems (Carlton, 2007)

[4] Czech Republic - Decree No. 13/1994 Sb. of Ministry of Environment, regulating some details of agricultural soil protection. Aqua regia MAC levels for non-light soils (Carlton, 2007)

[5] Finnish lower guideline value for soil contamination (Carlton, 2007)

[6] German Trigger levels for gardens and playing grounds (Carlton, 2007)

[7] Italian Limit values for surface and subsurface soil for Public (green) landuse (Carlton, 2007)

[8] Lithuanian maximum admissible concentrations (MAC) of dangerous substances in soil (Carlton, 2007)

[9] Poland - Soil quality standards for group B landuses (agricultural and forest land), data for topsoil 0-30 cm. Max permissible concentration (Carlton, 2007)

[10] Slovakian maximum allowable limits (B-limits) (uncorrected for clay or organic matter) (Carlton, 2007)

[11] Swedish EPA - Guideline values for contaminated soils - less sensitive land use, groundwater protection (Carlton, 2007)

[12] Romanian guideline values for total contents of heavy metals (alert values for sensitive soils) (Pope et al., 2005) [13] ICP Forests First soil condition report (Vanmechelen et al., 1997)

For **zinc** the median values of national soil critical levels is 300 mg/kg, exactly the same level as suggested in the first Forest Soil condition report (1stFSCR) (Vanmechelen et al., 1997). Most countries have values around this value except for Sweden (700 mg/kg).

The median critical level for **nickel** is 96.5 mg/kg conforming again with the level set in 1stFSCR. In contrast **chromium** critical level is mostly around 150 mg/kg, double as much as applied in the 1stFSCR.

For **copper** the median CL is set to 100 mg/kg, while in the 1stFSCR it was 60 mg/kg.

The most important change is for **lead**, for which the median critical value of all countries is 120 mg/kg, much smaller than the 500 mg/kg reported in the 1stFSCR.

The median critical level for **mercury** set by the countries is 2 mg/kg and for **arsenic**, not covered in this study, this is 25 mg/kg. The latter is added just for completeness.

Table 5.5 provides an overview of the baseline, trigger and critical values for all metals related to national legislative screening values for mineral soil.

Table 5.5: Overview of mineral topsoil baseline (BL), trigger (TV) and critical levels (CL) at the European level, based on national soil quality evaluation schemes. Values below LOQ cannot be quantified accurately.

Metal	LOQ	BL	TV	CL	CL:BL ratio
Cd	0.1	0.35	1.4	2.5	7.1
Zn	2	98	200	300	3.1
Ni	0.5	20	60	96.5	4.8
Cr	0.5	37	95	150	4.1
Cu	1	20	60	100	5.0
Pb	1	36	80	120	3.3
Hg	0.03	0.1	1	2	20.0
As		13.5	20	25	1.9

According to Tyler (1992), the trigger value is estimated as $(CL-BL)/2$ and rounded. The ratio CL:BL indicates the 'times current baseline' factor suggested by Tyler (1992) and related by him to measurable adverse effects on biota (soil organisms, plants) and soil processes

(respiration, N-transformation, ...). He found that most adverse effects show a CL:BL ratio starting from 3 to 5, depending on the metal.

Here we see that most metals show indeed CL:BL ratios below 5, except Cd (7) and Hg (20). Note also that the BL levels are way above the limit of quantification, so all concentration levels are reliably quantifiable.

Based on the evaluation scheme for concentrations in the topsoil (Table 5.5, an evaluation scheme for heavy metals stocks can easily be inferred when taking the average bulk density (i.e. 1 g/cm³) of the 0-10 cm topsoil into account (Table 5.6),

Table 5.6: Stock evaluation scheme for M01 layer

Evaluation	Cd (mg/m ²)	Zn (g/m ²)	Ni (g/m ²)	Cr (g/m ²)	Cu (g/m ²)	Pb (g/m ²)	Hg (mg/m ²)	As (g/m ²)
Background	<35	<9.8	<2	<3.7	<2	<3.6	<10	<1.35
Enriched	35-140	9.8-20	2-6	3.7-9.5	2-6	3.6-8	10-100	1.35-2
Contaminated	140-250	20-30	6-9.65	9.5-15	6-10	8-12	100-200	2-2.5
Polluted	>250	>30	>9.65	>15	>10	>12	>200	>2.5

These limits were used to present the stock evaluation maps.

5.1.4 EVALUATION OF THE EMPIRICAL DISTRIBUTIONS OF MINERAL TOPSOILS FOR LEVEL I PLOTS FOR BOTH SURVEYS

When applying the evaluation limits of Table 5.5 the number of plots qualifying for each class (background, enriched, contaminated, or polluted) may be determined from the empirical cumulative distribution function (ECDF) for each metal and for both surveys. For cadmium in mineral topsoil the ECDFs of S1 and S2 are given in Fig.5.1. The S1 distribution curve is clearly below the S2 distribution curve indicating more plots for a given concentration level in the first then in the second survey. The small table inside the figure shows the proportion of plots for each class. In the first survey 66% of all sampled LI plots are classified in the background class, while 80% during the second survey. About 5% of plots were considered polluted with Cd in the first survey but only 2% in the second.

These data are presented for all 7 metals in Figures 5.1 to 5.7, but in the latter (Hg) no data for S1 is available.

Two important conclusions can be made: (1) all metal concentrations are decreasing from the first to the second survey and some concentration ranges decrease more than others, depending on the metal and (2) overall only few percent of the level I plots is classified as polluted, 5-10% is classified as enriched and for all metals more than 50% of the level I plots is below the baseline concentration level (dashed green vertical line).

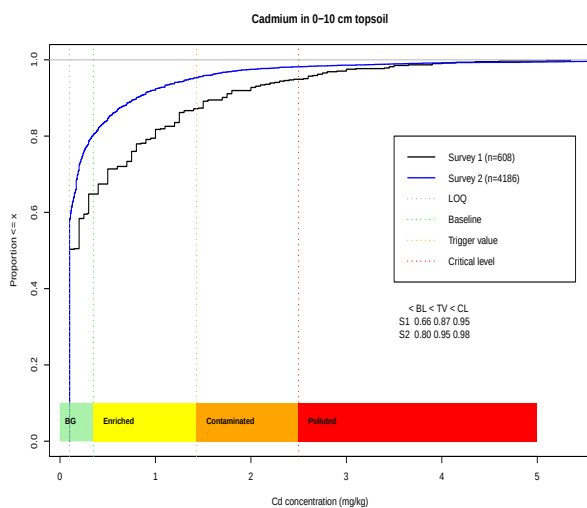


Figure 5.1: Empirical distribution function for Cd in the forest topsoil with evaluation limits.

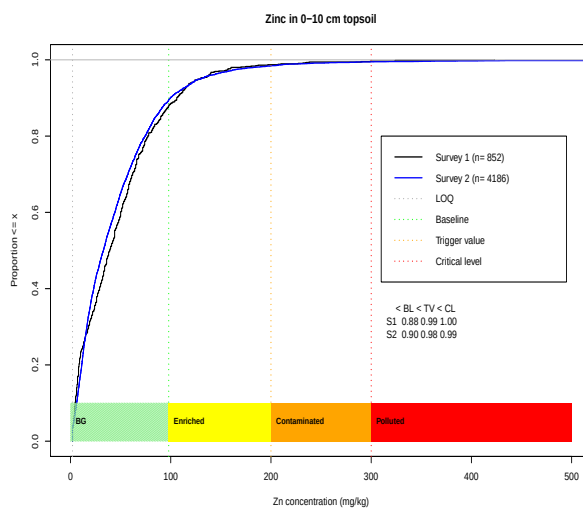


Figure 5.2: Empirical distribution function for Zn in the forest topsoil with evaluation limits.

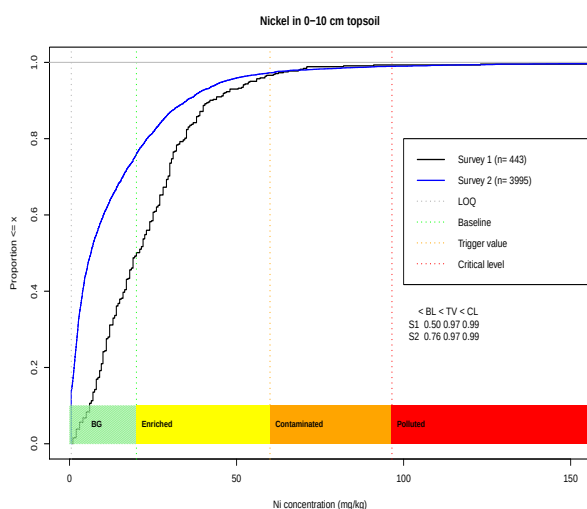


Figure 5.3: Empirical distribution function for Ni in the forest topsoil with evaluation limits.

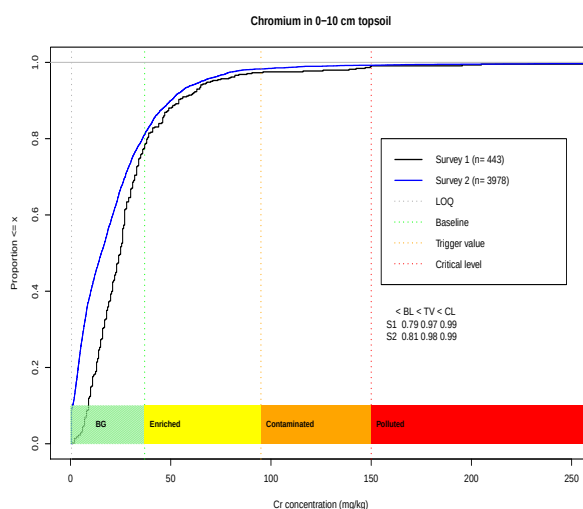


Figure 5.4: Empirical distribution function for Cr in the forest topsoil with evaluation limits.

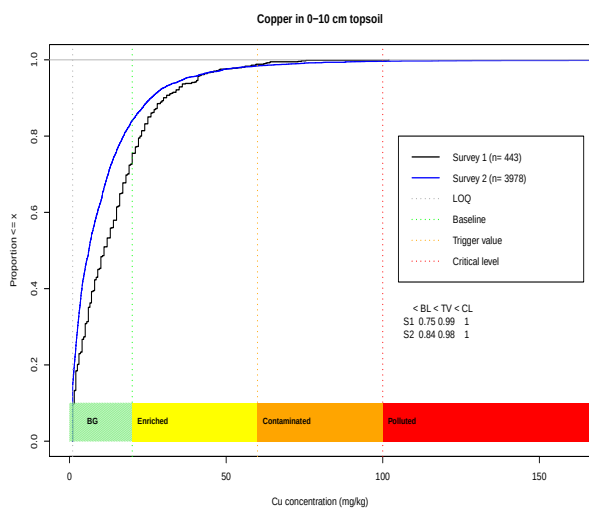


Figure 5.5: Empirical distribution function for Cu in the forest topsoil with evaluation limits.

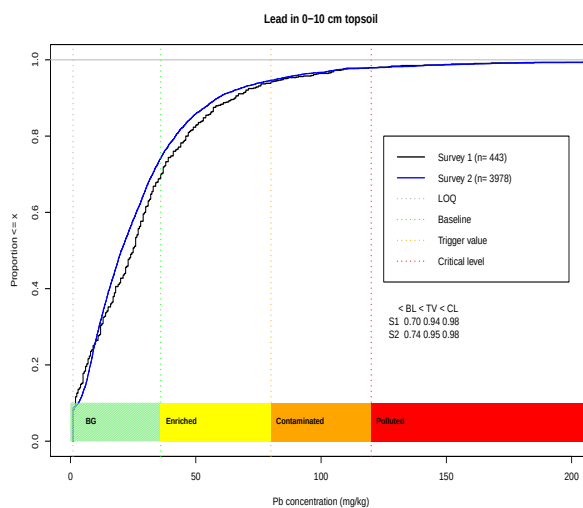


Figure 5.6: Empirical distribution function for Pb in the forest topsoil with evaluation limits.

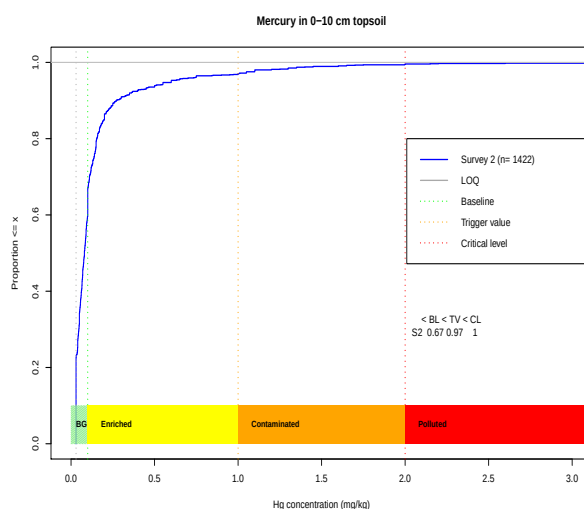


Figure 5.7: Empirical distribution function for Hg in the forest topsoil with evaluation limits.

5.1.5 CRITICAL LEVELS FOR HEAVY METALS IN FOREST FLOORS

Critical levels (CL) in forest floors are more difficult to assess than for mineral soils. Tyler (1992) estimated CL in Mor humus forms as follows: Cd: 3.5 mg/kg, Zn: 300 mg/kg, Cr: 30 mg/kg, Cu: 20 mg/kg, Pb: 150 mg/kg and Hg: 0.75 mg/kg.

De Vos (2003) developed the evaluation scheme in Fig 5.8 with critical limits that were generally higher than those of Tyler (1992), but with the same CL:BL ratio's for each of the metals. So this evaluation scheme system was in fact recalibrated for Belgian conditions.

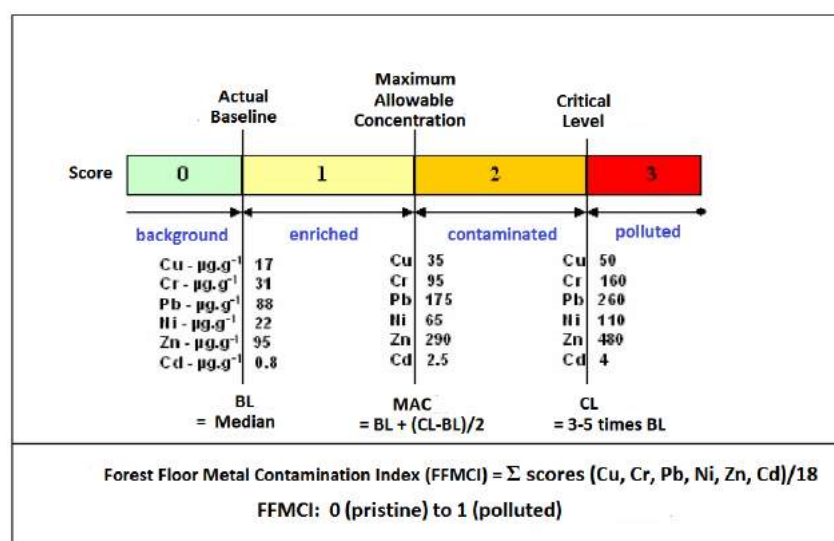


Figure 5.8: The Belgian Forest Floor contamination evaluation scheme for heavy metal concentrations and the calculated contamination index FFMCI

For any forest floor sample a score can be attributed for each heavy metal, based on the respective concentration class (see Fig 5.8). When scores for all metals are determined, the sum of scores divided by the sum of maximal scores provides a single forest floor contamination index (FFMCI). This index ranges from 0 (pristine, background concentrations) to 1 (highly polluted) forest floors.

In this study we applied the scores to the concentration levels of forest floors in S1 and S2 (Table 5.7).

Compared to S1, more than twice the number of plots could be evaluated in S2.

Using the Belgian evaluation scheme (Fig 5.8) over 75% of the FF are classified in the background range. This is the case for almost all plots for copper, but 76.5% of the plots for cadmium during S1, and 91% of the plots during S2. Consequently, about 23% and 8.5% of plots have 'enriched' Cd concentrations for S1 and S2 respectively. Less than 3% of plots are considered contaminated, mostly for Pb (Table 5.7). Similarly, when plots show polluted forest floors, this is mostly related to exceeding critical Pb concentrations.

Note the positive evolution from S1 to S2 and the general decrease in pollution levels.

Table 5.7: Percentage of plots in the first (S1) and second (S2) survey with their heavy metal concentration in forest floors classified as background, enriched, contaminated or polluted

Metal	Number of plots		Background (0)		Enriched (1)		Contamin. (2)		Polluted (3)	
	S1	S2	S1	S2	S1	S2	S1	S2	S1	S2
Cd	1419	3753	76.5	90.8	22.6	8.5	0.8	0.3	0.1	0.3
Zn	1746	3752	80.9	88.6	18.2	10.5	0.8	0.4	0.1	0.5
Ni	1104	3500	90.1	90.8	9.6	8.3	0.2	0.6	0.1	0.3
Cr	1148	3435	90.9	87.5	6.8	10.5	1.5	1.5	0.9	0.5
Cu	1559	3753	99.2	99.6	0.6	0.4	0.1	0.1	0.1	0.0
Pb	1564	3751	78.6	92.9	16.0	4.7	2.9	1.5	2.5	0.9

When calculating the contamination index (FFMCI) for the limited number of plots assessed during S1, the index ranged from 0 to 0.83, with 0.058 as the average. When considering S2 with much more plots and countries, the same range was found, but the average was 0.033, so the contamination index decreased with time. This might be related to a larger number of plots classified as background (0) in S2. However, if we consider only the paired plots ($n=1063$) then there is still an average decrease of the index of 0.031 and a maximum decrease on a specific plot of 0.28. Hence, for the countries that surveyed their FF during both surveys, the contamination index clearly decreases. However, this decrease might be partly explained by enhanced analytical accuracy for heavy metal determination in forest floor samples.

When mapping the contamination index for both surveys across Europe using the same scale (Figures 5.9 and 5.10), some specific spatial patterns emerge. A country effect is clearly visible for Lithuania. In S1 Lithuania is clearly different from Latvia, while this is not the case anymore in the S2 survey.

During S1 elevated indices are found West of Germany, East of Slovakia and along the Czech-German border. These spatial patterns roughly reappear in the S2 and are complemented with areas in North-West Slovenia, Northern Italy and North-east of Belgium. The potential is clearly shown for indicating contaminated areas by applying the FFMCI, but only if heavy metal concentrations of all 6 metals are known for all plots, full maps can be produced.

The evaluation scheme used as basis for the FFMCI could be improved and calibrated for each biogeographical region. The baseline values for each bioregion can be determined as in Table 5.2 and improved if more data from France, Switzerland, Croatia, South of Belgium (Wallonia), The Netherlands and Norway would be available. Literature reviews could help defining clear critical levels as for example in Bengtsson and Tranvik (1989). They suggested at that time for forest soil invertebrates maximum allowable metal concentrations in litter of 100-200 mg/kg Pb, <100 mg/kg Cu, <500 mg/kg Zn and 10-50 mg/kg Cd as limits that will cause no adverse effects. These limits conform with the CL presented in the evaluation scheme in Fig 5.8. Also for estimating the CL:BL ratio more ecotoxicological research is needed, linking in situ heavy metal concentrations to observable effects. Upon comparison of the CL:BL ratio's among European biogeographical regions, the hypothesis should be tested that there is no significant difference so that the same ratio's could be applied across Europe.

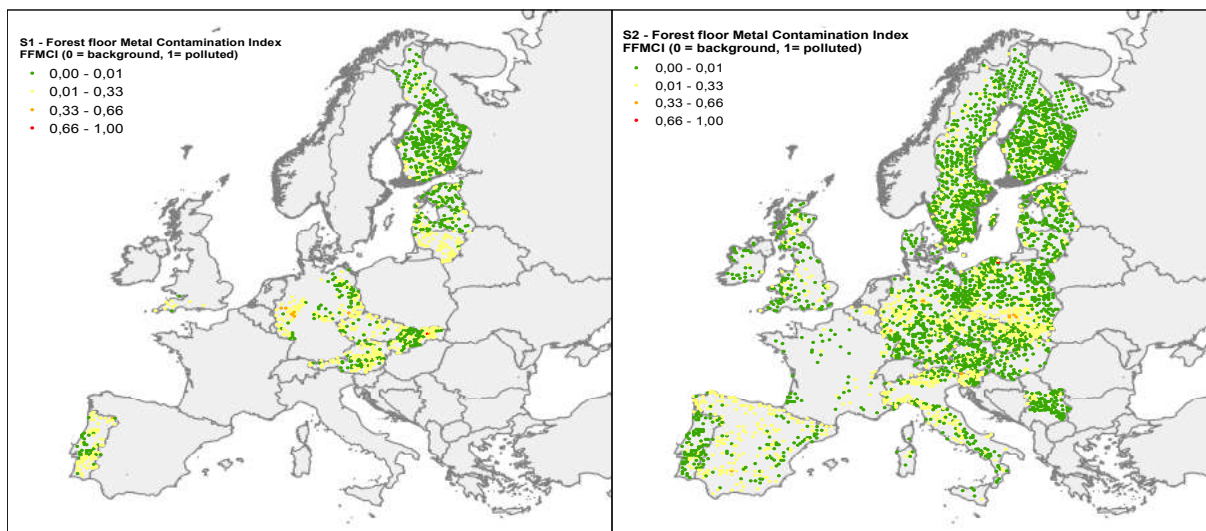


Figure 5.9: FFMCI of Level I plots of the first survey

Figure 5.10: FFMCI of Level I plots of the second survey

5.2 COMPARATIVE STUDY OF SPATIAL PATTERNS

In recent years, similar studies on spatial patterns of heavy metal concentrations in soils have been conducted. One of these studies was conducted by Tóth et al. (2016) and is based on topsoil samples collected all over the European Union (LUCAS Topsoil Survey), without differentiating between different land use types. We will discuss the differences and similarities between the maps of heavy metal concentration in forest topsoils produced in this study and the output maps produced by Tóth et al. (2016).

Another study was conducted by Frontasyeva et al. (2020) and is based on heavy metal concentrations in mosses throughout Europe. This research is part of a long-term monitoring effort coordinated by ICP Vegetation, investigating HM concentrations in mosses at five-yearly intervals. The HM concentration maps provided by this research will be compared to the maps produced in this study on heavy metal concentrations in forest floors. A qualitative assessment of the correlation between both types of maps is made.

Through the comparison with other independent HM studies we will be able to strengthen some conclusions hinted at in previous chapter, such as identifying areas with severe anthropogenic pollution.

5.2.1 HEAVY METALS FROM LUCAS TOPSOIL DATA

Tóth et al. (2016) mapped spatial distribution at 1 km resolution of Cd, Ni, Cr, Cu, Pb and Hg concentrations of ~ 23000 topsoil samples (upper 20 cm) using regression kriging. Unfortunately, Zn was not reported in their study although Zn was effectively assessed during the LUCAS 2009 and 2012 sampling campaigns.

When overlaying the Level I plots with the LUCAS HM 1km raster, a paired dataset was obtained and explored. The summary statistics of the paired dataset is provided in Table 5.8.

Table 5.8: Summary statistics of topsoil heavy metal concentrations (mg/kg) of S2 compared to LUCAS interpolations for Level I plot locations

Metal	Survey	Min.	1st Qu	Median	Mean	3rd Qu	Max.
Cd	S2	0.1	0.1	0.1	0.35	0.24	18.7
	LUCAS	0.07	0.07	0.07	0.09	0.09	1.24
Ni	S2	0.5	1.9	6.3	14.3	19.2	826
	LUCAS	1.35	5.47	10.4	14.3	18.8	235
Cr	S2	0.5	5	15.3	22.7	30.7	822
	LUCAS	2.45	9.05	14.6	18.3	23.7	168
Cu	S2	1	1.99	6.05	11.0	14.3	436
	LUCAS	1.41	5.32	8.68	10.8	13.8	111
Pb	S2	1	9.78	20.7	32.3	37	5000
	LUCAS	2.35	8.34	13.7	15.1	19.5	101
Hg	S2	0.03	0.04	0.08	0.16	0.14	12.2
	LUCAS	0.008	0.022	0.033	0.045	0.056	0.634

Note that the mean and maximum concentrations of the LUCAS dataset are generally smaller than the S2 observations. This is expected due to the averaging effect of the regression kriging between LUCAS observation points.

For each Level I location, the difference between the observation during S2 and the LUCAS observation in 2009/2012 was computed and bootstrapped to get 95% confidence intervals of the mean. Table 5.9 shows the bootstrapped values for each metal. The mean difference is not significantly different from zero for Ni and Cu, but positive for Cd, Cr, Pb and Hg indicating higher values for these metals in the forest topsoils (of Level I plots) compared to all landuses (LUCAS survey) at the EU level.

Table 5.9: Bootstrapped mean concentration (mg/kg) difference (S2-LUCAS) and S2/LUCAS ratio along with their 95% CI

Metal	mean diff	CI95LL	CI95UL	mean ratio	CI95LL	CI95UL
Cd	0.22	0.2	0.25	3.46	3.24	3.71
Ni	0.006	-0.669	1.036	0.96	0.93	1
Cr	4.39	3.58	5.46	1.23	1.19	1.27
Cu	0.19	-0.21	0.67	0.98	0.95	1.02
Pb	17.1	14.7	23.1	2.01	1.91	2.24
Hg	0.11	0.1	0.15	3.51	3.29	3.78

We also calculated the (bootstrapped) ratio of the S2 concentration relative to the LUCAS 'baseline' concentration (Table 5.9). Cd and Hg concentrations are a factor 3.5 higher than the predicted LUCAS concentrations, Pb about double as high and Cr a factor 1.23. Further details are systematically discussed for each heavy metal separately in next sections.

5.2.2 CADMIUM

A comparison between the maps in Figures 5.11 and 5.12 reveals some similar hotspots of elevated Cd concentration in Slovenia and southern Poland. However, the global patterns of Cd concentration in the United Kingdom and Spain diverge in both maps. Moreover, the

hotspots in northern Spain and Ireland visible on the map of Tóth et al. (2016) do not come back in the map of Cd concentration in forest topsoils.

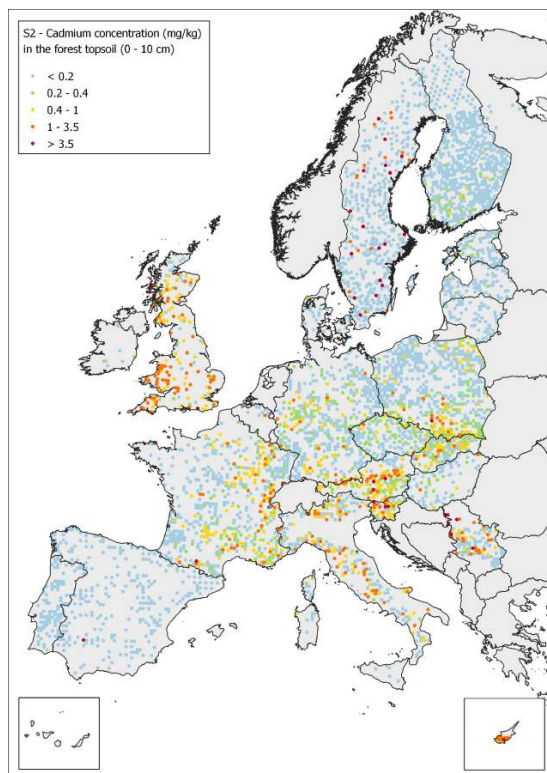


Figure 5.11: Cd concentration in forest topsoils.

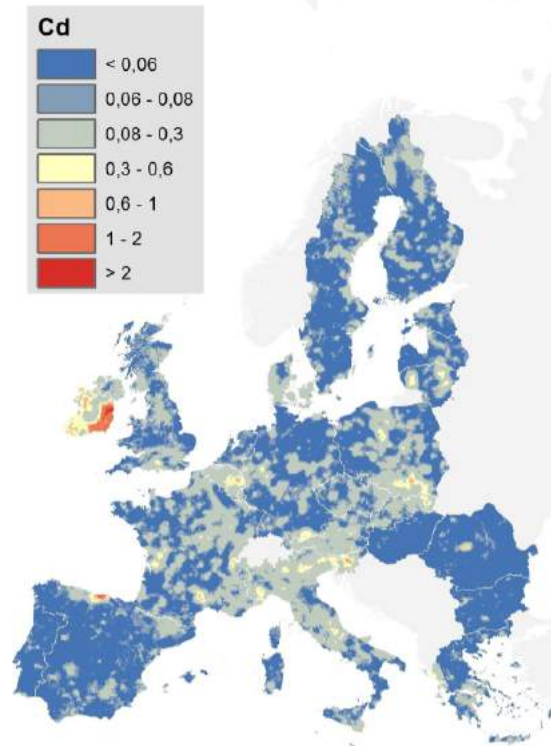


Figure 5.12: Cd concentration in topsoils of all land-use types. Adopted from Tóth et al. (2016)

Cd concentrations in forest floors are generally higher than in mosses. The spatial patterns of the concentrations in forest floors and mosses (Figures 5.13 and 5.14) are similar, with hotspots in Flanders, Slovenia and western Germany. Moreover, the spatial patterns of Cd concentration in mosses (Figure 5.14) do not reflect the spatial patterns of Cd concentration in the forest topsoil (Figure 5.11). This leads us to suspect that forest soils are good archives for historic pollution, but are not suitable as a proxy for atmospheric deposition of heavy metals given their capacity of accumulating heavy metals.

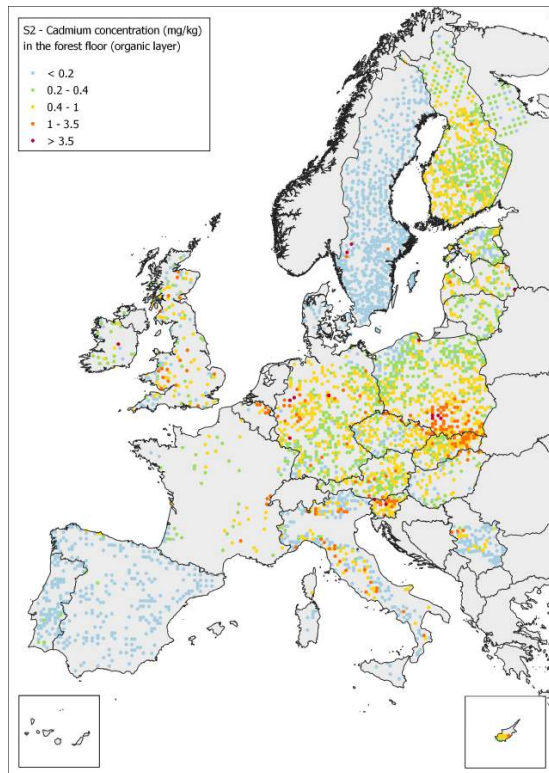


Figure 5.13: Cd concentration in forest floors.

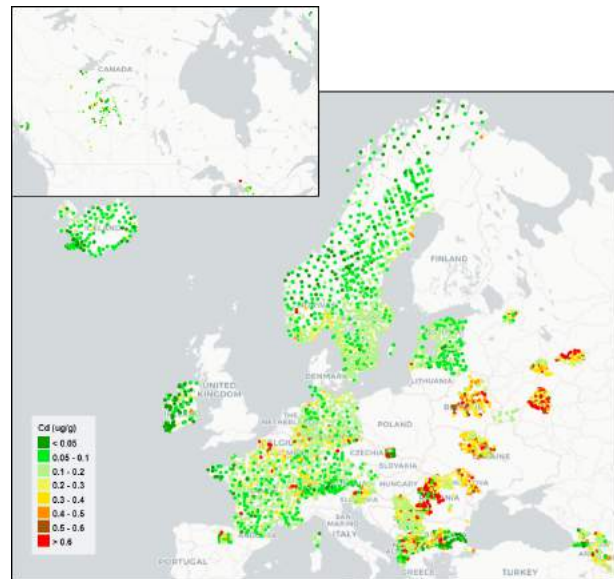


Figure 5.14: Cd concentration in mosses.
Courtesy of Frontasyeva et al. (2020).

5.2.3 CHROMIUM

Both in Figure 5.15 and in Figure 5.16 the boundary in Cr concentration as a result of the last glaciation period is clearly visible. The majority of the forest soils hold a Cr concentration between 30 and 75 mg/kg, whereas the average over all land-use types is situated between 15 and 50 mg/kg. Both maps show elevated Cr concentrations in the Po plain and hotspots around North Rhine-Westphalia.

The Cr concentration in mosses is generally lower than in the forest floor (Figure 5.17, Figure 5.18). The spatial patterns displayed in both maps are dissimilar for countries that took part in both surveys. Cr concentration in Spanish forest floors seems unreasonably high, given the discrepancy between Spanish and Portuguese forest floors. Moreover, the Cr concentration in Swedish forest floors seems unreasonably low in comparison to their Finnish counterparts. One could argue that these anomalies could be avoided by centralized sample analysis.

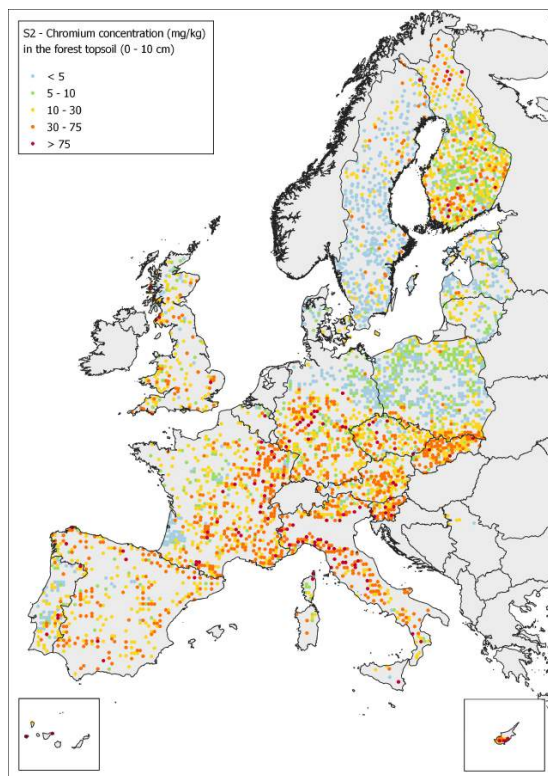


Figure 5.15: Cr concentration in forest topsoils.

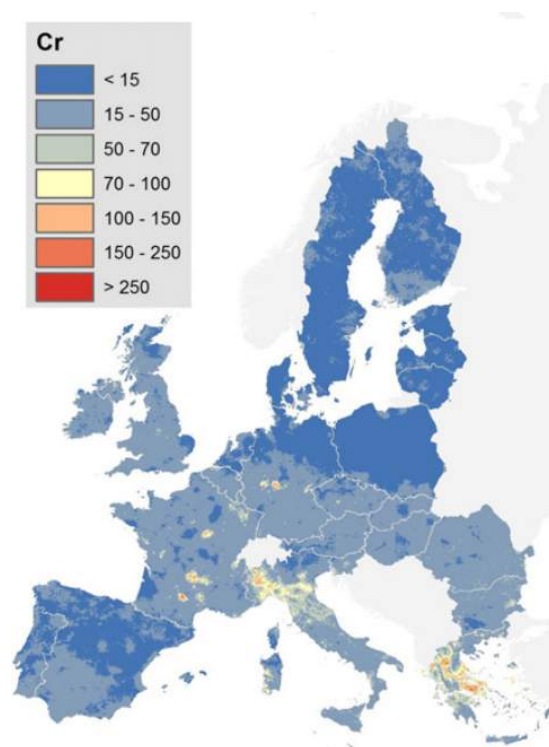


Figure 5.16: Cr concentration in topsoils of all land-use types. Adopted from Tóth et al. (2016)

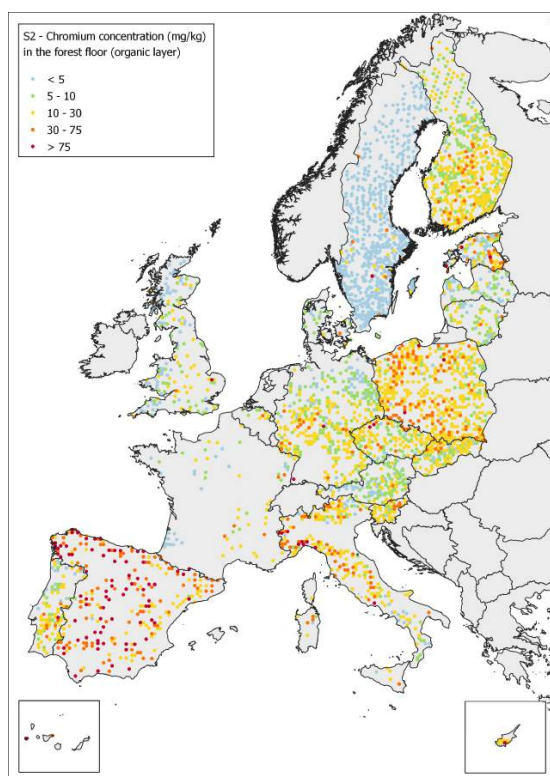


Figure 5.17: Cr concentration in forest floors.

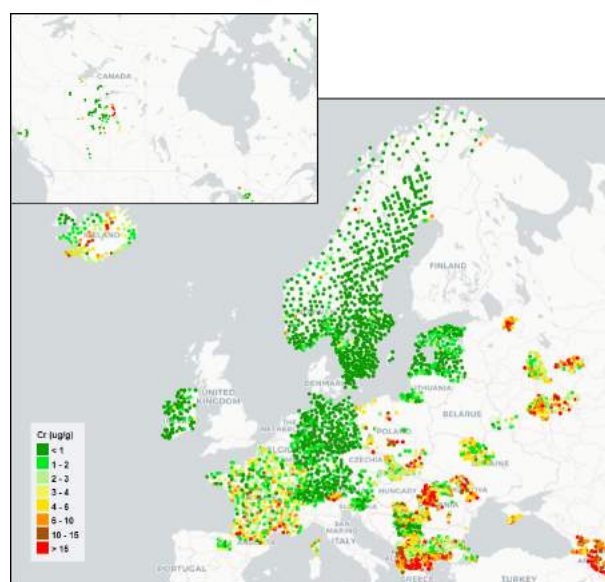


Figure 5.18: Cr concentration in mosses. Courtesy of Frontasyeva et al. (2020).

5.2.4 COPPER

High Cu concentrations on the Appenine peninsula are clear from both maps (Figure 5.19, Figure 5.20). Other regions with elevated Cu concentration in the both maps are southern Spain, southern France, central Germany . . .

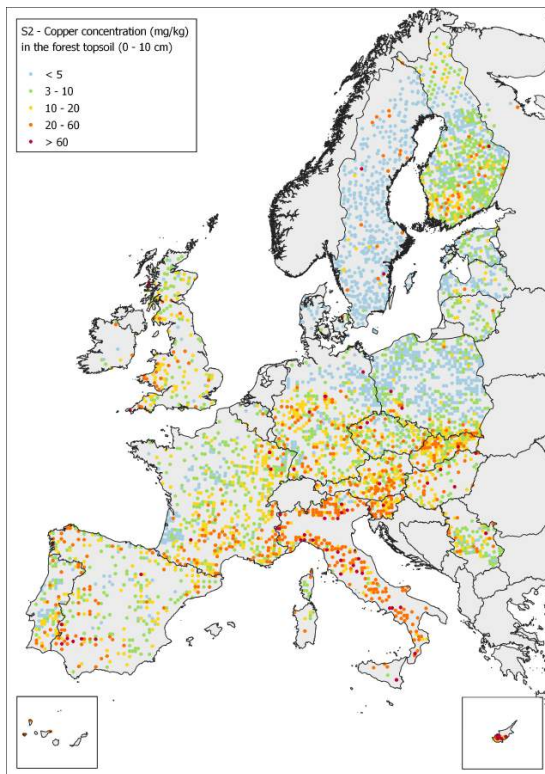


Figure 5.19: Cu concentration in forest topsoils.

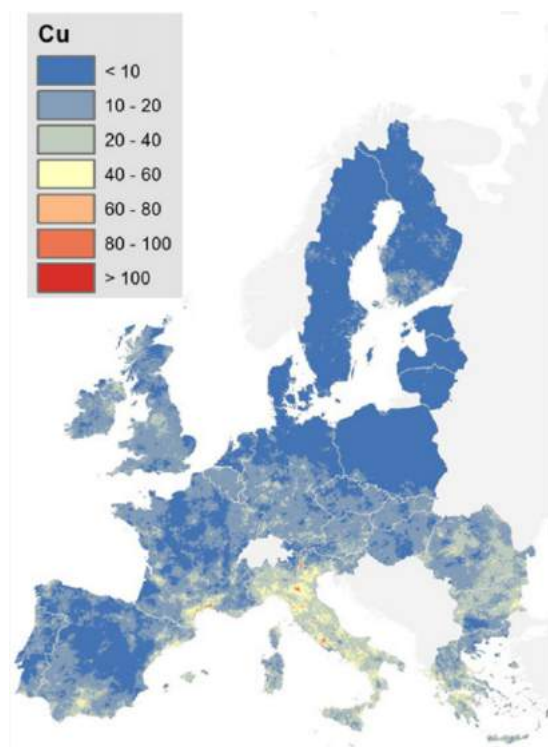


Figure 5.20: Cu concentration in topsoils of all land-use types. Adopted from Tóth et al. (2016).

A hotspot of elevated Cu concentration is clearly visible around Lubin, Poland (Figure 5.21, Figure 5.22). This region is home to the oldest mine in the Polish Copper Belt.

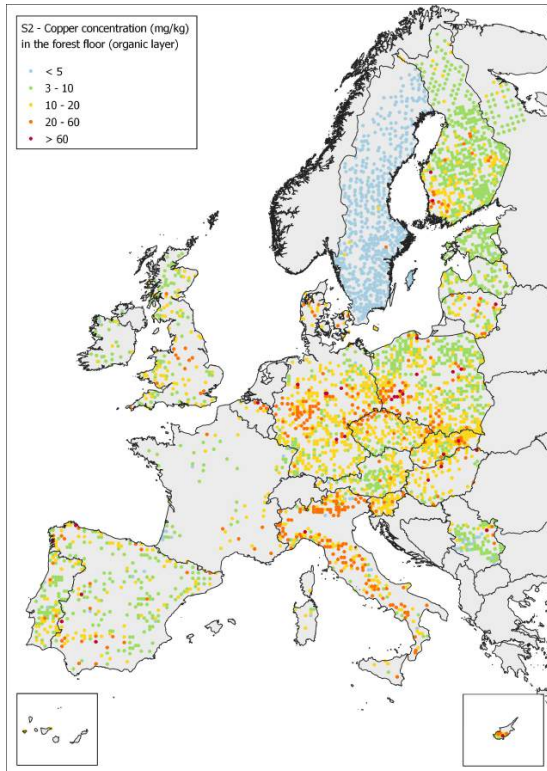


Figure 5.21: Cu concentration in forest floors.

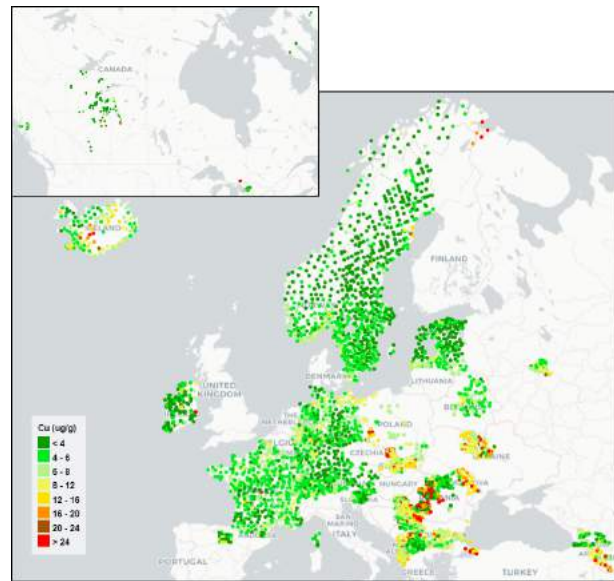


Figure 5.22: Cu concentration in mosses.
Courtesy of Frontasyeva et al. (2020).

5.2.5 NICKEL

The Ni concentration in topsoil was influenced by the last glaciation. The region with the highest overall Ni concentration is the Po Valley in Italy (Figure 5.23). Other hotspots include south-central France and central Germany. Northern Slovakia is indicated as a region with elevated Ni concentration in forest floors, but this isn't reflected in Figure 5.24.

Ni concentration is generally higher in forest floors than in mosses (Figure 5.25, Figure 5.26).

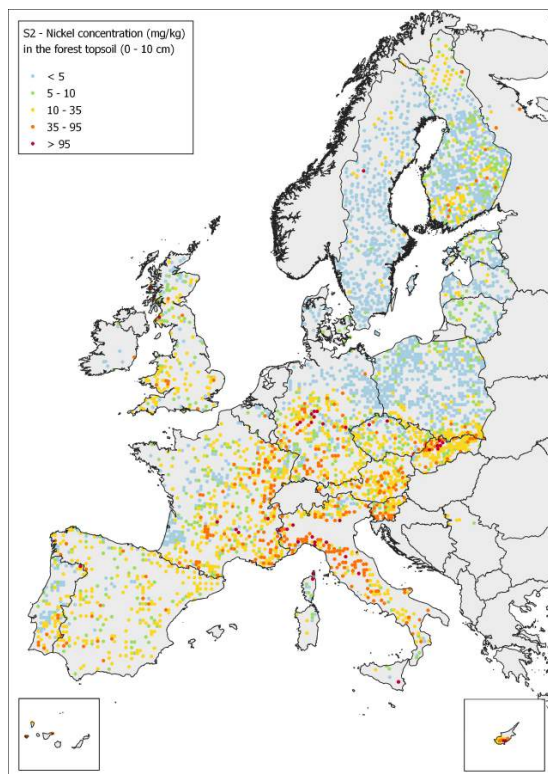


Figure 5.23: Ni concentration in forest topsoils.

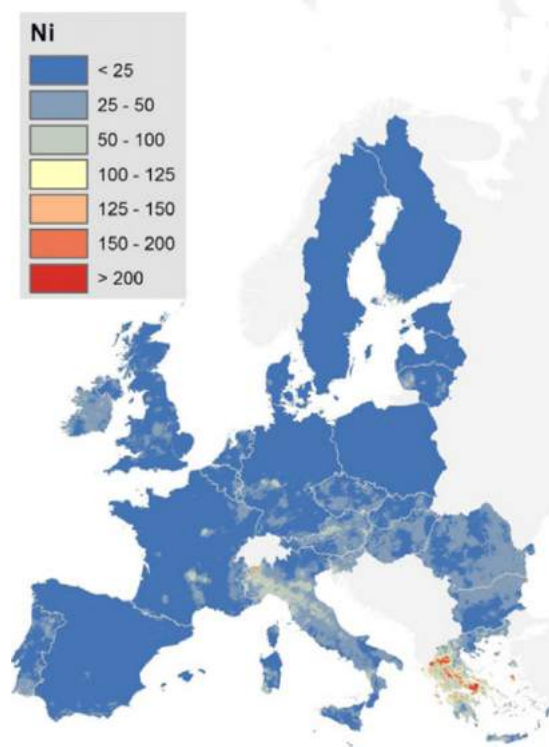


Figure 5.24: Ni concentration in topsoils of all land-use types. Adopted from Tóth et al. (2016).

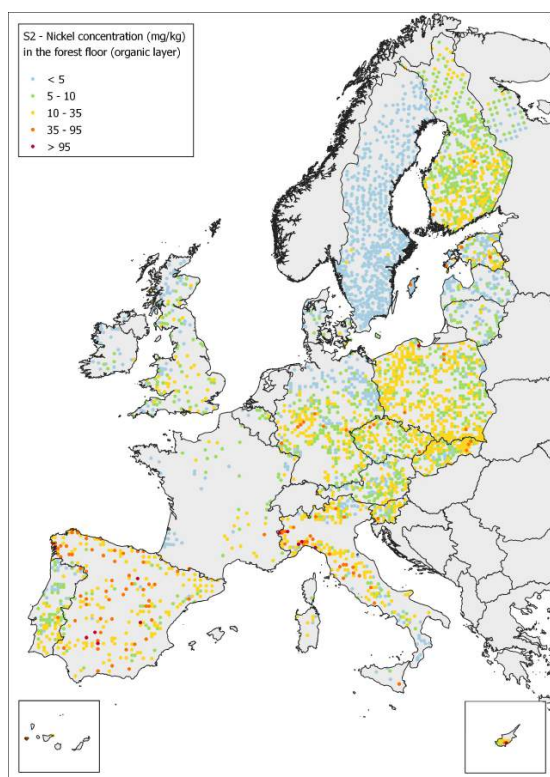


Figure 5.25: Ni concentration in forest floors.

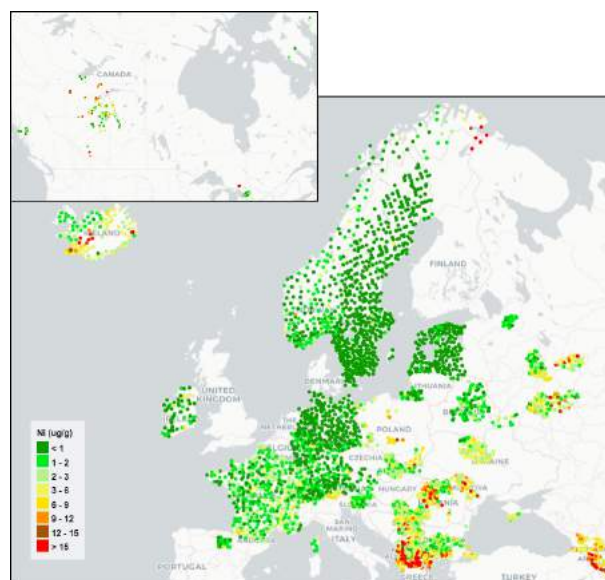


Figure 5.26: Ni concentration in mosses. Courtesy of Frontasyeva et al. (2020).

5.2.6 LEAD

The concentration of Pb in the topsoil is mostly of anthropogenic origin. The highest levels can be found where historical industrial activities were combined with mining. This is for example the case in the Harz mountain range, Germany and in the region around Montpellier, France (Figure 5.27, Figure 5.28). Tóth et al. (2016) also demonstrates a Pb hotspot around Rome, but this couldn't be verified given the scarcity of forested sites in the region.

Peaks of elevated Pb concentration in Sweden pop out against the otherwise low background concentration. Some of the hotspots in Swedish Lapland appear to be in close proximity of industrial mining sites. The region around Kraków, Poland is also classified as a highly polluted area on both maps.

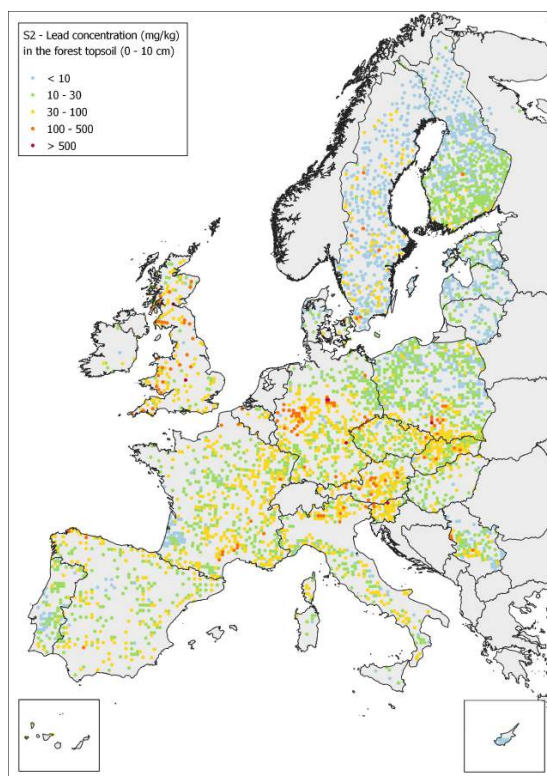


Figure 5.27: Pb concentration in forest topsoils.

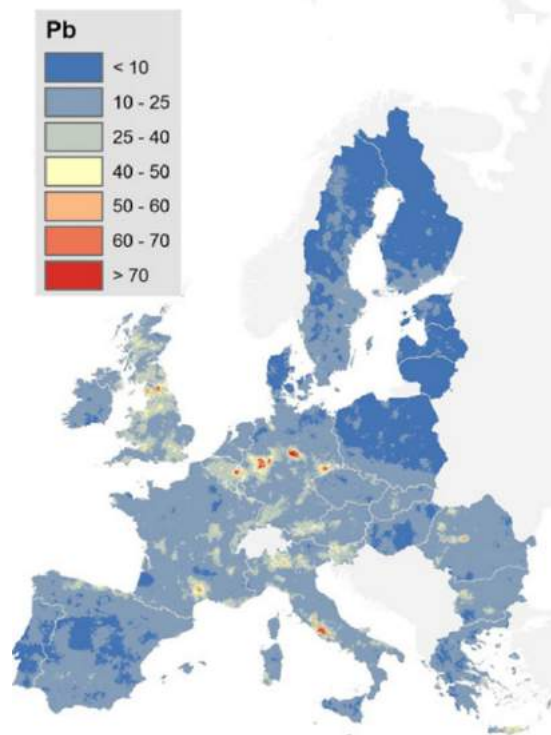


Figure 5.28: Pb concentration in topsoils of all land-use types. Adopted from Tóth et al. (2016).

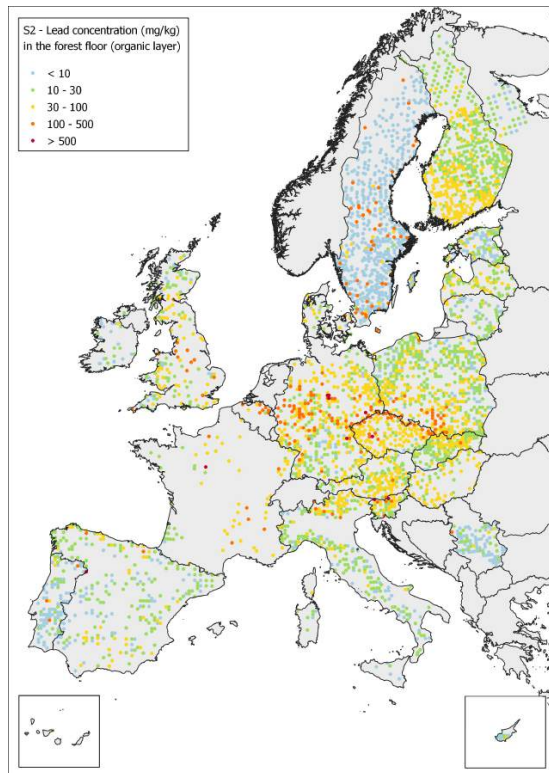


Figure 5.29: Pb concentration in forest floors.

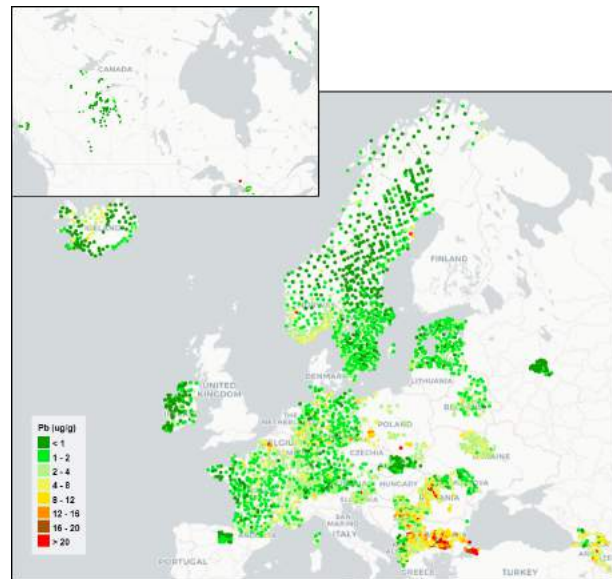


Figure 5.30: Pb concentration in mosses.
Courtesy of Frontasyeva et al. (2020).

5.2.7 MERCURY

Unfortunately, the geographic extent of Hg analysis is limited compared to the analysis of other heavy metals. However, the map of Tóth et al. (2016) partly confirms our findings on Hg concentrations in European topsoils (Figure 5.31, Figure 5.32).

Hotspots in Eastern Slovakia and Central Italy are clearly visible, as well as elevated Hg concentrations throughout the United Kingdom. High soil mercury concentrations in Britain were also reported in national surveys (Tipping et al., 2011).

The hotspot in eastern Slovakia is not only visible in forest topsoils (Figure 5.33), but also in forest floors (Figure 5.34) and in the mosses (Figure 5.35).

The relatively high Hg concentrations in French mosses (Figure 5.35) were not confirmed by elevated Hg concentrations in mineral topsoils but clearly visible in the forest floors (Figure 5.34) although the number of plots is limited. This is supporting the hypothesis that forest floors are better correlated with the moss survey than mineral topsoils.

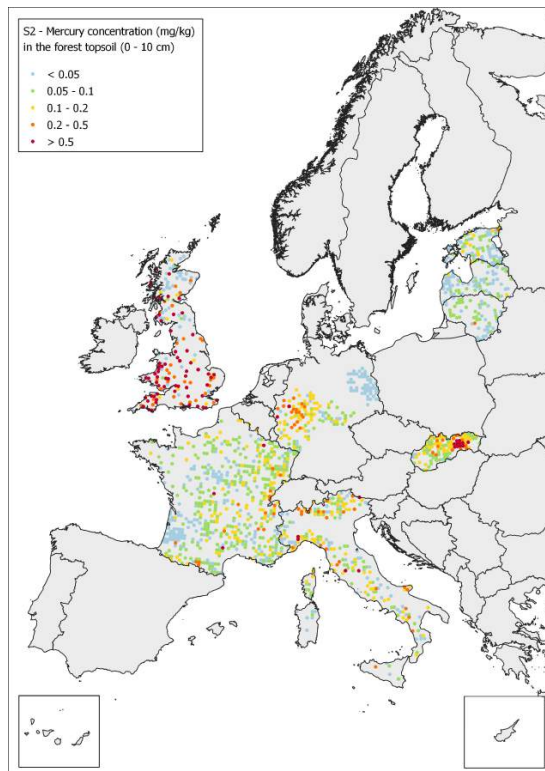


Figure 5.31: Hg concentration in forest topsoils.

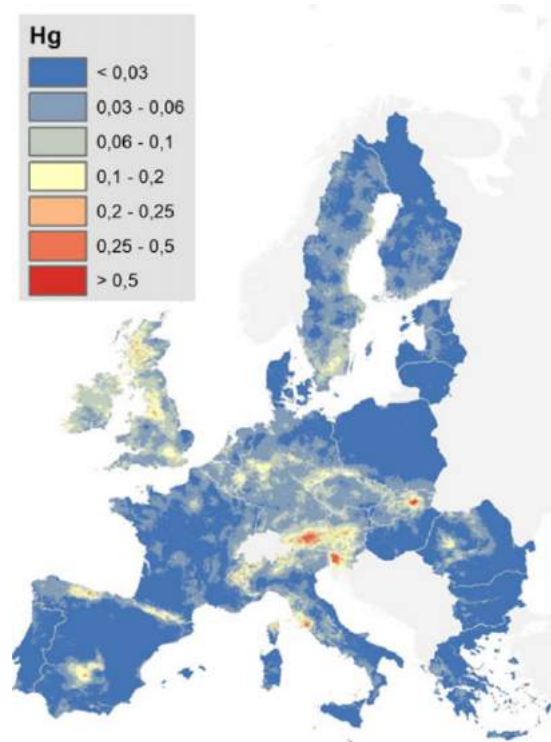


Figure 5.32: Hg concentration in topsoils of all land-use types. Adopted from Tóth et al. (2016).

5.3 RELATIONSHIPS WITH HEAVY METALS IN MOSSES

Heavy metal concentration in mosses are being monitored since 1990 by ICP Vegetation as an indicator of atmospheric heavy metal pollution and deposition (Frontasyeva et al., 2020; Harmens et al., 2008, 2010). Heavy metal concentrations are generally higher in forest floor and soil than in mosses, because these elements accumulate over time in the upper soil layers (metal pool or archive) while mosses reflect more the actual heavy metal deposition. This way, both indicators may complement each-other.

Table 5.10 shows the ranges of heavy metals in mosses in Europe compared to the concentrations in Forest floors and topsoils. Interestingly one can see that median concentration for Cd, Zn and Cu is higher in mosses than in forest floor.

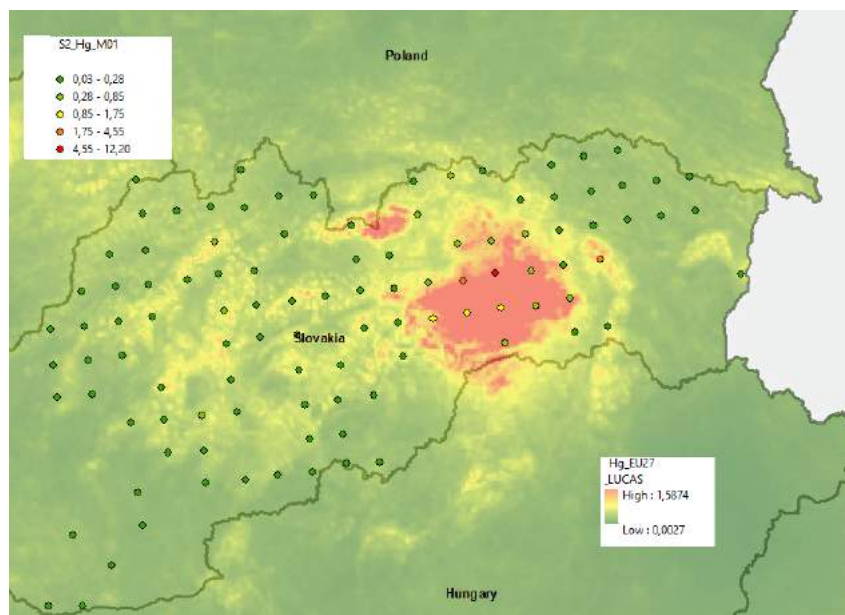


Figure 5.33: Detail of Hg concentration in topsoil compared to map based on LUCAS

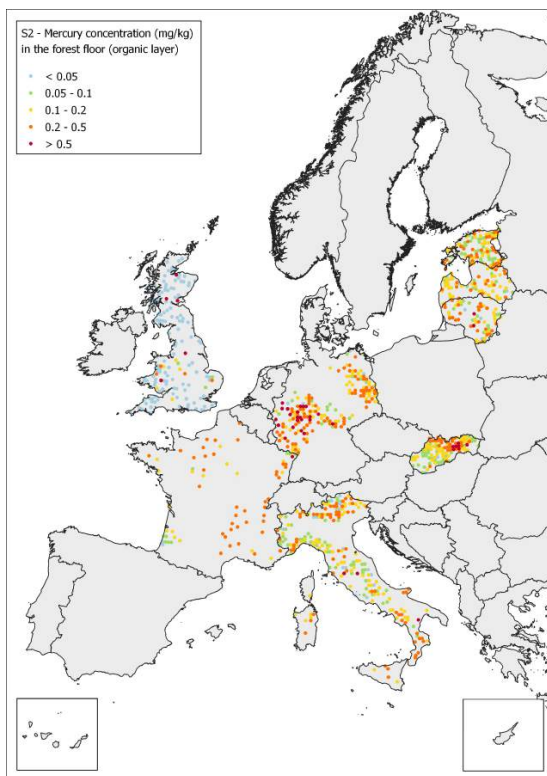


Figure 5.34: Hg concentration in forest floors.

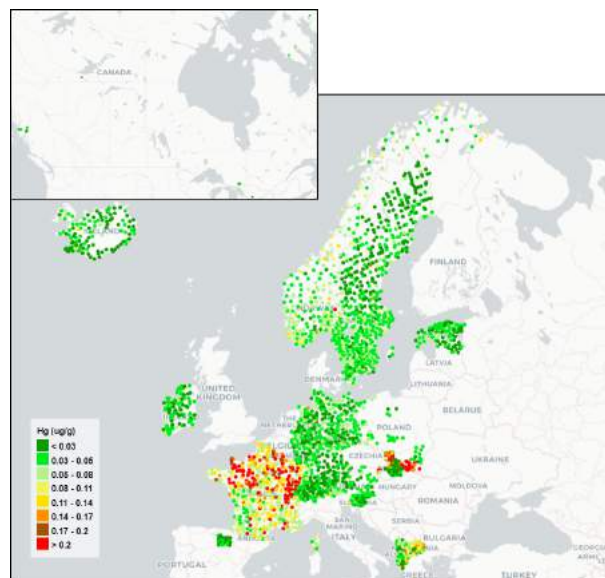


Figure 5.35: Hg concentration in mosses.
Courtesy of Frontasyeva et al. (2020).

Table 5.10: Comparison of summary statistics of Moss survey 2015/2016 and Second Level I survey (S2) for forest floor and topsoil.

		Concentration (mg/kg)			Ratio	
		Moss	Forest floor	Forest topsoil	Moss:Forest floor	Moss:Forest topsoil
Cadmium	N	3154	3736	4186	-	-
	Median	0.17	0.07	0.30	2.60	0.58
	P ₉₀ /P _{97.5}	3.55	2.60	1.34	1.37	2.64
	Max	11.60	32.40	18.70	0.36	0.62
Zinc	N	3562	3735	4186	-	-
	Median	32.9	28.0	52.8	1.18	0.62
	P ₉₀ /P _{97.5}	161.0	124.6	163.0	1.29	0.99
	Max	587.0	2919.0	2558.0	0.20	0.23
Nickel	N	3439	3501	3995	-	-
	Median	2.1	7.6	8.0	0.28	0.26
	P ₉₀ /P _{97.5}	50.2	74.3	40.5	0.68	1.24
	Max	547.0	222.0	916.0	2.46	0.60
Chromium	N	3497	3436	3978	-	-
	Median	2.7	11.9	10.9	0.23	0.25
	P ₉₀ /P _{97.5}	84.7	77.8	83.0	1.09	1.02
	Max	301.0	464.0	1067.0	0.65	0.28
Copper	N	2984	3736	4186	-	-
	Median	5.5	4.6	9.1	1.19	0.60
	P ₉₀ /P _{97.5}	27.1	45.0	35.7	0.60	0.76
	Max	374.0	211.0	982.0	1.77	0.38
Lead	N	2915	3734	4182	-	-
	Median	2.1	7.4	22.3	0.29	0.10
	P ₉₀ /P _{97.5}	19.7	49.1	168.0	0.40	0.12
	Max	460.0	5966.0	17114.0	0.08	0.03
Mercury	N	2294	952	1422	-	-
	Median	0.04	0.06	0.17	0.75	0.25
	P ₉₀ /P _{97.5}	0.23	2.20	0.61	0.10	0.38
	Max	0.63	9.13	12.20	0.07	0.05

Since 1990, heavy metal concentrations in mosses have systematically decreased.

Harmens et al. (2008) reported that geometric mean of Cd concentration in mosses decreased from 0.38 mg/kg in 1990 to 0.33 in 1995 and 0.23 in 2000, and Pb decreased from 15.1, over 10.2 to 6.4 mg/kg whereas no decrease was observed for Hg between 1995-2000. This change was significantly different between years and countries. This decrease could clearly be attributed to a decrease in atmospheric emission and deposition of heavy metals across Europe (Frontasyeva et al., 2020).

Schröder et al. (2013) found positive correlations between atmospheric deposition of Cd, Hg and Pb and their concentrations in mosses specified for ecological land classes. He recommended however to sample the mosses at the same locations as the EMEP monitoring stations and/or national deposition monitoring stations (like LII plots) in order to exclude spatial variation. For this study it is therefore important to mention that most plots of the moss survey are located outside forests, jeopardizing (spatial) comparability of the data.

Table 5.11 compares the overall decrease observed in mosses, emissions and depositions between 1990-2015 with the decrease we found in forest floors and topsoils.

Table 5.11: Median decrease (%) of heavy metal concentration in Europe between 1990 and 2015 in Level I forest floors and topsoils (ICP Forests), mosses (ICP Veg), emission (EEA) and deposition (EMEP, EU28)

Heavy metal	Forest floors	Topsoils (0-10 cm)	Mosses	Emissions	Deposition
Cd	-25.6	0	-63	-65	-53
Zn	-15	+0.7	-23	-39	
Ni	-17	-21	-25	-73	
Cr	-8.9	-17	-22	-71	
Cu	-14	-16	-37	+6.5	
Pb	-26	-6.8	-82	-74-82	-78
Hg	-	-	-2	-57	-23

The largest decrease over time in mosses was found for Pb (-82%) and Cd (-63%) and this is in accordance with the decrease of emissions in Europe (EEA) and for deposition by EMEP models. In forest soils however, we found a median decrease in forest floors (-26% both for Cd and Pb) but no or limited decrease in the topsoil, for Cd and Pb, respectively. These data seem to suggest that Cd and Pb concentrations are indeed decreasing but much slower than observed in mosses or by deposition timeseries. It is known that Pb forms very stable complexes with organomineral materials in soils (e.g. H-layer of forest floor) and is immobilized especially by high-molecular-weight humic acids (Alloway, 2012).

Conversely Cd is much more mobile in soils. No change could suggest that there is an increase of Cd leaching out of the forest floor. This should be evidenced in Level II plots where the vertical distribution of Cd and other heavy metals in the soil profile can be observed over time.

An important finding is that heavy metal concentrations are decreasing in the forest floor for all metals observed, whereas in the topsoil Cd and Zn concentrations do not decrease or slightly increase while Ni, Cr, Cu and Pb are decreasing as well.

Since we have no mercury data for the first survey, no changes can be inferred.

CHAPTER 6

CONCLUSIONS

6.1 ON DATA AVAILABILITY AND QUALITY

According to the ICP Forests soil manuals analysis of heavy metals was optional during the first survey and was mandatory only for Cu, Pb, Cd en Zn in forest floors and 0-10 cm mineral layers at the time of the second survey. Thanks to the EU cofunded BioSoil demonstration project 6 heavy metals became mandatory to report in all topsoil layers so that the data-gaps during the second survey were less prominent then in the first survey. However, large (national) data-gaps in the first survey seriously limit comprehensive comparison between both surveys, both spatially and with time.

Due to data-limitations, this study was based on available heavy metal concentrations of Cd, Zn, Ni, Cr, Cu, Pb and Hg in forest floor and mineral topsoil only. Incomplete datasets are present for deeper (> 20 cm) soil layers. No data for Hg was available from the 1st survey.

In order to calculate stocks, missing (measured) bulk density (BD) data for the topsoil layers could be readily estimated from BD information from the horizons of the profile description, the BD measured during the other survey (assuming constant) or by prediction using depth-specific pedo-transferfunctions.

6.2 ON HEAVY METAL CONCENTRATIONS LEVELS

All heavy metals studied had a specific concentration range, which followed both in the forest floor and mineral topsoil the common order (low to high): $Hg < Cd \ll Ni \approx Cr \approx Cu < Pb < Zn$.

Summary statistics in appendix B indicate that for cadmium and mercury, respectively up to 57% and 34% of the reported values were below limit of quantification. For the other metals this was generally well below 20%. Appropriate statistical handling of these left-censored data as we did in this study is important for correct comparison and interpretation of the heavy metal concentrations.

In appendix B2 we summarized all distribution statistics of concentrations and stocks arranged by survey, heavy metal and soil layer.

We considered the geometric mean as appropriate distribution metric for heavy metal concentration data, better than arithmetic mean or even median. Bootstrapping GM allowed us to compute 95% confidence intervals to detect significant factor differences or temporal changes.

6.3 ON SPATIAL VARIATION OF HEAVY METAL CONCENTRATIONS AND STOCKS IN FOREST FLOORS AND TOPSOILS

The spatial pattern of the heavy metal concentrations or stocks in forest floors and topsoils is metal-specific. However, similar patterns arise for metals with related geochemistry or emission sources, like for Ni & Cr, Cd & Zn, Cu & Pb. Spatial distribution of Hg shows an individual pattern.

For Cd, Cu, Pb, Zn, Hg the concentration levels in the forest floor are generally higher than in the forest topsoil, whereas the opposite is true for Cr and no clear pattern is observed for Ni.

Large differences exist between European countries in terms of background heavy metal concentrations, which are probably related to geology and climate. It is also clear from the maps that there is a lot of small-scale variability in heavy metal content, which can often be linked with local pollution sources. There were also indications that differences in analytical methodology during the first survey led to national differences in concentration levels which generally faded out during the second survey thanks to harmonised methods.

Stratification by biogeographical region seems useful to explain differences in baseline concentration levels. Lowest concentrations are often found in the Boreal region, intermediate levels in Atlantic and Continental zone and higher levels in Alpine and Mediterranean region, with some variation among metals.

Variation of heavy metal concentrations was correlated with reference soil groups. For instance, on Calcisols and Regosols, Cd concentrations are generally small while elevated in Histosols (peat soils) and Phaeozems. Conversely, Cr is elevated in Calcisols, but low in Histosols and Podzols.

Upon stratification of heavy metals by humus form, generally less variation was found compared to soil group. Mor types showed generally the lowest concentrations, but probably this is related to their vast presence in Nordic countries with generally lower metal concentration levels.

In general, similar spatial patterns of a given metal in forest floors and topsoils may be observed, with often more detail provided by the forest floor data. Hence concentrations in forest floors seem to be better pollution indicators than topsoil concentrations. Correlated patterns between concentration and stock maps are often less clear.

6.4 ON TEMPORAL CHANGE BETWEEN THE FIRST AND SECOND SOIL SURVEY

Concentration changes could be assessed for 9 countries only, mainly because heavy metal data of the first survey was lacking. Moreover, no paired measurements are available for Hg at all. More paired data is available for the forest floor than for mineral topsoil.

In general, the heavy metal concentration appears to have declined since the 1990's. However, the rate of change differs between countries. Although the evolution of analytical techniques might have contributed to the magnitude of differences observed, this is in line with the decrease observed in mosses and in deposition as reported in literature.

For about 750 to 1000 plots, paired observations (S1,S2) in forest floors indicate a significant decrease for all metals. In absolute concentrations, Pb showed the largest decline (-18.6 mg/kg) and Cd the smallest (-0.24 mg/kg). Except for Cr a significant decrease is found in more than half of all paired plots. For Pb, 62% of the plots show a decrease. No significant change is found for 15 to 37% of the plots, depending on the heavy metal. About a quarter of plots still show increasing concentrations in the forest floor, except for Pb. The agreement between S1 and S2 survey concentrations decreased in the order: Zn = Pb > Cu > Ni > Cd > Cr.

Temporal change in mineral topsoil could only be assessed on less than 500 plots (n=224-466) from few countries, so conclusions drawn at the EU scale are tentative. The decreases of Cd and Cr in topsoils are clearly significant, in contrast to Zn where no significant change is found. The Zn and Pb concentrations from S1 explain for more than 80% the variation in S2, whereas this temporal agreement is intermediate for Cu, Ni and Cd and lowest for Cr. This is the same order as found for forest floors. It evidences the persistence of heavy metals in mineral soil and forest floors, and is especially true for Pb.

6.5 ON CONTAMINATION AND POLLUTION LEVELS

In this study several approaches were tested for evaluating forest soil contamination with heavy metals. Paramount to all approaches is the definition of a reference level or geochemical baseline concentration, and a critical level harmful to the forest ecosystem, its species and processes.

Upon using the Geo-accumulation Index (I_{geo}), the most common heavy metal occurring in high levels in polluted ($I_{geo} > 1$) forest soils is Pb (53%), followed by Hg (20%), Cd (8%), Cu (6%), Zn (5%). Cr (2%) and Ni (1.6%). Pb pollution was also found most widespread across Europe.

The Nemorow Pollution Index ($PI_{Nemorow}$) assessed the overall degree of soil contamination. Unfortunately, due to the lack of data on heavy metals in deeper soil layers $PI_{Nemorow}$ could

only be computed in 10 countries. Only 6% of the sampling sites is classified as clean or "pristine" and 26% of the sites are on the verge of being classified as polluted and a relatively high share of sites (55%) is classified as "slightly polluted" while moderate and heavy pollution was found on 7% and 6% of the sampled sites respectively.

Another approach is applying national screening values (baseline and critical levels) that have been developed by most European countries as part of their legislation for soil quality assessment. Currently no clear screening values are published at the EU level for mineral soil nor forest floors. Based on 9 national frameworks, we computed median baseline values for all metals and compared these with quantified baseline values at the European level and for the 6 biogeographical regions. The estimated baselines for mineral soil are always less than the median values of national reference values, indicating that the estimated baselines are on the safe side compared to most national standards and that they indicate indeed pristine conditions which may be expected from the majority of forest soils. Also for forest floors, the estimated baselines are generally lower than national baselines. The use of biogeographically based reference baselines is generally supported.

This study synthesised critical levels for 8 heavy metals from 12 national legislative frameworks as well and evaluated the mineral topsoil concentrations with these. Generally only few percent of the level I plots exceeded the critical levels and is thus classified as polluted, 5-10% is classified as enriched and for all metals more than 50% of the level I plots is well below the baseline concentration level. In the second survey less plots exceeded the critical levels compared to the first survey for all metals investigated in mineral topsoils.

For forest floors, the Belgian evaluation scheme was applied at the EU level for producing maps, but recalibration of this scheme for each biogeographical region seems more appropriate, using the region-specific baseline values of forest floors.

6.6 ON COMPARISON WITH REFERENCE DATABASES AND MAPS

The maps of heavy metal concentration levels in forest soils from the second survey are compared with maps of metals in European topsoils derived from the LUCAS database for a similar time frame (roughly 2006-2012). This could be done for all investigated metals except for Zn.

We found no significant differences for Ni and Cu concentrations, but higher levels for Cd, Cr, Pb and Hg in the Level I forest topsoils compared to the interpolated topsoils of all landuses reported from the LUCAS survey. Cd and Hg concentrations are on average a factor 3.5 higher than the predicted LUCAS concentrations at LI plots, Pb about double as high and Cr a factor 1.23. These results support the hypothesis that forest soils accumulate more metals than agricultural land, especially for Cd, Hg and Pb.

When qualitatively comparing both maps, regional hotspots from LUCAS maps are clearly correlated with increased levels at the Level I sites, as expected. Similarly, increased levels

indicated by the maps of HM concentrations in mosses, produced by ICP Vegetation, are also related to the concentration in forest floors and topsoil, albeit less strongly than with LUCAS data.

The largest decrease between 1990 and 2015 in mosses was found for Pb (-82%) and Cd (-63%) and this is in accordance with the decrease of emissions in Europe (EEA) and for deposition predicted by EMEP models. In forest soils however, we found a median decrease in forest floors for all metals (up to -26% for Cd and Pb) but no or limited decrease in topsoil concentrations for Cd and Pb. These data seem to suggest that Cd and Pb concentrations are indeed decreasing but much slower than observed in mosses or by deposition timeseries.

Comparison with other datasets learns that heavy metals clearly accumulate and reside in forest soils and that their concentration levels are slightly higher than in mosses and agricultural soils. These findings are clearly in line with the known process that trees filter out airborne pollutants, including toxic heavy metals.

CHAPTER 7

FUTURE RESEARCH

OPPORTUNITIES

7.1 FUTURE SURVEYS

In order to investigate the evolution of the state of European forest soils, the engagement of each individual European country to participate in the surveys and collect samples according to a harmonized protocol is paramount. Taking samples at fixed depths facilitates further data progressing in a later stage of the research. On top of that, heavy metal records originating from deeper soil layers as reference level proved to be useful for comparison with topsoil concentrations and the calculation of various soil pollution indices. Concentration levels of deeper soil layers do not need to be repeated every 10-20 years, since they can serve mainly as baseline.

Therefore it is recommended:

- in the next level I survey to determine all metals (including Hg) mandatory in forest floors and M01 layers and if budget allows also in M12 and M24 layers
- at level II plots to sample the whole soil profile until 80 cm to determine vertical distribution patterns of heavy metals

We were unable to quantify the uncertainty related to (decentralised) analysis in national laboratories compared to a central lab as has been done by JRC for carbon analysis during BioSoil (S2) (Hiederer et al., 2010). For about 10% of the S2 plots (526 plots) all samples were analysed in a central lab (INRA) in order to assess the between lab-variation. It is unclear if heavy metal analyses were performed and if this dataset is available by now from ESDAC or the NFCs.

During BioSoil, about 3460 samples of the first survey (S1) taken from national soil archives (33 countries) were reanalysed by a central lab (INRA) (Hiederer et al., 2010). To our knowledge, data on heavy metals have never been published by the central lab. If heavy metals were analysed, these data could be very helpful in completing the S1 dataset.

Hence, centralized sample analysis of at least part of the samples should be considered in future forest soil surveys. Similarly as during BioSoil, it could be worthwhile to re-analyse samples taken in S1 and S2 to exclude the between-lab -variation in results caused by the unavoidable evolution of analytical techniques.

7.2 FURTHER DATA ANALYSIS

Due to the limited scope of this project, a lot of opportunities for further data exploration were still left undiscovered. Boosted regression trees for example could help to assess the influence of different parameters like pH, humustype, soiltype and organic carbon content on heavy metal concentrations and pools and the other way around, to assess the effect of heavy metal concentrations on litter decomposition and quality. But also the link with climatic variables as temperature (MAT) and precipitation (MAP) and geographical variables (altitude, slopes) is still left uncovered. In short: a statistical study selecting the best predictors for heavy metal concentration levels and stocks in EU forest soils.

Geostatistical mapping of the database also seems promising. Options include but are not limited to (1) kriging of concentrations to obtain continuous maps covering all European forests (2) spatially correlating heavy metal concentrations with each other and with external databases from other heavy metal surveys at the European scale.

Although the Level I database has many advantages such as its geographical extent, it falls short for certain types of research questions. One such question for which the Level II database might be more suited is the vertical migration of heavy metals in forest soils. Which heavy metals accumulate in the forest floor and which heavy metals leach more easily into deeper soil layers? To answer this research question a timeseries of the vertical distribution of heavy metals in soil profiles should be analysed to detect heavy metal migration and/or leaching and to reveal the processes behind these. This study suggests leaching of most metals from the forest floor downwards in the soil profile, which may be evidenced in soil solution at various depths which is monitored at Level II sites.

Finally, it would be interesting to see whether or not a link exists between heavy metal leaching and forest type or dominant tree species.

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APPENDIX A

FIGURES

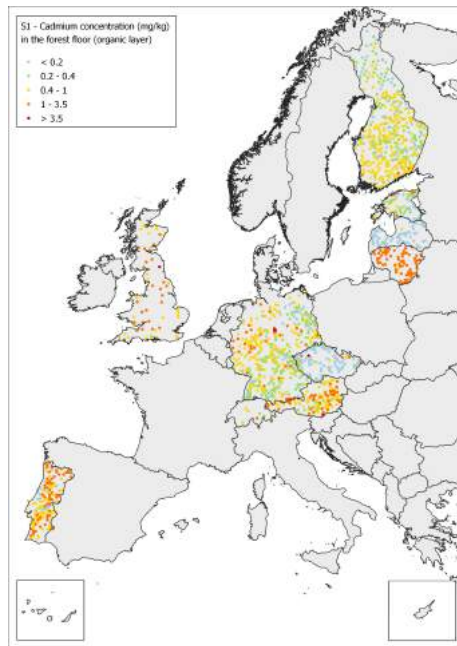


Figure A.1: Cadmium concentration in the forest floor in S1.

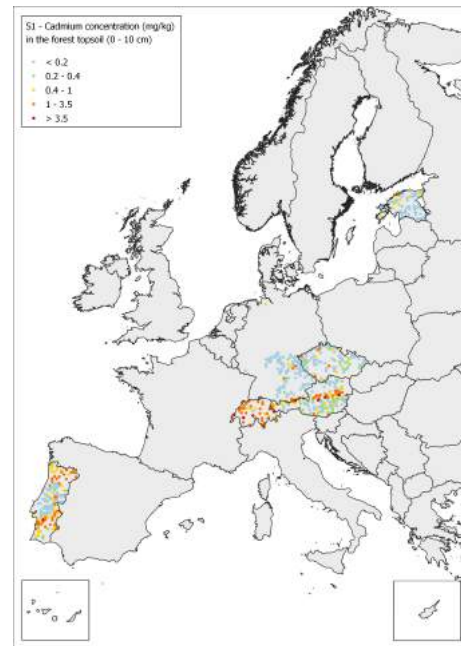


Figure A.2: Cadmium concentration in the forest topsoil in S1.

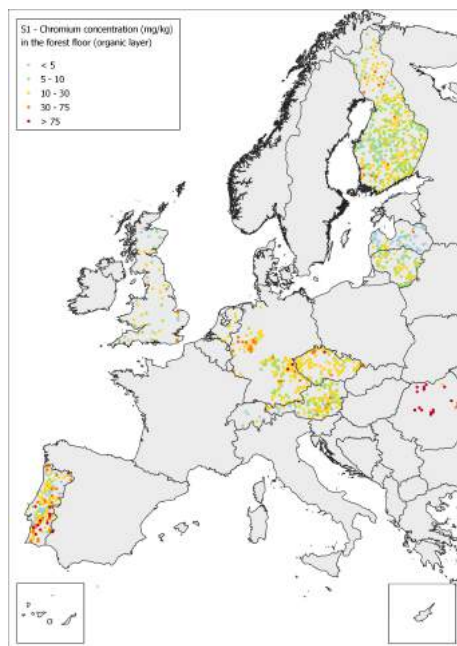


Figure A.3: Chromium concentration in the forest floor in S1.

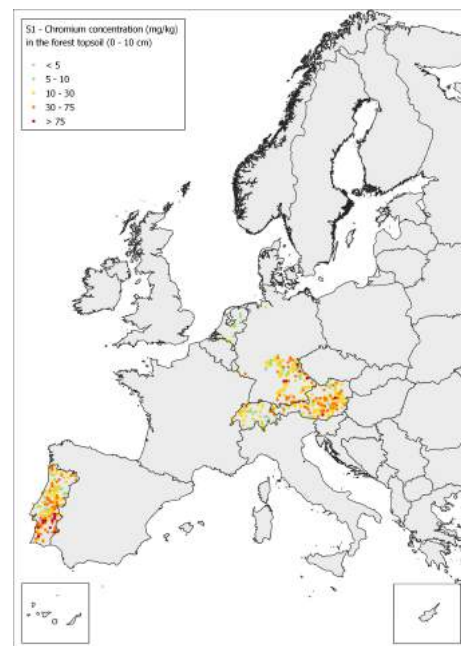


Figure A.4: Chromium concentration in the forest topsoil in S1.

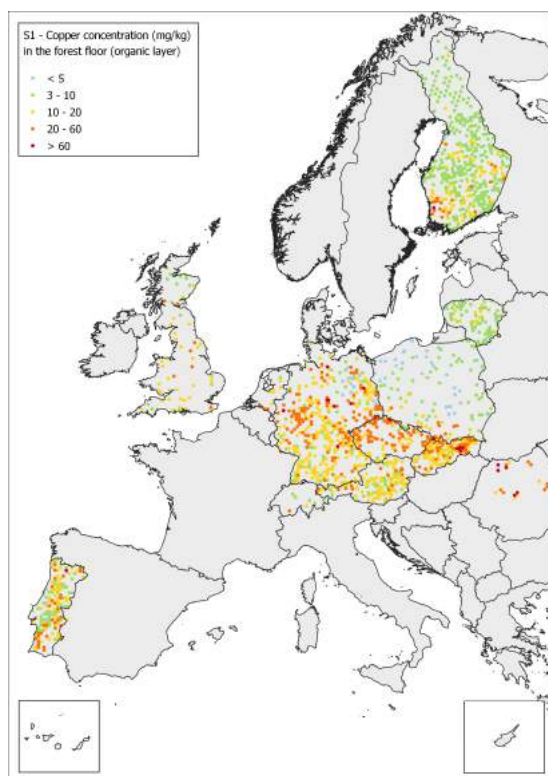


Figure A.5: Copper concentration in the forest floor in S1.

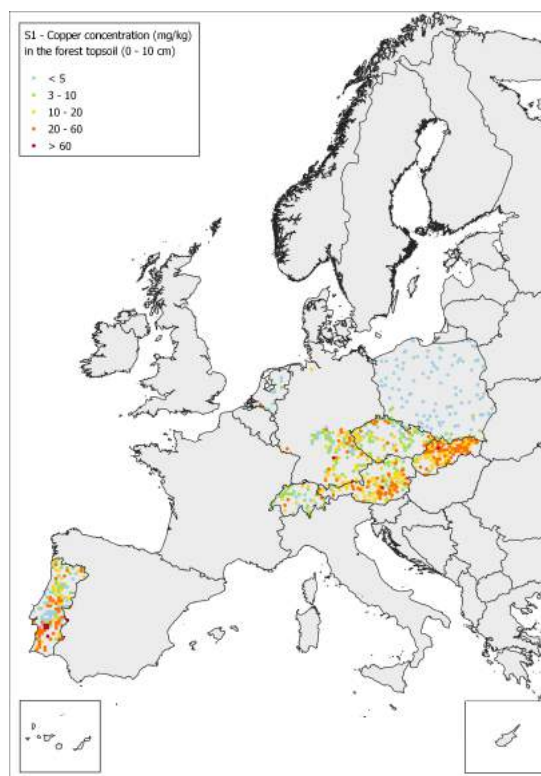


Figure A.6: Copper concentration in the forest topsoil in S1.

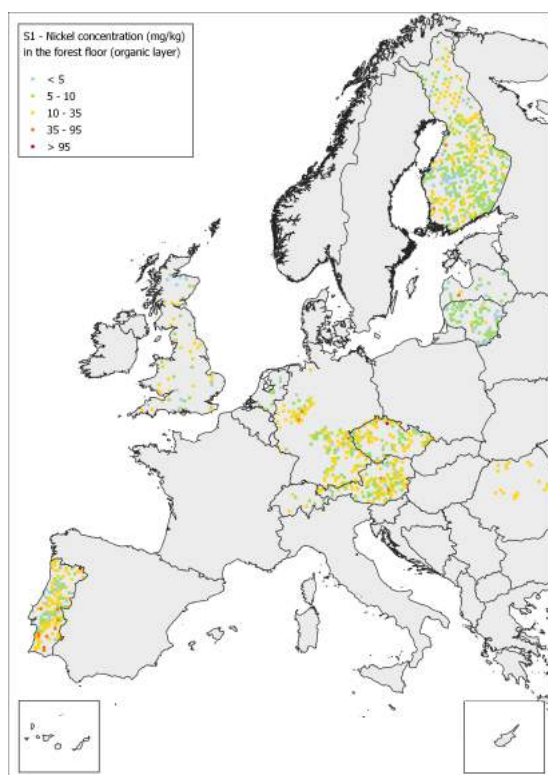


Figure A.7: Nickel concentration in the forest floor in S1.

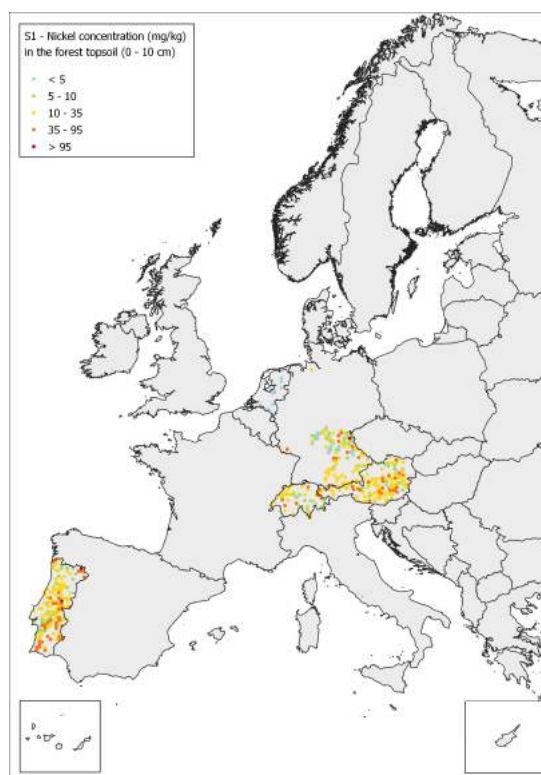


Figure A.8: Nickel concentration in the forest topsoil in S1.

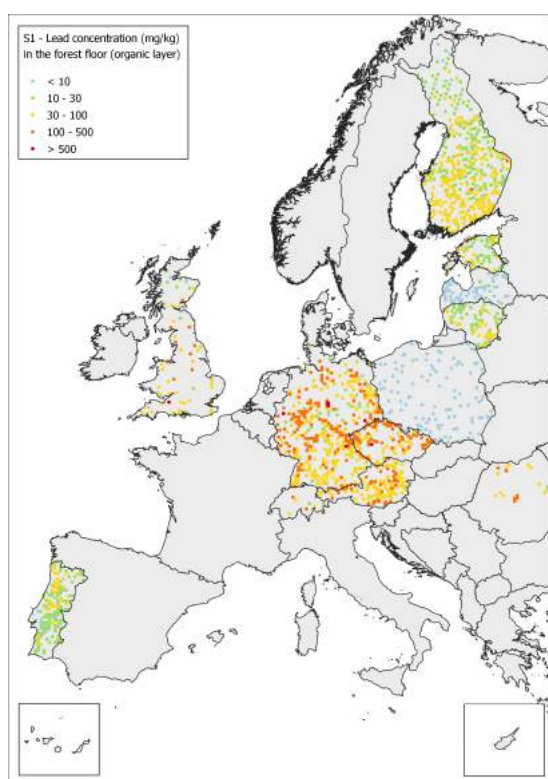


Figure A.9: Lead concentration in the forest floor in S1.

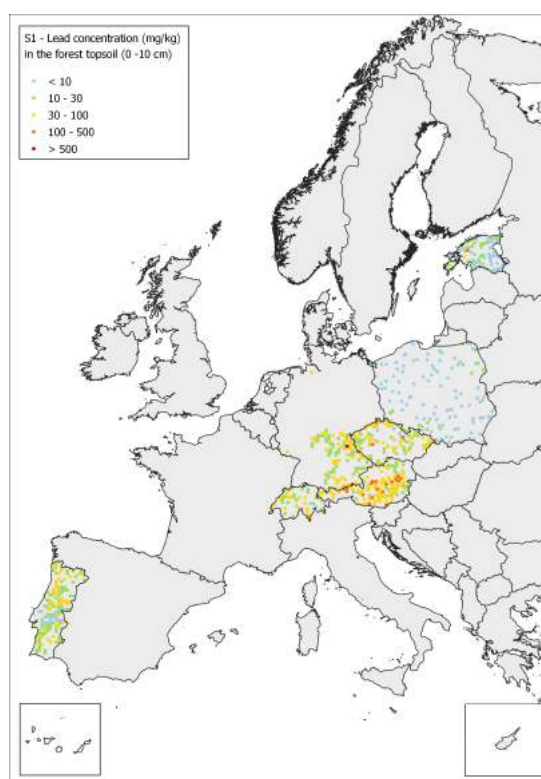


Figure A.10: Lead concentration in the forest topsoil in S1.

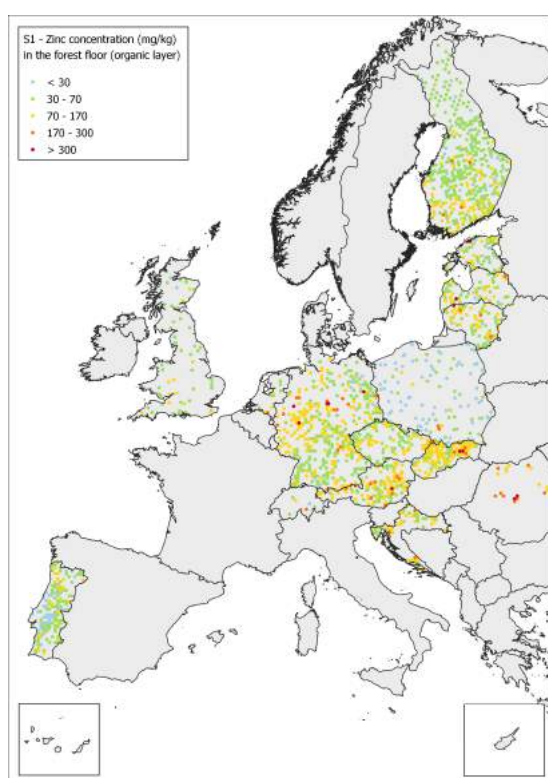


Figure A.11: Zinc concentration in the forest floor in S1.

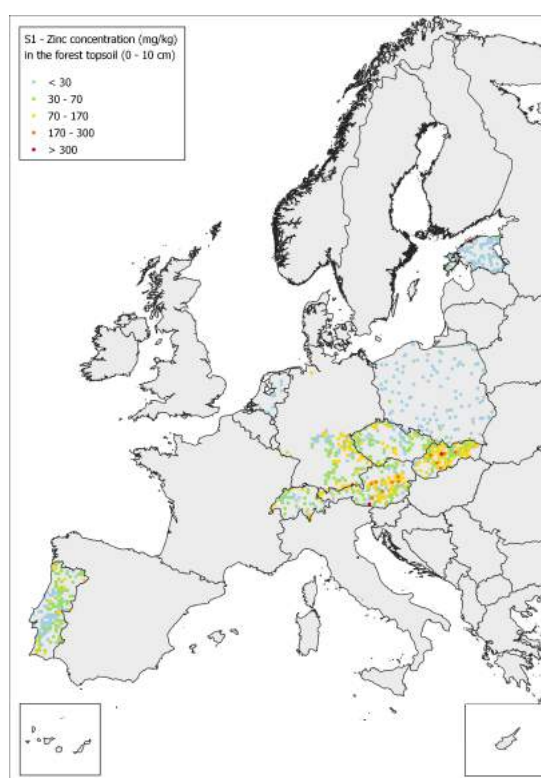


Figure A.12: Zinc concentration in the forest topsoil in S1.

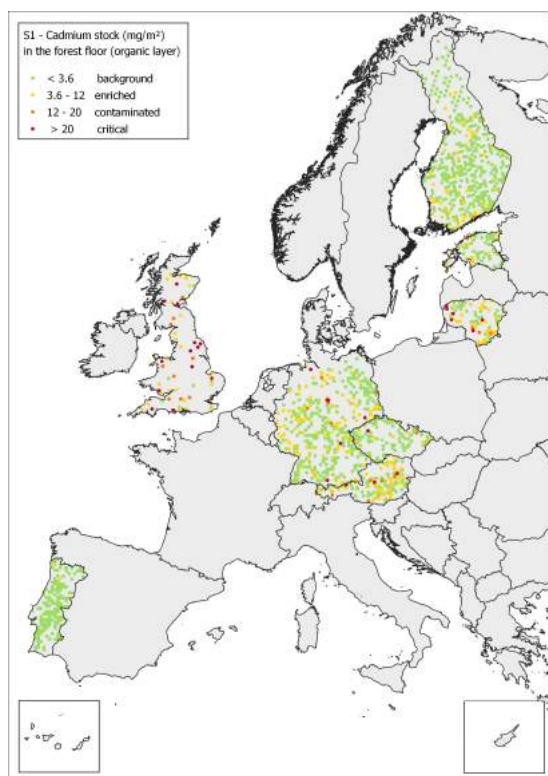


Figure A.13: Cadmium stock in the forest floor in S1.

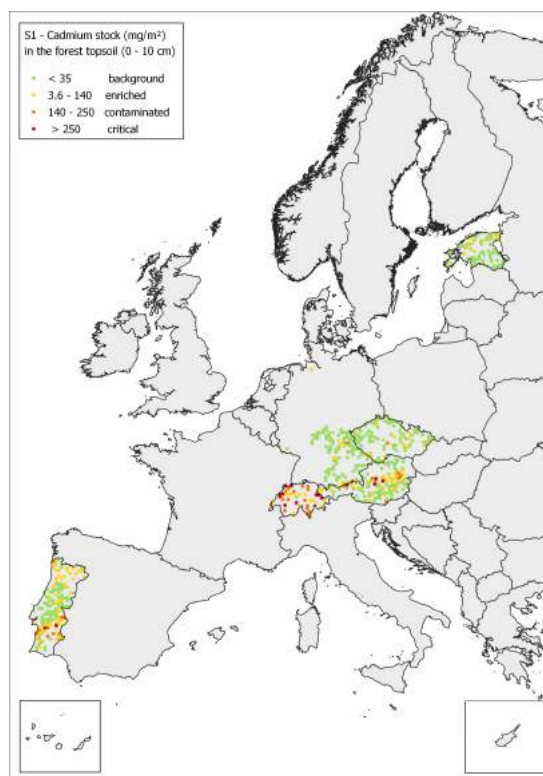


Figure A.14: Cadmium stock in the forest topsoil in S1.

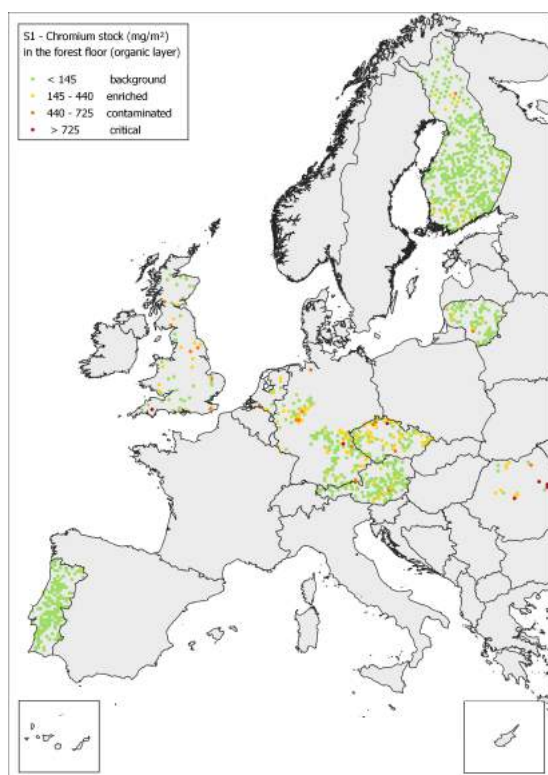


Figure A.15: Chromium stock in the forest floor in S1.

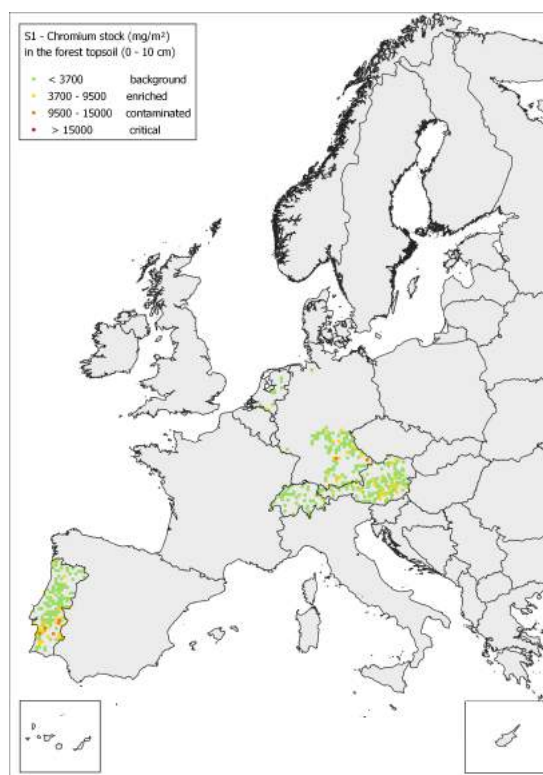


Figure A.16: Chromium stock in the forest topsoil in S1.

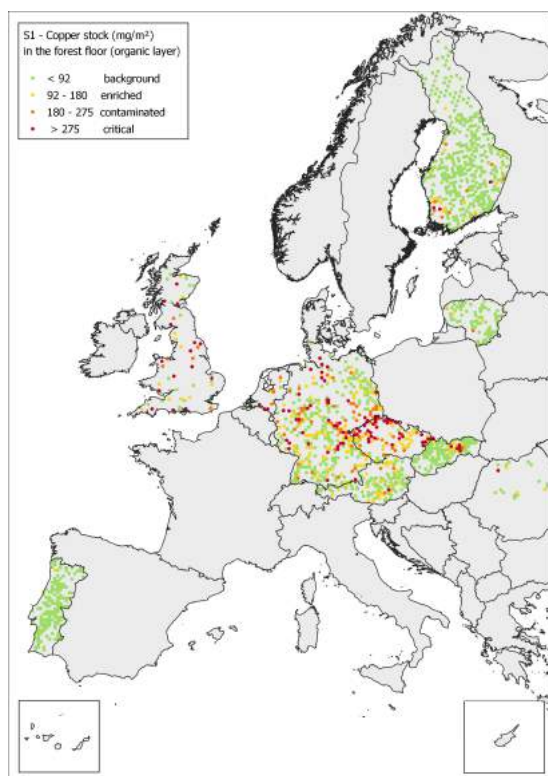


Figure A.17: Copper stock in the forest floor in S1.

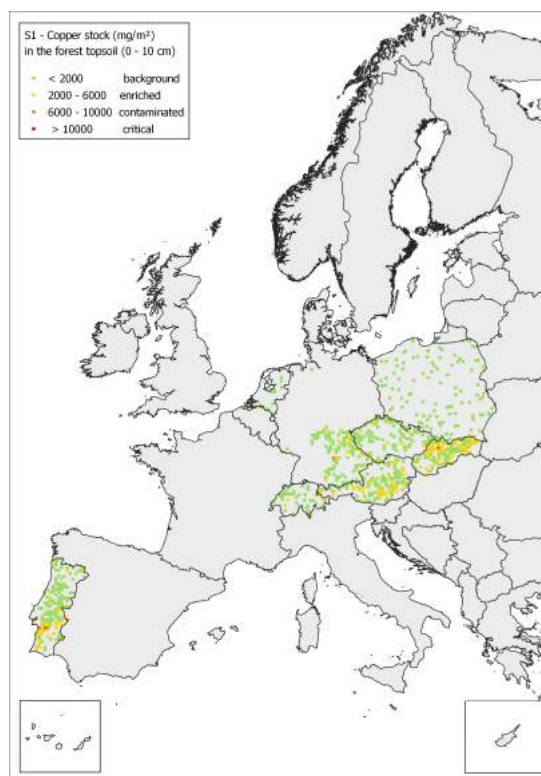


Figure A.18: Copper stock in the forest topsoil in S1.

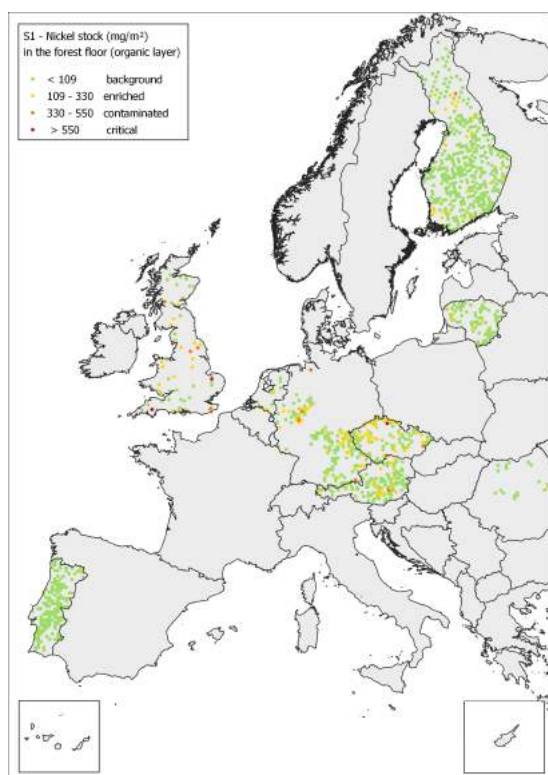


Figure A.19: Nickel stock in the forest floor in S1.

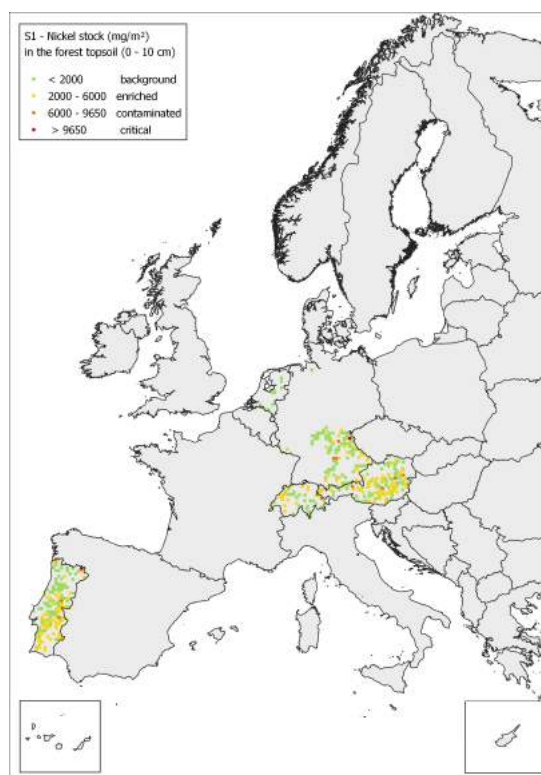


Figure A.20: Nickel stock in the forest topsoil in S1.

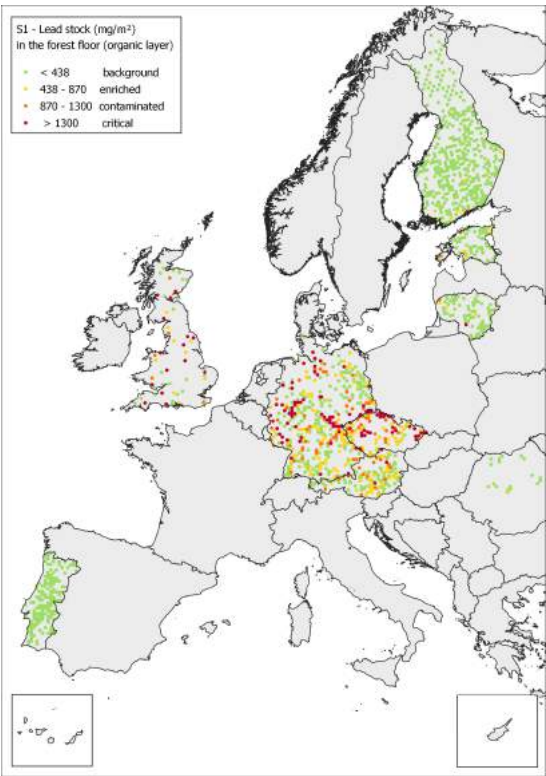


Figure A.21: Lead stock in the forest floor in S1.

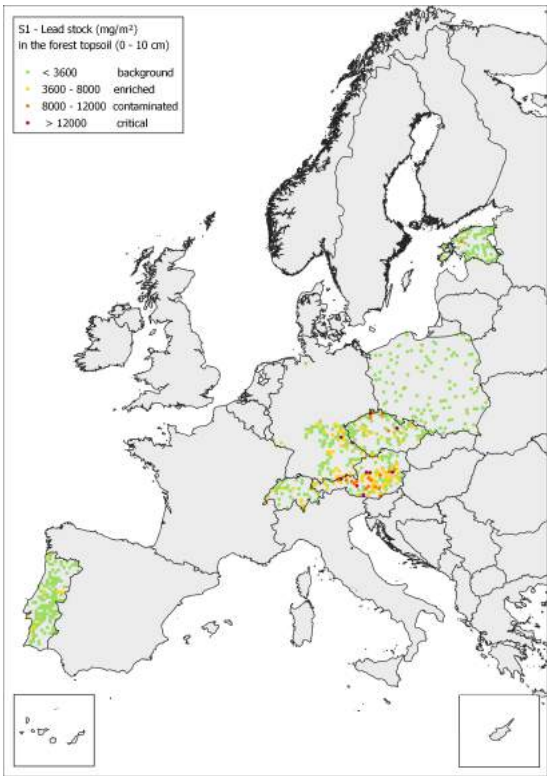


Figure A.22: Lead stock in the forest topsoil in S1.

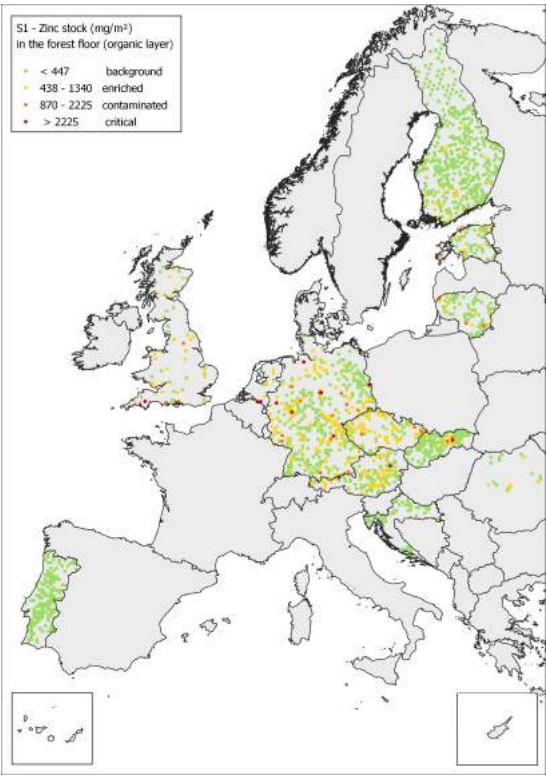


Figure A.23: Zinc stock in the forest floor in S1.

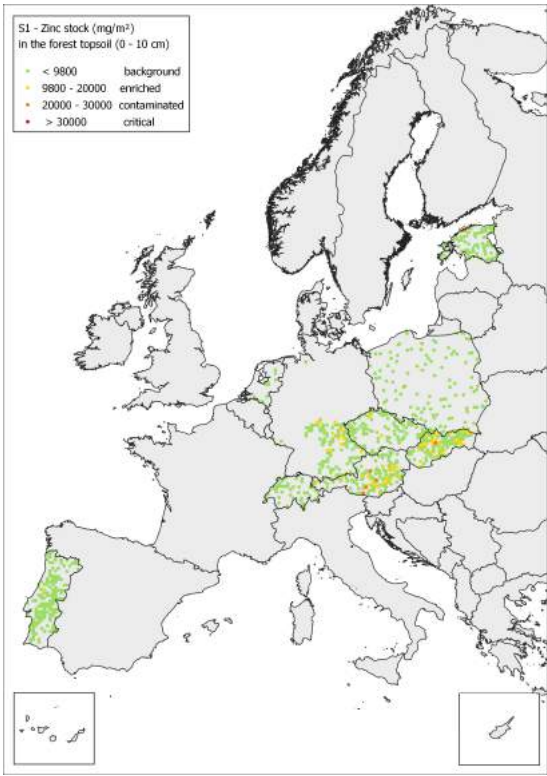


Figure A.24: Zinc stock in the forest topsoil in S1.

APPENDIX B

TABLES

B.1 DATA AVAILABILITY

Table B.1: Number of datapoints for the forest floors per country per heavy metal. The first value in each cell indicates the number of data points in S1, while the second value is the number of data points in S2.

Countries	Cadmium	Chromium	Copper	Mercury	Nickel	Lead	Zinc
Austria	124/130	124/130	124/130	0/0	124/130	124/130	124/130
Azores (Portugal)	0/0	0/0	0/0	0/0	0/0	0/0	0/0
Belgium	0/10	0/10	0/10	0/0	0/10	0/10	0/10
Bulgaria	0/0	0/0	0/0	0/0	0/0	0/0	0/0
Canaries (Spain)	0/2	0/2	0/2	0/0	0/2	0/2	0/2
Croatia	0/0	0/0	0/0	0/0	0/0	0/0	60/0
Cyprus	0/15	0/15	0/15	0/0	0/15	0/15	0/15
Czech Republic	100/146	100/146	100/146	0/0	100/146	100/146	100/146
Denmark	0/25	0/25	0/25	0/0	0/25	0/25	0/25
Estonia	61/92	0/92	0/92	0/92	0/92	61/92	61/92
Finland	400/493	400/493	400/493	0/0	400/493	400/493	400/493
France	0/67	0/67	0/67	0/67	0/67	0/67	0/67
Germany	381/420	145/371	387/420	0/182	145/371	387/420	387/420
Greece	0/0	0/0	0/0	0/0	0/0	0/0	0/0
Hungary	0/75	0/0	0/75	0/0	0/0	0/75	0/75
Ireland	0/29	0/0	0/29	0/0	0/27	0/27	0/29
Italy	0/236	0/236	0/236	0/219	0/236	0/236	0/236
Latvia	66/69	63/69	0/69	0/69	19/69	65/69	65/69
Lithuania	73/62	73/62	73/62	0/62	73/62	73/62	73/62
Luxembourg	0/0	0/0	0/0	0/0	0/0	0/0	0/0
Netherlands	0/0	11/0	11/0	0/0	11/0	0/0	11/0
Norway	0/0	0/0	0/0	0/0	0/0	0/0	0/0
Poland	0/480	0/480	122/480	0/0	0/480	122/480	122/480
Portugal	148/103	148/103	148/103	0/0	148/103	148/103	148/103
Romania	0/0	18/0	18/0	0/0	18/0	18/0	18/0
Russian Federation	0/38	0/0	0/38	0/0	0/38	0/38	0/38
Serbia	0/109	0/0	0/109	0/0	0/0	0/109	0/109
Slovakia	0/112	0/112	110/112	0/112	0/112	0/112	111/112
Slovenia	0/45	0/45	0/45	0/0	0/45	0/45	0/45
Spain	0/245	0/245	0/245	0/0	0/245	0/245	0/245
Sweden	0/584	0/584	0/584	0/0	0/584	0/584	0/583
Switzerland	8/0	8/0	8/0	0/0	8/0	8/0	8/0
United Kingdom	58/149	58/149	58/149	0/149	58/149	58/149	58/149

Table B.2: Number of datapoints for the forest topsoil (0 - 10 cm) per country per heavy metal. The first value in each cell indicates the number of data points in S1, while the second value is the number of data points in S2.

Countries	Cadmium	Chromium	Copper	Mercury	Nickel	Lead	Zinc
Austria	131/135	131/135	131/135	0/0	131/135	131/135	131/135
Azores (Portugal)	0/0	0/0	0/0	0/0	0/0	0/0	0/0
Belgium	0/10	0/10	0/10	0/0	0/10	0/10	0/10
Bulgaria	0/0	0/0	0/0	0/0	0/0	0/0	0/0
Canaries (Spain)	0/3	0/3	0/3	0/0	0/3	0/3	0/3
Croatia	0/0	0/0	0/0	0/0	0/0	0/0	0/0
Cyprus	0/15	0/15	0/15	0/0	0/15	0/11	0/15
Czech Republic	99/146	0/145	99/146	0/0	0/145	99/146	99/146
Denmark	0/25	0/25	0/25	0/0	0/25	0/25	0/25
Estonia	77/83	0/83	0/83	0/83	0/83	77/83	77/83
Finland	0/567	0/567	0/567	0/0	0/567	0/567	0/567
France	0/542	0/542	0/542	0/542	0/542	0/542	0/542
Germany	110/412	110/412	110/412	0/172	110/412	110/412	110/412
Greece	0/0	0/0	0/0	0/0	0/0	0/0	0/0
Hungary	0/75	0/0	0/75	0/0	0/0	0/75	0/75
Ireland	0/11	0/0	0/11	0/0	0/11	0/11	0/11
Italy	0/238	0/238	0/238	0/213	0/238	0/238	0/238
Latvia	0/77	0/77	0/77	0/77	0/77	0/77	0/77
Lithuania	0/56	0/56	0/56	0/57	0/56	0/56	0/56
Luxembourg	0/0	0/0	0/0	0/0	0/0	0/0	0/0
Netherlands	0/0	11/0	11/0	0/0	11/0	0/0	11/0
Norway	0/0	0/0	0/0	0/0	0/0	0/0	0/0
Poland	0/524	0/524	122/524	0/0	0/524	122/524	122/524
Portugal	147/103	147/103	147/103	0/0	147/103	147/103	147/103
Romania	0/0	0/0	0/0	0/0	0/0	0/0	0/0
Russian Federation	0/6	0/0	0/6	0/0	0/6	0/6	0/6
Serbia	0/128	0/13	0/128	0/0	0/13	0/128	0/128
Slovakia	0/112	0/112	111/112	0/112	0/112	0/112	111/112
Slovenia	0/45	0/45	0/45	0/0	0/45	0/45	0/45
Spain	0/267	0/267	0/267	0/0	0/267	0/267	0/267
Sweden	0/440	0/440	0/440	0/0	0/440	0/440	0/440
Switzerland	44/0	44/0	44/0	0/0	44/0	44/0	44/0
United Kingdom	0/166	0/166	0/166	0/166	0/166	0/166	0/166

B.2 SUMMARY STATISTICS OF HEAVY METAL CONCENTRATIONS

Table B.3: Summary statistics including left-censored values of Aqua Regia extractable **Cd (mg/kg)** for the first forest soil condition survey (1985 - 2000).

Layer	n	Cen %	P _{2.5}	P ₂₅	P ₅₀	P ₇₅	P _{97.5}	Mean	MeanCI _{95%}		Max
									LCL	UCL	
O	1419	9.7	0.056	0.200	0.400	0.600	3.620	0.653	0.624	0.683	6.600
M01	608	21.4	0.010	0.100	0.100	0.750	3.000	0.579	0.512	0.646	5.350
M12	483	29.0	0.007	0.061	0.200	0.900	3.195	0.622	0.541	0.702	6.400
M24	106	2.8	0.075	0.102	0.198	0.438	2.368	0.438	0.311	0.566	4.686
H	83	3.6	0.088	0.300	0.500	0.800	2.100	0.600	0.427	0.773	4.900

Table B.4: Summary statistics including left-censored values of Aqua Regia extractable **Cd (mg/kg)** for the second forest soil condition survey (2000 - 2015).

Layer	n	Cen %	P _{2.5}	P ₂₅	P ₅₀	P ₇₅	P _{97.5}	Mean	MeanCI _{95%}		Max
									LCL	UCL	
O	3736	30.6	0.002	0.019	0.067	0.240	2.600	0.404	0.381	0.427	32.441
M01	4186	53.1	0.048	0.141	0.300	0.490	1.343	0.345	0.323	0.368	18.735
M12	1686	57.1	0.003	0.025	0.080	0.240	2.000	0.383	0.346	0.421	8.000
M24	1409	53.5	0.002	0.024	0.080	0.270	2.470	0.428	0.384	0.472	7.800
M48	1316	57.9	0.003	0.027	0.092	0.300	2.880	0.380	0.335	0.425	13.244
H01	202	37.1	0.046	0.133	0.300	0.460	1.076	0.406	0.269	0.543	13.400
H12	197	42.1	0.008	0.046	0.120	0.331	1.446	0.391	0.230	0.552	13.400
H24	162	55.6	0.003	0.022	0.066	0.198	1.394	0.327	0.154	0.500	13.400
H48	51	43.1	0.010	0.041	0.100	0.230	1.375	0.257	0.168	0.346	1.432

Table B.5: Summary statistics including left-censored values of Aqua Regia extractable **Hg (mg/kg)** for the second forest soil condition survey (2000 - 2015).

Layer	n	Cen %	P _{2.5}	P ₂₅	P ₅₀	P ₇₅	P _{97.5}	Mean	MeanCI _{95%}		Max
									LCL	UCL	
O	952	14.9	0.001	0.020	0.058	0.700	2.200	0.202	0.181	0.224	9.134
M01	1422	21.1	0.030	0.090	0.172	0.251	0.613	0.164	0.141	0.186	12.200
M12	464	21.8	0.008	0.039	0.080	0.137	1.050	0.320	0.273	0.368	4.100
M24	456	26.3	0.005	0.038	0.100	0.300	1.900	0.378	0.320	0.435	4.800
M48	391	34.3	0.002	0.026	0.082	0.400	2.200	0.457	0.389	0.526	3.000
H01	37	0.0	0.100	0.200	0.200	0.300	0.410	0.229	0.196	0.262	0.500
H12	42	61.9	0.007	0.024	0.051	0.100	0.395	0.138	0.101	0.175	0.800
H24	34	55.9	0.002	0.012	0.038	0.100	1.635	0.224	0.090	0.357	1.800
H48	25	56.0	0.007	0.024	0.052	0.100	0.540	0.148	0.097	0.199	0.600

APPENDIX B. ANNEX TABLES

Table B.6: Summary statistics including left-censored values of Aqua Regia extractable **Cr (mg/kg)** for the first forest soil condition survey (1985 - 2000).

Layer	n	Cen %	P _{2.5}	P ₂₅	P ₅₀	P ₇₅	P _{97.5}	Mean	MeanCI _{95%}		Max
									LCL	UCL	
O	1148	1.3	2.0	5.0	9.0	13.0	45.9	18.5	16.4	20.7	567.0
M01	443	0	5.0	14.5	25.0	34.8	95.7	30.7	27.6	33.7	373.0
M12	318	0	4.0	16.0	26.0	41.0	112.2	33.2	29.8	36.7	320.0
M24	120	0	10.0	21.4	29.0	39.2	80.2	31.9	28.8	35.0	92.4
H	55	0	2.0	8.0	11.0	17.0	78.3	11.4	8.6	14.2	51.0

Table B.7: Summary statistics including left-censored values of Aqua Regia extractable **Cr (mg/kg)** for the second forest soil condition survey (2000 - 2015).

Layer	n	Cen %	P _{2.5}	P ₂₅	P ₅₀	P ₇₅	P _{97.5}	Mean	MeanCI _{95%}		Max
									LCL	UCL	
O	3436	16.7	1.1	4.3	11.9	31.0	77.8	17.3	16.4	18.2	464.0
M01	3978	8.9	1.0	4.5	10.9	20.3	83.0	23.1	22.0	24.3	1067.0
M12	1587	3.7	0.9	5.0	15.4	30.8	80.3	22.8	21.5	24.1	343.3
M24	1304	3.5	1.2	5.1	17.0	32.7	78.3	21.7	20.3	23.2	326.7
M48	1213	4.2	1.1	5.0	13.0	31.3	77.9	21.0	19.6	22.4	348.9
H01	178	39.3	0.1	0.7	2.0	4.2	24.2	4.2	2.9	5.5	91.5
H12	177	24.9	0.1	0.8	2.8	9.4	43.3	7.7	5.9	9.4	91.1
H24	149	22.8	0.1	0.9	2.5	13.0	44.7	8.7	6.7	10.6	58.6
H48	45	8.9	0.3	1.5	7.3	14.9	70.3	12.9	7.3	18.5	90.9

Table B.8: Summary statistics including left-censored values of Aqua Regia extractable **Cu (mg/kg)** for the first forest soil condition survey (1985 - 2000).

Layer	n	Cen %	P _{2.5}	P ₂₅	P ₅₀	P ₇₅	P _{97.5}	Mean	MeanCI _{95%}		Max
									LCL	UCL	
O	1559	0.8	4.1	7.0	10.0	20.0	63.4	15.8	14.8	16.7	438.0
M01	775	4.1	0.9	4.0	11.0	20.0	48.0	14.3	13.4	15.3	102.0
M12	650	6.0	0.6	3.0	10.0	21.0	50.8	14.2	13.1	15.3	86.0
M24	120	0.0	5.0	12.3	20.0	28.1	48.3	21.6	19.3	23.9	74.8
H	45	0.0	2.0	8.0	12.0	19.0	47.0	17.0	11.9	22.1	96.0

Table B.9: Summary statistics including left-censored values of Aqua Regia extractable **Cu (mg/kg)** for the second forest soil condition survey (2000 - 2015).

Layer	n	Cen %	P _{2.5}	P ₂₅	P ₅₀	P ₇₅	P _{97.5}	Mean	MeanCI _{95%}		Max
									LCL	UCL	
O	3736	15.8	0.2	1.2	4.6	16.1	45.0	11.3	10.9	11.7	211.0
M01	4186	14.5	2.0	5.9	9.1	14.0	35.7	11.5	10.8	12.2	982.0
M12	1687	15.5	0.4	2.0	6.1	14.5	49.2	11.9	10.9	13.0	531.0
M24	1409	20.6	0.3	1.5	6.0	15.1	51.3	10.7	9.9	11.5	177.0
M48	1316	23.7	0.2	1.2	4.9	14.9	47.7	11.0	10.0	12.0	450.3
H01	202	36.6	0.6	2.1	4.4	8.9	22.9	6.7	5.8	7.5	37.4
H12	197	23.4	0.5	1.8	4.6	10.0	37.7	9.5	6.5	12.5	261.1
H24	161	21.7	0.5	1.8	5.2	11.7	35.5	9.1	7.2	11.1	111.1
H48	51	9.8	0.7	2.7	4.9	10.0	40.8	9.1	5.4	12.7	82.1

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Table B.10: Summary statistics including left-censored values of Aqua Regia extractable **Ni (mg/kg)** for the first forest soil condition survey (1985 - 2000).

Layer	n	Cen %	P _{2.5}	P ₂₅	P ₅₀	P ₇₅	P _{97.5}	Mean	MeanCI _{95%}		Max
									LCL	UCL	
O	1104	0.4	2.2	6.0	9.0	12.8	33.4	12.7	12.0	13.3	233.0
M01	443	0.0	2.0	11.0	20.0	31.0	63.9	23.9	21.9	25.9	298.0
M12	318	0.0	2.0	14.0	26.0	35.0	64.1	27.1	25.2	29.1	147.0
M24	120	0.0	8.9	20.4	31.2	41.7	77.5	32.7	29.7	35.7	88.1
H	46	2.2	3.0	8.0	10.0	15.0	34.0	11.3	8.2	14.4	68.0

Table B.11: Summary statistics including left-censored values of Aqua Regia extractable **Ni (mg/kg)** for the second forest soil condition survey (2000 - 2015).

Layer	n	Cen %	P _{2.5}	P ₂₅	P ₅₀	P ₇₅	P _{97.5}	Mean	MeanCI _{95%}		Max
									LCL	UCL	
O	3501	17.5	0.4	2.4	7.6	25.0	74.3	10.6	10.2	11.0	221.8
M01	3995	13.6	1.0	3.6	8.0	13.1	40.5	14.7	13.7	15.7	916.0
M12	1611	6.4	0.3	1.9	6.4	19.4	61.6	15.7	14.7	16.7	228.8
M24	1332	6.3	0.5	2.4	8.5	22.0	66.8	16.7	15.5	18.0	224.2
M48	1241	6.4	0.4	2.5	7.0	22.1	76.7	17.5	16.1	19.0	311.6
H01	201	36.8	0.3	1.0	2.3	3.8	13.6	3.3	2.6	4.1	44.6
H12	196	23.5	0.3	1.1	2.8	5.3	20.8	4.4	3.6	5.2	38.9
H24	161	23	0.3	1.0	2.7	6.3	21.6	4.9	3.9	5.9	54.4
H48	51	7.8	0.3	1.6	4.3	8.5	39.8	8.8	4.0	13.6	117.8

Table B.12: Summary statistics including left-censored values including left-censored values of Aqua Regia extractable **Pb (mg/kg)** for the first forest soil condition survey (1985 - 2000).

Layer	n	Cen %	P _{2.5}	P ₂₅	P ₅₀	P ₇₅	P _{97.5}	Mean	MeanCI _{95%}		Max
									LCL	UCL	
O	1564	7.9	2.0	17.5	23.0	33.0	181.4	64.6	59.3	69.9	2114.0
M01	730	6.2	1.0	9.1	25.0	41.0	108.8	32.7	28.1	37.2	1520.0
M12	605	11.4	1.0	4.0	17.0	31.0	77.8	22.2	20.2	24.2	206.0
M24	120	0.0	8.0	18.9	26.1	35.9	76.5	30.9	27.3	34.5	139.0
H	83	0.0	2.6	22.0	38.0	79.2	255.9	38.1	26.8	49.3	334.0

Table B.13: Summary statistics including left-censored values of Aqua Regia extractable **Pb (mg/kg)** for the second forest soil condition survey (2000 - 2015).

Layer	n	Cen %	P _{2.5}	P ₂₅	P ₅₀	P ₇₅	P _{97.5}	Mean	MeanCI _{95%}		Max
									LCL	UCL	
O	3734	15.6	0.7	2.7	7.4	15.6	49.1	39.0	34.1	43.8	5965.7
M01	4182	8.8	1.8	8.6	22.3	40.5	168.0	34.8	26.4	43.2	17114.0
M12	1685	3.9	2.3	9.5	20.3	36.7	107.9	37.4	11.5	63.4	22300.0
M24	1408	4.9	2.0	7.8	17.7	30.8	91.5	15.9	14.6	17.1	539.3
M48	1317	7.1	1.1	4.0	10.4	20.7	63.0	12.3	11.1	13.5	541.8
H01	200	35.5	3.0	8.6	17.7	27.1	101.2	25.3	18.6	32.0	541.8
H12	196	21.4	0.9	5.5	12.6	22.9	119.8	340.0	-279.6	959.6	61940.0
H24	161	21.1	0.4	2.2	5.9	11.4	96.7	78.2	-47.9	204.4	10350.0
H48	51	17.6	0.2	2.2	4.7	11.3	106.8	62.1	-37.1	161.4	2584.0

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Table B.14: Summary statistics including left-censored values of Aqua Regia extractable **Zn (mg/kg)** for the first forest soil condition survey (1985 - 2000).

Layer	n	Cen %	P _{2.5}	P ₂₅	P ₅₀	P ₇₅	P _{97.5}	Mean	MeanCI _{95%}		Max
									LCL	UCL	
O	1746	0.1	4.1	23.0	33.0	49.5	104.9	70.8	68.6	73.1	638.0
M01	852	2.1	2.0	12.5	39.0	68.0	157.0	49.0	45.9	52.1	423.0
M12	727	3.0	2.0	8.0	34.0	65.0	134.0	44.0	40.7	47.3	445.0
M24	120	0.0	18.5	46.0	64.7	83.9	184.3	70.7	63.0	78.4	301.5
H	83	0.0	12.0	44.0	60.0	84.0	188.0	39.5	33.4	45.5	170.0

Table B.15: Summary statistics including left-censored values of Aqua Regia extractable **Zn (mg/kg)** for the second forest soil condition survey (2000 - 2015).

Layer	n	Cen %	P _{2.5}	P ₂₅	P ₅₀	P ₇₅	P _{97.5}	Mean	MeanCI _{95%}		Max
									LCL	UCL	
O	3735	1.4	3.4	10.3	28.0	61.9	124.6	63.0	60.7	65.2	2918.9
M01	4186	3.3	13.9	39.2	52.8	71.2	163.0	47.5	45.6	49.5	2557.5
M12	1722	1	2.7	13.4	32.8	64.8	165.8	47.8	44.4	51.3	2460.0
M24	1438	1	3.7	14.5	34.7	65.0	152.0	42.9	40.8	45.1	382.0
M48	1341	0.9	3.2	13.3	30.7	63.0	144.1	41.4	38.8	43.9	662.3
H01	202	3	4.2	18.9	33.2	58.2	248.5	56.8	44.0	69.7	821.0
H12	183	2.7	2.1	6.4	13.5	35.1	139.8	32.9	23.3	42.6	662.3
H24	152	3.3	0.8	3.8	9.4	29.8	136.9	30.2	18.8	41.6	662.3
H48	47	6.4	1.0	4.1	11.2	21.8	58.0	18.1	11.4	24.7	134.6

Table B.16: Summary statistics cadmium stocks (mg/m²) per soil layer in S1.

Layer	n	P _{2.5}	P ₂₅	P ₅₀	P ₇₅	P _{97.5}	Mean	MeanCI _{95%}		Max
								LCL	UCL	
O	1342	0.1	1.0	2.0	3.7	16.6	3.4	3.2	3.8	108.2
M01	608	2.8	9.4	13.3	52.8	260.9	45.1	40.1	51.1	432.8
M12	483	4.5	9.6	15.1	61.3	271.9	49.8	44.1	57.8	465.0
H	59	0.8	3.8	7.0	16.9	456.3	56.3	28.3	134.0	1138.4

Table B.17: Summary statistics cadmium stocks (mg/m²) per soil layer in S2.

Layer	n	P _{2.5}	P ₂₅	P ₅₀	P ₇₅	P _{97.5}	Mean	MeanCI _{95%}		Max
								LCL	UCL	
O	3453	0.04	0.3	0.8	2.0	8.4	1.9	1.7	2.5	526.3
M01	3961	2.6	7.5	11.6	19.7	116.2	22.9	21.7	24.6	1609.2
M12	1675	4.3	11.1	14.7	25.9	172.4	34.0	31.0	38.4	830.7
M24	1387	8.7	25.8	30.3	52.0	381.8	66.3	61.2	73.1	1296.4
M48	1297	11.9	53.1	60.5	89.8	916.0	143.1	128.7	160.2	2772.8
H01	202	0.3	1.8	3.6	6.1	24.5	5.5	4.6	6.9	77.5
H12	197	0.2	1.3	2.3	4.7	43.6	5.6	4.4	7.8	72.1
H24	162	0.5	2.1	3.4	7.1	48.6	8.1	6.1	11.8	163.2
H48	51	2.6	5.0	6.1	13.3	67.2	14.1	10.4	22.1	107.6

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Table B.18: Summary statistics chromium stocks (mg/m²) per soil layer in S1.

Layer	n	P _{2.5}	P ₂₅	P ₅₀	P ₇₅	P _{97.5}	Mean	MeanCI95%		Max
								LCL	UCL	
O	1074	2.0	25.0	46.3	94.7	431.9	88.0	80.0	99.1	2335.3
M01	443	188.8	1170.8	1925.9	3094.5	9780.4	2581.2	2360.0	2870.7	23699.5
M12	318	254.5	1167.4	2014.4	3285.8	10584.4	2784.6	2491.0	3145.8	23025.6
H	44	13.1	81.8	162.5	425.5	11670.2	841.2	289.2	2190.8	12530.2

Table B.19: Summary statistics chromium stocks (mg/m²) per soil layer in S2.

Layer	n	P _{2.5}	P ₂₅	P ₅₀	P ₇₅	P _{97.5}	Mean	MeanCI95%		Max
								LCL	UCL	
O	3217	1.0	7.7	28.1	67.3	306.3	61.7	57.5	66.9	2996.8
M01	3868	30.9	430.4	1051.3	2330.7	6694.1	1778.7	1707.4	1883.8	64237.8
M12	1576	52.1	654.2	1312.3	2789.3	7208.8	2032.8	1928.7	2146.5	29593.2
M24	1285	105.3	1253.8	2346.9	5317.7	14977.7	4033.7	3792.5	4348.9	77071.7
M48	1194	297.9	2266.6	4393.7	11362.0	33569.3	8332.1	7779.4	8920.8	155190.7
H01	178	1.2	6.6	20.1	49.1	497.0	75.5	53.7	120.7	2051.8
H12	177	1.2	7.3	41.9	156.8	761.5	134.5	107.7	183.5	1697.6
H24	149	2.2	15.9	67.9	385.5	1786.4	323.6	254.0	447.5	4642.0
H48	45	18.9	66.7	371.7	765.4	5238.7	776.4	475.6	1266.1	5961.6

Table B.20: Summary statistics copper stocks (mg/m²) per soil layer in S1.

Layer	n	P _{2.5}	P ₂₅	P ₅₀	P ₇₅	P _{97.5}	Mean	MeanCI95%		Max
								LCL	UCL	
O	1426	2.3	23.4	43.6	99.0	455.4	94.7	87.1	107.0	4305.6
M01	775	74.1	251.6	850.0	1658.1	4688.6	1195.5	1112.1	1281.5	9690.0
M12	650	78.5	264.0	718.1	1710.9	4991.4	1236.9	1132.7	1358.9	9141.3
H	44	35.3	91.3	138.1	390.5	9479.3	1147.7	564.3	2897.9	18499.0

Table B.21: Summary statistics copper stocks (mg/m²) per soil layer in S2.

Layer	n	P _{2.5}	P ₂₅	P ₅₀	P ₇₅	P _{97.5}	Mean	MeanCI95%		Max
								LCL	UCL	
O	3453	1.6	8.5	21.4	48.3	220.9	44.6	42.2	48.2	2004.8
M01	3961	51.6	174.2	436.3	1060.6	3713.2	870.7	823.2	930.0	45528.4
M12	1676	71.1	195.5	530.2	1293.2	4614.5	1073.7	995.7	1223.5	59369.5
M24	1388	158.2	323.2	815.0	2375.4	9578.1	1935.0	1817.0	2077.4	23010.0
M48	1297	398.8	644.0	1577.8	5783.4	19980.6	4219.3	3917.4	4562.7	75650.4
H01	202	2.3	18.0	52.4	99.6	585.8	112.0	89.8	139.4	1411.5
H12	197	2.3	20.0	72.1	155.2	904.5	181.7	136.6	287.0	5247.6
H24	161	3.7	30.1	157.7	403.8	1985.6	339.7	271.7	445.4	3925.9
H48	51	37.0	111.8	245.1	594.8	2925.3	542.5	378.3	832.0	4201.5

Table B.22: Summary statistics mercury stocks (mg/m²) per soil layer in S2.

Layer	n	P _{2.5}	P ₂₅	P ₅₀	P ₇₅	P _{97.5}	Mean	MeanCI95%		Max
								LCL	UCL	
O	921	0.08	0.1	0.2	0.9	3.7	0.8	0.7	1.0	60.5
M01	1421	0.9	3.9	6.1	10.2	58.3	11.6	10.5	14.2	957.3
M12	463	1.6	4.3	7.5	22.2	132.5	23.2	20.2	26.9	253.3
M24	455	3.1	8.1	10.9	57.2	353.7	58.3	50.2	68.3	694.7
M48	389	2.6	14.0	19.0	215.7	845.1	159.6	134.0	188.3	1711.2
H01	37	1.2	2.7	4.7	5.6	9.2	4.6	3.8	5.5	11.7
H12	42	0.2	0.4	0.6	2.1	9.3	1.9	1.3	3.6	17.3
H24	34	0.4	0.7	1.5	4.1	55.2	7.4	3.0	23.3	122.4
H48	25	0.8	0.9	2.0	5.6	33.3	6.4	3.6	13.9	50.9

Table B.23: Summary statistics nickel stocks (mg/m²) per soil layer in S1.

Layer	n	P _{2.5}	P ₂₅	P ₅₀	P ₇₅	P _{97.5}	Mean	MeanCI95%		Max
								LCL	UCL	
O	1074	2.8	21.5	41.1	78.0	268.1	64.3	59.7	71.2	1476.6
M01	443	141.1	859.2	1530.9	2707.4	6022.2	1971.9	1831.5	2160.4	18934.2
M12	318	224.8	985.7	1758.3	2986.2	6632.7	2207.2	2034.1	2396.0	9714.3
H	44	6.8	72.1	132.3	263.0	7402.5	684.6	317.2	1525.0	9676.4

Table B.24: Summary statistics nickel stocks (mg/m²) per soil layer in S2.

Layer	n	P _{2.5}	P ₂₅	P ₅₀	P ₇₅	P _{97.5}	Mean	MeanCI95%		Max
								LCL	UCL	
O	3244	1.0	6.0	20.5	46.0	166.0	36.2	34.4	38.3	1234
M01	3885	27.0	157.0	474.0	1408.0	5329.4	1148.1	1081.2	1228.7	64544
M12	1600	38.0	304.0	716.5	1819.8	6293.4	1391.8	1297.1	1494.2	23453
M24	1311	83.8	653.0	1336.0	3622.5	15004.5	3020.4	2802.4	3296.3	53763
M48	1222	264.0	1294.5	2775.0	8586.2	28907.7	6529.5	6066.9	7093.1	131550
H01	201	1.0	9.0	25.0	51.0	366.0	64.0	47.2	107.1	2043
H12	196	1.0	9.8	42.0	92.2	476.8	86.3	67.3	118.0	1508
H24	161	2.0	19.0	73.0	205.0	1303.0	183.6	144.2	241.4	1869
H48	51	16.0	71.0	213.0	469.0	2222.2	494.6	315.0	912.0	6031

Table B.25: Summary statistics lead stocks (mg/m²) per soil layer in S1.

Layer	n	P _{2.5}	P ₂₅	P ₅₀	P ₇₅	P _{97.5}	Mean	MeanCI95%		Max
								LCL	UCL	
O	1366	4.2	85.0	182.2	534.5	2679.1	504.0	453.2	601.7	32833
M01	730	101.9	703.8	1714.6	3374.8	9336.3	2683.8	2355.7	3774.7	198360
M12	605	99.3	450.2	1390.5	2470.2	5628.9	1710.7	1591.8	1874.3	16911
H	59	116.6	234.3	365.4	1011.5	31595.3	3375.6	1787.9	6542.0	38124

Table B.26: Summary statistics lead stocks (mg/m²) per soil layer in S2.

Layer	n	P _{2.5}	P ₂₅	P ₅₀	P ₇₅	P _{97.5}	Mean	MeanCI95%		Max
								LCL	UCL	
O	3451	0.9	10.2	48.5	168.9	1329.3	219.3	194.5	265.3	44340
M01	3957	63.8	751.0	1722.7	2862.8	7488.8	2573.5	2210.5	3866.3	1224327
M12	1674	92.0	956.6	1638.7	2707.2	7622.1	3104.8	2130.8	7820.4	1575208
M24	1387	183.4	1036.1	2001.0	3731.2	10262.1	2954.4	2782.3	3410.5	140651
M48	1298	443.1	1398.5	2727.4	5931.4	21801.8	4767.5	4453.6	5132.9	79402
H01	200	2.5	21.6	165.2	383.6	1873.0	358.9	273.6	483.1	6941
H12	196	2.5	96.4	179.9	331.5	2540.5	27551.6	342.8	136294.0	5326840
H24	161	4.7	63.7	164.3	318.3	2537.0	11412.5	329.2	55663.1	1780200
H48	51	47.8	91.1	240.6	584.2	4853.3	17931.0	438.0	87721.6	888896

Table B.27: Summary statistics zinc stocks (mg/m²) per soil layer in S1.

Layer	n	P _{2.5}	P ₂₅	P ₅₀	P ₇₅	P _{97.5}	Mean	MeanCI95%		Max
								LCL	UCL	
O	1074	2.8	21.5	41.1	78.0	268.1	64.3	59.7	71.2	1477
M01	443	141.1	859.2	1530.9	2707.4	6022.2	1971.9	1831.5	2160.4	18934
M12	318	224.8	985.7	1758.3	2986.2	6632.7	2207.2	2034.1	2396.0	9714
H	44	6.8	72.1	132.3	263.0	7402.5	684.6	317.2	1525.0	9676

Table B.28: Summary statistics zinc stocks (mg/m²) per soil layer in S2.

Layer	n	P _{2.5}	P ₂₅	P ₅₀	P ₇₅	P _{97.5}	Mean	MeanCI95%		Max
								LCL	UCL	
O	3452	8.0	64.0	162.0	311.0	1560.1	317.7	289.9	369.2	44367
M01	3961	181.0	1031.0	2306.0	4968.0	12430.0	3577.9	3458.0	3765.7	182962
M12	1711	387.5	1644.5	3023.0	5839.0	13726.2	4356.8	4150.5	4717.4	173767
M24	1417	726.8	3097.0	5401.0	11038.0	24003.0	7949.0	7626.2	8341.1	72072
M48	1322	1488.6	5237.0	9700.5	21914.2	48858.0	15337.1	14605.4	16186.1	147874
H01	202	35.0	189.5	359.0	734.8	5380.0	928.4	731.3	1337.5	19132
H12	183	29.3	97.5	165.0	368.5	2130.9	362.6	292.5	461.2	3924
H24	152	51.0	117.8	196.0	548.8	2973.0	526.9	419.6	679.0	4554
H48	47	102.0	183.0	469.0	1183.0	3296.7	916.3	665.1	1446.9	6892