Schlutow *et al. Environ Sci Eur (2021) 33:7*
https://doi.org/10.1186/s12302-020-00391-w

Environmental Sciences Europe

RESEARCH

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Assessing the relevance of atmospheric heavy metal deposition with regard to ecosystem integrity and human health in Germany

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Abstract

Background: The critical values for heavy metal fluxes for protecting the human health and ecosystem's integrity in Germany, especially the Federal Immission Control Act (BImSchG in Gesetz zum Schutz vor schädlichen Umwelteinwirkungen durch Luftverunreinigungen, Geräusche, Erschütterungen und ähnliche Vorgänge (Bundes-Immissionsschutzgesetz-BImSchG), 1974/2020) with its implementing ordinances (especially the 39th BImSchV in Neununddreißigste Verordnung zur Durchführung des Bundes-Immissionsschutzgesetzes Verordnung über Luftqualitätsstandards und Emissionshöchstmengen vom 2. August 2010, zuletzt geändert durch Art. 2 V v. 18.7.2018 I 1222, 2010, 2018), the Federal Soil Protection Ordinance (BBodSchV in Bundes-Bodenschutz- und Altlastenverordnung (BBodSchV) (GBBl. I S. 1554 vom 12. Juli 1999, zuletzt durch Artikel 3 Absatz 4 der Verordnung vom 27. September 2017 (BGBl. I S. 3465) ge-ändert, 1999/2015) and the Technical Instructions on Air Quality Control (Luft in Erste Allgemeine Verwaltungsvorschrift zum Bundes–Immissionsschutzgesetz (Technische Anleitung zur Reinhaltung der Luft – TA Luft), 2002), were analysed, assessed with regard to the possibilities and applicability of the risk assessment, and were prepared for evaluation in comparison to the respective atmospheric deposition modelled with the chemical transport model LOTOS-EUROS. For a comparison of the critical values, the critical loads for cadmium, lead and mercury inputs were updated for Germany on a scale of 1:1 Mio, and critical loads for additional heavy metals (arsenic, copper, zinc, chromium and nickel) were computed, respectively. Due to the methodological differences of their derivation, the critical values of the individual regulations are only conditionally comparable to one another and to the critical loads. Sometimes major differences exist due to different levels of protection, various protective goods and the effect relationship. Only with the critical load calculations, inputs and outputs can be balanced.

Results: For two unregulated metals (thallium and vanadium) a preliminary rough estimate of the risk of inputs in the receptors was provided as a calculated balance for in- and acceptable outputs. The uncertainty analysis shows, that the highest deviations occurred in the metal contents in plants used to calculate the output through the harvesting of the biomass. The critical load calculation has the highest sensitivity to changes in the pH value. The critical loads for heavy metal fluxes for protecting the human health ($CL(M)_{drink}$) and ecosystem's integrity $CL(M)_{eco}$) for arsenic, nickel, zinc and chromium were not exceeded in Germany for 2009–2011. $CL(M)_{drink}$ and $CL(M)_{eco}$ are exceeded by Hg and Pb inputs, especially in the low rainfall regions of Germany (Brandenburg, lowlands of Saxony-Anhalt, Leipzig Bay, Ruhr valley) with wood vegetation; in addition $CL(Cu)_{eco}$ is exceeded by copper deposition 2010 in the

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area surrounding Berlin and in the Ruhr valley. The critical loads for cadmium for the protection of drinking water $CL(Cd)_{drink}$ and for the protection of human food from wheat products $CL(Cd)_{food}$ are not exceeded in the German data set due to atmospheric deposition in 2010, but in the worst-case scenario the maximum atmospheric deposition in 2010 could exceeded the lowest $CL(Cd)_{drink}$ and $CL(Cd)_{food}$.

Conclusions: That assessment of risks was based on deposition from the atmosphere, which represents only a fraction of the inputs compared to the inputs from the use of fertilisers and other sources. This study suggests the conclusive recommendation to methodically deepen and broaden the assessment and evaluation of atmospheric deposition. This is especially true for the spatial validation and specification of exposure for ecosystem types.

Keywords: Heavy metals, Assessment values of heavy metals, Critical loads for the protection of human health, Critical loads for the protection of ecosystems

Background

Besides natural geochemical processes, anthropogenic sources contribute to the input of heavy metals into the soil, plants and groundwater. These are in particular heavy metal depositions from emissions of dust and aerosols from industrial and power generation plants, the use of metal-contaminated mineral phosphate fertilisers and sewage sludge in agriculture, tyre wear in road traffic, surface runoff from mining waste dumps contaminated with heavy metals, waste water irrigation in agriculture, etc. [1, 2]. However, the present study is mainly limited to the atmospheric input of heavy metals into soil, plants and groundwater.

The extent and temporal and spatial distribution of heavy metal inputs from the atmosphere can be determined with technical and biological collectors such as mosses and chemical transport models (EMEP [3], LOTOS-EUROS) [4–6]. The aim of this contribution was to assess heavy metal deposition rates in terms of their effects and compliance with legal requirements and environmental quality objectives. As heavy metals can be transported in the atmosphere over long distances and across national borders, both national and international regulations and assessment methods have to be considered thereby.

The risk potential for human health of increased concentrations of heavy metals in air, food and drinking water has been known for a long time, as has that of heavy metal enrichment for aquatic and terrestrial ecosystems. In order to prevent harmful effects and avert dangers, the German Federal Immission Control Act [7], the Federal Immission Control Acts (BImSchV) and the Technical Instructions Air [8], regulate the limitation of heavy metal emission (lead, cadmium, mercury, arsenic, nickel) and immission or deposition. The 39th Federal Immission Control Act [9] implements[1] the EU Directives 2008/50/EC [10, 11] and 2004/107/EC [12].

At the end of 2013, the EU presented a new package of measures for clean air in Europe to update existing legislation. The objective is to further reduce emissions of air pollutants in order to reduce or eliminate impacts on human health and the environment. The package includes a “Clean Air for Europe” programme, the initial aim of which is to ensure that existing objectives are met. In addition, new air quality targets for 2020 and 2030 have also been formulated. The objective of this strategy for 2020 is to reduce air pollution to levels that no longer have a significant impact on human health or the environment. The assessment of the relevance of heavy metals deposition presented in this article was also intended to evaluate whether this objective can be achieved with the existing regulations.

The European Directive 2008/50/EC prescribes a limit value for lead in PM10 dust of 500 ng/m^3. This limit value has been in force since 2005. Directive 2004/107/EC contains target values for nickel, arsenic and cadmium. The target values correspond to those of the EU position paper 2000 [13]. When setting EU limit and target values, not only health considerations, but also technical feasibility and economic effects are taken into account. Article 21(5) of Directive 2010/75/EU [14] obliges EU Member States to adapt the permit requirements for the construction or modification of a pollutant-emitting installation to new or revised BAT (= best available techniques) conclusions. The European Commission has been publishing new BAT reference documents on a regular basis since 2001.

Another international regulation binding under international law is the Heavy Metals Protocol of the Convention on Long-range Transboundary Air Pollution (CLRTAP, also known as the Århus Protocol on Heavy Metals). It came into force at the end of 2003 and was revised in December 2012 and adapted to the modern requirements of industrial plants. In this protocol, emissions of Pb, Cd, Hg into the air are regulated, e.g. by

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[1] http://www.umweltbundesamt.de/themen/luft/regelungen-strategien/luftreinhaltung-in-der-eu.

technical standards for industries that emit heavy metals. It also regulates the use of lead in petrol or the use of cadmium and mercury in certain products. In the Convention on Long-range Transboundary Air Pollution (CLRTAP), the impact assessment of heavy metal inputs is carried out using the critical loads approach, which has long been proven for the assessment of inputs of eutrophic nitrogen or acid into ecosystems. This method enables a comprehensive risk assessment for large areas as, e.g. for Germany, the EU or the EMEP region [15]. The determination of deposition required for the classification of the risk of exceeding the critical loads is carried out by measurement and modelling in the EMEP programme [4] and is supported by biomonitoring with mosses [6].

The German Ordinance on Air Quality Standards and Emission Ceilings of 2 August 2010, last amended in 2018 [9] serves to implement European requirements and their national implementation. It contains immission target values for arsenic, cadmium and nickel for the protection of human health and the environment (as an average of a calendar year). The responsible immission control authorities of the Länder are obliged to carry out periodic measurements of heavy metal concentrations in the air. If these are exceeded regionally, the authorities are obliged to draw up air pollution control plans. In practice, this initially involves a close-meshed grid measurement. The emission sources are determined on this basis. Clean air plans to reduce emissions are then drawn up and appropriate agreements are made with plant operators who have been identified as the main sources. For industrial installations covered by Directive 2008/1/EC [11], this means that the best available techniques (BAT) within the meaning of Article 2(12) of that Directive must be applied. If an operator refuses or fails to comply with a voluntary agreement, the competent authority shall impose a subsequent order. Within the framework of the precautionary obligations under Article 5 para. 1 No. 2 of the Federal Immission Control Act, the main point is that installations must retrofit to the state of the art (in accordance with the relevant BAT reference document). If the state of the art changes after the issue of a permit, a subsequent order pursuant to §17 para. 1 sentence 1 BImSchG may require that the state of the art be implemented in plants that have already been granted a permit, for example by installing filter systems or similar. If the operator of a plant subject to approval does not comply with a subsequent order, the competent authority may prohibit operation in whole or in part until the subsequent order is complied with, if a violation of the subsequent order causes an immediate danger to human health or constitutes an immediate significant danger to the environment (§20 (1) BImmSchG).

The Federal Soil Protection and Contaminated Sites Ordinance of 12 July 1999, last amended in 2017, (BBodSchV) regulates the planned investigation of harmful soil changes and their evaluation by the competent authorities on the basis of precautionary, test and measure values or permissible deposition rates. Concrete indications that give rise to sufficient suspicion of harmful soil changes or contaminated sites are generally available if investigations show that test values are exceeded. In this case, a detailed investigation should determine whether hazards arise from spatially limited accumulations of pollutants within a suspected area and whether and how a demarcation of uncontaminated areas is advisable. If a test value is exceeded at the site of sampling, it shall be determined in each individual case whether the pollutant concentration in the leachate at the site of assessment exceeds the test value. In order to assess the risks to groundwater from suspected areas, a leachate prognosis shall be prepared in order to estimate and evaluate in each individual case to what extent it can be expected that the pollutant concentration in the leachate will exceed the test value at the place of assessment. The place of assessment is the area of transition from the unsaturated to the saturated zone. Insofar as harmful soil changes and contaminated sites are present in the water-saturated soil zone, they shall be assessed with regard to a hazard to groundwater in accordance with water law regulations. The geogenically conditioned background situation of the respective groundwater region must be taken into account when applying the test values. The results of the detailed investigation are to be evaluated with regard to the extent to which measures are necessary, taking into account the circumstances of the individual case, in particular on the basis of measure values. In the event that measure values are locally exceeded, the BBodSchV contains requirements for danger prevention by decontamination and safety measures, protective and restrictive measures for individual existing installations. The procedures that then follow correspond to those according to BImSchV.

In addition to the precautionary regulations on immission control, soil protection regulations are relevant in Germany which limit the input of heavy metals including atmospheric deposition if the concentrations in the soil have already reached a certain level. Permissible additional loads aim at avoiding or reducing further accumulations of pollutants in the soil if precautionary values have already been exceeded. These are critical input rates of heavy metals in the approval procedure of individual plants. They assume an acceptable increase in concentrations in the soil if precautionary values have already been exceeded by the existing pollution. The permissible additional loads are therefore only of limited precautionary character in the sense of a sustainable avoidance of risks

Table 1 Assessment values for heavy metal fluxes or concentrations for the protection of ecosystems and human health

Metal	TA Luft Tab. 6[a]	TA Luft Tab.8[b]	BBodSchV[c]	39th BImSchV[e,f]	EU-Directive 2004/107/EG[e]	EU-Directive 2008/50/EG[e]
	Emitter-related			General load		
	$[\mathrm{g\ ha^{-1}\ a^{-1}}]$					
Mercury (Hg)	4	Field: 110 Grassland: 11	1.5			
Cadmium (Cd)	7	Field: 9 Grassland: 117	6	Housing settlement: 4.4 Coniferous forest: 7 Deciduous forest: 4 Grassland: 2.5 Field: 2.5	Housing settlement: 4.4 Coniferous forest: 7 Deciduous forest: 4 Grassland: 2.5 Field: 2.5	
Lead (Pb)	365	Field: 675 Grassland: 6935	400	Housing settlement: 435 Coniferous forest: 716 Deciduous forest: 420 Grassland: 250 Field: 250		Housing settlement: 435 Coniferous forest: 716 Deciduous forest: 420 Grassland: 250 Field: 250
Arsenic (As)	15	Field: 4271 Grassland: 219		Housing settlement: 5.2 Coniferous forest: 6 Deciduous forest: 4 Grassland: 2.2 Field: 2.2	Housing settlement: 5.2 Coniferous forest: 6 Deciduous forest: 4 Grassland: 2.2 Field: 2.2	
Nickel (Ni)	55		100	Housing settlement: 17.4 Coniferous forest: 28 Deciduous forest: 17 Grassland: 10 Field: 10	Housing settlement: 17.4 Coniferous forest: 28 Deciduous forest: 17 Grassland: 10 Field: 10	
Copper (Cu)			360			
Zinc (Zn)			1200			
Chrome (Cr)			300			
Thallium (Tl)	7	26				

[a] TA Luft = Technical Instructions for Air pollution control (deposition values to protect human health)

[b] TA Luft = Technical Instructions for Air pollution control (deposition values as reference points for the special case examination to protect environment)

[c] BBodSchV = Federal Soil Protection Ordinance (permissible additional load according to §11 para. 2)

[d] 39th BImSchV = 39th Federal Immission Control Ordinance

[e] Converted from assessment values for concentrations [4]: Tables 33 and 34)

of harmful effects due to accumulation of pollutants. They are more comparable with a bagatelle or irrelevant threshold.

Finally, the Water Framework Directive [16] contains priority substances, including the heavy metals lead, cadmium, nickel and mercury. These effect concentrations are to be included in the assessment of heavy metal inputs from a variety of entry paths, even if critical deposition cannot be directly derived from them. Table 1 in conjunction with Additional file 1: Table S1.1 provides an overview of existing legally binding assessment values. The regulations and recommendations compiled in Table 1 and Additional file 1: Table S1.1 contain different categories of assessment values which differ with regard to their protective purpose, the respective level of protection and protective objective. For this reason, this study uses the overarching term "assessment value", but takes over the nomenclature of quotations from the rules and regulations. In addition, a distinction is made between precautionary assessment values and those which serve to avert danger. Precautionary assessment values indicate limits of resilience (concentrations in environmental compartments or substance flows) below which there is no concern of significant impairment of ecosystems and their functions and services to humans. They apply generally, i.e. beyond the sphere of influence of concrete facilities, projects or management measures, and they are independent of usage claims. In law, the concept of danger is always linked to a certain probability of the occurrence of significant, harmful changes. In principle, assessment values that serve to avert hazards permit higher pollutant concentrations or inputs than precautionary ones. As a rule, they serve to assess concrete (including planned) facilities, projects or management measures and are derived from specific uses (e.g. test values and measure values in soil protection). Table 1 compiles the assessment values used in this study to compare them with critical loads. Due to the methodological differences in their derivation, they are only comparable to each other to a limited extent and with critical loads. The differences, some of which are clear, are due to different levels of protection, protection objectives and the relationship between effects (Additional file 1: Table S1.1).

Objective

The protection of human health and ecosystems and their functions against adverse effects from air pollutant deposition is generally ensured if heavy metal inputs are completely avoided. However, this is currently not a realistic assumption. On the basis of empirical evidence, it is assumed that protection of these objects of protection is possible if specific critical concentrations of heavy metals in environmental media are not reached for reasons of eco- and human toxicology. But only with the critical load calculations the balance between inputs and outputs can be proved. Critical loads for Germany are therefore determined below.

Critical loads for Cd, Pb, Hg have already been calculated for the entire EMEP[2] region. They serve as policy advice, in particular to examine and justify whether further emission reductions are necessary. To date, they have not been designed as binding immission or deposition values. The critical loads indicate the total input rate below which adverse effects on ecosystems and human health (paths atmosphere–soil–groundwater for drinking water use and atmosphere–soil–food wheat (only for Cd)) can be excluded in the long term according to current knowledge. Consequently, if the critical loads are complied with, risk minimisation is achieved below the classic danger threshold, which means that the assessment values are very precautionary.

The critical load concept focuses on the budgets of substances in ecosystems. Ecosystem-specific features (soil, climate, use, etc.) are taken into account when calculating the critical load values. As a result, there is no only one "critical load", but rather a range of values that allows a comprehensive, regionalised representation of the sensitivity of ecosystems, food crops and drinking water to heavy metals.

In addition to natural and semi-natural ecosystems, agricultural land is also considered both as ecosystems and as areas where human and ecotoxicological values must be respected. Critical loads aimed at protecting ecosystems are hereinafter referred to as $CL(M)_{eco.}$ Critical loads aimed at protecting human health, e.g. drinking water, are abbreviated $CL(M)_{drink}$ and those aimed at protecting food for humans $CL(M)_{food}$, where (M) stands for heavy metal and can be replaced by the respective element symbol (Cd, Pb, Hg,…). The determination of $CL(M)_{eco}$ is based exclusively on ecotoxicological threshold values. This means that the $CL(M)_{eco}$ are determined on the basis of effects. Experimentally determined zero effect threshold values (NOEC or PNEC[3]) are used as "critical limits" in the calculation of the $CL(M)_{eco}$. For the $CL(M)_{drink,}$ internationally agreed critical concentrations were used in drinking water and for $CL(Cd)_{food}$ in food wheat.

Materials and methods for calculation of critical loads for heavy metals in Germany

Basic principles for determination of critical loads for heavy metal deposition

In the following, an assessment of the input rates into ecosystems in the equilibrium of inputs and outputs will be carried out according to the critical loads concept. Their mapping for Germany is carried out on a scale of 1:1 million and provides an overview of the sensitivity of terrestrial ecosystems to nine heavy metals. Ecosystem integrity [17] and human health are regarded as protection goals.

By definition, critical loads for heavy metals are the highest total input rate of the metal under consideration (from atmospheric deposition, fertilisers and other anthropogenic sources) below which no long-term adverse effects on human health and on the structure and function of ecosystems are to be expected according to the current state of knowledge [18]. Critical load is calculated according to the mass balance approach assuming a chemical equilibrium in the system under consideration and a steady state at a concentration level defined by the critical limit. This is an impact-based derived limit concentration in certain ecosystem compartments below which significant adverse effects on human health as well as on defined sensitive components of ecosystems can be excluded according to the current state of knowledge.

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[2] Co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe (inefficially 'European Monitoring and Evaluation Programme' = EMEP).

[3] *NOEC* no observed effect concentration, *PNEC* predicted no-effect concentration.

Table 2 Receptor types and their area proportions according to CORINE [20] in Germany

CORINE code	Description of the CORINE code	Area in Germany [ha]	Surface area in Germany [%]	Proportion of total receptors [%]
211	Arable land	13410853	37.53	47.9
231	Meadows and pastures	4266058	11.94	15.2
311	Deciduous forests	2359267	6.60	8.4
312	Coniferous forests	5436535	15.21	19.4
313	Mixed forests	2302725	6.44	8.3
321	Natural grassland	99061	0.28	0.4
322	Heaths and moor heaths	35776	0.10	0.1
411	Marshes	19755	0.06	0.1
412	Peat bogs	58577	0.16	0.2
Sum of receptor surfaces		27988609	78.32	100.0

Cadmium has been identified as an important pollutant in relation to the maintenance of food quality for the protection of human health. With this metal, uptake from the soil into the vegetation is comparatively high, so that accumulations in the soil entail the potential danger of health effects via plant food. Wheat was selected as the indicator plant. Wheat grain accounts for a significant proportion of food in Germany (as in Europe) and its cultivation accounts for a large proportion of agricultural land in Germany (and other European countries) [19]. Critical loads for the protection of drinking water are mapped for all ecosystem types. Critical loads are therefore determined below for three objects of protection:

1. $CL(M)_{eco}$: critical load for a metal (M stands for Hg, Cd, Pb, Cu, Zn, Ni, As, Cr, Zn) to protect the sensitive biota of the ecosystem;
2. $CL(M)_{drink}$: critical load for a metal (M stands for Hg, Cd, Pb, Cu, As, Cr, Zn) for Protection of drinking water for human beings;
3. $CL(Cd)_{food}$: critical load for cadmium for the protection of arable crops (here: wheat-producing as a food for human beings.

Data base

For the critical load calculation, the necessary data is spatially linked with the geographical information system ArcView and transferred to a database. Both original data such as precipitation and derived data such as values for the organic matter content (OM) and pH values derived from the soil overview map BÜK1000N are used. The storage, evaluation and presentation of the data are done in polygons, which result from the intersection of the input data.

Biotope type and land use mapping

The spatial distribution of the investigated receptors in Germany is taken from the CORINE Land Cover 2006 [20]. Critical loads are calculated for natural and semi-natural ecosystems and for agricultural land (arable and intensive grassland). Settlement areas, water areas, etc. (21.8% of the area of Germany) are not included as receptor areas. The following legend units of the [20] are therefore regarded as receptor surfaces (Table 2).

Soil map

The land use-differentiated soil overview map of the Federal Republic of Germany on a scale of 1:1,000,000 (BÜK1000N Version 2.3.1; BGR [21]) shows the spatial distribution of soil forms, summarised in soil associations (=soil units). In contrast to the BÜK 1000 [22] with its 71 pedological legend units, the polygons of the BÜK1000N are significantly characterised by soil and land use information. Thus, 66 legend units are combined with land use arable land, 56 with grassland and 63 legend units with forest. Taking into account the differentiation achieved by regionalisation (European climate zones), a total of 675 legend descriptions and guiding soil profiles are available for these three main uses. For each soil profile, the humus form of the organic layers, the (fine) soil types of the mineral horizons, the horizon sequence with thickness data and for each horizon the soil systematic unit, the total nitrogen content and the carbonate class, the pH level, the bulk density, the storage density, the field capacities, the total pore volume, the humus class and the concentrations of exchangeable cations are indicated.

Long-term mean of temperature and precipitation

The following grid databases have been made available by the German Weather Service in Offenbach (DWD), Climate and Environment Department:

4. Average monthly air temperature for the months January–December from the period 1981–2010 [23] and
5. Average monthly rainfall for the months January–December from the period 1981–2010 [24].

The data are available as ASCII file and results in a matrix of 650 × 880 points. Each of these points embodies the value of a 1×1 km^2 cell. The limits of the data field range from right value 3,280,000 to right value 3,930,000 and from high value 5,230,000 to high value 6,110,000 of the Gauss–Krüger coordinate system.

Average annual leachate rate

The data on the land-use-differentiated mean annual leachate rate from soil for the climate period 1981–2010 were made available digitally by the BGR in October 2014 [25]. The regional allocation of land use classes is based on CORINE Land Cover 2006 [20]. The data set describes the spatial distribution of the leachate rates with a grid resolution of 1×1 km^2 on the geometric reference base of the ATKIS-DLM 1000.

Derivation and regionalisation of ecological receptors

While the data basis for the soil-specific parameters, which are included in the simple mass balance, with the BÜK1000N [21], in particular with the use type-specific leading soil profiles, is sufficiently accurate for determining the sensitivity of ecosystems, the rough biotope type and land use types of the CORINE Land Cover 2006 [20] are not sufficient for all vegetation-specific parameters for the mass balance. For this reason, this study assigned typical semi-natural vegetation units and crop rotations to the leading soil profiles of the BÜK1000N. The usage differentiation of the BÜK1000N is, however, also too rough for this. For example, guide soil profiles are only available for arable land, grassland and forests. The allocation of the vegetation units to guide soil profiles was therefore carried out at the following levels:

6. BÜK guide soil profile "Grassland" differentiated according to meadows and pastures (CORINE class 231), natural grassland (CORINE class 321), heaths and moorland (CORINE class 322), swamps (CORINE class 411) and peat bogs (412),
7. BÜK guide soil profile "forests" differentiated according to deciduous forest (CORINE class 311), coniferous forest (CORINE class 312) and mixed forest (CORINE class 313)
8. BÜK guide soil profile "Arable land" undifferentiated for CORINE class 211.

The assignment of the semi-natural vegetation units is based on the database of the BERN model [26, 27]. For the intensively used vegetation complexes, the currently typical vegetation units were assigned to the combinations of BÜK1000N guide soil profile and CORINE unit, i.e. e.g. for the "coniferous forest" predominantly forest associations, for the "meadows and pastures" predominantly meadow associations. For the CORINE classes deciduous forest (311), natural grassland (CORINE class 321), heaths and moor heaths (CORINE class 322), marshes (CORINE class 411) and peat bogs (412), the semi-natural or near-natural plant community was assigned in each case, which is to be expected as typical on the basis of the site conditions according to the information of the BÜK1000N on the leading soil profile and the climate area. 226 plant communities were assigned to the 210 guide soil profiles, each with 7 CORINE classes. For forests in particular, this means that it is now possible to take account of a site-typical mixture of tree species, so that a more sensitive mixed tree species may also determine the critical limit instead of the less sensitive dominant main tree species, as has been customary to date. The potential yield can also be more finely differentiated for mixtures of species such as those found in deciduous and mixed forests, but also in open country.

The CORINE class arable land (2.1.1) was assigned arable crop rotations that correspond to good professional practice according to the soil shape. The distribution of cultivated areas was checked against the data of the Federal Statistical Office [28] for the years 2007–2013 (mean value for federal states) and adjusted accordingly. Additional file 1: Table S1.2 contains the assumed crop rotations according to good professional practice on the soil units of BÜK1000 as well as the typical area distribution of crop rotation members assumed for the calculation of critical loads.

Methodological approach of the critical load calculation

The methodological approach for the calculation of critical loads for heavy metals in this study follows the recommendations in the manual of the ICP Modeling and Mapping ([18, 29, 30], Chapter V.5). All relevant fluxes into or from a certain soil layer, in which the essential substance conversions occur or in which the receptors have their distribution focus and which is therefore relevant for the effects in the system, are compared. The consideration of heavy metal fluxes, reserves and concentrations refers to mobile or potentially mobilisable metals, only they are relevant for the consideration of substance fluxes.

The mass balance equation includes as output paths from the terrestrial ecosystem the uptake into the biomass with subsequent harvest and the output with the leachate flow as follows:

$$CL(M) = M_u + M_{le(crit)},$$

with CL(M) as critical load of the metal M [g ha^{-1} a^{-1}], M_u as net uptake of the metal M into harvestable plant parts [g ha^{-1} a^{-1}], $M_{le(crit)}$ the tolerable (critical) leaching of the metal M from the considered soil layer with exclusive consideration of vertical rivers (leachate) [g ha^{-1} a^{-1}].

The inclusion of further terms is in accordance with the recommendations of the Expert Panel for Heavy Metals to the ICP Modeling and Mapping [31, 19]. There have been no changes to this approach since 2004 [19].

Calculations

Removal of heavy metals

The removal rate of heavy metals with the harvest of biomass results from the yield of the biomass to be harvested, multiplied by the substance content as follows:

$$M_u = [M]_{ha} \cdot E,$$

with M_u as heavy metal removal rate [g $ha^{-1}a^{-1}$], $[M]_{ha}$ as metal content in the dry matter of the harvest [mg kg^{-1}], and E as the dry matter yield of the crop [kg ha^{-1} a^{-1}].

By definition, critical loads are not intended to cause long-term adverse effects on human health or on the structure and function of ecosystems. Thus, they should not reflect the status quo in terms of farming methods and the resulting cultivation conditions and yields, but should follow long-term principles of sustainable agriculture and forestry. Therefore, the critical load approach is based on the following assumptions about the management of receptor areas:

1. *Forests*

   In the long term, it can be assumed that the conversion to near-natural forest management, which has already begun nationwide, in combination with the trend towards a reduction in nitrogen inputs, will regulate the potential timber yield expectation and the material content to a sustainable and stable equilibrium. For this reason, conservative assumptions were made for earnings and salary estimates, which are derived from measurement data at more or less unpolluted locations.
2. *Acre*
   The field yields were derived from current harvest statistics. In contrast to forest management, there are no discernible trends towards extensification in arable farming in Germany (apart from organic farming, whose share of land has remained stable at a low level in recent years). Even after its amendment, the Fertiliser Ordinance still tolerates a high level of excess fertilisation with nitrogen. With regard to crop rotations, i.e. for the cultivation conditions of the individual crop types, it is assumed, however, that the rules of good professional practice (in particular phytosanitary favourable, nutrient-effective and soil-preserving crop rotations) are applied, even if at present in particular the cultivation conditions, but also the use of fertilisers and thus the yields in agriculture are predominantly made dependent on support programmes and on the market. This must not be assumed in the following, since on the one hand the critical loads are to apply in the long term, but on the other hand cultivation conditions in the longer term should not be predicted on the basis of today's market conditions. For the future, it can be assumed that the cultivation structure will correspond to good professional practice in the long term.
3. *Open woodless country*
   A distinction was made between unused openland ecosystem types (peat bogs, swamps, moor heaths) and those that are regularly used (natural grassland, dry heaths, salt marshes). The estimation of the dry matter yield in openland habitats in use assumes that a minimum use or maintenance use is necessary to maintain the stock. However, this necessary minimum use also depends on the biomass production potential of the respective location.

Heavy metal contents in the biomass

The annual heavy metal removal (M_u) for used forests results from the estimated biomass removal by the annual increase in solid wood and bark of the main and secondary tree species of the current stocking at the site, multiplied by the average content of heavy metals in solid wood and bark (Table 3). These contents can be regarded as sustainably compatible and thus acceptable in the long term, since only measured values from areas that are not specifically contaminated were evaluated for this purpose. For the compilation of the heavy metal contents by Jacobson et al. [32], data from 45 sites in Germany were evaluated. Reinds et al. [33] considered values from three sites in Europe.

M_u for grassland biotopes and arable crops used results from the growth rate of above-ground green matter in the year [t ha^{-1} a^{-1}] and the heavy metal contents in the harvest mass (from investigations without specific load) according to Table 4.

Assessment of the plant physiological yield potential of biomass to be harvested

The export of biomass must be estimated from the biomass productivity depending on the yield potential of the site, taking into account the plant physiologically possible

Table 3 Heavy metal contents (mg kg^{-1} dry matter) in solid wood with bark of main tree species ($n = 45$)

Tree species	Heavy metal content $[M]_{ha}$ (mg kg^{-1} dry matter)							
	Pb[a]	Cd[a]	Hg[a]	Cu[a]	Ni[a]	Zn[a]	As[b]	Cr[a]
Oak	2.97	0.13	0.02	2.19	1.58	5.27	0.02	0.74
Beech	1.52	0.15	0.02	1.77	1.28	10.53	0.02	0.54
Spruce	1.29	0.36	0.02	1.67	1.18	31.2	0.01	0.42
Pine	1.75	1.31	0.02	1.35	1.85	25.24	0.01	0.35
All others on average	1.81	0.29	0.02	1.91	1.48	11.20	0.015	0.53

Sources: [a] Jacobsen et al. [32], [b] Reinds et al. [33]

Table 4 Heavy metal contents (mg kg^{-1} dry matter) of arable crops and grassland

Plant species	N	Heavy metal content $[M]_{ha}$ (mg kg^{-1} dry matter)							
		Pb	Cd	Hg	Cu	Ni	Zn	As	Cr
Winter wheat[a]	24	0.03	0.03	0.005	4.6	0.23	20	0.035	0.48
Rye	23	0.07	0.02	0.005	4.6	0.44	26	0.035	0.25
Winter barley[b]	30	0.1	0.02	0.01	3.6	0.23	25	0.035	0.27
Rapeseed[c]	18	0.1	0.08	0.003	3.8	0.81	39	0.035	1.7
Potatoes	32	0.04	0.09	0.001	4.6	0.23	14	0.035	0.17
Sugar beet	30	0.2	0.08	0.01	3.9	0.8	12	0.035	0.47
Silage maize[e]	24	0.2	0.04	0.02	3.5	0.58	19	0.035	0.73
Grass and grassland plants[d]	160	0.99	0.13	0.03	6.2	0.91	49.5	0.1	0.395

Source: Knappe et al. [54]

[a] The share of the area under spring wheat is negligibly small compared to the area under winter wheat [28] and is therefore not considered in crop rotation

[b] The share of the area under spring barley is negligibly small compared to the area under winter barley [28] and is therefore not considered in crop rotation

[c] The proportion of sunflower area cultivated is negligibly small compared to the area under rape [28] and is therefore not considered in crop rotation

[d] The share of the area under legumes is negligibly low compared to the area under grassland [28] and is therefore not considered in crop rotation

[e] Silage maize is defined here as energy maize, green maize and feed silage maize

biomass growth. The basis for the site type-specific estimation of the potential wood yield in forests is provided by yield tables of the growth of tree species at non-influenced sites, in particular from as old measurements as possible. Over 100 years, the average annual increase for yield class I and the worst yield class of the tree species is determined from the yield tables (Table 5). The fixed measurement increments (DGZ 100) determined in this way are converted into weight measurement increments with the aid of the tree species-specific wood and bark density [19].

The estimation of the dry matter yield in the semi-natural open land receptor areas as well as for cultivated meadows and pastures (Table 6) assumes that a use or maintenance use is carried out.

The crop yields from intensive agriculture (Table 7) are taken from the data of the Federal Statistical Office [28] for the years 2007–2013 (mean value). The lower range limits were taken from the data from the federal state with the lowest yields, and the upper range limit also corresponds to the average of the years 2007–2013 of the federal state with the highest yields of this type of fruit.

The biomass yield to be harvested depends on the yield potential of the respective location. Based on the site-specific yield potential (soil fertility), a potential yield can be interpolated within the specified yield ranges.

Soil-specific yield potential

The method described below serves to concretise a discrete soil-typical yield value within the vegetation type-specific yield range (Tables 8, 9), taking into account the different soil characteristics. First of all, the best possible assessment of soil fertility as a function of the soil types of the horizons of the leading soil profiles of the BÜK1000N [21] has to be esteemed (Additional file 1: Table S1.3). The respective model for that was developed by Schlutow et al. [27]. Various soil properties were assessed as very unfavourable (score 1) to very favourable (score 5) in terms of yield formation. These values refer to the horizons of the guide soil profiles from the

Table 5 Range of yield potential of main and secondary tree species

Tree species	Range of the average annual growth rates after 100 years [DGZ 100]				Yield board from
	Yield potential the best yield class I for trunk wood with bark $E_{max(Phyto)}$		Yield potential the worst yield class for trunk wood with bark $E_{min(Phyto)}$		
	[m^3 ha^{-1} a^{-1}]	[m^3 ha^{-1} a^{-1}]	[m^3 ha^{-1} a^{-1}]	[m^3 ha^{-1} a^{-1}]	
Scots pine	7.8	3.1	2.0	0.8	Wiedemann [67][a]
Norway spruce	12.0	4.9	7.5	3.2	Wiedemann [68][a]
White fir		3.5		3	Schober [69][a]
European larch		2.5		2	Schober [69][a]
Beech	7.8	4.9	3.7	2.4	Schober [69][a]
Common and sessile oak	6.7	4.0	2.1	1.4	Mitscherlich [70]
Black alder	8.0	4.3	4.5	2.5	Mitscherlich [70]
Birch, all species	4.9	2.8	3.6	2.1	Schwappach [71]
Willows, all species	5.0	2.3	3.4	1.6	Schober [72]
Ash	6.2	3.7	4.1	2.5	Wimmenauer [73]
Mountain ash		2.1		1.6	Erteld [74]
Lime tree. all species	8.8	5.2	5.0	3.0	Böckmann [75]
Maple, all species		3.5		2.5	Schober [76]
Poplars, aspen	13.2	4.5	3.0	1.1	Knapp [77]
Hornbeam		5.6		2.5	Schober [76]

[a] In Schober [72]

Table 6 Yield potentials of the different vegetation types of the forest-free near-natural/semi-natural ecosystems

Vegetation type	Dry matter yield with extensive grassland use [t ha^{-1} a^{-1}]	
	$E_{max(Phyto)}$	$E_{min(Phyto)}$
Nutrient-poor grassland	1.5	0.65
Heathen	1.4	0.8
Dry lime turf	1.7	0.11
Wet and wet meadows	2.5	0.1
Flood meadows and floodplain meadows	1.6	0.8
Fresh meadows/fresh pastures	1.5	0.65

Sources: Bobbink and Hettelingh [78]. Bohner et al. [79]. Bolte [80]. Brenner et al. [81]. Briemle et al. [82]. Brünner and Schöllhorn [83]. Dierschke and Briemle [84]. Elsäßer [85]. Keienburg and Prüter [86]. Klapp [87]. Luthardt et al. [53]. Petersen [88]. Quade [89]. Ruhr-Stickstoff-Aktiengesellschaft [90]. Stein-Bachinger et al. [91]. Tischew [92]

BÜK-1000N database. In order to check the yield potential the map of the "Arable yield potential of soils in Germany" [34] based on the "Soil Quality Rating" (SQR) [35] was used. A complete adoption of this map was not productive, as this method was developed only for arable land and not also for forests, natural open land, meadows and pastures. The comparison of the scores, however, led to changes in the valuation with regard to the groundwater and evapotranspiration influence and with regard to rootability in Additional file 1: Table S1.3.

Data compilation

The individual criteria described here to indicate the yield potential cannot be equally weighted in the estimation of the yield potential, because individual criteria have a greater influence on plant growth than others and sometimes affect several different physiological processes.

Table 7 Yield ranges $E_{min(Phyto)}$–$E_{max(Phyto)}$ throughout Germany, averaged over the years 2007–2013

Yields in t dry matter per year $E_{min(Phyto)}$ (="min") $E_{max(Phyto)}$ (="max")															
Wheat		Rye		Barley		Roughage		Beta beet		Potatoes		Rape seed		Silage maize	
Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
6.2	8.8	4.2	6.5	5.3	7.6	5.3	8.6	58	72	35	48	3.4	3.9	34	51

Source: Federal Statistical Office [28]

Table 8 Main factors influencing yield potential of the soils

Individual parameter	Synthesis to the main influencing factors
Usable field capacity Porosity with dead water (tendency to waterlogging) risk of dehydration Influence of groundwater and backwater	Soil water balance
Cation exchange capacity Usable field capacity Humus content	Nutrient balance
Thoroughness Rootability Hardening tendency	Soil structure

For this reason, the individual parameters in Additional file 1: Table S1.3 have been combined in accordance with Table 8 to form the main factors influencing yield formation and the mean values of the classes have been calculated. The mean value was then determined from the 3 main influencing factors. It corresponds to the yield potential of the soil horizon $EP_{(geo\text{-}hor)}$ in the last column of Additional file 1: Table S1.3.

The relative yield potential of the soil $EP_{(geo\text{-}hor)}$ was now assigned for each horizon of the soil profile of the BÜK1000N based on the data of the soil type and then averaged to the rooting depth (following section) using a depth-weighted average. This corresponds to the yield potential of the reference profile $EP_{(geo\text{-}prof)}$.

Determination of the rooted soil depth as a function of vegetation- and soil-specific root penetration potentials

The vegetation-specific root penetration depth of the dominant and characteristic species could be estimated on the basis of the assigned plant community (Sect. 3.3). This was the prerequisite for averaging the horizontal data of the critical load-relevant parameters from the guide soil profiles. On the other hand, the depth actually rooted by plants also depends on the rootable depth of the soil. Starting from the potential length of the main root habit (=80% of the total root mass) of the characteristic main tree species or the characteristic type of herb layer [36], the potential root penetration depths for the main stands shown in Table 9 can be given. These potential root lengths are limited by the upper edge of the terrestrial subsoil horizon (C horizons) for most vegetation types (except for the pioneer tree species mountain pine, aspen and birch), by the upper edge of the oxygen-free (reduced) groundwater or backwater horizon (Gr/Sr horizons) for wet-avoiding tree species, or by the upper edge of the reduced-gas horizon

Table 9 Length of the main root mass according to Köstler et al. [36] and horizons cutting off the root mass that cannot be rooted through (from Nagel et al. [19], supplemented and updated)

Vegetation type/main tree species	Potential main root length [cm]	Horizons that cannot be rooted through (according to soil mapping instructions KA 5. p. 83ff)
Arable crops	40	C C;P;Gr;Y;F;Sr;Sd;Sg
Natural grassland	40	C;P;Gr;Y;F;Go;S
Heaths and moor heaths	20	C;P;Gr;Y;F;Sr;S
Marshes	110	C; P; Y; Fr
Peat bogs	90	C; P; Y; Fr
Meadows and pastures	60	C C;P;Gr;Y;F;Sr;Sd;Sg
Scots pine	180	C;P;Gr;Y;F;Sr;Sd;Sg
Spruce	80	C;P;Gr;Y;F;Sr;Sd;Sg
Copper beech	80	C;P;Gr;Y;F;Go;Sr;Sd;Sg
Alder, ash tree	80	C;P;Gr;Y;F;Sr;Sd;Sg
Oak (all species)	180	C;P;Gr;Y;F;Sr;Sd;Sg
Larch, Douglas fir	100	C;P;Gr;Y;F;Go;S
Maple (all species)	80	C;P;Gr;Y;F;Go;S
Poplars, aspen	120	
Mountain pine	180	
Black pine	180	C;P;Gr;Y;F;Sr;Sd;Sg
Birch	100	
Lime tree (all species), hornbeam, *Robinia*	100	C;P;Gr;Y;F;Go;S
Willows and elms (all species)	60	C;P;Gr;Y;F;Sr;Sd;Sg

(Y horizons) for all vegetation types. This means that the vegetation-typical potential root length is cut off by the site-specific soil profile in cases where the potential root length is greater than the upper depth of the uppermost non-rootable horizon (= physiological thoroughness).

The thickness of each soil horizons was taken from BÜK1000N. The soil-specific yield potential of each horizon $\mathrm{EP}_{\mathrm{geo}}$ was then averaged over all rooted horizons, taking into account the respective horizon thickness. The result is then corrected as a function of climate parameters in the manner explained below.

Determination of climate-specific yield potentials

So far, only soil and vegetation type-specific parameters have been included in the determination of yield potentials. The length of the vegetation period is a highly significant climate–ecological influencing factor. The longer the vegetation period in the year (number of days in the year with an average air temperature of ≥ 10 °C), the greater the net primary production. Good to very good growth rates are promoted by vegetation periods ranging from 100 days (medium montane sites) to 200 days (planar lowland sites), while in high montane and alpine regions (60–100 days) net primary production falls significantly below the soil-specific yield potential. Therefore, the soil-specific yield potential was related to the vegetation period as follows:

$$\mathrm{EP}_{(\text{climate corr})} = \mathrm{EP}_{(\text{geo}-\text{prof})} \cdot \left(1 + \frac{\mathrm{VZ} - 165}{200 - 100}\right),$$

where $\mathrm{EP}_{(\text{klima-korr})}$ is the climate-adjusted yield potential; $\mathrm{EP}_{(\text{geo-prof})}$, the soil-specific yield potential of the rooted soil profile (between 1 and 5); VZ, the duration of vegetation (long-term average number of days per year with an average air temperature of ≥ 10 °C), where 165 days is the mean value in Germany, 100–200 days is the span in Germany.

Calculation of the biomass yield

The difference between the minimum and maximum yields according to the yield tables (Tables 7, 8) was interpolated according to the relative yield potential $\mathrm{EP}_{(\text{klima-korr})}$. The yield was thus as follows, taking into account the vegetation-specific yield ranges and the site-specific relative yield potential:

$$E = E_{\min(\text{Phyto})} + \left(((E_{\max(\text{Phyto})} - E_{\min(\text{Phyto})})/4)(\mathrm{EP}_{\text{klima}-\text{karr}} - 1\right).$$

Table 10 Seepage water rates used for the calculation of the heavy metal leaching with the seepage water for the various protective goods

M	Drinking water	Ecosystems	Food (wheat)
	Seepage water rate used		
Pb	$Q_{\mathrm{le}(z)}$	$Q_{\mathrm{le}(z)}$	
Cd	$Q_{\mathrm{le}(z)}$	$Q_{\mathrm{le}(z)}$	$Q_{\mathrm{le}(z)}$
Hg	$Q_{\mathrm{le}(z)}$	$Q_{\mathrm{le}(z)}$	
ace	$Q_{\mathrm{le}(z)}$	$Q_{\mathrm{le}(z)}$	
Cu	$Q_{\mathrm{le}(z)}$	$Q_{\mathrm{le}(z)}$	
Ni		$Q_{\mathrm{le}(z)}$	
Zn		$Q_{\mathrm{le}(z)}$	
Cr	$Q_{\mathrm{le}(z)}$	$Q_{\mathrm{le}(z)}$	

Output of heavy metals with the leaching

The tolerable (critical) leaching of the metal M ($\mathrm{M}_{\mathrm{le(crit)}}$) out of the considered soil layer with exclusive consideration of vertical fluxes (leachate) [g ha^{-1} a^{-1}] results from the product of leachate rate (Q_{le}) and critical concentration of the metal in the leachate ($[\mathrm{M}]_{\mathrm{sdw(crit)}}$). Different soil horizons and, accordingly, leachate rates in these soil horizons are relevant for the various objects of protection (Table 10). The map of the leachate rate for Germany [25] provides the basic information for determining the water leaching from the soil layer under consideration. The original BGR data set contains values smaller than or equal to 0 for approx. 3.3% of the raster cells. When the critical loads were calculated using the simple mass balance method, negative leachate rates showed implausible results. Therefore, a method was applied which is proposed in the Mapping Manual [30] p. V - 48) to correct the original seepage rates with the help of the precipitation data (long-term mean 1981–2010) of the DWD as follows: for each grid, the annual precipitation was calculated multiplied by 0.05 (= 5% of the precipitation). Then the original leachate rate from BGR [25] in each grid is compared with 5% of precipitation. The higher value represents the new value for the leachate rate in the grid. With this method negative values could be excluded.

These corrected water flows are equal to the seepage water rates below the rooted soil layer (z) ($Q_{\mathrm{le}(z)}$). These water flows were used unchanged in the calculation of $\mathrm{CL(M)}_{(\text{drink})}$. It is assumed that the protection of groundwater against exceeding the drinking water limit values by anthropogenic pollutant inputs is guaranteed if the limit values in the leachate directly below the root zone are not exceeded. Possible interactions

Table 11 Current internationally used guideline and limit values for the concentration of heavy metals in drinking water

Directive or regulation	Reference and limit values for the concentration in drinking water [mg l^{-1}]						
	Pb	Cd	Hg	As	Cr	Cu	Zn
Drinking Water Ordinance for Germany [38]	*0.01*	*0.003*	*0.001*	*0.01*	*0.05*	*2*	*–*
WHO guideline [93]	0.01	0.003	0.001[a] 0.006[b]	0.01	0.05	2	–
EU-Directive 2013/39/EU [16]	0.01	0.005	0.001	0.01	0.05	2	
USA [94]	0.015	0.005	0.002	0.01	0.1	–	
Canada [95]	0.01	0.005	0.001	0.01	0.05	1	5

[a] For total mercury

[b] For inorganic mercury

of washed-out metals with exchanger sites in deeper layers of the water-saturated soil zone are neglected.

Soil microorganisms, invertebrates and sensitive plant species of the herb layer are predominantly found or rooted in the humus-rich O and A horizons. Therefore, for the $CL(M)_{eco}$ and $CL(Cd)_{(food)}$ the less thick biologically active soil layer (e.g.) is considered, where the water output (here referred to as soil water) is higher. The differential amount of water to the leachate flow below the root zone is absorbed in the deeper soil layers by plant roots and is subject to transpiration.

The leachate rate below the biologically active soil horizons $Q_{le(zb)}$ was calculated as follows:

$$Q_{le(zb)} = Q_{le(z)} + \left(1 - f_{ET(zb)}\right) * (P - (P * fi)),$$

where $Q_{le(zb)}$ is the leachate rate below the biologically active soil horizons (zb); $Q_{le(z)}$, the leachate rate below the total rooted soil layer (z) (corresponds to the rate from the leachate map of the BGR [25]; P, the precipitation (average annual sum over 30 years 1981–2010); $f_{ET(zb)}$, the factor for determining the proportion of evapotranspiration from the biologically active soil layer (e.g.),and $fi_{(zb)}$ is the factor for calculating the share of interception in annual precipitation.

The following generalising assumptions were made [19]:

$f_{ET(zb)} = 0.25$ for $CL(Hg)_{eco.}$
$f_{ET(zb)} = 0.5$ for $CL(Pb)_{eco}$,, $CL(Cd)_{eco}$, $CL(As)_{eco}$, $CL(Cu)_{eco}$, $CL(Ni)_{eco}$, $CL(Zn)_{eco}$, $CL(Cr)_{eco.}$
$fi_{(zb)} = 0.15$ for arable and grassland vegetation.
$fi_{(zb)} = 0.25$ for red beech and hornbeam.
$fi_{(zb)} = 0.20$ for all other deciduous trees.
$fi_{(zb)} = 0.35$ for conifers.

Critical concentrations for the protection of human health

Protection of drinking water

There are currently several legal limits or guideline values for the concentration of heavy metals in drinking water (Table 11).

The critical limits for heavy metals in drinking water specified in the Mapping Manual [18, 29, 30] with reference to the WHO guideline [37] for Pb, Cd, Hg correspond to the limit values of the currently valid Drinking Water Ordinance for Germany [38]. For this reason, the limit concentrations of the Drinking Water Ordinance for Germany [38] were generally used for the CL(M) calculation in this project (Table 11, 1st line, italics type).

Protection of vegetable foods (wheat grain)

The EU limit value for cadmium in wheat grain of 0.2 [mg kg^{-1}] (Commission of the European Communities (2001), EC No 466/2001) was not derived on the basis of effects. Therefore, in the present study, the cadmium limit value for wheat was used instead of the EU Regulation (EC No. 1881/2006) as recommended in the ICP Modeling and Mapping Manual [18] (Table 12, 2nd line) [19].

Since the concentration (critical limit) for the plant ($[Cd]_{ha(crit)}$) is given, the critical concentration in the soil solution ($[Cd]_{sdw(crit)}$) can be determined iteratively with transfer functions according to Römpkens et al. [39] (details see [19]). $[Cd]_{sdw(crit)}$ is then 0.8 [mg m^{-3}].

Table 12 Critical concentrations of cadmium in wheat

Directive or regulation	Object of protection	Unit	Cd
EU Regulation (EC No. 1881/2006) [2]	Food products	mg kg^{-1}	0.2
Manual of the ICP Modeling and Mapping [18] –2017)	Wheat grain	mg kg^{-1}	0.1

Table 13 Coefficients for the calculation of the critical concentration of free ions as a function of the concentration of free ions with protective effect (=function of the pH value) according to De Vries et al. [51]

Coefficients	Cd	Pb	Cu	Ni	Zn
α	− 0.32	− 0.91	− 1.23	− 0.64	− 0.31
γ	− 6.34	− 3.8	− 2.05	− 2.59	− 4.63

Critical concentrations for the protection of ecosystems and biodiversity

The ecotoxicological effect of heavy metal ions depends on their concentration in soil water, as only free active ions are absorbed into the biomass and thus interact with the organisms. Hettelingh et al. [40] and Reinds et al. [33] compiled critical limits for heavy metals. The determination of the critical total concentration of heavy metals in soil water related to soil microorganisms, invertebrates and plants has to be carried out for each considered heavy metal according to its chemical properties according to different approaches as follows.

Determination of critical concentration of free heavy metal ions Cd, Pb, Cu, Zn and Ni in soil solution

For a number of heavy metals (Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}) toxicity is highly dependent on the simultaneous presence of non-toxic cations (Na^{+}, Ca^{2+}, H^{+}) which restrict the uptake of toxic heavy metals into organisms and thus protect them. The concentration of the protective competing cations is closely correlated with the pH value. The concentration of free heavy metal ions (Table 13) is therefore a function of the pH value of the soil water:log $[M]_{free,swd(crit)} = \alpha \cdot pH + \gamma$. [41, 42].

Calculation of critical total concentrations of reactive metals in soil for Cd, Pb, Cu, Zn, Ni.

Metals occur in soil water not only as free ions, but also in the form of soluble complexes:

1. Inorganic complexes ($[M]OH^{+}$, $[M]HCO^{3+}$, $[M]Cl^{+}$, etc.);
2. Metals bound to the dissolved organic mass (DOM) ($[M]_{DOM}$);
3. Metals bound to suspended particles (SPM) ($[M]_{SPM}$.

After the critical limit functions for the concentration of free heavy metal ions have been derived, the next step for the critical load calculation was to derive the critical total concentrations in the soil solution $[M]_{swd(crit)(eco)}$, which is required for the calculation of the tolerable leaching. Manual chapter 5.5 [30] recommends that this transformation be performed using a chemical specification model, e.g. the Windemere Humic Aqueous Model, WHAM [43, 44]. This model (version 6) was specially adapted to the requirements of the critical limit derivation for soils (W6S-MTC2). For the German data set of the critical load for Cd, Pb, Cu, Zn and Ni, the critical total concentrations were calculated with the latest model version on the basis of the site-specific input data required for this, which are described below.

Table 14 Assignment matrix of pH classes from BÜK1000N to an average pH value per horizon of the soil profiles according to KA5 ([45]. p. 367)

pH classes original from BÜK1000N	$pH(CaCl_2)$ of	$pH(CaCl_2)$ to	$pH(CaCl_2)$ middle
a0/s0	6.8	7.2	7
a1	7.2	7.9	7.6
s1	6.1	6.8	6.4
s2	5.4	6.1	5.8
s3	4.7	5.4	5.0
s4	4	4.7	4.4
s5	3.3	4	3.6

Table 15 Classification matrix of base saturation to an average pH value per horizon of the guide soil profiles according to KA5 ([45]. p. 371)

BS (%) of	BS (%) to	$pH(CaCl_2)$ of	$pH(CaCl_2)$ to	$pH(CaCl_2)$ middle
0.1	5	2.8	3.3	3.1
6	20	3.3	3.8	3.6
21	50	3.8	4.8	4.3
51	80	4.8	6	5.4
81	100	6	8	7

pH levels

In the database of the BÜK1000N [21] on the soil profiles, pH classes are given for each horizon of the profiles of the grassland and arable land use types. These classes can be transformed in $pH(CaCl_2)$ ranges according to the Soil Science Mapping Guide KA5 [45], from which the mean value can be assigned to each horizon[4] (Table 14). Subsequently, the depth step-weighted mean value was calculated over the horizons up to the considered depth, i.e. over the O and A horizons.

The database on soil profiles does not contain pH data for the profiles of the forest use type, but the concentrations of the exchangeable cations, from which the base

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[4] If a logarithmic method were used to calculate the mean value, e.g. de-logarithmic–averaging–logarithmic, a pH value of 4.18 would result instead of an average value of pH 4.2. In view of the classification into ranges of 0.7 pH units, this deviation has no significant influence on the results.

Table 16 Assignment of the organic mass content to the horizons of the soil profiles of BÜK1000N, based on the humus class data

Land use	Humus class from BÜK1000N (BGR [21] 2014)	Organic matter content OM Mass % of	Organic matter content OM Mass % to
Forests	h0	0	0
Forests	h1	0.1	1
Forests	h2	1.1	1.9
Forests	h3	2	4.9
Forests	h4	5	9.9
Forests	h5	10	14.9
Forests	h6	15	29.9
Forests	h7	30	55
Arable land	h0	0	0
Arable land	h1	0.1	1
Arable land	h2	1.1	1.9
Arable land	h3	2	3.9
Arable land	h4	4	7.9
Arable land	h5	8	14.9
Arable land	h6	15	29.9
Arable land	h7	30	55
Grassland	h0	0	0
Grassland	h1	0.1	1
Grassland	h2	1.1	1.9
Grassland	h3	2	3.9
Grassland	h4	4	7.9
Grassland	h5	8	14.9
Grassland	h6	15	29.9
Grassland	h7	30	55

saturation can be calculated according to KA5 [45], p. 371. The pH($CaCl_2$) range could again be derived from the base saturation (Table 15), so that the procedure could then be followed as described above.

Organic matter content (OM)

A humus class is specified horizontally in the database for the soil profiles. According to KA5 [45], p. 112, a range for the content of organic matter was assigned to each humus class, differentiated according to type of use (Table 16). Subsequently, the horizontal minimum contents (conservatively) were averaged to the considered depth.

Determination of the content of dissolved organic carbon (DOC) and dissolved organic substance (DOM)

There is currently no data available on soils in connection with the vegetation type for this purpose that would be representative and thus transferable to the soil forms and vegetation types occurring in Germany. Therefore, the recommendation in the ICP Modeling and Mapping Manual [18, 29, 30], Chapter 5.5) for "default" values for forest, grassland and arable land was used (Table 17). For forest soils, a differentiation of the DOC contents according to coniferous and deciduous forest as well as according to depth levels according to De Vries et al. [46]: Appendix 11 is available.

Table 17 Classification of dissolved carbon (DOC) contents as a function of vegetation type

	DOC [mg l^{-1}]		
Depth step:	**− 5 to 0**	**0–10**	**0–30**
Coniferous forest[a]	40	23	16
Deciduous forest[a]	32	21	12
Mixed forest	36	22	14
Grassland[b]		15	
Field[b]			10

Sources: [a] deVries et al. [46]. [b] Manual of ICP Modeling and Mapping [18, 29, 30]: Chapter 5.5)

Table 18 Assignment of the factor of the multiple of the atmospheric CO_2 partial pressure to the depth levels of the guide soil profiles of the BÜK1000N, based on the information in the manual of the ICP Modeling and Mapping [18, 29, 30]

Upper depth [cm]	Lower depth [cm]	Multiplication factor with the atmospheric CO_2 partial pressure
0	5	5.0
5	10	5.0
10	15	6.7
15	20	7.5
20	25	8.0
25	30	8.3
30	35	10.0
35	40	11.3
40	45	12.2
45	50	13.0
50	55	13.6
55	60	14.2

In the manual of the ICP Modeling and Mapping [18, 29, 30], Chapter 5.5) it is stated that the content of organic matter (DOM) is about twice the DOC content.

Partial pressure of CO_2 in the soil solution (pCO_2)

The partial pressure of CO_2 in the soil solution is generally higher than in the atmosphere above, because CO_2 in the soil is released by the plants through respiration, thus increasing the pressure in the soil. The manual of the ICP Modeling and Mapping [18, 29, 30], Chapter 5.5 provides simplifying estimates based on extensive regional studies: 5–10 times atmospheric CO_2 partial pressure for organic horizons, 5–15 times atmospheric CO_2 partial pressure for A horizons, 15–20 times atmospheric CO_2 partial pressure for B horizons, 15–30 times atmospheric CO_2 partial pressure for C horizons.

Taking into account the depth levels of the horizons described in the BÜK1000N [21], the following allocation matrix for the factor of the multiple of the atmospheric CO_2 partial pressure was established for this project, which was produced by interpolation of the estimated figures given in the manual (Table 18). Subsequently, the depth step-weighted mean value was calculated up to the considered depth.

Concentration of suspended particles (SPM)

For the CL(M) data set, it was assumed for reasons of simplification that the concentration of suspended particles (SPM) in the soil solution is negligibly low. PSM was therefore set to *ZERO* in all analysis cells in Germany.

Table 19 Total critical concentration of heavy metal ions that can be used independently of pH

Object of protection	Unit	As	Cr
Ecosystems	$\mu g\ l^{-1}$	70	44

Calculation of the critical total concentration of Hg in the soil solution

Mercury occurs as far as possible only bound to humus complexes, so that it is not necessary to determine the free ion concentration in the soil solution. Thus, it makes sense to determine the critical concentration of Hg below the humus layer, in particular of forests, by relating the critical concentration to the organic matter content. On this basis, the critical concentration (only of humus-bound ions) in the soil solution $[Hg]_{swd(crit)eco}$ [mg m^{-3}] can be determined according to the following equation:

$$[\mathrm{Hg}]_{\mathrm{swd(crit)eco}} = [\mathrm{Hg}]_{\mathrm{OM(crit)}} \cdot \mathrm{f_f} \cdot [\mathrm{DOM}]_{\mathrm{swd}},$$

with $[Hg]_{OM(crit)}$ as the critical limit for Hg based on solid organic substance (OM) in humus layer; f_f, the factor to describe the ratio of Hg in solid organic substance (OM) to Hg in dissolved organic matter (DOM) [-], and $[DOM]_{swd}$ as the concentration of dissolved organic matter in the soil solution of humus layer [g m^{-3}].

Meili et al. [47] recommend the critical limit of 0.5 mg Hg kg^{-1} OM [18]. This results in an Hg/OM ratio of 0.0000005 kg kg^{-1}. The calculation of $[Hg]_{swd(criteco)}$ also requires information on the ratio of Hg concentrations in solid and dissolved organic matter (f_f) and on the concentration of DOM in the soil solution $[DOM]_{swd}$. A Swedish study [47–49] showed that the concentration of Hg in solid and dissolved organic matter is usually approximately the same even under different environmental conditions (soil, climate), so that according to the current state of knowledge the value $f_f = 1$ can be defined as standard. The allocation of [DOM] was made on the basis of a Table 17, whereby the DOC contents for the calculation of [DOM] were doubled.

Determination of the critical total concentration of the heavy metal ions As and Cr in the soil solution

Ecotoxicological effects of arsenic on ecosystem compartments could be excluded by Doyle et al. [50] at a value of 70 μg l^{-1} in soil water (no-effect value—ENEV) (Table 19). A dependence of this no-effect value on soil chemical parameters could not be determined, so that a critical limit function is unnecessary.

For Cr, De Vries et al. [51] and Lofts et al. [42] could not find sufficient data to parameterise a function of the

Table 20 Overview of the 5, 25, 50, 75 and 95 percentiles, minima and maxima as well as arithmetic mean values of the critical loads in the receptor areas in Germany

	Nickel g ha^{-1} a^{-1}	Copper	Zinc	Lead	Arsenic	Chrome	Cadmium	Mercury
Drinking water								
Min		484	1234	3	2	12	0.8	0.3
5 Perc.		1070	2848	9	6	28	2.5	0.6
25 Perc.		4091	10428	24	21	104	7.1	2.1
50 Perc.		6172	15,628	35	31	156	10.2	3.2
Mean		6168	15,609	35	31	156	10.2	3.2
75 Perc.		7956	20,093	44	40	200	12.9	4.1
95 Perc.		11,268	28,316	61	56	282	18	5.7
Max		27,533	69,133	142	138	688	42.6	13.8
Ecosystems								
Min	37	7	81	2	115	78	1.5	0.1
5 Perc.	109	13	189	6	181	115	4.1	0.2
25 Perc.	197	27	313	9	311	198	6.4	0.3
50 Perc.	518	74	565	21	414	263	10.5	0.4
Mean	981	158	543	122	421	267	15.6	0.4
75 Perc.	1363	118	695	102	501	317	20.9	0.4
95 Perc.	3338	710	1032	601	711	448	42.4	0.6
Max	11,232	3384	2457	2603	1669	1049	127.6	1.1
Food (wheat products)								
Min							1.9	
5 Perc.							3	
25 Perc.							4.9	
50 Perc.							6	
Mean							6.1	
75 Perc.							7.1	
95 Perc.							9.3	
Max							19.2	

critical concentration and therefore recommend the lowest effect-based threshold value (for an invertebrate species in fresh water) of 44 µg l^{-1} (Table 19).

However, the adoption of impact thresholds from investigations in water bodies for anhydromorphic sites is controversial (Advisory Committee for Existing Substances "Risk Assessment of Substances in Soils" [52]) and can only be used as an alternative under the simplistic assumption that the sensitivity of biota in water bodies is comparable with the sensitivity of microorganisms in soil water [53].

Results

Spatial patterns of critical load calculation for Pb, Cd, Hg, As, Cu Ni, Zn and Cr

Additional file 1: Figures S1.1, S1.2, S1.3, S1.4, S1.5, S1.6, S1.7, S1.8, S1.9, S1.10, S1.11, S1.12, S1.13, S1.14, S1.15 show the results of the critical load calculation for the heavy metals lead, cadmium, mercury, arsenic, copper, nickel, zinc and chromium in cartographic form.

Statistical distribution of critical loads

Table 20 shows the results of statistic evaluation of the area-based critical load calculation.

It can be seen that the sensitivity of the different objects of protection for the same heavy metal can vary in magnitudes. For example, for copper, zinc and mercury the sensitivity of ecosystems is higher than the requirements for drinking water protection, for arsenic, chromium and cadmium it is vice versa. With regard to lead, the CL range for drinking water protection is within the CL range for ecosystem protection. $CL(Cd)_{food}$ for wheat products is significantly lower than $CL(Cd)_{drink}$ for drinking water or ecosystem protection.

Validity

Soil yield potential

The best available yield statistics are available in summary form for the administrative districts of Germany. These statistics do not provide a direct basis for this study because the arable crops and their yields are not broken down by soil type (or group). The approach taken by Knappe et al. [54] of combining the area shares of arable crops in a county with the area shares of soil forms of the BÜK1000 in a county according to the area shares of arable crops may allow a snapshot to be taken, as was be the aim in the study by Knappe et al. [54]. However, this is not sufficient for a long-term forecast of soil-typical yields of the various arable crops. For this reason, the more or less long-term unchangeable soil-specific yield potentials were estimated in this study. This approach is also the basis of the map of the “Arable yield potential of soils in Germany” [34] based on the “Soil Quality Rating” (SQR) [35]. This map was compared with the results of the present study. Where plausible differences were found in relation to the influence of groundwater and backwater and in relation to rootability in Table 6, the assessment in the present study was adapted to the map of the ‘arable yield potential of soils in Germany’ [34].

The largest differences in the valuation result from the Münsterland, Ostfriesland and Oderhaff regions. This applies to the areas with the BÜK1000N soil form “Mainly Gley podzol and Gleye, low distribution of podzols from sandy river sediments; low distribution of Plaggen ash and Treposole” with a reference profile PP (norm podzol) for field use. The relevant horizon to a depth of 30 cm (Aep) consists of weakly loamy sand. The yield potential calculated here is 2.94 (on the scale between 1 and 5), which corresponds to 49 points on the BGR scale (on the scale between 0 and 102). The BGR card shows 60–80 points for the same areas. Reasons for the far more positive evaluation by the BGR could not be determined, therefore no adjustment of the evaluation to the BGR was made for this profile. At the same time, the BGR also indicates the same yield potential of 60–80% for cambisol vega from clayey loamy floodplain sediments in the Oderbruch as for podzol from 60 to 80% for arable land use. According to the method used in this study, a relative yield potential of 3.86 (on the scale between 1 and 5) results for this soil form in the Oderbruch; this corresponds to 73 points on the BGR scale (on the scale between 0 and 102). In the case of the cambisol vega, the assessments of both procedures are well in line.

Another significant difference is shown by the evaluation of the “Predominantly Chernosema” with a reference profile TTn (Norm Chernosema) for arable land use in the Magdeburger Börde. With the method for this study, a yield potential of 3.6 (= 66 BGR points) was determined, while the BGR card represents > 80 points. The reference profile shows a strongly clayey silt for the Ap horizon. With the method used here, the danger of waterlogging due to the high clay content (Table 6) is evaluated negatively, while the BGR does not evaluate this hazard indicator negatively for this soil profile. In this case, too, no adjustment was made to the BGR valuation. Areas for which higher yield potentials were determined in the present study than in the BGR map are not identifiable. In this respect, the possible underestimation of yields always leads to lower critical loads and these are thus “on the safe side”. If, however, the areas with the greatest deviations from the yield potential of the BRGs were taken as a basis, i.e. the yield potential for the slightly loamy–sandy podzol in the Münsterland was 70 points according to BGR (corresponds to 3.75 on the scale from 1 to 5), the following changes in $CL(M)_{eco}$ would result for wheat, barley and rapeseed, for example (Table 21).

If the BGR assessment of the yield potential is applied to determine the yield, which in extreme cases is approx. 28% higher, the ecosystem-related critical loads for lead, cadmium, mercury, nickel, zinc, arsenic, copper and chromium would only increase by a few percentage points. The highest deviation is 5.9% for the critical load for copper on wheat fields.

The yields of arable crops, as used in the present case to calculate critical loads, are subject to greater variation than the wood yields of forests and grassland yields, as actual arable yields are used instead of potential wood and grassland yields (Sect. 3.5). While in the forests and semi-natural grassland a tendency towards extensification of production has been apparent for several years, this is not evident in arable farming. While in forests and natural open land nitrogen inputs from the air are decreasing, more nitrogen is fertilised on fields.

Heavy metal concentration in harvested crop

Literature studies on heavy metal contents in the harvestable parts of agricultural crops have already been carried out in earlier projects [55, 56]. The calculated median values for the Cd, Pb and Hg contents in cereal grain, beet, potatoes, maize, grass and other forage plants, oil and legume seeds are significantly higher than the values used for the calculations in this paper. The earlier data bases [19] for calculating mean concentrations (medians) in crop plants date from the late 1980s [57] and early 1990s [58]. Since then, the deposition of heavy metals, especially Pb, has decreased. This has led to lower concentrations later [54]. The median values used here for the concentrations of lead, cadmium and mercury are taken from Knappe et al. [54], p. D 59 for arable crops. However, the authors also indicate higher concentrations of

Table 21 Sensitivity analysis using an example calculation for the $\mathrm{CL(M)_{eco}}$ with different yield potential estimates (t dry matter $\mathrm{ha^{-1}\ a^{-1}}$) and otherwise the same input data at a site in the Münsterland region

	Soil	Yield class	Yield $\mathrm{t\ ha^{-1}\ a^{-1}}$	$\mathrm{CL\ (Pb)_{eco}}$ $\mathrm{g\ ha^{-1}\ a^{-1}}$	$\mathrm{CL\ (Cd)_{eco}}$	$\mathrm{CL\ (Hg)_{eco}}$	$\mathrm{CL\ (Ni)_{eco}}$	$\mathrm{CL\ (Zn)_{eco}}$	$\mathrm{CL\ (As)_{eco}}$	$\mathrm{CL\ (Cu)_{eco}}$	$\mathrm{CL\ (Cr)_{eco}}$
Wheat	Podzol from weak loamy sands	2.94[a]	7.5	10.6	6.3	0.09	356	277	233	40	150
Wheat		3.75[b]	8.0	10.6	6.3	0.09	356	287	233	43	150
Barley		2.94[a]	6.4	11.0	6.2	0.11	356	288	233	29	148
Barley		3.75[b]	6.9	11.0	6.2	0.12	356	300	233	31	148
Rapeseed		2.94[a]	3.6	10.7	6.4	0.06	357	269	233	20	152
Rapeseed		3.75[b]	3.7	10.7	6.4	0.06	357	273	233	20	152
Deviations [%]											
Wheat		27.6	6.9	0.1	0.2	3.0	0.0	3.7	0.0	5.9	0.2
Barley		27.6	7.2	0.4	0.1	4.0	0.0	4.0	0.0	5.7	0.1
Rapeseed		27.6	2.5	0.1	0.1	0.5	0.0	1.3	0.0	1.8	0.1

[a] According to own estimation given in Sect. 3.5

[b] According to BGR [34]

Table 22 Sensitivity analysis using an example calculation for CL(Pb)$_{eco}$ with different Pb contents and otherwise the same input data at a site with cambisol vega from clayey loamy outer sediments in the subcontinental climate zone

	Yield	t dry mass ha^{-1} a^{-1}	Silage maize	Sugar beets	Wheat	Barley
			46.0	67.8	8.0	6.9
Input data and results used in this paper	Pb content[a]	g t^{-1}	0.2	0.2	0.03	0.1
	CL(Pb)$_{eco}$	g ha^{-1} a^{-1}	10.9	15.3	2.0	2.4
Alternative input data and results	Pb content[b]	g t^{-1}	0.6	0.44	0.14	0.21
	CL(Pb)$_{eco}$	g ha^{-1} a^{-1}	25.2	71.6	2.4	3.3
Deviations	Pb content	%	300	220	466	210
	CL(Pb)$_{eco}$	%	169	106	45	32

[a] According to Knappe et al. [54]. p. D59ff, medians, as used in this present study

[b] According to Knappe et al. [54]. p. D 59ff, 90 Perz

Table 23 Sensitivity analysis using an example calculation for the CL(Cd)$_{eco}$ with different cadmium contents in stem wood with bark and otherwise the same input data at a site in the subcontinental climate zone

Tree species	Soil	Yield t ha^{-1} a^{-1}	Cd content g t^{-1} dry mass	CL(Cd) $_{eco}$ g ha^{-1} a^{-1}
Pine	Cambisol from sands	1.7	1.31[a]	7.36
			0.3[b]	5.62
Deviations in %			− 77.1	− 23.6

[a] According to Jacobson et al. [32], as used in this present investigation

[b] According to ICP Modeling and Mapping Manual [18, 29, 30]

lead in the usual arable crops on the market (90 s percentiles) (Table 22).

The critical loads for lead (ecosystem related) in the example would increase by up to 169% compared to the CL(Pb)$_{eco}$ determined here if the 90 percentile of lead concentrations according to Knappe et al. [54] were applied, which in this case are 300% higher than those used here. In particular, the Cu, Cr and Ni contents in the stem wood of typical tree species in Germany are significantly dependent on the concentration in the soil [59]. Therefore, in this study, the low values published by Jacobsen et al. [32] were included in the CL calculation, which corresponds to the worst case. An exception is the Cd content in stem wood with pine bark. The median value from 45 studies by Jacobsen et al. [32] deviates more than four times from the range shown in the manual. For this reason, the sensitivity of the critical load is also shown for the low Cd content in the pine stem according to the ICP Manual [18] using an example (Table 23).

If one assumes the lowest value reported in the literature (manual of the ICP Modeling and Mapping—[18] for the Cd content, which deviates by −77% from the value used here according to Jacobsen et al. [32], the CL(Cd)$_{eco}$ would decrease by around 24%. The contents of the heavy metals vary predominantly depending on the metal content in the soil. For example, the arsenic content in wheat varies from 0.01 to 0.34 mg kg^{-1} dry mass, in maize from 0.06 to 0.47 mg kg^{-1} dry mass and in grassland from 0.07 to 1.11 mg kg^{-1} dry mass [60]. The copper content in wheat varies from 3.8 to 6.17 mg kg^{-1} dry mass, in maize from 1.9 to 7 mg kg^{-1} dry mass and in grassland from 6.4 to 21.5 mg kg^{-1} dry mass [61]. The zinc content in wheat ranges from 33 to 94 mg kg^{-1} dry mass, in maize from 28 to 174 mg kg^{-1} dry mass and in grassland from 38 to 176 mg kg^{-1} dry mass [61].

The zinc contents according to Knappe et al. [54], p. D 59ff (Sect. 3.5) used in the present study are partly at approx. 60% of the lower range limit stated by Van Driel et al. [61], but significantly higher for grassland. The arsenic contents applied here according to Knappe et al. [54], p. D 59ff are for wheat only 30%, but for maize and grass 200% of the lower range limits according to Wiersma et al. [60]. The copper contents according to Knappe et al. [54], p. D 59ff used for the CL calculation in this paper are higher for wheat and maize, but somewhat lower for grassland than the lower range limits according to Van Driel et al. [61]. The effect of applying older data for metal concentrations on the respective critical load for the protection of the ecosystem is calculated using an example area with a very high yield potential, where the highest deviations in terms of metal uptake are to be expected.

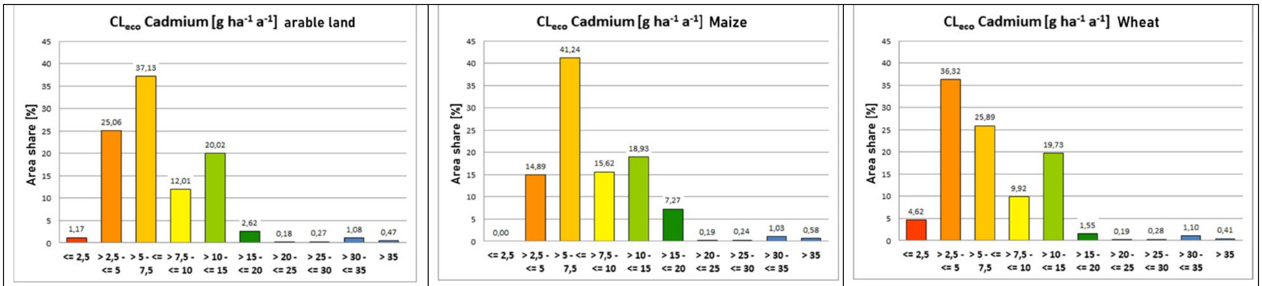
Table 24 Sensitivity analysis using an example calculation for CL(M)$_{eco}$ with different metal contents and otherwise the same input data at a site with cambisol vega from clayey–loamy sediments in the subcontinental climate zone

	Alternative, older input data and results			Input data and results used in this study			Deviations [%]		
	Wheat	Silage maize	Meadow	Wheat	Silage maize	Meadow	Wheat	Silage maize	Meadow
Zn content [g t^{-1}]	33[b]	28[b]	38[b]	20[c]	19[c]	49.5[c]	65	47	− 23
As content [g t^{-1}]	0.01[a]	0.06[a]	0.07[a]	0.035[c]	0.035[c]	0.1[c]	− 71	71	− 30
Cu content [g t^{-1}]	3.8[b]	1.9[b]	6.4[b]	4.6[c]	3.5[c]	6.2[c]	− 17	-46	3
CL(Zn) $_{eco}$ [g ha^{-1} a^{-1}]	286.7	1309.4	311.5	182.1	895.3	399.3	57	46	− 22
CL(As) $_{eco}$ [g ha^{-1} a^{-1}]	38.6	41.3	39.0	38.8	40.1	39.3	− 0.5	2.9	− 0.6
CL(Cu) $_{eco}$ [g ha^{-1} a^{-1}]	31.5	88.4	49.9	38.0	162.0	48.3	− 17	− 45	3

[a] According to Wiersma et al. [60]

[b] According to Van Driel et al. [61]

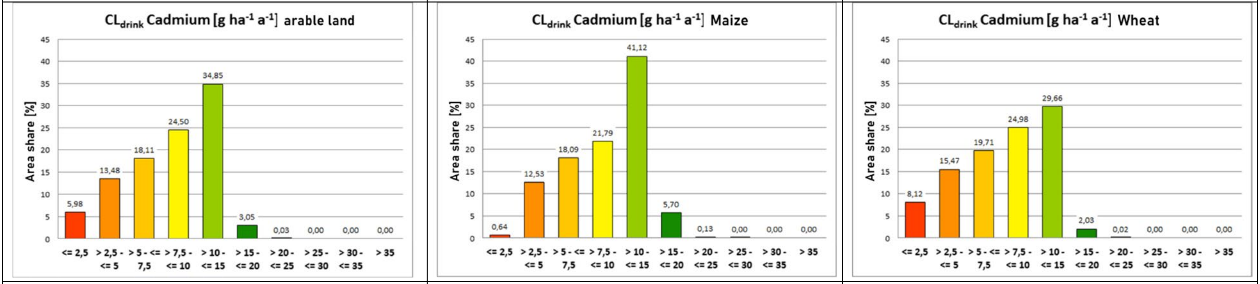
[c] According to Knappe et al. [54]



Area shares of the CL(Cd)$_{eco}$ with ideal crop rotation

Area shares of CL(Cd) $_{eco}$ for monoculture Maize

Area shares of CL(Cd) $_{eco}$ for monoculture wheat



Area shares of the CL(Cd)$_{drink}$ in ideal crop rotation

Area shares of CL(Cd)$_{drink}$ in monoculture Maize

Area shares of CL(Cd)$_{drink}$ in monoculture wheat

Fig. 1 Comparison of the area share in Germany in the critical load classes for cadmium for the protected goods ecosystem (CL(Cd) $_{eco}$) and drinking water (CL(Cd)$_{drink}$), in each case in the variants "crop rotation according to good professional practice" (left), "monoculture maize" (centre), "monoculture wheat" (right)

The greatest negative differences between the contents used in this study and the older lower range limits mentioned above are found in the As contents in wheat (− 71%) and maize (+ 71%). However, these only lead to a relatively small reduction in the CL(As)$_{eco}$ (− 0.5 to + 2.9%). The deviation of the zinc content for wheat (+ 65%) and maize (+ 47%) would lead to an increase of CL(Zn)$_{eco}$ by 57% and 46%, respectively. For copper, the use of the older content data would lead to a reduction of CL(Cu)$_{eco}$ (Table 24).

Crop rotations

The assumption of ideal–typical crop rotations according good professional practice in agriculture does not currently correspond to the practice everywhere in Germany. Currently, more silage maize and wheat are cultivated than is needed to ensure sustainable soil fertility.

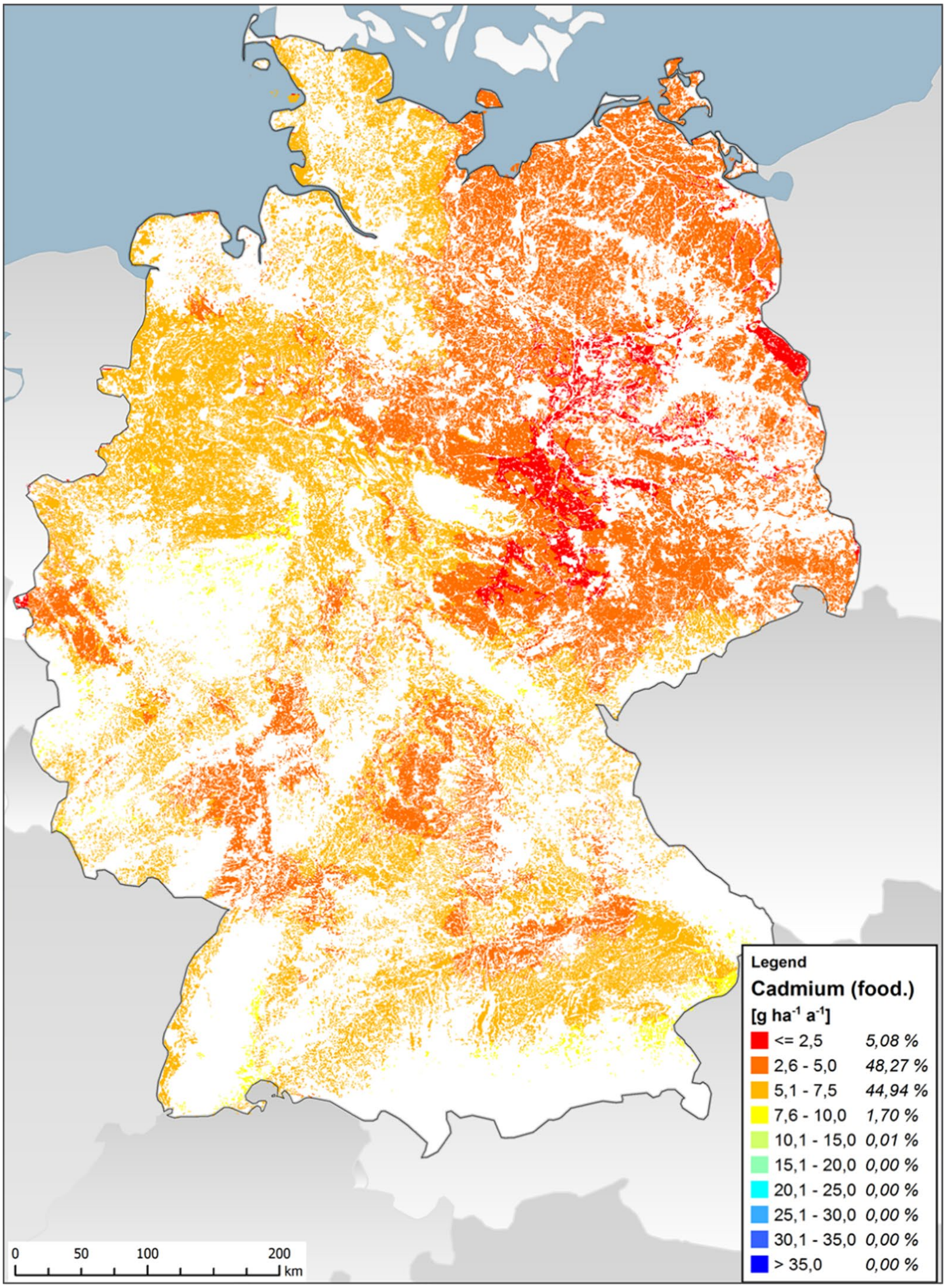


Fig. 2 Critical load for cadmium to protect human health when consuming wheat products in the case of a nationwide monoculture with wheat on arable land in Germany

The worst case can be a monoculture with silage maize or a monoculture with wheat (Figs. 1, 2).

There is a slight increase in the critical loads for the “monoculture maize” variant, but a significant decrease in the critical loads for the “monoculture wheat” variant, both for the ecosystems protected and for drinking water protection (Fig. 1). The comparison of the area shares in the critical load classes $CL(Cd)_{food}$ shows a clear shift to the more sensitive classes for monoculture wheat (Fig. 3).

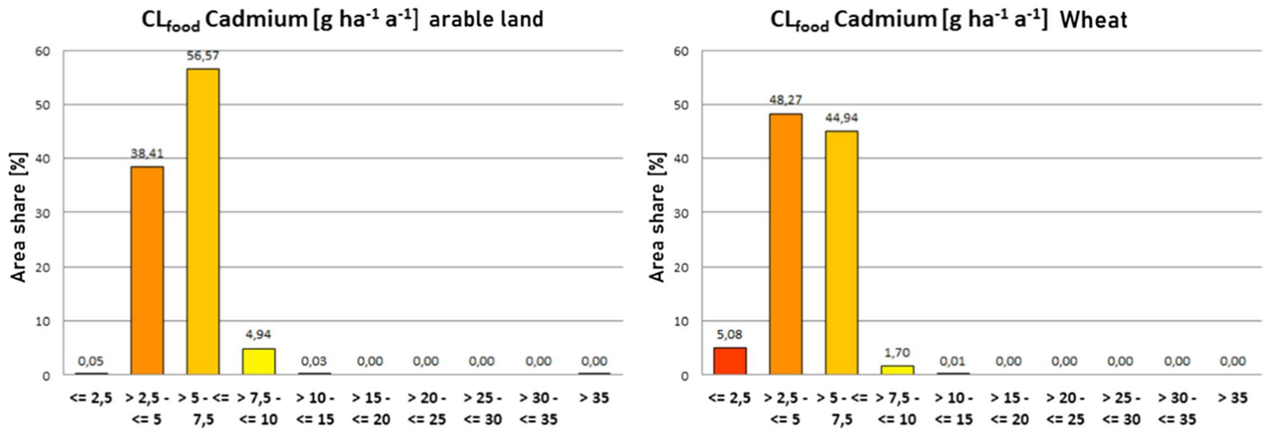


Fig. 3 Comparison of the proportions of arable land in Germany in the classes of critical load for cadmium for human health ($CL(Cd)_{food}$, in the variant "crop rotation according to good professional practice" (left), "monoculture wheat" (right)

Table 25 Sensitivity analysis using an example calculation for $CL(M)_{drink}$ with different leaching rates and otherwise the same input data at a field site with cambisol vega from clayey–loamy sediments and at a forest site with sand-cambisol in the subcontinental climate zone of Brandenburg

		Seepage rate mm a^{-1}	$CL(Pb)_{drink}$ g ha^{-1} a^{-1}	$CL(Cd)_{drink}$	$CL(Hg)_{drink}$	$CL(As)_{drink}$	$CL(Cu)_{drink}$	$CL(Cr)_{drink}$
Input data and results used in this paper	Wheat	66.0[a]	6.8	2.2	0.05	6.9	1357.0	36.9
	Silage maize	66.0[a]	15.8	3.8	0.93	8.2	1481.0	66.6
	Meadow	66.0[a]	14.2	3.0	0.24	7.4	1367.4	36.0
	Pine	66.0[a]	9.6	4.2	0.06	6.6	1322.5	33.6
Alternative input data and results	Wheat	111.0[b]	11.3	3.6	0.05	11.4	2257.0	59.4
	Silage maize	111.0[b]	20.3	5.2	0.93	12.7	2381.0	89.1
	Meadow	111.0[b]	18.7	4.3	0.25	11.9	2267.4	58.5
	Pine	111.0[b]	14.1	5.6	0.08	11.1	2222.5	56.1
Deviations [%]	Wheat	68.2	65.8	60.8	64	60.8	67.0	29.1
	Silage maize	68.2	28.5	35.3	28	40.2	61.7	7.9
	Meadow	68.2	33.2	47.2	51	61.1	67.0	30.0
	Pine	68.2	46.8	31.8	65	68.0	68.1	66.9

[a] According to BGR [21] (2014)

[b] According to MUGV [62]

Leaching rate

The comparison of leaching rates according to BGR [25] with corresponding larger-scale surveys on groundwater recharge in the north-eastern German lowlands shows large discrepancies. For example, an average seepage rate of 66 mm a^{-1} according to BGR for Brandenburg is offset by an average seepage rate of 111 mm a^{-1} according to a publication of the Brandenburg Ministry for the Environment, Health and Consumer Protection [62]. For Saxony-Anhalt, too, the data differ from an average of 56 mm a^{-1} [25] to an average of 90 mm a^{-1} [63]. Even if the regional data are obviously not yet based on the 30-year average 1981–2010, as in the case of the BGR map, such large deviations cannot result from the temporal offset.

The seepage rate has a significant influence on the result of the critical load calculation (Table 25).

The percentage deviation of the leaching rate, assuming otherwise the same input values, is reflected at most in the same percentage deviation of the $CL(M)_{drink}$ for wheat and pine as well as for all receptors with respect to copper. The $CL(Cr)_{drink}$ has the smallest deviation.

Heavy metal concentration in leachate

The critical concentrations of metals in leachate used in this study to calculate critical loads for ecosystem

Table 26 Comparison of insignificance threshold values for the metal concentration in leachate [65] with the critical total concentrations in leachate used in this study

	Critical concentration used			Insignificance thresholds[e]	
	Ecosystem protection		Drinking water protection[h]	Ecosystem and drinking water protection	
		µg l^{-1}			µg l^{-1}
As	PNEC[i]	70[a]	10	Base value[f]	3.2
Cr(III)	NOEC[j]	44[b]	50	Ecotoxicological impact threshold[f]	3.4
Cu	PNEC	1-50[c]	2000	Base value[g]	5.4
Ni	NOEC	25-700[c]	–	Base value[g]	7
Zn	NOEC	20-90[c]	–	Base value[g]	60
Pb	NOEC	0.08-71.5[c]	10	Ecotoxicological impact threshold[f]	1.2
Cd	NOEC	0.43–7.16[c]	3	Base value[g]	0.3
Hg	NOEC	0.058–17.4[c]	1	Base value[g]	0.1

[a] Doyle et al. [50] in Reinds et al. [33]

[b] Crommentuijn et al. [96] in Reinds et al. [33]

[c] WHAM modeling results [97]

[d] Reinds et al. [33]

[e] Zeddel et al. [65]

[f] Ecotoxicological impact threshold < human toxicological impact threshold

[g] The lower value based on ecotoxicity was below the base value, so that the JRC is reported at the level of the base value

[h] Drinking Water Ordinance for Germany [38]

[i] Predicted no-effect concentration = the predicted concentration of a substance that is normally dangerous to the environment and up to which no effects on the environment are observed

[j] No Observed Effect Concentration = corresponds to the highest exposure concentration of a substance in subchronic or chronic studies at which no statistically significant effect can be observed

protection correspond to the specifications of Reinds et al. [33]. Accordingly, the critical total concentrations for copper, nickel, zinc, lead and cadmium were calculated model-based according to their bioavailability depending on the soil-specific pH value and the content of organic mass and dissolved organic carbon [18, 29, 30]. The modelling is based on PNEC values (for As and Cu) and NOEC values (for Cr, Ni, Zn, Pb, Cd and Hg). From the soil-specific modelling on the basis of the reference profiles of the BÜK1000N, value ranges of the total concentration result for Cu, Ni, Zn, Pb, Cd and Hg (Table 26).

A joint working group with representatives of LAWA,[5] LABO[6] and LAGA[7] updated the report "Derivation of Insignificance Thresholds for Groundwater" [64] from 2013 to 2015 and prepared the corresponding amendments and the reformulation of a chapter "Principles for the Application of Insignificance Thresholds" [65]. The comparison of low-minimity threshold values for the metal concentration in leachate [65] with the critical total concentrations in leachate used in this paper is shown in Table 28.

The low thresholds for copper, zinc, lead and mercury lie within the respective ranges of the soil-specific modelled results for ecosystem protection. However, the lowest thresholds for arsenic, chromium, nickel and cadmium are below the critical concentrations used to calculate the critical loads in this paper. The largest differences are for arsenic, chromium and nickel, so that the critical loads result in deviations in the result of up to −95% when using the low-value thresholds as input values in the calculation as an alternative (Table 27).

The percentage deviation of the critical limits in the case of alternative use of the lowest thresholds according to Zeddel et al. [65] is reflected in an almost equally high percentage deviation of the $CL(M)_{eco}$.

pH

In the pH range considered in Table 28, higher pH values result in lower critical loads. The pH values used in the determination of the pH-dependent critical limits and thus in the calculation of the $CL(M)_{eco}$ were derived from the classes of the acidity per horizon of the BÜK1000N soil profiles. These are average values for the typical soil types in Germany under the respective use. Since

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[5] Working Group of the Federal States for Water protection.

[6] Working Group of the Federal States for Soil protection.

[7] Working Group of the Federal States for Waste Recovery.

Table 27 Sensitivity analysis using an example calculation for $CL(M)_{eco}$ with different critical total concentrations in leachate and otherwise the same input data at an arable site with cambisol vega from clayey loamy fluviatile sediments in the sub-Atlantic climate zone and at a forest site with sandy cambisol in the subcontinental climate zone

		Metal concentration in leachate ($\mu g\ l^{-1}$)			Critical loads ecosystem protection ($g\ ha^{-1}\ a^{-1}$)		
		$[As]_{crit}$	$[Cr]_{crit}$	$[Ni]_{crit}$	$CL(As)_{eco}$	$CL(Cr)_{eco}$	$CL(Ni)_{eco}$
Input data and results used in this paper	Wheat	70.0	44.0	106.8	205.6	132.9	315.0
	Silage maize	70.0	44.0	106.8	206.9	162.6	339.8
	Meadow	70.0	44.0	106.8	206.1	132.1	320.1
	Pine	70.0	44.0	197.9	46.2	29.7	133.9
Alternative input data (here: minority thresholds according to Zeddel et al. [65] and results	Wheat	3.2	3.4	7.0	9.7	13.8	22.4
	Silage maize	3.2	3.4	7.0	11.0	43.6	47.2
	Meadow	3.2	3.4	7.0	10.1	13.0	27.5
	Pine	3.2	3.4	7.0	2.1	2.9	7.9
Deviations [%]	Wheat	− 95.4	− 92.3	− 93.4	− 95.3	− 89.6	− 92.9
	Silage maize	− 95.4	− 92.3	− 93.4	− 94.7	− 73.2	− 86.1
	Meadow	− 95.4	− 92.3	− 93.4	− 95.1	− 90.2	− 91.4
	Pine	− 95.4	− 92.3	− 96.5	− 95.4	− 90.3	− 94.1

Table 28 Sensitivity analysis based on an example calculation for $CL(M)_{eco}$ with different pH values and otherwise the same input data at a forest site with sand-cambisol in the Atlantic climate zone of northwest Germany

	Low pH		High pH		Deviation [%]	
	Beech	Pine	Beech	Pine	Beech	Pine
Soil	Cambisol from nutrient-poor sands		Cambisol from nutrient-rich sands			
pH [–]	4.1	4.1	4.9	4.9	19.9	19.9
Yield [t dry mass $ha^{-1}\ a^{-1}$]	4.4	1.7	4.7	1.9	5.7	7.7
$CL(Pb)_{eco}$ [$g\ ha^{-1}\ a^{-1}$]	41.7	30.7	13.4	8.2	− 67.9	− 73.2
$CL(Cd)_{eco}$ [$g\ ha^{-1}\ a^{-1}$]	9.1	9.0	5.4	6.2	− 40.9	− 31.4
$CL(Ni)_{eco}$ [$g\ ha^{-1}\ a^{-1}$]	586.1	462.0	268.2	210.6	− 54.2	− 54.4
$CL(Zn)_{eco}$ [$g\ ha^{-1}\ a^{-1}$]	213.1	174.8	153.4	128.9	− 28.0	− 26.3
$CL(Cu)_{eco}$ [$g\ ha^{-1}\ a^{-1}$]	32.0	21.3	12.5	5.8	− 60.9	− 73.0

a large number of input parameters are included in the WHAM modelling of the critical limits in addition to the pH value, soil profiles had to be sought for the sensitivity analysis with regard to the pH value in order to compare soil profiles in which all other input data (seepage rate, OM, DOM, DOC contents, pCO_2) are the same and only the depth-stage-weighted mean value of the pH value deviates. However, the yields are not identical in a low-base and a base-rich soil according to the calculation of the yield potentials on which this report is based. Although a higher yield tends to result in higher critical load, the opposite influence of pH on the critical load far outweighs the effect (Table 28).

Although the pH value differs by only approx. 20% and at the same time the yield variations tend to have a compensating effect, the $CL(M)_{eco}$ deviates between 26 and 73%. Implausible pH values can be seen in some conductive soil profiles under forest. For example, for stagnic chernozems from loess over clay and marl rocks under forest in the top 30 cm of the mineral soil, the contents of exchangeable cations result in a base saturation of 7.1%, which corresponds to a pH value of 3.2. This seems much too low for this soil form. In raised bogs, the high contents of Ca and Mg result in a base saturation of 100% and a pH value of 6.8. This cannot be explained for raised bogs. Implausible values for 4 of the above-mentioned reference soil profiles were therefore not included in the CL calculation, but replaced by expert estimates. This, however, creates some uncertainty.

Organic matter content

The organic matter content was derived from the humus class for the horizons of the guide soil profiles of the BÜK1000N. An exemplary comparison of the CL

Table 29 Sensitivity analysis using an example calculation for CL(M)$_{eco}$ with different organic mass contents and otherwise the same input data at grassland sites with boulder clay in the subcontinental climate zone of Northeast Germany

Vegetation Soil	Weed Luvic arenosols from boulder clay	Weed Distric gley from boulder clay	Deviations [%]
OM [mass %]	1	15	– 93.3
CL(Pb)$_{eco}$ [g ha^{-1} a^{-1}]	13.0	14.8	– 12.2
CL(Cd) $_{eco}$ [g ha^{-1} a^{-1}]	5.3	5.5	– 3.6
CL(Hg) $_{eco}$ [g ha^{-1} a^{-1}]	0.22	0.22	– 2.2
CL(Ni) $_{eco}$ [g ha^{-1} a^{-1}]	273.3	280.8	– 2.7
CL(Zn) $_{eco}$ [g ha^{-1} a^{-1}]	358.9	370.1	– 3.0
CL(Cu) $_{eco}$ [g ha^{-1} a^{-1}]	36.7	46.4	– 20.9

results therefore requires the comparison of two leading soil profiles with clearly differing humus classes and otherwise the same parameter values as occur on soils of the same soil form group under grassland use (Table 29).

The effects of a high deviation of the OM content of 93% only have a dampened effect on the respective critical load. The maximum deviation of the CL(Cu)$_{eco}$ is 21%. When deriving the OM contents from the humus classes, no implausibilities were noticed.

Dissolved organic matter and dissolved organic carbon content

The values for deciduous and coniferous forest used in this study are taken from De Vries et al. [46]. In the manual of the ICP Modeling and Mapping [18, 29, 30], Chapter 5.5 only one value is given for forest in general. Kalbitz et al. [66] published results of a field study at 23 reference sites with spruce stands. The DOC average over the O horizons is therefore 41.3 mg l^{-1}. These data from German forests fit very well with the Dutch data for coniferous forests [46]. Their range is from approx. 22–83 mg l^{-1}. The manual points out that the number of investigated sites is not yet sufficient to derive generalisations for reliable reference values. This parameter is still subject to a very high degree of uncertainty. Therefore, Table 30 shows the results with the variants according to De Vries et al. [46] and according to Manual [30], as well as with a fictitious extremely low value and an extremely high value. Since mercury largely occurs only in the organic layer, the CL(Hg)$_{eco}$ is particularly sensitive to the DOC/DOM content compared to the other metals (Manual: Table 5.21).

The deviations of the CL(Hg)$_{eco}$ results for extreme variants from the results of this study are very high (maximum 131%). However, the deviation of the results with the variants according to De Vries et al. [46] and according to Manual [18, 29, 30] is only small (maximum: – 10%).

The multi-factorial influence of pH and DOC on the variability of the critical load is shown in Table 31.

Exceeding critical loads

After completion of the investigations described in Additional file 2, it became known that the emission data for the years considered were updated as the basis for the deposition modelling by TNO and EMEP for the years considered and that new concentration and deposition data are now available from EMEP in 0.1° x 0.1° resolution, at least for Pb, Cd, Hg. As soon as these are available and other prerequisites for the recalculation of

Table 30 Sensitivity analysis using an example calculation for CL(Hg)$_{eco}$ with different contents of dissolved organic mass and otherwise the same input data at a coniferous forest and a deciduous forest site with boulder clay in the subcontinental climate zone of north-eastern Germany

		DOC g m^{-3}	CL(Hg)$_{eco}$ g ha^{-1} a^{-1}	Deviation CL(Hg)$_{eco}$ %
Input data and results in this study[a]	Beech	32	0.2288	
	Pine	40	0.1736	
Input data according to Manual[b]	Beech	35	0.2420	6
	Pine	35	0.1562	– 10
Alternative input data and results from fictitious assumptions of extremes	Beech	1	0.0924	– 60
	Pine	1	0.0380	– 78
	Beech	100	0.5279	131
	Pine	100	0.3822	120

Sources: [a]deVries et al. [46]. [b] Manual of the ICP Modeling and Mapping [18, 29, 30]: Chapter V.5)

Table 31 Sensitivity analysis using an example calculation for CL(Cd)$_{eco}$ and CL(Pb)$_{eco}$ with different pH and dissolved organic mass contents and otherwise identical input data at a coniferous forest and a deciduous forest site with rendzic leptosol from marl in the subcontinental climate zone of north-eastern Germany

		DOC g m^{-3}	pH –	CL(Cd)$_{eco}$ g ha^{-1} a^{-1}	CL(Pb)$_{eco}$ g ha^{-1} a^{-1}	Deviations CL(Cd)$_{eco}$ %	Deviations CL(Pb)$_{eco}$ %
DOC data and results in this study[a]	Beech	32	4.0	8.97	42.7		
	Pine	40	4.0	8.89	31.8		
DOC according to Manual[b]	Beech	35	4.0	8.97	42.7	0	0
	Pine	35	4.0	8.83	31.5	− 1	− 1
alternative input data and results from fictitious assumptions of extremes	Beech	1	4.0	8.84	40.1	− 1	− 6
	Pine	1	4.0	8.73	29.5	− 2	− 7
	Beech	100	4.0	9.28	48.5	3	14
	Pine	100	4.0	9.07	36.0	2	14
DOC data and results used in this study[a]	Beech	32	7.0	9.03	26.0		
	Pine	40	7.0	9.73	21.6		
DOC according to Manual[b]	Beech	35	7.0	9.08	26.0	0	0
	Pine	35	7.0	8.91	18.3	− 8	− 15
Alternative input data and results from fictitious assumptions of extremes	Beech	1	7.0	1.92	7.5	− 79	− 71
	Pine	1	7.0	3.26	3.7	− 67	− 83
	Beech	100	7.0	15.15	63.5	68	144
	Pine	100	7.0	13.71	47.9	41	121

[a] According to De Vries et al. [46]

[b] According to ICP Modeling and Mapping Manual [18, 29, 30]: Chapter 5.5)

Table 32 Maximum possible deviations of the input values in Germany and the resulting maximum possible deviations of the critical loads

	Possible deviation of the input value from the CL input value of this operation [%].	Maximum possible deviation of the varying CL from the CL of this work [%].	Quotient from Columns 2 and 3	CL with the greatest possible deviation
(1)	(2)	(3)	(4)	(5)
Yield	28	5.9	0.2	CL(Cu) $_{eco}$ for podzol from weak loamy sands
Metal content in harvested crop	300	169	0.6	CL(Pb)$_{eco}$ on silage maize fields
Leachate rate	68	68	1.0	CL(As)$_{drink}$ and CL(Cu)$_{drink}$ for pine forest in Brandenburg
Critical limit	96.5	94.1	1.0	CL(Ni)$_{eco}$ for pine
pH	19.9	− 73	− 3.7	CL(Pb)$_{eco,}$ CL(Cu)$_{eco}$ for pine forests
OM content	− 93	− 21	0.2	CL(Cu) $_{eco}$ for grassland

critical load exceedances based on them are fulfilled, the results presented in Additional file 2 could be updated accordingly.

Discussion

The random sensitivity calculations were designed in such a way that the possible range of deviations of the input data used in this study for CL determination from alternative values is reflected (Table 32).

Table 32 shows that even minor positive pH deviations have the greatest negative effects on critical loads. The pH value is therefore the input parameter to which all critical loads react most sensitively. However, the pH values, as used in this study for the CL calculation, are derived from the BÜK1000N database [21] from nationwide measurement campaigns, i.e. representative of the typical soil forms in Germany and also quality-checked and one of the sources with the lowest uncertainties. In a restrictive manner, reference must be made to the 8 reference profiles of a total of 675 profiles in the BÜK database, for which the pH values do not appear plausible from our expert point of view.

The largest deviations in the input data were found for the metal contents in the biomass to be harvested. However, the influence of this deviation on the respective CL(M) is damped. Negatively deviating OM contents also have a reducing effect on CL, but less drastically than the pH value. However, no data on OM contents could be found in the literature in addition to the BÜK1000N database used here, so that a comparison with values from other sources was not possible. For this parameter, too, it can be estimated that the BÜK1000N values used in this paper are based on a reliable database.

For all other input values, a comparison with other literature references shows that the values used here for the CL calculation are below the span or in the lower half of the value ranges of other data sources. Thus, this study results in conservative critical loads based on conservatively estimated leachate rates, metal contents in the harvested crop and DOC contents in the soil. The input values used or derived from the BÜK1000N (yield potential, pH values, OM contents) are to be evaluated as robust. The leachate rates according to BGR [25] are also quality-tested. There are major uncertainties in the determination of DOC contents, which are recommended by [46] (Manual of ICP Modeling and Mapping [18, 29, 30], but for which validation is still required.

The total critical concentrations of lead, cadmium and mercury used are based on NOEC values for plants, invertebrates and soil microorganisms and are therefore based on thresholds for terrestrial ecosystems. The threshold values for the concentration of copper, nickel and zinc have been determined on the basis of NOEC and PNEC values of soil water organisms. In this respect, it has yet to be proven that plants are no more sensitive than the microorganisms in soil water. The critical threshold values for arsenic and chromium have been transferred from NOEC or PNEC values of aquatic organisms to terrestrial ecosystems. For these two metals, therefore, the greatest uncertainties remain. From the latest ecotoxicological studies on organisms in leachate, minor threshold values were derived [65], which for chromium and arsenic are far below the PNEC and NOEC values documented in Reinds et al. [33].

The critical loads maps offer a Germany-wide overview of the sensitivity of the receptor surfaces on a scale of 1:1 million. In particular, they enable a comparison with the current entries for a Germany-wide assessment of the risks for humans and the environment. However, they also offer a relative comparison of the sensitivity of the receptor surfaces to each other as well as the identification of regional differences in national or international evaluations. They are not suitable for large-scale or site-specific evaluation due to the small map scale.

In particular the CL data bases for lead, cadmium, mercury can be considered well validated, but also the CL for copper, nickel and zinc can be recommended for the above-mentioned small-scale applications. However, the uncertainties of the $CL(As)_{eco}$ and $CL(Cr)_{eco}$ cards are still considerable. Further research is required in particular with regard to the determination of ecotoxicological critical limits for arsenic and chromium.

Conclusions

A comparison of the critical loads determined for Germany with the assessment values of binding legal regulations reveals clear differences (Table 33).

The comparison shows that there are regions in Germany where the protection of drinking water is possibly not sufficiently guaranteed by the applicable assessment values. The need for protection, as shown by the critical loads ($CL(M)_{drink}$), is significantly higher in Brandenburg, Saxony-Anhalt and in the north-east of Saxony and Mecklenburg-Western Pomerania with regard to the input of Hg, Cd, Pb, As, and Cr into groundwater than the guarantee of protection by existing binding assessment values. Only for Cu and Zn are the assessment values of existing regulations for drinking water protection sufficient.

The protection of health during the consumption of wheat products is largely guaranteed by the assessment values for Cd inputs, with the exception of arable land in the Heinsberg district on the Dutch border. Here the $CL(Cd)_{food}$ is lower than the mandatory assessment values in small areas.

The protection of ecosystems throughout Germany is possibly only guaranteed by binding assessment values for As and Ni. The $CL(Hg)_{eco}$ are even lower than the binding assessment values throughout Germany. For all other metals, Cd, Pb, Cu, Zn and Cr, the critical loads ($CL(M)_{eco}$) in some regions indicate significantly more sensitive ecosystems.

The comparison of the human toxicologically derived assessment values with the atmogenic inputs in 2013 (mercury) and 2010 (all other metals) shows that the critical loads for drinking water protection for lead and mercury are not complied with in some regions of Germany and that there could therefore be a long-term risk to human health if drinking water is consumed, provided that the mercury actually arrives in groundwater. Especially the rain poor regions of Germany (especially Brandenburg, lowlands of Saxony-Anhalt, Leipziger Bucht, Ruhr area) with forest vegetation are affected by exceedances by Hg- and Pb-entries. This area proportion

Table 33 Comparison of the assessment values of binding legal regulations and the critical loads for Germany

Metal	TA Luft Tab. 6[a]	TA Luft Tab.8[b]	BBodSchV[c]	39th BImSchV[d,e] 2004/107/EG[e] 2008/50/EG[e]	CL(M)$_{\text{drink}}$	CL(M)$_{\text{food}}$	CL(M)$_{\text{eco}}$
	Emitter-related			General load			
	g ha^{-1} a^{-1}						
Hg	4	11–110	1.5		0.3–13.8		0.1–1.1
Cd	7	9–117	6	2.5–7	0.8–42.6	1.9–19.2	1.5–127.6
Pb	365	675–6935	400	250–716	3–142		2–2603
As	15	219–4271		2.2–6	2–138		15–1669
Ni	55		100	10–17.4			37–11,232
Cu		300			484–27,533		7–3384
Zn		1200			1234–69,133		81–2457
Cr		300			12–688		78–1049

[a] TA Luft = Technical Instructions for Air pollution control (deposition values to protect human health)

[b] TA Luft = Technical Instructions for Air pollution control (deposition values as reference points for the special case examination to protect environment)

[c] BBodSchV = Federal Soil Protection Ordinance (permissible additional load according to §11 para. 2)

[d] 39th BImSchV = 39th Federal Immission Control Ordinance

[e] Converted from assessment values for concentrations [4]: Tables 30 and 31)

may be higher, since the German CL dataset may not reflect areas where maximum deposition rates meet a very low critical load (worst case).

Although the critical loads for cadmium for drinking water protection $\text{CL(Cd)}_{\text{drink}}$ and for the protection of human food from wheat products $\text{CL(Cd)}_{\text{food}}$ will not be exceeded by the atmospheric depositions in 2010 in the receptor areas of the German dataset, the German dataset may not reflect smaller areas where maximum deposition rates meet a very low critical load (worst case). In these cases, the maximum atmospheric deposition in 2010 would have exceeded $\text{CL(Cd)}_{\text{drink}}$ and $\text{CL(Cd)}_{\text{food}}$. Although no critical loads for drinking water protection could be calculated for nickel, since the BTrinkwV does not specify a limit concentration for nickel, a comparison of the 2010 entries with the recommended assessment concentrations for nickel, converted into annual input rates in the EU position paper (2000), shows an exceedance on fields and grassland in the worst case (maximum deposition meets lowest permissible input value).

If one compares the heavy metal input 2013 (mercury) or 2010 (all other metals) with the ecotoxicologically justified assessment values, the picture is the same as for the assessment values derived from human toxicology: The critical loads for ecosystem protection $\text{CL(M)}_{\text{eco}}$ are exceeded by the mercury and lead inputs in some regions of Germany (in particular Brandenburg, Leipzig Bay, Saxony-Anhalt, Ruhr area) with forest vegetation; in addition, the $\text{CL(Cu)}_{\text{eco is}}$ exceeded by copper inputs in 2010 in the Berlin environs and in the Ruhr area (around 1% of the receptor area). In the worst case, $\text{CL(Cd)}_{\text{eco}}$ could be exceeded by the maximum cadmium inputs in 2010. For example, the forests of sub-continental climatic areas are exposed to potential risks (low precipitation, high evaporation rate) due to atmospheric heavy metal inputs, but also the habitat types according to Annex 1 of the Habitats Directive with restricted or prohibited use (humid and slope forests, dry and humid heaths, moors, humid high-growing shrub meadows along watercourses, etc.). The FFH-Annex-I-habitats 91D0, 91E0, 9180, 91T0, 91U0 must therefore be regarded as particularly sensitive.

However, this rough risk assessment must be discussed in the context of uncertainties and assumptions: Since the 2010 deposition data set for Germany shows higher average depositions than the 2009 and 2011 data sets, the comparison of the 2010 depositions with the assessment values tends to show unfavourable conditions and is therefore a rather conservative view. The uncertainties of the emission rates underlying atmospheric transport modelling are very high for some metals. This uncertainty is of course transferred to the calculated deposition values.

The deposition calculations by Schaap et al. [4] do not reflect any small-scale limited direct loads in the vicinity of individual emitters. This is also shown by empirically determined deposition values, some of which are significantly higher than the deposition model values. This clarifies the character of the modelled values as background deposition and explains why the plant-related assessment values of the TA Luft and the BBodSchV are not exceeded by these deposition rates. Airborne depositions represent only a fraction of the inputs compared to inputs with fertilisers and other inputs. Including all entry paths, exceedances of the critical loads and the permissible additional loads of the BBodSchV could occur more widely or be significantly higher, especially on fields. As with critical loads for the protection of human health, if critical loads for ecosystem protection are exceeded, the ecosystem may accumulate without damage as long as the critical limits have not yet been reached. If the critical limits are reached, an impairment of the protected property must be expected, even if only after a corresponding reaction time of the ecosystem. Particularly in the case of heavy metal inputs, it can take centuries before a visible negative change in the protected goods occurs if the critical loads are permanently exceeded. For example, soils have a very high buffering capacity against mercury inputs. Other metals such as cadmium and nickel are more mobile and accumulate proportionally to the soil content in the biomass, so that the assumptions about the uptake rates with the biomass for the critical loads calculation are very conservative, because this calculation was generally carried out with very low concentrations in the biomass (literature values).

The objectives of the EU Air Pollution Strategy, not to allow unacceptable impacts on humans and the environment by 2020, have not yet been met by the 2010 deposition rates. For the goal of the National Biodiversity Strategy by 2015 of establishing ecosystem-based impact thresholds for pollutants that describe the impacts on biological diversity, the critical loads for the protection of ecosystems provide a very precautionary scientific basis for discussion. Since cadmium, lead and mercury are transported far in the atmosphere, both national and international measures to reduce them are necessary in addition to plant- and project-related emission limits. In the case of other metals, the focus should be on plant-related reductions within Germany. A first step could be the mandatory measurement and reporting of actual emission levels (especially for mercury emissions) in the operation of large emitters. However, special attention must also be paid to farm inputs, especially to protect agricultural land from harmful accumulations of substances.

Supplementary information

Supplementary information accompanies this paper at https://doi.org/10.1186/s12302-020-00391-w.

Additional file 1. Figures and Tables.

Additional file 2. Exceeding critical loads.

Abbreviations

As: arsenic, here limited to As(V), the stable form in aerobic environment (humus topsoil); Cd: cadmium; $CL(Cd)_{food}$: critical load for cadmium for the protection of arable crops (here: wheat products) as food for humans; $CL(M)_{drink}$: critical load for a metal (M stands for the chemical symbol for the metal in question) to protect drinking water as a foodstuff for humans; $CL(M)_{eco}$: critical load for a metal (M stands for the chemical symbol for the metal under consideration) for the protection of the considered ecosystem; CLC: corine landcover; Co: cobalt; Cr: chromium, here limited to Cr(III), the stable form in the considered humus-containing topsoil horizons; Cu: copper; $[DOM]_{swd}$: concentration of dissolved organic matter in the soil solution of the humus layer [g m^{-3}]; DWD: German Meteorological Service; ECMF: European Centre for Medium Range Weather Forecasts; EEA: European Environmental Agency; EMEP: European Monitoring and Evaluation Programme; GIS: Geographic Information System; Hg: mercury, sum of organically bound Hg in methyl mercury ($CH_3 Hg^+$) and Hg in inorganic forms; $[Hg]_{OM(crit)}$: critical limit for Hg relative to solid organic matter (OM) in humus layers; CLRTAP: Convention on Long-Range Transboundary Air Pollution; $[M]_{free,sdw(crit)}$: critical concentration of free metal ions in the seepage water; $[M]_{ha}$: metal content in the dry matter of the crop [mg kg^{-1} TS^{-1} or eq kg^{-1} TS^{-1}]; $[M]_{sdw(crit)}$: critical total concentration of metals in leachate and bound to organic, inorganic and suspended particles; $Mle_{(crit)}$: tolerable leaching of the metal M from the soil layer under consideration with exclusive consideration of vertical rivers (leachate) [g ha^{-1} a^{-1}]; Mn: manganese; Mon: molybdenum; M_u: net uptake of the metal M into harvestable parts of plants [g ha^{-1} a^{-1}]; Ni: nickel.

Acknowledgements

We would like to thank the Federal Environment Agency for financial support and expert assistance for the study.

Authors' contributions

WS headed the investigation and drafted the manuscript. AS and TS carried out the calculations. All authors read and approved the final manuscript.

Funding

The investigation was funded by the Federal Environment Agency of Germany.

Availability of data and materials

It is planned to archive the data in a repository.

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that there are no competing interests.

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Received: 6 June 2020 Accepted: 19 August 2020

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