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Comparison of Existing Legal Assessment Values for Heavy Metal Deposition in Western Europe and Calculation of Assessment Values for Luxembourg

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Abstract: The protection against eco- and human-toxicological impairments caused by atmospheric deposition of heavy metals requires legally defined assessment values. Since such values are missing for Luxembourg, the aim of this investigation was to evaluate different approaches to derive assessment values for the regulation of heavy metals that are in accordance with scientific and legal standards. To this end, assessment values for heavy metals were derived from the compilation of respective values implemented in European countries. In addition, (1) precipitation-related assessment values for the protection of soil for Cr, Zn, and Cu and (2) precautionary assessment values (critical loads for Cr, Zn, and Cu, as well as As, Cd, Ni, and Pb) for the protection of human health and ecosystems were calculated. The calculation of the regionally differentiated precipitation-related assessment values resulted in ranges of 17–272 g Cu ha^{-1} a^{-1}, 167–2672 g Zn ha^{-1} a^{-1} and 17–272 g Cr_{total} ha^{-1} a^{-1}. The critical loads for drinking water protection vary in the ranges from 1.23 to 2.14 g Cd ha^{-1} a^{-1}, from 4.05 to 8.63 g Pb ha^{-1} a^{-1}, from 2.6 to 5.9 g As ha^{-1} a^{-1}, from 258 to 564 g Cu ha^{-1} a^{-1}, from 1292 to 2944 g Zn ha^{-1} a^{-1}, and from 12.9 to 29.9 g Cr_{total} ha^{-1} a^{-1}. Ecosystems are significantly more sensitive to Pb, Cu, and Zn inputs than humans. For As and Cr, humans react much more sensitively than ecosystems. For Cd, the critical loads for drinking water, ecosystems, and wheat products are about the same.

Keywords: critical loads for drinking water; ecosystems; wheat products

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1. Introduction

When, in the middle of the last century, several thousand people in the Japanese cities of Minamata and Niigata became ill from damage to the nervous system and some also died, the international public became aware for the first time of the environmental pollution caused by heavy metals. The cause of this poisoning, later referred to as Minamata disease, was wastewater contaminated with Hg from plastic production that was discharged into the sea. The Hg accumulated in fish via the food chain and led to symptoms of poisoning, particularly in humans, who mainly fed on fish. By the time of the first court case in 1973, 78 deaths had already been reported [1], a total of about 3000 people were poisoned, and more than 1800 of these cases were fatal.

As trace elements, some heavy metals are essential for life processes in the biological system. On the other hand, above a certain quantity, they contribute to pollution and can have toxic or carcinogenic effects. Accumulation is possible via the food chain, which can ultimately also endanger human health. For this reason, regulations have been established at both a national and international level to limit the input of heavy metals to a tolerable level in order to protect human health.

The First Environmental Action Program of the EU 1973–1976 [2] therefore already listed the heavy metals Pb and V (Group 1) and Ni, cadmium, and antimony (Group 2) among the air pollutants to be investigated as a priority.

In Germany, a maximum level for Hg in fishery products of 1 mg kg^{-1} was set as early as 1975 for consumer health protection. In order to protect human health, EU-wide maximum levels for Pb and Cd have been in force since April 2002 in various foodstuffs such as cereals, vegetables, fruit, food supplements, food for infants and young children, and meat and fishery products.

Since the sources and pathways of heavy metals require an approach that goes beyond national borders, the United Nations Economic Commission for Europe (UNECE) has addressed this issue. A milestone in this process was the Convention on Long-Range Transboundary Air Pollution (CLRTAP). Signed in 1979 and in force since 1983, this convention brings together 51 member countries from Europe, the European Union (EU) as a whole, as well as the United States and Canada. "The Convention is the only negotiating forum beyond the EU that is binding under international law to combat transboundary air pollution. At the same time, it is a model for other regions of the world facing similar problems" [3].

CLRTAP's goals were implemented through protocols. To date, eight such protocols have been adopted, including one to mitigate pollution from heavy metals (Heavy Metals Protocol 1989: Regulation to Reduce Emissions of the Heavy Metals Cd, Pb, and Hg). The UNECE Heavy Metals Protocol, also known as the Aarhus Protocol after the city of signature, entered into force in 2003. This protocol only regulates emissions to air, such as technical standards for industries that emit heavy metals. It also regulates the use of Pb in gasoline or Hg in certain substances.

The Aarhus Protocol was revised in December 2012 and adapted to modern requirements for industrial plants [4]. In particular, the countries of the former Soviet Union (EECCA region) should be facilitated in their ratification by the revision, which for example provides for longer transition periods for technical adaptations and more flexible base years for reporting deadlines of these countries. The focus on applying the state of the art identifies mitigation potentials in the UNECE. In particular, Eastern Europe and the former Soviet Union have the greatest emission reduction potentials due to the currently still lower environmental standards and the condition of industrial plants there.

The EU presented a new package of measures for clean air in Europe at the end of 2013, which aims to update existing legislation. The aim is to further reduce emissions of air pollutants so that impacts on human health and the environment are reduced or avoided altogether. Part of the package is a "Clean Air for Europe" program, which initially aims to ensure compliance with existing targets. In addition, new air quality targets are also formulated for the years 2020 and 2030.

The 2020 target of this strategy is to reduce air pollution to the point where it no longer has an unacceptable impact on people and the environment. Part of this strategy has already been implemented with the Directive on ambient air quality and cleaner air for Europe, which came into force on 11 June 2008. Directive 2008/50/EC confirms the existing limit values. By 10 June 2010, the new directive had to be transposed into the national laws of the member states. In Germany, implementation took place with the 39th Ordinance on the Implementation of the Federal Emission Control Act.

Overall, the synopsis of national and international regulations shows that there is no summary document on assessment values for heavy metals. Rather, an assessment of exposure or limitation of input is carried out according to input pathways (air, water, and soil), according to objects of protection (foodstuffs, drinking water, and ecosystems), or also in relation to the emitters, whereby the best available technique (BAT) is to be applied.

Since legally defined assessment values for the protection against eco- and human-toxicological impacts due to atmospheric heavy metals deposition are still missing for Luxembourg, the first aim of this investigation was to evaluate different approaches to derive assessment values for the regulation of heavy metals that are in accordance with scientific and legal standards. Founded by this comprehensive evaluation, it should be worked out whether the existing regulations in Luxembourg's neighboring countries can be applied to Luxembourg or whether new limit values should be set according to the critical loads determined by the authors on the basis of models for specific regions of Luxembourg. Based on the compilation and comparative analysis of existing legal and sublegal assessment values for atmospheric deposition of As, Cd, Cr, Cu, Ni, Pb, and Zn in the Western European countries France, the Netherlands, Belgium, Switzerland, Austria, Germany, and in the EU (Schlutow et al. 2021), the second aim of this investigation was to establish regionalized assessment values for Luxembourg for the first time. The methodology applied to this end was developed and already applied by the authors for Germany [5,6] but extended and further developed for Luxembourg:

1. Precipitation-based assessment values for soil protection for Cr, Zn, and Cu (Section 2.1).
2. Precautionary assessment values (critical loads) for Cr, Zn, and Cu, as well as, Cd, Ni, and Pb for the protection of human health and ecosystems (Section 2.2).

2. Methods

2.1. Comparison of Legal Regulations

The regulations and recommendations considered below contain different categories of assessment values that differ in their protective purpose, their level of protection, and their protective objective. Therefore, this paper uses the overarching term "assessment value" but adopts the nomenclature of the regulations when quoting from them.

In the following section, we distinguish between precaution-oriented assessment values and those that serve to avert danger: Assessment values that serve to avert danger permit, in principle, higher pollutant concentrations or discharges than precaution-oriented ones. In contrast to precaution-oriented assessment values, they generally serve to assess concrete (including planned) facilities, projects, or management measures and are derived on a use-specific basis (e.g., test values and measure values in soil protection).

For the protection of human health, assessment values for concentrations in air are contained in the following Western European regulations, directives, and recommendations. These can be converted into deposition values in order to compare them with other assessment criteria. In this context, not only the depositions on arable land and grassland, which are important for humans as primary links in the food chain, but also forests where people spend time for recreation are considered. The assessment values of the recommendations, laws, and sub-legislative regulations are summarized in Table 1.

Table 1. Comparison of assessment values from legal and sublegal regulations in Western Europe, critical depositions after conversion by means of deposition rates according to Schaap et al. [7].

Rulebook	Protection Target	Protected Property	Pb	Cd	Cu	Ni	Zn	As	Cr
			[g ha^{-1} a^{-1}]						
European Union									
EU Position Paper (2000) [8]	General load	Man, soil, plants	250–716	2.5–7		5–43.5		1.5–13	
EU Directive 2008/50/EC [9]	General load	Human and environment	250–716						
EU Directive 2004/107/EC [10]	General load	Man, soil, plants		2.5–7		7–28		2.2–6	
UNECE-CLRTAP (Critical Loads in Central Europe) [11]	General load	Humans, ecosystems, soil organisms, and plants	3–5	1–2					

Table 1. *Cont.*

Rulebook	Protection Target	Protected Property	Pb	Cd	Cu	Ni	Zn	As	Cr
						[g ha^{-1} a^{-1}]			
					Germany				
German 39th BImSchV (2010, 2018) [12]	General load	Human and environment	250–716	2.5–7		7–28		2.2–6	
German BBodSchV (1999, 2017) [13]	Project-related load	Humans (via soil, plants, groundwater)	400	6	360	100	1200		300
German TA Luft (2021) [14]	Project-related load	Human and environment	365	7		55		15	
GermanTA Luft (2021) [14]	Project-related load	Environment	675–6935	9.1–116.8				219–4270	
UNECE-CLRTAP (Critical Loads in Germany) (2018) [15]	General load	Man	9–61	2.5–18	1070–11,268		2848–28,316	6–56	28–282
		Ecosystems	6–601	4.1–42.4	13–710	109–3338	189–1032	181–711	115–448
					Switzerland				
Swiss Ordinance on Air Pollution Control (LRV) (1985, 2018) [16]	Project-related load	Humans, animals, soil, ecosystems	365	7.3			1460		
					Belgium				
Flemish Decree on Environmental Permitting (1995/2012) [17]	Project-related load	Man	890	73					
	General load			26.4					
					Austria				
Austrian Emmission Control Act—Air (1997/2018) [18]	General load	Man	365	7.3		7–28		2.2–6	
					France				
Environmental Code 2016 [19]	Project-related load	Human and environment	365	7		55		15	

Due to the methodological differences in their derivation, the assessment values compiled in Table 1 are only comparable with each other and with the critical loads to a limited extent. The partly significant differences exist due to different protection levels, protection goals, and the impact reference (Table 2).

Table 2. Protection levels, protection goals and the impact references for regulations in Western Europe.

Rulebook	Heavy Metal	Legally Binding	Protection Level	Effect Indicator	Methods
		European Union			
EU Position Paper (2000) [8]	Cd, As, Ni	Recommendation	Precaution and hazard prevention	Human toxicological effect thresholds	Expert estimate: Concentration limits in the air above the ground
EU Directive 2004/107/EC [9]	Cd, As, Ni, Hg	Recommendation	Precaution and hazard prevention	Human toxicological effect thresholds	Expert estimate: Concentration limits in the air above the ground
EU Directive 2008/50/EC [10]	Pb	Legally binding	Precaution and hazard prevention	Human toxicological effect thresholds	Expert estimate: Concentration limits in the air above the ground

Table 2. *Cont.*

Rulebook	Heavy Metal	Legally Binding	Protection Level	Effect Indicator	Methods
UNECE-CLRTAP (Critical Loads in Central Europe) [11]	Cd, Pb, Hg	Recommendation	Precaution	Human toxicological effect thresholds (Drinking water, food crops) and ecotoxicological thresholds (NOEC, LOEC of the most sensitive microorganisms and plants)	Balancing of permissible inputs to tolerable outputs
		Germany			
German 39th BImSchV (2010, 2018) [12]	Pb	Legally binding	Precaution and hazard prevention	Human toxicological effect thresholds	Expert estimate: Concentration limits in the air above the ground
	Cd, As, Ni, Hg	Recommendation	Precaution and hazard prevention	Human toxicological effect thresholds	Expert estimate: Concentration limits in the air above the ground
German BBodSchV (1999, 2017) [13]	Cd, Pb, Cr, Cu, Hg, Ni, Zn	Legally binding	Precaution	Human and ecotoxicological thresholds	Calculation of concentration limits in soil from background concentrations in soil
	Pb, Cd, Cr, Cu, Ni, Hg, Zn	Legally binding	Precaution	Human and ecotoxicological thresholds	Determination of tolerable input rates when the precautionary values have already been reached
	As, Pb, Cd, Cr, Cu, Ni, Hg Zn	Legally binding	Hazard prevention	human toxicological effect thresholds	Calculation of concentration limits in soil from background concentrations in soil
German TA Luft -(2021) [14]	Cd, Pb, As, Ni, Hg, Th	Legally binding	Hazard prevention	Human toxicological effect thresholds	Calculation of tolerable input rates from background concentrations in soil
German TA Luft (2021) [14]	Cd, Pb, As, Hg, Th	Legally binding	Hazard prevention (Protection against significant disadvantages or significant nuisances)	Human toxicological effect thresholds	Determination of tolerable input rates when the precautionary values have already been reached
UNECE-CLRTAP (Critical Loads in Germany) (2017) [15]	Cd, Pb, Hg, As, Cu, Zn, Cr, Ni, V, Th	Recommendation	Precaution	Human toxicological effect thresholds (Drinking water, food crops) and ecotoxicological thresholds (NOEC, LOEC of the most sensitive microorganisms, and plants)	Balance of inputs to tolerable harmless outputs
		Austria			
Austrian Emmission Control Act—Air (1997/2018) [18]		Legally binding	Precaution and hazard prevention	Human toxicological effect thresholds	Concentration limits in the air above the ground

Table 2. *Cont.*

Rulebook	Heavy Metal	Legally Binding	Protection Level	Effect Indicator	Methods
			Switzerland		
Swiss Ordinance on Air Pollution Control (LRV) (1985, 2018) [16]	Pb, Cd, Zn	Legally binding	Precaution and hazard prevention	Human toxicological effect thresholds	
			Belgium		
Flemish Decree on Environmental Permitting (1995/2012) [17]	Cd	Legally binding	Precaution and hazard prevention	Human toxicological effect thresholds	Concentration limits in the air above the ground
	Pb	Legally binding	Precaution and hazard prevention	Human toxicological effect thresholds	Tolerable deposition rate up to 1000 meters from the operating limit
	Cd, Pb	Legally binding	Precaution and hazard prevention	Human toxicological effect thresholds	Tolerable deposition rate up to 1000 meters from the operating limit
			France		
Environmental Code 2016 [19]	As, Cd, Cr, Ni, Pb	Recommendation	Precaution and hazard prevention	Human toxicological effect thresholds for inhalation	Concentration limits in the air
			Netherlands		
Dutch Emission Directive Air (2007/2009) [20–22]	Cd	Legally binding	Precaution and hazard prevention	Human toxicological effect thresholds	Concentration limits in the air
	Pb	Legally binding	Precaution and hazard prevention	Human toxicological effect thresholds	Concentration limits in the air
	Cr	Legally binding	Precaution and hazard prevention	Human toxicological effect thresholds	Concentration limits in the air

2.2. *Calculation of Assessment Values for the Regions of Luxembourg on Empirical Data Basis*

2.2.1. Precipitation-Related Values for Soil Protection

The technical bases according to Prinz and Bachmann [23] for the derivation, including in particular the test and/or measure values as well as the assumptions on soil thickness and density, predominantly still correspond to the current status (explanatory memorandum to the new version of the TA Luft [24]. The calculation of the precipitation-limiting values is based on the following calculation procedure [23]:

$$NW = \frac{(BW - HW) \cdot D \cdot M}{A} \quad (1)$$

with:

NW = Precipitation-limiting value [10^3 ng m^{-2} d^{-1}].
BW = Soil value [ng kg^{-1}]
HW = Background value [ng kg^{-1}]
D = Soil density [t m^{-3}]
M = Soil thickness [m]
A = Enrichment period (=200 × 365 days [d])

Soil Values

Precipitation-limiting values are primarily to be based on test values of soil protection (Tables 3–5), since a situation is certainly to be regarded as undesirable, in which an exceeding of test values would be foreseeable as a consequence of airborne pollutants. If, instead of the test values, only measure values are available as the starting point for the calculation, Prinz and Bachmann [23] recommend that, when converting to precipitation-limiting values, a discount be taken into account to compensate for possible uncertainties. However, the amount of the recommended discount is not specified. Therefore, no discount is applied in this paper.

Table 3. Test values according to § 8 paragraph 1 sentence 2 no. 1 of the Federal Soil Protection Act [25] for the direct uptake of pollutants on children's playgrounds, in residential areas, parks and recreational facilities, and industrial and commercial sites (in mg kg^{-1} dry matter, fine soil).

Metal	Children's Play Areas	Residential Areas	Park and Leisure Facilities	Industrial and Commercial Properties
As	25	50	125	140
Pb	200	400	1000	2000
Cd	10 (2 in home gardens and allotments)	20	50	60
	200	400	1000	1000
Ni	70	140	350	900

Table 4. Test and measure values for the pollutant transition from soil to crop on arable land and in kitchen gardens as well as on grassland with regard to plant quality (in mg kg^{-1} dry matter, fine soil).

Metal	Fields and Kitchen Gardens		Grassland
	Test Value	Action Value	Action Value
	(mg kg^{-1} Dry Mass)		
As	200 [(a)]	-	50
Cd	-	0.04/0.1 [(b)]	20
Pb	0.1	-	1200
Cu			1300 [(c)]
Ni			1900

[(a)] For soils with intermittent reducing ratios, a test value of 50 mg/kg dry matter applies. [(b)] On areas with bread wheat cultivation or cultivation of vegetables with high cadmium content, the action value shall be 0.04 mg/kg dry matter; otherwise, the action value shall be 0.1 mg/kg dry matter. [(c)] For grassland use by sheep, the measure value shall be 200 mg/kg dry matter.

Table 5. Test values for assessing the soil–groundwater impact pathway (in µg/L).

Metal	Test Value (µg L^{-1})
As	10
Pb	25
Cd	5
Cr_{total}	50
Cr(VI)	8
Cu	50
Ni	50
Zn	500

Accumulation Period, Soil Density and Thickness

A period of 200 years is taken as the time period for which a still tolerable enrichment is to be calculated. The heavy metals introduced via atmospheric deposition are primarily bound in the topsoil and thus enriched there. The use of the soils results in varying degrees of mixing of the upper soil layers, so that depending on the use, soil layers of varying thickness must be assumed in which the heavy metals accumulate. Likewise, the soils have different storage densities. For the calculations, the soil thicknesses and storage densities listed in Table 6 were used in accordance with the report of the subcommittee "Impacts" of the State working group on Emission (LAI) "Emission values for mercury compounds" [26].

Table 6. Convention for the inclusion of soil thickness and storage density in the calculation of precipitation-limiting values for the protection of the soil.

Land-Use Type	Soil Thickness = Soil Layer Relevant for Assessment (m)	Soil Density = Assumed Average Storage Density (t m^{-3})
Field	0.00–0.30	1.5
Grassland	0.00–0.10	1.3
Forest floor	Depending on horizon thickness	
Support humus		0.3
Humic topsoil (Ah horizon)		0.8
Mineral soil		1.5

Determination of Background Values for Luxembourg

Measured values of heavy metal levels in Luxembourg were provided by the Administration de l'environnement, Unité stratégies et concepts, as of 5 February 2020 [27]. Soil samples were collected and analysed at 308 sites, including 113 arable, 124 grassland, 5 vineyard, and 66 forest sites, each at 2–3 depth levels. Heavy metal contents were determined both after aqua regia digestion and with ammonium nitrate extract. In the following section, however, only the values determined with aqua regia digestion are considered, because this corresponds to the methodology of Prinz and Bachmann [23] and thus to TA Luft [14,28]. In the following section, only the data sets corresponding to the assessment-relevant soil layers (Table 6) are used.

Prinz and Bachmann [23] used the 90th percentile of the contents determined in comparable studies in arable soils and forest soils in rural areas with certain widespread parent rocks of soil formation for the calculation as the background value of the ubiquitous distribution of substances in soils. Prinz and Bachmann [23] point out "that background contents could be much higher, especially for some bedrock soils, for geogenic reasons alone. In extreme cases, they can be so high that the test values are already exceeded, at least in part, by the geogenic heavy metal contents. In this case, the Soil Protection and Contaminated Sites Ordinance [29] provides for special assessment regulations. Within the framework of the calculation of precipitation-limiting values presented by Prinz and Bachmann [23], which are based on typical regulatory conditions, such extreme locations were not included, however, since this would lead to negative calculation results. The consideration of these aspects must be reserved for a special case examination."

Therefore, in the present paper, a determination of outlier values and extreme values was carried out first. First, the 25th and 75th percentiles (perc.) of Cr, Cu, and Zn contents in aqua regia digestion were determined for the data sets of the soil layers relevant to the assessment within the soil-use types. Then, the outlier values were determined according to the following equations:

- If(measured value > ((75th Perc. − 25th Perc.) · 1.5) + 25th Perc., then measured value = outlier above.
- If(Measured value < 75th Perc. − ((75th Perc. − 25th Perc.) 1.5, then measured value = outlier below
- Extreme values were determined according to the following equations:
- If(measured value > ((75th Perc. − 25th Perc.) 3) + 25th Perc., then measured value = extreme value above.
- If(measured value < 75th Perc. − ((75th Perc. − 25th Perc.) · 3, then measured value = extreme value below

Now the typical profiles and their background values without outliers and extremes resulted in the statistics contained in Table 7.

Table 7. Here, 50th and 90th percentile (perc.) of the Luxembourg background database for chromium, copper and zinc by land use, after elimination of special cases and outliers.

Land Use	Cr_{total} (mg kg^{-1})		Cu (mg kg^{-1})		Zn (mg kg^{-1})	
	50th Perc.	90th Perc.	50th Perc.	90th Perc.	50th Perc.	90th Perc.
Field	41.3	53.0	15.0	25.4	85.0	124.0
Grassland	46.5	59.0	16.0	28.0	95.5	164.9
Forest	31	43.9	12.0	19.8	59.2	101.3

Calculation of Precipitation-Limiting Values

As in Prinz and Bachmann [23], we used the following input data for the soil-human impact pathway as the basis for calculating precipitation-limiting values for settlement areas:

- The test value for children's play areas from the German Federal Soil Protection Ordinance [25]. However, such a test value is only available for Cr_{total} (Table 1).
- Background values from fields (topsoil),
- Storage density 1.5 t m^{-3}
- Thickness of the soil layer relevant to the enrichment: 2 cm
- Accumulation period: 200 years.

The input data used for the soil-crop impact pathway were [23]:

- Test and action values for the pollutant transition soil—crop on arable land and in kitchen gardens as well as on grassland. Only the measure value for Cu on grassland can be used for this project (Table 4).
- Background values on grassland (topsoil),
- Storage density for grassland 1.3 t m^{-3}
- Thickness of the assessment-relevant soil layer for grassland 0.1 m
- Accumulation period: 200 years

With the limitation that an adequate methodological basis was only available for Pb and Cd, Prinz and Bachmann [23] additionally considered the heavy metal transport from soil to groundwater. The underlying regression analyses were performed only on data sets of arable soils for Pb and Cd; therefore, the supplementary consideration of Prinz and Bachmann [23] was limited to these two elements only.

In a very simplified way, the approach of Prinz and Bachmann [23] for Cd could also be applied to Cr, Cu, and Zn. Here, it was assumed that the input is equal to the output, i.e., uptake by vegetation is neglected. Prinz and Bachmann [23] set the determination of the leachate quantity at a flat rate of 30% of the precipitation quantity. Since a calculation of the leachate quantities for the determination of critical loads for groundwater protection was carried out on the basis of land-use-differentiated reference values depending on soil permeability and slope, it was better to fall back on these values here, especially since the leachate share of the annual precipitation total in Germany of 11–42% corresponds quite well with the average value of 30% [23].

In Luxembourg, the annual precipitation sum in the 30 year average (1971–2000) is 871 mm a^{-1} on average, according to Geo-Portal Luxembourg [30]. The standard deviation within the country is 36 mm a^{-1}, so that the use of the mean value is sufficient for this rough estimate. The seepage fraction in Luxembourg's soils [31] is:

- In arable land and grassland: 22–23%, mean: 22.5%.
- In deciduous forest: 14–19%, mean: 16.5%.
- In coniferous forest: 11–17%, mean: 14%.

The test values, with which the seepage rate was multiplied, were taken from Table 8.

Table 8. Precautionary values for metals (in mg kg^{-1} dry matter, fine soil, and aqua regia digestion) (BBodSchV, Annex 2).

Soil Texture	Cd	Pb	Cr_{total}	Cu	Hg	Ni	Zi
Clay	1.5	100	100	60	1	70	200
Loam/silt	1	70	60	40	0.5	50	150
Sand	0.4	40	30	20	0.1	15	60

2.2.2. Critical Loads

In this paper, the methodological approach for calculating critical loads for heavy metals follows the recommendations in the ICP Modelling and Mapping [32] (Chapter V.5). Here, all relevant fluxes into or out of a specific soil layer, in which the main substance transformations 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, stocks, and concentrations refer to the mobile or potentially mobilizable metals, and only they are relevant for the consideration of the substance fluxes. The mass balance equation includes as discharge pathways from the terrestrial ecosystem the uptake into the biomass with subsequent harvesting and the discharge with the leachate flux as follows:

$$CL(M) = M_u + M_{le(crit)} \tag{2}$$

with:

$CL(M)$ = Critical Load of the metal M [g ha^{-1} a^{-1}].

M_u = Uptake rate of the metal M in harvestable plant parts [g ha^{-1} a^{-1}].

$M_{le(crit)}$ = Tolerable (critical) leaching rate of the metal M from the soil layer under consideration when only vertical fluxes (leachate) are considered [g ha^{-1} a^{-1}].

where by

$M_{le(crit)} = [M]_{crit} - Q$

with:

$[M]_{crit}$ = Critical concentration of the metal M in the leachate [g m^{-3}].

Q = Leachate rate [m^3 ha^{-1} a^{-1}]

In accordance with the recommendations of the Expert Panel for Heavy Metals to the ICP Modelling and Mapping [33,34], there have been no changes to this approach since 2004 [35,36].

Harvest Withdrawal of Heavy Metals

The removal rate of heavy metals with biomass harvesting is derived from the yield of the biomass to be harvested and multiplied by the substance content as follows:

$$M_u = [M]_{con} - E \tag{3}$$

with:

M_u = Uptake rate of the heavy metal [g ha^{-1} a^{-1}].

$[M]_{con}$ = Metal content in the dry matter of the harvested crop [mg kg^{-1}].

E = Yield of dry matter of the crop [kg ha^{-1} a^{-1}].

The critical load approach-related assumptions about the management of receptor areas are detailed in the following.

With regard to forests, it can be assumed that in the long term that the conversion to near-natural forest management, which has already begun nationwide, in combination with the trend decrease in nitrogen inputs, regulates the potential wood yield expectation as well as the substance contents to a sustainable stable equilibrium. Therefore, conservative assumptions are made for yield and content estimation, derived from measured data at more or less unpolluted sites [5,15]. The distribution of the main tree species was derived as a rough generalization from the soil types of the 1:100,000 soil map of Luxembourg [31], including climate data [30] and elevation levels [31].

Crop yields for intensive agriculture are taken from Luxembourg's 2010–2018 crop statistics. Unlike forest management, there are no discernible trends of extensification in arable farming (except for organic farming, but its share of land is small). However, with regard to crop rotations, i.e., for the cultivation ratios of the individual crop types, it is assumed that the rules of good professional practice (in particular phytosanitary favourable, nutrient-effective and soil-preserving crop rotations) are applied. In the following, this must be assumed, since the critical loads are intended to apply in the long term. For the future, the cropping structure should be assumed to be in accordance with good professional practice in the long term. The crop rotations are derived in rough generalization from the soil types of the soil map 1:100,000 of Luxembourg [31], taking into account the climate data [30] and the altitude levels [31].

The estimation of dry matter yield in utilized grassland habitats assumes extensive use (2–3 ash mowing or grazing predominantly with cattle) with only stand-maintaining fertilizer applications. For dry slope grasslands, minimum conservation use or maintenance use (mowing or grazing primarily with sheep and goats) is assumed to prevent natural scrub encroachment. However, this necessary minimum use also depends on the biomass production potential of the respective site. The grassland types are derived as a rough generalization from the soil types of the soil map 1:100,000 of Luxembourg [31], taking into account the climate data [30] and the altitude levels [31]. Yield determination was performed according to the method of Schlutow et al. [5,15].

The annual heavy metal removal (M_u) for exploited forests is derived from the estimated biomass removal by the annual increment of rough wood and bark of the main and secondary tree species of the current stand at the site, multiplied by the average contents of heavy metals in rough wood and bark (Table 9). These contents can be regarded as sustainably tolerable and thus acceptable in the long term, since only measured values from areas not specifically contaminated were evaluated for this purpose. The M_u for used grassland biotopes and arable crops results from the growth rate of above-ground grass mass in the year (dry matter) and the heavy metal contents in the harvested mass (from studies without specific contamination) according to Table 9.

Table 9. Heavy metal contents (mg kg^{-1}) in the dry matter of rough wood with bark of the main tree species, of arable crops and grassland [37–39].

Species	Heavy Metal Contents $[M]_{con}$ (mg kg^{-1})							
	N	Pb	Cd	Cu	Ni	Zn	As	Cr_{total}
Oak	45	2.97	0.13	2.19	1.58	5.27	0.02	0.74
Beech	45	1.52	0.15	1.77	1.28	10.53	0.02	0.54
Spruce	45	1.29	0.36	1.67	1.18	31.2	0.01	0.42
Pine	45	1.75	1.31	1.35	1.85	25.24	0.01	0.35
All other tree species on average	45	1.81	0.29	1.91	1.48	11.2	0.015	0.53
Wheat	24	0.03	0.03	4.6	0.23	20	0.035	0.48
Rye	23	0.07	0.02	4.6	0.44	26	0.035	0.25
Barley	30	0.1	0.02	3.6	0.23	25	0.035	0.27
Rapeseed	18	0.1	0.08	3.8	0.81	39	0.035	1.7
Potatoes	32	0.04	0.09	4.6	0.23	14	0.035	0.17
Sugar beet	30	0.2	0.08	3.9	0.8	12	0.035	0.47
Silage maize	24	0.2	0.04	3.5	0.58	19	0.035	0.73
Grass and grassland plants	160	0.99	0.13	6.2	0.91	49.5	0.1	0.395

Discharge of Heavy Metals with Water Runoff

The basic information for determining the water runoff from the soil layer under consideration is provided by the map of annual precipitation totals in the 30 year mean of the years 1971–2000 [30]. From the map of annual precipitation totals, 4 significantly different zones emerge.

- Southeast: from 744 to <800 mm a^{-1}

- Central South: from 800 to <850 mm a^{-1}
- North and southwest: from 850 to <900 mm a^{-1}
- Extreme southwest and west (2 small areas on the border): from 900 to 967 mm a^{-1}.

The seepage rate $Q_{le(z)}$ (subsurface runoff) results from the difference of precipitation, minus evapotranspiration rate and surface runoff. The calculation of total runoff is based on the methodology of Renger et al. [40]. In a rough generalization, taking into account the soil-type-specific permeability, the mean annual total evapotranspiration by vegetation according to BMVBS [41] and the surface runoff on slopes [41], the following ratio of infiltration rate of precipitation can be assumed (Table 10).

Table 10. Reference value ranges and mean values for the ratio of infiltration rate of the annual precipitation total [%] depending on soil type, relief, and vegetation [41].

Location Type	Vegetation Type	Share of Infiltration Rate of the Annual Precipitation Sum [%].		
		from	to	Mean Value
An-to slightly hydromorphic sandy brown earth, shallow Loamy pararendzina, wavy Calcareous rendzina, hanging	Arable and grassland:	38	45	42
	Deciduous forest:	18	25	22
	Coniferous forest	11	18	15
An-to slightly hydromorphic sandy and loamy brown earth, undulating Loamy parabrown earth, flat Clayey brown earths, parabrown earths, and pelosols, wavy-domed	Arable and grassland:	18	27	23
	Deciduous forest:	18	19	19
	Coniferous forest	15	18	17
An-to slightly hydromorphic sandy brown earth, dome-hanging Loamy brown earth and parabrown earth, wavy, or domed; Clayey brown earths, parabrown earths, and pelosols, shallow	Arable and grassland:	18	25	22
	Deciduous forest:	13	15	14
	Coniferous forest	9	13	11
Hydromorphic soils, flat to sloping	Arable and grassland:	15	20	18
	Deciduous forest:	13	15	14
	Coniferous forest	9	13	11

The assignment of the soil forms (from soil map 1:100,000 Luxembourg [31]) to slope classes, in which the soil forms predominantly occur, was carried out by overlaying the layers of the Geoportal Luxembourg. The classification was performed as follows: Slope 0–10°—flat, 10–20°—undulating, and 20–30°—dome-shaped >30°—sloping. It was assumed that the protection of groundwater with regard to the exceeding of drinking water limits by anthropogenic pollutant inputs is guaranteed if the limits are not exceeded in the leachate directly below the root zone. Possible interactions of the leached metals with exchange 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 distributed or rooted in the more humus-rich O and A horizons. Therefore, for $CL(M)_{eco}$ and $CL(Cd)_{food}$, the lower-thickness biologically active soil layer (zb) was considered, where water runoff (referred to here as soil water) is higher. The difference water flow to the seepage flow below the root zone $Q_{le(z)}$ is absorbed in the deeper soil layers by plant roots and is subject to transpiration. $Q_{le(zb)}$ was calculated as follows:

$$Q_{le(zb)} = Q_{le(z)} + (1 - f_{ET(zb)})\,(P - (P \cdot f_{i(zb)})) \quad (4)$$

where by:

$Q_{le(zb)}$ = Seepage rate below the biologically active soil horizons (zb);

$Q_{le(z)}$ = Seepage rate below the total rooted soil layer (z);

P = Precipitation (30 year average of annual precipitation totals);

$f_{ET(zb)}$ = Factor for determining the proportion of evapo-transpiration from the biologically active soil layer (zb);

$f_{i(zb)}$ = Factor for calculating the shares of interception in annual precipitation.

The following generalizing assumptions were made [35]:

$f_{ET(zb)}$ = 0.5 for $CL(Pb)_{eco}$, $CL(Cd)_{eco,}$ $CL(As)_{eco}$, $CL(Cu)_{eco,}$ $CL_{(}Ni)_{eco}$, $CL(Zn)_{eco}$, $CL(Cr)_{eco}$;

$f_{i(zb)}$ = 0.15 for arable and grassland vegetation;

$f_{i(zb)}$ = 0.25 for copper beech and hornbeam;

$f_{i(zb)}$ = 0.20 for all other deciduous trees;

$f_{i(zb)}$ = 0.35 for conifers.

Critical Concentrations for the Protection of Human Health

In order to protect the groundwater as a drinking water reservoir, the limit values for heavy metal contents can be found in the Grand-Ducal Regulation on the Quality of Water Intended for Human Consumption in Luxembourg [42]. Currently, there are various legal limits or guideline values for the concentration of heavy metals in drinking water worldwide. An overview is given in Table 11.

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

Directive or Ordinance	Guideline and Limit Values for the Concentration in Drinking Water [mg L^{-1}].					
	Pb	**Cd**	**As**	**Cr_{total}**	**Cu**	**Zn**
Luxembourg Regulation 2002/2017 [43]	0.01	0.005	0.01	0.05	1	
WHO guideline [44]	0.01	0.003	0.01	0.05	2	-
Canada [45]	0.01	0.005	0.01	0.05	1	5
Drinking Water Ordinance for Germany [46]	0.01	0.003	0.01	0.05	2	-

The critical limits for heavy metals in drinking water $[M]_{crit(drink)}$ as given in the Mapping Manual [32,35,36] with reference to the WHO guideline [43] for Pb, As, and Cr correspond to the limits of the currently valid drinking water regulations for Luxembourg [42] and Germany [45]. The Cd limit in Luxembourg is higher than according to WHO and in Germany, while the Cu limit is lower. Therefore, the respective lower limit concentrations were applied in this study (marked in bold).

In Order to protect soils for the production of plant pood, the EU limit value for Cd in wheat grain of 0.2 mg kg^{-1} dry matter (Commission of the European Community [46] is not derived based on effects. Therefore, in this study, the Cd limit $[Cd]_{con}$ for wheat used according to the recommendation of the Manual of ICP Modelling and Mapping [32,35,36] instead of the EU regulation [47] (Table 12) [34].

Table 12. Critical concentrations of cadmium in wheat.

Directive or Ordinance	Protected Property	Unit	$[Cd]_{con}$
Manual of the ICP Modelling and Mapping [33,36,37]	Wheat grain	mg kg^{-1}	0.1

Since the concentration (critical limit) for the plant is given, the critical concentration in the soil solution $[Cd]_{crit(food)}$ can be determined iteratively with transfer functions according to Römpkens et al. [48]. $[Cd]_{crit(food)}$ is then 0.8 mg m^{-3}.

Critical Concentrations (Critical Limits) for the Protection of Ecosystems and Biodiversity

The ecotoxicological effect of heavy metal ions depends on their concentration in soil water, since only free active ions are taken up into the biomass and thus interact with organisms. In a Europe-wide survey on CL(M), critical limits for a number of heavy metals were compiled from the literature in 2006/07 [39,49]. Determination of the total critical concentration of heavy metals in soil water with effect on soil microorganisms, invertebrates, and plants must be performed for each heavy metal under consideration according to its chemical properties using different approaches as follows:

Determination of the Critical Concentration of the Free Heavy Metal Ions Cd, Pb, Cu, Zn and Ni in the Soil Solution $[M]_{crit(free)}$

For a number of heavy metals (Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+}), toxicity is highly dependent on the simultaneous presence of nontoxic cations (Na^{+}, Ca^{2+}, H^{+}), which limit the uptake of the toxic heavy metals into organisms and thus protect the organisms. The concentration of protective competing cations is closely correlated with pH values. Thus, the concentration of free heavy metal ions is the following function of soil water pH in connection with Table 13 [50]:

$$[M]_{crit(free)} = 10^{\alpha \cdot pH + \gamma} \quad (5)$$

Table 13. Coefficients for the calculation of the critical concentration of free ions as a function of the concentration of free ions with a 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

Calculation of Total Critical Concentrations [M]crit(eco) of Reactive Metals in Soil for Cd, Pb, Cu, Zn, and Ni

Metals occur in soil water not only as free ions but also in the form of soluble complexes. Manual [32] (Chapter V.5) recommends that the transformation be performed using a chemical speciation model, e.g., the Windemere Humic Aqueous Model, WHAM [52,53]. This model (version 6) was specifically adapted to meet the requirements of the critical limit derivation for soils (W6S-MTC2). The critical concentrations of metals in leachate used in the calculation of critical loads for ecosystem protection in this study are consistent with those specified in Reinds et al. [39]. Accordingly, the total critical concentrations for Cu, Ni, Zn, Pb, and Cd were calculated based on models differentiated by their bioavailability as a function of soil-specific pH and organic matter and dissolved organic carbon content (see also [32]). The modelling was based on PNEC values (for As and Cu) or on NOEC values (for Cr, Ni, Zn, Pb, and Cd).

3. Results

3.1. Precipitation-Related Assessment Values for Soil Protection in Luxembourg

3.1.1. Soil–Man Impact Pathway

The calculation for Luxembourg analogous to Prinz and Bachmann [23] results in a precipitation-limiting value for Cr_{total} in settlement areas of 219 g ha^{-1} a^{-1} (Table 14).

Table 14. Input data and result of the calculation of the precipitation-limiting value for chromium in settlement areas.

	Test Value	Background Value	Soil Layer	Storage Density	Period	Result
	(mg kg^{-1})	(mg kg^{-1})	m	t m^{-3}	d	µg m^{-2} d^{-1}
Cr	200	53.0	0.02	1.5	73,050	60.370

The calculation for Luxembourg analogous to Prinz and Bachmann [23] results in precipitation-limiting values for copper in sheep pastures of 1117 g ha^{-1} a^{-1} and in other grassland of 8267 g ha^{-1} a^{-1} (Table 15).

Table 15. Input data and result of the calculation of the precipitation-limiting value for copper in grassland areas.

Cu	Action Value	Background Value	Soil Layer	Storage Density	Period	Result
	mg kg^{-1}	mg kg^{-1}	m	t m^{-3}	d	µg m^{-2} d^{-1}
Grassland (sheep pasture)	200	28	0.1	1.3	73,050	306.092
Other Grassland	1300	28	0.1	1.3	73,050	2263.655

3.1.2. Soil–Groundwater Impact Pathway

The result of the rough estimate of the precipitation-limiting assessment values for the protection of groundwater as a drinking water reservoir is shown in Table 16.

Table 16. Rough estimate of the precipitation-limiting assessment values for the protection of groundwater as a drinking water reservoir in Luxembourg.

Land Use		Field, Grassland	Deciduous Forest	Coniferous Forest
Precipitation	mm a^{-1}	871	871	871
Seepage rate	L m^{-2} a^{-1}	196	144	122
Test value Cr_{total}	µg L^{-1}	50	50	50
Test value Cr(VI) (Chromate)	µg L^{-1}	8	8	8
Test value Cu	µg L^{-1}	50	50	50
Test value Zi	µg L^{-1}	500	500	500
Precipitation-limiting assessment value Cr_{total}	µg m^{-2} d^{-1}	26.846	19.687	16.704
Precipitation-limiting assessment value Cr(VI) (Chromate)	µg m^{-2} d^{-1}	4.295	3.150	2.673
Precipitation-limiting assessment value Cu	µg m^{-2} d^{-1}	26.846	19.687	16.704
Precipitation-limiting assessment value Zn	µg m^{-2} d^{-1}	268.459	196.870	167.041

3.2. *Critical Loads for Heavy Metals Deposition in Luxembourg*

3.2.1. Protection of Human Health

The results of the determination of critical loads for the protection of human health through compliance with the drinking water limit concentrations in groundwater under the different vegetation types (arable land, grassland, deciduous forest, coniferous forest, and mixed forest) is differentiated according to the 27 soil types of the soil map 1:100,000 Luxembourg [31] are presented in Table 17.

Table 17. Values of the critical loads for drinking water protection in Luxembourg.

Soil Forms (BK 100 Luxembourg)	Land-Use Type	Seepage Rate	CL $(Pb)_{drink}$	CL $(Cd)_{drink}$	CL $(Cu)_{drink}$	CL $(As)_{drink}$	CL $(Cr)_{drink}$	CL $(Zn)_{drink}$
		$m^3\ a^{-1}$	g $ha^{-1}\ a^{-1}$					
1 Loamy, slightly stony brown earth, not to moderately gleyed.	Field	1991	29.6	7.4	4066	21.1	108	10,605
	Grassland	1991	26.4	6.7	3983	20.5	100	9962
	Deciduous forest	1637	21.8	5.7	3275	16.4	82	8187
	Coniferous forest	1460	19.8	6.2	2921	14.6	73	7304
	Mixed forest	1549	20.8	6.0	3098	15.5	77	7745
2 Stony–loamy brown soils of slate and phyllad, not gleyed	Field	1903	29.7	7.2	3897	20.3	104	10,222
	Grassland	1903	25.3	6.4	3806	19.6	95	9520
	Deciduous forest	1239	17.7	4.5	2478	12.4	62	6195
	Coniferous forest	974	14.8	4.7	1947	9.8	49	4870
	Mixed forest	1106	16.3	4.6	2213	11.1	55	5533
3 Stony–loamy brown soils of weathered slate and phyllad, not gleyed	Field	1903	28.7	7.1	3889	20.2	103	10,162
	Grassland	1903	25.5	6.5	3806	19.7	95	9520
	Deciduous forest	1239	17.8	4.5	2478	12.4	62	6195
	Coniferous forest	974	14.9	4.8	1947	9.8	49	4870
	Mixed forest	1106	16.4	4.7	2213	11.1	55	5533
4 Stony–loamy brown soils of slate and phyllad, weakly to moderately gleyed	Field	1991	30.0	7.8	4099	21.4	109	10,695
	Grassland	1991	26.5	6.7	3983	20.5	100	9963
	Deciduous forest	1637	24.4	6.0	3275	16.4	82	8187
	Coniferous forest	1460	19.8	6.3	2921	14.6	73	7304
	Mixed forest	1549	22.7	6.4	3098	15.5	77	7746
5 Stony–loamy brown earths of slate and sandstones, not gleyed	Field	1991	32.2	7.7	4087	21.4	110	10,772
	Grassland	1991	26.3	6.7	3983	20.5	100	9962
	Deciduous forest	1637	21.8	5.7	3275	16.4	82	8187
	Coniferous forest	1460	19.7	6.2	2921	14.6	73	7304
	Mixed forest	1549	20.8	6.0	3098	15.5	77	7745
6 Stony–loamy brown earths of weathered slates and sandstones, not gleyed	Field	1991	32.2	7.7	4087	21.4	110	10,772
	Grassland	1991	26.3	6.7	3983	20.5	100	9962
	Deciduous forest	1637	21.8	5.7	3275	16.4	82	8187
	Coniferous forest	1460	19.7	6.2	2921	14.6	73	7304
	Mixed forest	1549	20.8	6.0	3098	15.5	77	7745
7 Stony–loamy brown earths of slate and Sandstones, weakly to moderately gleyed	Field	1903	29.1	7.6	3922	20.5	105	10,253
	Grassland	1903	25.6	6.5	3806	19.7	95	9520
	Deciduous forest	1239	20.4	4.8	2478	12.4	62	6195
	Coniferous forest	974	15.0	4.8	1947	9.8	49	4870
	Mixed forest	1106	18.3	5.1	2213	11.1	55	5533
8 Stony–loamy brown earths of clay slate and sandstones, weakly to moderately gleyed.	Field	1991	30.0	7.8	4099	21.4	109	10,695
	Grassland	1991	26.5	6.7	3983	20.5	100	9963
	Deciduous forest	1637	24.4	6.0	3275	16.4	82	8187
	Coniferous forest	1460	19.8	6.3	2921	14.6	73	7304
	Mixed forest	1549	22.7	6.4	3098	15.5	77	7746
9 Stony–loamy brown soils from slate, not gleyed	Field	1903	29.7	7.2	3897	20.3	104	10,222
	Grassland	1903	25.3	6.4	3806	19.6	95	9520
	Deciduous forest	1239	17.7	4.5	2478	12.4	62	6195
	Coniferous forest	974	14.8	4.7	1947	9.8	49	4870
	Mixed forest	1106	16.3	4.6	2213	11.1	55	5533
10 Stony–loamy and stony–clayey brown earths and parabrown earths with quartzitic boulders, not to moderately gleyed.	Field	1843	29.1	7.0	3776	19.7	101	9921
	Grassland	1843	24.9	6.3	3685	19.1	92	9219
	Deciduous forest	1200	17.5	4.4	2400	12.0	60	5999
	Coniferous forest	943	14.6	4.7	1885	9.5	47	4716
	Mixed forest	1071	16.1	4.6	2143	10.7	54	5358

Table 17. *Cont.*

Soil Forms (BK 100 Luxembourg)	Land-Use Type	Seepage Rate	CL $(Pb)_{drink}$	CL $(Cd)_{drink}$	CL $(Cu)_{drink}$	CL $(As)_{drink}$	CL $(Cr)_{drink}$	CL $(Zn)_{drink}$
		$m^3\ a^{-1}$	$g\ ha^{-1}\ a^{-1}$					
11 Stony–clayey brown earths of dolomite, not gleyed	Field	1660	16.6	5.0	3327	16.7	84	8331
	Grassland	1660	17.7	5.1	3320	16.7	83	8300
	Deciduous forest	1081	17.1	4.2	2162	10.8	54	5405
	Coniferous forest	849	14.1	4.6	1698	8.5	42	4249
	Mixed forest	965	15.6	4.4	1930	9.7	48	4827
12 Stony–clayey brown earths of lime, not gleyed	Field	3943	49.1	13.6	7997	40.8	206	20,425
	Grassland	3943	40.5	12.0	7885	39.5	197	19,714
	Deciduous forest	2043	26.4	7.0	4085	20.4	102	10,213
	Coniferous forest	1378	19.3	6.1	2755	13.8	69	6890
	Mixed forest	1710	22.8	6.6	3420	17.1	86	8552
13 Sandy, loamy–sandy and sandy–loamy brown earths and parabrown earths of calcareous sandstone, sand or weathered clay, not gleyed	Field	1843	30.1	7.2	3784	19.9	102	9984
	Grassland	1843	25.4	6.3	3685	19.1	92	9219
	Deciduous forest	1200	18.0	4.5	2400	12.0	60	5999
	Coniferous forest	943	14.9	4.8	1885	9.5	47	4716
	Mixed forest	1071	16.5	4.7	2143	10.7	54	5358
14 Sandy, loamy–sandy and sandy–loamy parabrown soils over clay, weakly to moderately gleyed	Field	1843	29.4	7.1	3779	19.8	101	9940
	Grassland	1843	25.1	6.3	3685	19.1	92	9219
	Deciduous forest	1200	20.2	4.7	2400	12.0	60	5999
	Coniferous forest	943	14.7	4.7	1885	9.5	47	4716
	Mixed forest	1071	18.0	5.0	2143	10.7	54	5358
15 Sandy–loamy and sandy–clayey brown earths and parabrown earths from red sandstones, not gleyed	Field	1660	27.7	6.5	3420	18.0	90	9037
	Grassland	1660	23.1	5.7	3320	17.2	83	8305
	Deciduous forest	1081	16.3	4.1	2162	10.8	54	5404
	Coniferous forest	849	13.7	4.4	1698	8.5	42	4249
	Mixed forest	965	15.0	4.3	1930	9.7	48	4826
16 Sandy–loamy and loamy parabrown soils from loess loam, not to moderately gleyed	Field	1843	29.0	7.5	3807	19.9	102	9990
	Grassland	1843	25.4	6.3	3685	19.1	92	9219
	Deciduous forest	1200	18.0	4.5	2400	12.0	60	5999
	Coniferous forest	943	14.9	4.8	1885	9.5	47	4716
	Mixed forest	1071	16.5	4.7	2143	10.7	54	5358
17 Sandy–loamy and loamy parabrown soils from loess loam, strongly to very strongly gleyed	Field	1500	25.9	6.1	3093	16.3	84	8226
	Grassland	1500	16.0	4.6	3000	15.1	75	7500
	Deciduous forest	1200	17.8	5.3	2400	12.0	60	6000
	Coniferous forest	943	14.9	4.8	1885	9.5	47	4716
	Mixed forest	1071	16.5	5.1	2143	10.7	54	5358
18 Clay and heavy clay brown earths, parabrown earths and terra fusca over limestone, not gleyed	Field	2138	31.5	8.3	4392	22.8	116	11,430
	Grassland	2138	22.4	6.5	4275	21.5	107	10,688
	Deciduous forest	1758	23.0	6.1	3515	17.6	88	8788
	Coniferous forest	1568	20.8	6.6	3135	15.7	78	7840
	Mixed forest	1663	21.9	6.3	3325	16.6	83	8314
19 Clayey brown earths and parabrown earths from Macigno, not gleyed	Field	1991	30.9	7.5	4076	21.3	109	10,683
	Grassland	1991	26.8	6.8	3983	20.6	100	9963
	Deciduous forest	1637	22.3	5.8	3275	16.4	82	8187
	Coniferous forest	1460	20.0	6.3	2921	14.6	73	7304
	Mixed forest	1549	21.2	6.1	3098	15.5	77	7745
20 Clayey parabrown soils from Macigno, weakly to moderately gleyed	Field	1991	20.0	6.0	3990	20.0	100	9988
	Grassland	1991	26.5	6.7	3983	20.5	100	9963
	Deciduous forest	1637	24.4	5.9	3275	16.4	82	8187
	Coniferous forest	1460	19.8	6.3	2921	14.6	73	7304
	Mixed forest	1549	22.7	6.4	3098	15.5	77	7746
21 Clayey parabrown soils of clay, weakly to moderately gleyed	Field	3673	47.7	12.6	7439	38.1	193	19,091
	Grassland	3673	39.0	11.3	7346	36.9	184	18,366
	Deciduous forest	1903	19.7	5.8	3806	19.0	95	9514
	Coniferous forest	1283	15.3	4.7	2567	12.8	64	6418
	Mixed forest	1593	17.6	5.2	3186	15.9	80	7965
22 Clayey parabrown soils from shelly sandstone, not to moderately gleyed	Field	1991	31.7	7.7	4083	21.4	109	10,737
	Grassland	1991	27.0	6.8	3983	20.6	100	9963
	Deciduous forest	1637	22.5	5.8	3275	16.4	82	8187
	Coniferous forest	1460	20.2	6.4	2921	14.6	73	7304
	Mixed forest	1549	21.4	6.1	3098	15.5	77	7745

Table 17. *Cont.*

Soil Forms (BK 100 Luxembourg)	Land-Use Type	Seepage Rate	CL $(Pb)_{drink}$	CL $(Cd)_{drink}$	CL $(Cu)_{drink}$	CL $(As)_{drink}$	CL $(Cr)_{drink}$	CL $(Zn)_{drink}$
		$m^3\ a^{-1}$	$g\ ha^{-1}\ a^{-1}$					
23 Clayey and heavy clayey brown earths, parabrown earths and pelosols of limestone and marl, not to moderately gleyed	Field	1928	29.0	7.6	3969	20.7	106	10,354
	Grassland	1928	26.4	6.6	3857	20.0	97	9648
	Deciduous forest	1585	21.6	6.4	3171	15.9	79	7928
	Coniferous forest	1414	19.7	6.3	2828	14.2	71	7073
	Mixed forest	1500	20.8	6.4	3000	15.0	75	7501
24 Clay and heavy clay brown earths, Pararendzina Pelosols and pelosols of marl, not gleyed	Field	1928	30.7	7.4	3956	20.7	104	10,352
	Grassland	1928	26.2	6.6	3857	19.9	97	9648
	Deciduous forest	1585	21.8	5.6	3171	15.9	79	7928
	Coniferous forest	1414	19.6	6.2	2828	14.2	71	7073
	Mixed forest	1500	20.7	6.0	3000	15.0	75	7500
25 Heavy clayey brown earths, parabrown earths and pelosols of marl, weakly to very strongly gleyed.	Field	1928	30.9	7.4	3955	20.7	106	10,413
	Grassland	1928	26.2	6.6	3857	19.9	97	9648
	Deciduous forest	1585	21.7	6.4	3171	15.9	79	7928
	Coniferous forest	1414	19.6	6.2	2828	14.2	71	7073
	Mixed forest	1500	20.8	6.4	3000	15.0	75	7501
26 Valley slopes and valley floors	Field	1843	30.2	7.2	3785	19.9	102	9994
	Grassland	1843	25.4	6.3	3685	19.1	92	9219
	Deciduous forest	1200	17.9	5.3	2400	12.0	60	6000
	Coniferous forest	943	14.9	4.8	1885	9.5	47	4716
	Mixed forest	1071	16.5	5.1	2143	10.7	54	5358
27 Source zones	Field	1843	18.4	5.5	3685	18.4	92	9213
	Grassland	1843	19.7	5.7	3685	18.5	92	9214
	Deciduous forest	1200	17.7	5.2	2400	12.0	60	6000
	Coniferous forest	943	14.7	4.7	1885	9.5	47	4716
	Mixed forest	1071	16.3	5.0	2143	10.7	54	5358

The results of the determination of critical loads for Cd in wheat and wheat products for the protection of human health are presented for the 27 soil types of the soil map 1:100,000 Luxembourg [31] differentiated in Table 18.

Table 18. Critical loads for Cd in wheat and wheat products for the protection of human health in Luxembourg.

Soil Forms (BK 100 Luxembourg)	$CL(Cd)_{food}$
	$g\ ha^{-1}\ a^{-1}$
1 Loamy, slightly stony brown earth, not to moderately gleyed.	4.6
2 Stony–loamy brown soils of slate and phyllad, not gleyed	4.5
3 Stony–loamy brown soils of weathered slate and phyllad, not gleyed	4.5
4 Stony–loamy brown soils of slate and phyllad, weakly to moderately gleyed	4.6
5 Stony–loamy brown earths of slate and sandstones, not gleyed	4.6
6 Stony–loamy brown earths of weathered slates and sandstones, not gleyed	4.6
7 Stony–loamy brown earths of slate and sandstones, weakly to moderately gleyed	4.5
8 Stony–loamy brown earths of clay slate and sandstones, weakly to moderately gleyed.	4.6
9 Stony–loamy brown soils from slate, not gleyed	4.5
10 Stony–loamy and stony–clayey brown earths and parabrown earths with quartzitic boulders, not to moderately gleyed.	4.4
11 Stony–clayey brown earths of dolomite, not gleyed	3.9
12 Stony–clayey brown earths of lime, not gleyed	6.3
13 Sandy, loamy–sandy and sandy–loamy brown earths and parabrown earths of calcareous sandstone, sand or weathered clay, not gleyed	4.4
14 Sandy, loamy–sandy and sandy–loamy parabrown soils over clay, weakly to moderately gleyed	4.4
15 Sandy–loamy and sandy–clayey brown earths and parabrown earths from red sandstones, not gleyed	3.9
16 Sandy–loamy and loamy parabrown soils from loess loam, not to moderately gleyed	4.4
17 Sandy–loamy and loamy parabrown soils from loess loam, strongly to very strongly gleyed	4.1
18 Clay and heavy clay brown earths, parabrown earths and terra fusca over limestone, not gleyed	4.9
19 Clayey brown earths and parabrown earths from Macigno, not gleyed	4.6
20 clayey parabrown soils from Macigno, weakly to moderately gleyed	4.6

Table 18. *Cont.*

Soil Forms (BK 100 Luxembourg)	$CL(Cd)_{food}$ g ha^{-1} a^{-1}
21 clayey parabrown soils of clay, weakly to moderately gleyed	5.9
22 clayey parabrown soils from shelly sandstone, not to moderately gleyed	4.6
23 Clayey and heavy clayey brown earths, parabrown earths and pelosols of limestone and marl, not to moderately gleyed	4.4
24 Clay and heavy clay brown earths, Pararendzina pelosols and pelosols of marl, not gleyed	4.4
25 Heavy clayey brown earths, parabrown earths and pelosols of marl, weakly to very strongly gleyed	4.4
26 Valley slopes and valley floors	4.4
27 Source zones	4.4

3.2.2. Protection of Ecosystems

The results of the determination of critical loads for the protection of plants, soil invertebrates, and microorganisms for the different vegetation types (arable, grassland, deciduous, coniferous, and mixed forest), differentiated according to the 27 soil types of the Soil Map 1:100,000 Luxembourg [31] are presented in (Table 19).

Table 19. Critical loads for the protection of plants, soil invertebrates and microorganisms for the different vegetation types in Luxembourg.

Soil Forms (BK 100 Luxembourg)	Land-Use Type	CL $(Pb)_{eco}$	CL $(Cd)_{eco}$	CL $(Cu)_{eco}$	CL $(Ni)_{eco}$	CL $(Zn)_{eco}$	CL $(As)_{eco}$	CL $(Cr)_{eco}$
		g ha^{-1} a^{-1}						
1 Loamy, slightly stony brown earth, not to moderately gleyed.	Field	14.2	7.8	87.6	326	798	401	259
	Grassland	13.0	7.7	12.4	330	165	403	253
	Deciduous forest	11.0	6.8	10.6	284	137	347	218
	Coniferous forest	10.1	7.1	9.3	249	122	304	191
	Mixed forest	10.6	7.0	9.9	266	130	325	204
2 Stony–loamy brown soils of slate and phyllad, not gleyed	Field	15.1	7.9	95.0	322	855	395	256
	Grassland	12.7	7.6	12.2	325	162	397	249
	Deciduous forest	10.1	6.3	6.8	269	126	319	201
	Coniferous forest	9.1	6.5	5.8	227	109	270	169
	Mixed forest	9.6	6.4	6.3	248	117	294	185
3 Stony–loamy brown soils of weathered slate and phyllad, not gleyed	Field	14.2	7.7	87.5	321	795	395	255
	Grassland	10.9	7.1	4.0	312	154	397	249
	Deciduous forest	9.0	6.0	3.2	251	120	319	201
	Coniferous forest	8.2	6.2	2.7	212	103	270	169
	Mixed forest	8.6	6.1	2.9	232	111	294	185
4 Stony–loamy brown soils of slate and phyllad, weakly to moderately gleyed	Field	14.6	8.3	120.3	329	889	401	261
	Grassland	16.7	9.2	10.7	454	193	403	253
	Deciduous forest	16.8	8.4	9.2	391	161	347	218
	Coniferous forest	12.9	8.3	8.0	342	143	304	191
	Mixed forest	15.4	8.6	8.6	366	153	325	204
5 Stony–loamy brown earths of slate and sandstones, not gleyed	Field	14.8	6.0	108.3	178	923	401	261
	Grassland	9.0	5.1	4.0	165	114	403	253
	Deciduous forest	13.7	5.7	12.7	147	117	347	218
	Coniferous forest	12.4	6.2	11.1	128	105	304	191
	Mixed forest	13.1	6.0	11.9	137	111	325	204
6 Stony–loamy brown earths of weathered slates and sandstones, not gleyed	Field	16.8	8.2	108.4	329	965	401	261
	Grassland	11.7	7.4	7.0	322	160	403	253
	Deciduous forest	10.6	6.8	7.4	292	137	347	218
	Coniferous forest	9.7	7.1	6.5	256	122	304	191
	Mixed forest	10.2	7.0	7.0	274	130	325	204
7 Stony–loamy brown earths of slate and sandstones, weakly to moderately gleyed	Field	14.5	8.2	120.3	324	886	395	257
	Grassland	16.6	9.1	10.5	447	190	397	249
	Deciduous forest	16.1	7.8	8.4	359	148	319	201
	Coniferous forest	12.0	7.6	7.1	304	128	270	169
	Mixed forest	14.6	8.0	7.8	331	138	294	185

Table 19. *Cont.*

Soil Forms (BK 100 Luxembourg)	Land-Use Type	CL $(Pb)_{eco}$	CL $(Cd)_{eco}$	CL $(Cu)_{eco}$	CL $(Ni)_{eco}$	CL $(Zn)_{eco}$	CL $(As)_{eco}$	CL $(Cr)_{eco}$
		$g\ ha^{-1}\ a^{-1}$						
8 Stony–loamy brown earths of clay slate and sandstones, weakly to moderately gleyed.	Field	14.6	8.3	120.3	329	889	401	261
	Grassland	16.7	9.2	10.7	454	193	403	253
	Deciduous forest	16.8	8.4	9.2	391	161	347	218
	Coniferous forest	12.9	8.3	8.0	342	143	304	191
	Mixed forest	15.4	8.6	8.6	366	153	325	204
9 Stony–loamy brown soils from slate, not gleyed	Field	15.1	7.9	95.0	322	855	395	256
	Grassland	16.3	9.1	10.5	447	190	397	249
	Deciduous forest	13.3	7.5	8.4	359	148	319	201
	Coniferous forest	11.9	7.5	7.1	304	128	270	169
	Mixed forest	12.6	7.5	7.8	331	138	294	185
10 Stony–loamy and stony–clayey brown earths and parabrown earths with quartzitic boulders, not to moderately gleyed.	Field	15.0	7.7	94.9	313	851	382	248
	Grassland	16.2	8.8	10.2	432	184	385	242
	Deciduous forest	13.3	7.3	8.1	348	144	309	194
	Coniferous forest	11.8	7.4	6.9	294	124	261	164
	Mixed forest	12.5	7.4	7.5	321	133	285	179
11 Stony–clayey brown earths of dolomite, not gleyed	Field	5.6	3.1	13.6	99	111	343	216
	Grassland	6.9	3.2	6.4	98	81	346	217
	Deciduous forest	15.4	4.3	10.1	90	81	278	175
	Coniferous forest	13.4	4.8	8.6	76	71	235	148
	Mixed forest	14.4	4.6	9.4	83	76	257	161
12 Stony–clayey brown earths of lime, not gleyed	Field	18.7	6.7	122.4	174	841	557	358
	Grassland	10.4	5.1	10.3	159	130	559	351
	Deciduous forest	18.9	5.6	14.2	126	114	392	247
	Coniferous forest	15.8	5.7	11.4	101	93	313	196
	Mixed forest	17.3	5.7	12.8	114	104	352	222
13 Sandy, loamy–sandy and sandy–loamy brown earths and parabrown earths of calcareous sandstone, sand or weathered clay, not gleyed	Field	15.9	7.8	102.7	314	914	382	249
	Grassland	11.3	7.0	3.9	302	150	385	242
	Deciduous forest	10.7	6.2	6.6	260	122	309	194
	Coniferous forest	9.4	6.5	5.6	220	106	261	164
	Mixed forest	10.1	6.4	6.1	240	114	285	179
14 Sandy, loamy–sandy and sandy–loamy parabrown soils over clay, weakly to moderately gleyed	Field	15.2	7.7	97.2	313	870	382	248
	Grassland	11.0	7.0	3.9	302	150	385	242
	Deciduous forest	12.8	6.4	6.6	260	122	309	194
	Coniferous forest	9.2	6.4	5.6	220	106	261	164
	Mixed forest	11.6	6.7	6.1	240	114	285	179
15 Sandy–loamy and sandy–clayey brown earths and parabrown earths from red sandstones, not gleyed	Field	15.0	7.0	104.0	283	866	345	222
	Grassland	10.4	6.3	3.5	272	135	346	218
	Deciduous forest	8.6	5.3	2.8	219	104	278	175
	Coniferous forest	7.8	5.7	2.4	185	91	235	148
	Mixed forest	8.2	5.5	2.6	202	97	257	161
16 Sandy–loamy and loamy parabrown soils from loess loam, not to moderately gleyed	Field	14.9	8.1	126.0	315	919	382	249
	Grassland	11.3	7.0	3.9	302	150	385	242
	Deciduous forest	13.8	7.4	8.1	348	144	309	194
	Coniferous forest	12.1	7.5	6.9	294	124	261	164
	Mixed forest	13.0	7.5	7.5	321	134	285	179
17 Sandy–loamy and loamy parabrown soils from loess loam, strongly to very strongly gleyed	Field	15.0	7.3	97.0	294	861	358	233
	Grassland	6.8	6.3	11.0	295	143	360	226
	Deciduous forest	11.3	7.4	7.1	287	130	309	194
	Coniferous forest	10.1	6.8	6.0	243	112	261	164
	Mixed forest	10.8	7.1	6.5	265	121	285	179
18 Clay and heavy clay brown earths, parabrown earths and terra fusca over limestone, not gleyed	Field	12.8	6.4	121.0	190	857	430	279
	Grassland	5.9	5.5	8.4	191	133	432	272
	Deciduous forest	12.3	5.0	8.9	127	102	372	234
	Coniferous forest	11.2	5.5	7.8	111	92	326	205
	Mixed forest	11.7	5.2	8.4	119	97	349	219
19 Clayey brown earths and parabrown earths from Macigno, not gleyed	Field	15.5	8.0	97.4	328	877	401	260
	Grassland	13.4	7.7	12.4	330	165	403	253
	Deciduous forest	12.1	7.3	7.9	323	145	347	218
	Coniferous forest	10.8	7.6	6.9	282	129	304	191
	Mixed forest	11.5	7.5	7.4	302	137	325	204

Table 19. *Cont.*

Soil Forms (BK 100 Luxembourg)	Land-Use Type	CL $(Pb)_{eco}$	CL $(Cd)_{eco}$	CL $(Cu)_{eco}$	CL $(Ni)_{eco}$	CL $(Zn)_{eco}$	CL $(As)_{eco}$	CL $(Cr)_{eco}$
		g ha^{-1} a^{-1}						
20 Clayey parabrown soils from Macigno, weakly to moderately gleyed	Field	4.6	6.5	11.3	315	181	400	252
	Grassland	13.1	7.7	12.4	330	165	403	253
	Deciduous forest	14.1	7.4	7.9	323	145	347	218
	Coniferous forest	10.6	7.5	6.9	282	129	304	191
	Mixed forest	12.9	7.8	7.4	303	137	325	204
21 Clayey parabrown soils of clay, weakly to moderately gleyed	Field	14.2	7.1	98.5	225	866	519	334
	Grassland	11.5	9.9	11.8	484	219	521	327
	Deciduous forest	7.2	6.8	8.3	340	152	366	230
	Coniferous forest	7.6	6.2	6.6	271	122	291	183
	Mixed forest	7.5	6.5	7.4	305	137	328	206
22 Clayey parabrown soils from shelly sandstone, not to moderately gleyed	Field	14.3	6.0	104.0	178	888	401	261
	Grassland	11.7	5.9	7.9	178	130	403	253
	Deciduous forest	12.5	4.8	8.3	118	95	347	218
	Coniferous forest	11.2	5.4	7.3	103	86	304	191
	Mixed forest	11.9	5.1	7.8	111	91	325	204
23 Clayey and heavy clayey brown earths, parabrown earths and pelosols of limestone and marl, not to moderately gleyed	Field	13.9	6.5	119.7	185	829	388	252
	Grassland	11.4	5.6	7.6	173	124	391	245
	Deciduous forest	13.8	6.4	12.3	142	114	336	211
	Coniferous forest	12.7	6.2	10.8	124	102	294	185
	Mixed forest	13.4	6.4	11.6	133	108	315	198
24 Clay and heavy clay brown earths, Pararendzina pelosols and pelosols of marl, not gleyed	Field	15.8	7.9	103.2	319	856	388	251
	Grassland	12.8	7.5	8.5	329	160	391	245
	Deciduous forest	11.0	6.7	7.2	283	133	336	211
	Coniferous forest	9.9	7.0	6.3	248	119	294	185
	Mixed forest	10.4	6.9	6.8	265	126	315	198
25 Heavy clayey brown earths, parabrown earths and pelosols of marl, weakly to very strongly gleyed.	Field	15.8	6.4	106.3	185	887	388	253
	Grassland	11.2	5.6	7.6	173	124	391	245
	Deciduous forest	13.9	6.4	12.3	142	114	336	211
	Coniferous forest	12.5	6.1	10.8	124	102	294	185
	Mixed forest	13.3	6.3	11.6	133	108	315	198
26 Valley slopes and valley floors	Field	16.1	7.8	103.9	314	923	382	249
	Grassland	16.6	8.9	10.2	432	185	385	242
	Deciduous forest	13.7	8.2	8.2	348	144	309	194
	Coniferous forest	12.1	7.5	6.9	294	124	261	164
	Mixed forest	13.0	7.9	7.5	321	134	285	179
27 Source zones	Field	4.1	4.7	7.2	169	114	381	239
	Grassland	5.5	4.9	7.4	170	117	384	241
	Deciduous forest	13.1	6.0	11.3	131	105	309	194
	Coniferous forest	11.5	5.6	9.6	110	90	261	164
	Mixed forest	12.4	5.9	10.5	120	98	285	179

4. Discussion

The assessment values for the protection of human health are based on different criteria. While the values of the TA Luft [14], the 39th BImSchV [12] and the EU Position Paper [8] (from which the assessment values of most other laws and regulations were derived) as well as the value for settlements according to Prinz and Bachmann [23] focus on the protection of humans in case of direct contact with soil in settlement areas, the assessment values for the soil–groundwater impact pathway of the BBodSchV [13] as well as the $CL(M)_{drink}$ consider the protection of humans in case of ingestion of drinking water from the groundwater reservoir. The $CL(M)_{food}$ considers the protection of plants for human consumption. Due to different pedo-transfer processes in soil, from soil into plants, and from soil into groundwater, the results can only be compared to a limited extent (Table 20). Nevertheless, it is noticeable that the assessment values for Cd, As, Ni, and Cr are close to each other several times.

Table 20. Assessment values [μg m^{-2} d^{-1}] for the protection of human health (in brackets: values for noncomparable exceptions and special cases).

Metal	German BbodSchV [13], German TA Luft [14], Swiss LRH Ordinance [16], Flemish VO [17]	EU position [8], EU-RL [9,10], German 39th BImmSchV [12], Austrian ImmSVO [18], Flemish VO [17]	Calculation According to Prinz and Bachmann [23] for Luxembourg Settlement/Coniferous Forest/Deciduous Forest/Open Land	$CL(M)_{food}$ Luxembourg 5th–95th Perc.	$CL(M)_{drink}$ Luxembourg 5th–95th Perc.
	Project Related		**General Related**		
Cd	1.6–2 (20)	1.2–2 (7.2) [(a)]		1.1–1.7	1.23–2.14
Pb	100–110 (243)	100–110 [(a)]			4.05–8.63
As	4.1	0.96–3.1 [(a)]			2.6–5.9
Ni	15.1–27.4	2.4–4.8 [(a)]			
Cu	98.6	-	17–27 [(b)]		258–564
Zn	329	-	167–267 [(b)]		1292–2944
Cr_{total}	82.2	-	60 [(c)]; 17–272 [(b)]		12.9–29.9

[(a)] Converted from assessment values for concentrations using the deposition rate for settlements according to Schaap et al. [7]. [(b)] Calculated from measure values of the BBodSchV [13] for the soil–groundwater impact pathway (for forest and open land) taking into account the Luxembourg background concentrations. [(c)] Calculated from the test value of the BBodSchV for the soil–human pathway on playgrounds, regarding the Luxembourg background concentrations.

The assessment value for $Cr_{(total)}$ on settlement areas (children's play areas) calculated according to Prinz and Bachmann [23] for the soil–human impact pathway on the basis of the test value in relation to the background levels in Luxembourg corresponds exactly to the value in the draft TA Luft [24]. The calculation results of Prinz and Bachmann [23] show a range of 16–70 μg m^{-2} d^{-1} for Germany, so that the value for Luxembourg is validated as plausible.

The assessment value for Cu on sheep pastures for the soil–plant–animal pathway based on the measure value relative to background levels in Luxembourg (306 μg m^{-2} d^{-1}) is in the range of 230–335 μg m^{-2} d^{-1} calculated by Prinz and Bachmann [23] for Germany. Likewise, the assessment value for other grassland for the soil–plant effect pathway with 2264 μg m^{-2} d^{-1} is within the range of 2189–2294 μg m^{-2} d^{-1} for Germany of Prinz and Bachmann [23].

Prinz and Bachmann [23] did not determine any assessment values for the soil–groundwater impact pathway. A comparison with this is therefore not possible. If the calculation results calculated according to the method of Prinz and Bachmann [23] (Section 2.1) are compared with the critical loads for the protection of groundwater as a drinking water reservoir (Section 2.2), there is an exact agreement for Cr as a whole. For Cu, the critical loads are about 40× higher and for Zn about 10× higher than the calculation results, according to the method of Prinz and Bachmann [23].

The reasons are obvious. For example, the Drinking Water Ordinance for Germany [45] contains a 40× higher limit concentration for Cu. The limit concentration for Zn (according to Health Canada [44]) is ten times higher than the test value according to BBodSchV Germany [13].

Assessment values for the protection of plants, animals, biodiversity, and ecosystems (Table 21) as a whole are based in the legal and sublegal regulations on the assumption that human toxicological threshold values protect ecosystems to a sufficient degree. Ecotoxicological thresholds do not underlie these assessment values. Thus, the assessment values are also largely identical to those for the protection of human health. A comparison with the critical loads shows that this thesis does not apply in every case. The $CL(M)_{eco}$ are based exclusively on ecotoxicological threshold values (PNEC, LOEC, and NOEC).

Table 21. Assessment values for the protection of arable, grassland, deciduous, and coniferous forest ecosystems.

	German BBodSchV [13], German TA Luft [14], Swiss LRH Ordinance [16]	EU position [8], EU-RL [9,10], German 39th BImmSchV [12], Austrian ImmSVO [18]	Calculation according to Prinz and Bachmann [23] for Luxembourg	$CL(M)_{eco}$ Luxembourg 5–95 Perz.
	Plant-Related	General Strain		
	$\mu g\ m^{-2}\ d^{-1}$			
Cd	1.6–2.5 (32)	0.7–2 [(a)]		1.34–2.38
Pb	100–185 (1900)	69–196 [(a)]		2.0–4.6
As	4.1–60 (1170)	0.41–3.1 [(a)]		72–110
Ni	15.1–27.4	1.4–7.7 [(a)]		30–110
Cu	98.6	-	Sheep pasture: 306 [(b)] Other. Grassland: 2264 [(b)]	1–33
Zn	329	-		25–243
Cr_{total}	82.2	-		45–72

[(a)] Converted from assessment values for concentrations using deposition rates for arable land, grassland, deciduous forest, and coniferous forest, according to Schaap et al. [7]. [(b)] Calculated from the BBodSchV measure value for the soil–plant pathway for grassland [13], taking into account the Luxembourg background concentrations.

The comparison of the critical loads in Luxembourg (Tables 17–19) shows that the sensitivity of humans cannot be equated with the sensitivity of ecosystems with their plants, animals, and microorganisms. Thus, ecosystems are significantly more sensitive to Pb, Cu, and Zn inputs than humans. In particular, Cu and Zn, as essential trace elements for humans, are rather insufficient in drinking water and in food crops, so that deficiency symptoms are commonly observed in humans. The situation is different for As and Cr. Here, humans react much more sensitively than ecosystems, especially to Cr(VI) compounds, e.g., chromate [54]. For Cd, the critical loads for drinking water, ecosystems, and wheat products are about the same.

5. Conclusions

From the comparison of existing legal regulations with assessment values calculated on an empirical basis, a number of indications for further scientific and political work in connection with the determination and application of assessment values for heavy metal discharges emerge.

1. The assessment values of the considered recommendations, laws, and sub-legislative regulations are only conditionally comparable with each other and with calculated precipitation-related values or with the critical loads due to the methodological differences of their derivation. The differences, some of which are significant, are due to different levels of protection, protection goals, and the impact relationship.
2. With regard to human health, other heavy metals are of immense importance, especially Hg [55], Tl [56], and Cr [57]. There is an urgent need for research on these metals. Comparing the calculation results calculated according to the method of Prinz and Bachmann [23] (Section 2.1) with the critical loads for the protection of groundwater as a drinking water reservoir (Section 2.2), there is an exact match for Cr_{total} at 60 $\mu g\ m^{-2}\ d^{-1}$. This value was also included in the draft of the draft TA Luft as of 2016 [24]. Unfortunately, this value was not included in the current TA Luft [14]. Previously regulated assessment values for Zn, on the other hand, are rather superfluous, because for people in Europe there is rather a zinc deficiency than a toxic overdose.
3. The assessment values for depositions of dusts containing heavy metals, as given in the Flemish Ordinance on Environmental Permitting [17], in the Swiss Air Pollution Control Ordinance [16], in the German Federal Soil Protection Ordinance [13], and in the German TA Luft [14], do not or not sufficiently take into account the regional and especially the geogenic differences in accumulation. As shown by the

determinations of precipitation-related values based on natural background levels in soil both in Luxembourg (see Tables 17–19) and in Germany [5], the partly strong regional differentiation cannot be neglected. The derivation of a tolerable annual total input rate from the assessment values alone is not meaningful. However, it can be calculated from the difference between the background value and the assessment value, differentiated by region, as precipitation-related assessment values, as was performed for Luxembourg using the method of Prinz and Bachmann [23].

4. Although the precipitation-related assessment values according to the method of Prinz and Bachmann [23], such as the critical loads for heavy metals, take into account all input pathways (air, management, possibly others), they differ significantly from the critical loads in their methodological approach. They assume an acceptable increase in concentrations in the soil when precautionary values have already been exceeded, whereas CL(M) are calculated assuming an equilibrium between inputs and outputs at the concentration level of the critical limits (the impact thresholds), regardless of the current concentration in the soil. The precipitation-related assessment values therefore have only a limited precautionary character in the sense of sustainable prevention of risks of adverse effects due to pollutant accumulation. They are more comparable to a de minimis threshold or irrelevance threshold.
5. Higher safety is provided by assessment values for acceptable additional input rates that ensure a balance with the harmless discharges (critical loads). If the balanced assessment values are observed, further enrichment beyond critical concentrations can be ruled out in the long term if they are currently undercut. If the critical concentrations are already exceeded today, a depletion can also take place under favourable conditions (tolerable discharges higher than inputs).

All assessment values set by law and sub-law for the protection of natural assets are based on human toxicological threshold values. Therefore, they are only conditionally suitable for application to ecological protected goods.

The comparison of the critical loads in Luxembourg—as well as in Germany [5]—shows that the sensitivity of humans cannot be equated with the sensitivity of ecosystems with their plants, animals, and microorganisms.

For the goal of the European Biodiversity Strategy for 2030 to set ecosystem-based impact thresholds for pollutants that describe the effects on biodiversity, the critical loads for the protection of ecosystems provide a very precautionary scientific basis for discussion.

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Abbreviations

As	Arsenic; here limited to As(V), the stable form in aerobic environment (humus topsoil)
BAT	Best available technique
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
CLRTAP	Convention on Long-range Transboundary Air Pollution
Cr	Chromium
Cr(III)	Trivalent compounds of chromium, the stable form in the considered humus-containing topsoil horizons
Cr(VI)	Hexavalent compounds of chromium, e.g., chromate
Cr_{total}	Sum of Chromium compounds
Cu	Copper
Hg	Mercury, sum of organically bound Hg in methyl mercury (CH_3Hg^+) and Hg in inorganic forms
LAI	German State working Group on Emission control
LOEC	Lowest Observed Effect Concentration
$[M]_{crit(free)}$	Critical concentration of free metal ions in the seepage water
$[M]_{crit(eco)}$	Critical concentrations of metals in leachate used in the calculation of critical loads for ecosystem protection
Ni	Nickel
NOEC	No Observed Effect Concentration
Pb	Lead
PNEC	Predicted no effect concentration
UNECE	United Nations Economic Commission for Europe
V	Vanadium
Zn	Zinc

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