



Sustainable sewage sludge management fostering phosphorus recovery and energy efficiency



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Quantitative risk assessment of potential hazards for humans
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Table of content

1	Introduction.....	1
2	Background on Risk Assessment.....	1
3	General system characteristics and scope.....	3
3.1	Hazard selection.....	3
3.2	Product definition	3
3.3	Endpoint definition and “standard environment”	7
3.4	Scope.....	8
4	Hazard characterization.....	10
4.1	Endpoint soil organisms.....	10
4.2	Endpoint humans	11
4.3	Endpoint groundwater.....	13
5	Exposure assessment.....	14
5.1	Substance-specific parameters for organic substances	14
5.1.1	Assumptions.....	14
5.1.2	Discussion.....	15
5.2	Substance-specific parameters for heavy metals	16
5.2.1	Assumptions.....	16
5.2.2	Discussion.....	17
5.3	Atmospheric boundary conditions and initial conditions	18
5.3.1	Assumptions.....	18
5.3.2	Discussion.....	19
5.4	Boundary condition for product application	20
5.5	Data-quality of products	22
5.6	Exposure	22
5.6.1	Kinetic model by TGD	22
5.6.2	Results and Discussion	24
5.7	Evaluation of results regarding Cd- and Zn-distributions between precipitated and ionic species (MINTEQ-software).....	26
5.8	Sensitivity analysis on exposure assessment	28
6	Risk characterization.....	30
6.1	Product comparison	33
6.2	Derivation of critical concentrations in phosphorus fertilizers for cadmium and zinc	34

7	Conclusion	36
7.1	Summary	36
7.2	Recommondations and Outlook.....	37
8	Literature.....	38
9	Annex	43
9.1	Safety-parameters and BCF for approach of PNEC for endpoint humans	43
9.2	Substance-specific parameters for organic substances	44
9.3	Substance-specific parameters for heavy metals	45
9.4	Initial and atmospheric boundary conditions	47
9.5	Description of solute transport model (HYDRUS).....	49
9.6	Results of exposure assessment by kinetic model (TGD).....	52
9.7	Results of exposure assessment by solute transport model (HYDRUS).....	62
9.8	Results of risk characterization.....	66

List of figures

Figure 1: Steps of risk management process according to (van Leeuwen & Vermeire 2007)	2
Figure 2: Pathways for exposure, endpoints and midpoints in the risk assessment	7
Figure 3: Inputs (upper boundary conditions) and outputs in the kinetic model according to (IHCP 2003) for organic substances (left), and modified for heavy metals (right), The solute transport model in refinement for heavy metals consider the same boundary conditions and processes	8
Figure 4: Iterations of risk assessment in this study (left for organic substances, right for heavy metals). Adjusted according to (IHCP 2003 p.174 Fig.17)	9
Figure 5: Saturation concentration and product concentration including daily atmospheric deposition calculated on infiltration water of one day in selected pH-range for cadmium and zinc.....	28
Figure 6: Range of Risk Characterization Ratio (PEC/PNEC-Ratio) on particular hazards for the endpoint soil organisms, TSP Pot-trails and atmospheric deposition for comparison.....	31
Figure 7: Range of Risk Characterization Ratio (PEC/PNEC-Ratio) on particular hazards for the endpoint human, TSP Pot-trails and atmospheric deposition for comparison	31
Figure 8: Range of Risk Characterization Ratio (PEC/PNEC-Ratio) on particular hazards for the endpoint groundwater, TSP Pot-trails and atmospheric deposition for comparison.....	32
Figure 9: Ratio of average phosphorus related mass flow per square meter soil and year for hazards; for atmospheric deposition all mass flows set to 1; for products proportional ratio	33
Figure 10: $PEC_{topsoil}$ and $PEC_{leachate}$ for PCDD/F and dl-PCB and PAH over 100 years of application averaged for the first 30 days after application in due consideration of initial concentrations and PNEC from hazard characterization	52
Figure 11: $PEC_{topsoil}$ for single-substance of PAH (model refinement) over 100 years of application averaged for the first 30 days after application in due consideration of initial concentrations and PNEC from hazard characterization	53
Figure 12: $PEC_{topsoil}$ and $PEC_{leachate}$ for As, Cr and Cu over 100 years of application averaged for the first 30 days after application in due consideration of initial concentrations and K_d -value from risk assessment reports and PNEC from hazard characterization	54
Figure 13: $PEC_{topsoil}$ and $PEC_{leachate}$ for Hg and Pb over 100 years of application averaged for the first 30 days after application in due consideration of initial concentrations and K_d -value from risk assessment reports and PNEC from hazard characterization	55
Figure 14: $PEC_{topsoil}$ and $PEC_{leachate}$ for Cd over 100 years of application averaged for the first 30 days after application in due consideration of initial concentrations and variable K_d -values in dependency from soil-pH-value for pH 5,0; pH 5,5 and pH 6,0 in Table 20 and PNEC from hazard characterization.....	56
Figure 15: $PEC_{topsoil}$ and $PEC_{leachate}$ for Cd over 100 years of application averaged for the first 30 days after application in due consideration of initial concentrations and variable K_d -values in dependency from soil-pH-value for pH 6,5 and pH 7,0 in Table 20 and K_d -value from risk assessment report in Table 21 and PNEC from hazard characterization	57

Figure 16: $PEC_{topsoil}$ and $PEC_{leachate}$ for Ni over 100 years of application averaged for the first 30 days after application in due consideration of initial concentrations and variable K_d -values in dependency from soil-pH-value for pH 5,0; pH 5,5 and pH 6,0 in Table 20 and PNEC from hazard characterization.....	58
Figure 17: $PEC_{topsoil}$ and $PEC_{leachate}$ for Ni over 100 years of application averaged for the first 30 days after application in due consideration of initial concentrations and variable K_d -values in dependency from soil-pH-value for pH 6,5 and pH 7,0 in Table 20 and K_d -value from risk assessment report in Table 21 and PNEC from hazard characterization	59
Figure 18: $PEC_{topsoil}$ and $PEC_{leachate}$ for Zn over 100 years of application averaged for the first 30 days after application in due consideration of initial concentrations and variable K_d -values in dependency from soil-pH-value for pH 5,0; pH 5,5 and pH 6,0 in Table 20 and PNEC from hazard characterization.....	60
Figure 19: $PEC_{topsoil}$ and $PEC_{leachate}$ for Zn over 100 years of application averaged for the first 30 days after application in due consideration of initial concentrations and variable K_d -values in dependency from soil-pH-value for pH 6,5 and pH 7,0 in Table 20 and K_d -value from risk assessment report in Table 21 and PNEC from hazard characterization	61
Figure 20: $PEC_{topsoil}$ over 100 years and $PEC_{leachate}$ and flux to groundwater over 1000 years for Cd in due consideration of initial concentrations and variable K_d -values in dependency from soil-pH-value for pH 5,0; pH 5,5 and pH 6,0 in Table 20 and PNEC from hazard characterization	62
Figure 21: $PEC_{topsoil}$ over 100 years and $PEC_{leachate}$ and flux to groundwater over 1000 years for Cd in due consideration of initial concentrations and variable K_d -values in dependency from soil-pH-value for pH 6,5 and pH 7,0 in Table 20 and K_d -value from risk assessment report in Table 21 and PNEC from hazard characterization	63
Figure 22: $PEC_{topsoil}$ over 100 years and $PEC_{leachate}$ and flux to groundwater over 1000 years for Zn in due consideration of initial concentrations and variable K_d -values in dependency from soil-pH-value for pH 5,0; pH 5,5 and pH 6,0 in Table 20 and PNEC from hazard characterization	64
Figure 23: $PEC_{topsoil}$ over 100 years and $PEC_{leachate}$ and flux to groundwater over 1000 years for Zn in due consideration of initial concentrations and variable K_d -values in dependency from soil-pH-value for pH 6,5 and pH 7,0 in Table 21 and K_d -value from risk assessment report in Table 21 and PNEC from hazard characterization	65

List of tables

Table 1: Phosphorus-and hazard concentrations in dry matter of products.....	5
Table 2: Concentrations of singular poly aromatic hydrocarbons in products for model refinement regarding PAH	6
Table 3: General characteristics for “standard environment”	8
Table 4: PNEC in mg per kg topsoil for hazards regarding soil organisms	10
Table 5: Calculated tolerable concentrations in soil for cadmium and lead according to pH-value (Schütze et al. 2002)	11
Table 6: Tolerable daily intake via food for a person of 70 kg bodyweight, tolerable wheat and soil concentration.....	12
Table 7: PNEC in mg per kg topsoil for hazards regarding human consumption.....	13
Table 8: PNEC in µg per L leachate (minor threshold values) (LAWA 2004).....	14
Table 9: Average total heavy metal content on arable land and geogenic heavy metal content in Germany in comparison with calculated heavy metal content in Table 23	19
Table 10: Annual mass flow of hazards per ha soil by fertilizer application of 60 kg P ₂ O ₅ /ha·yr	21
Table 11: Overview on results of exposure assessment and PNECs from hazard characterization	24
Table 12: Average heavy metal discharge from agricultural ecosystems	26
Table 13: Expected anions and concentrations (Lindsay 1979) in agricultural soil for calculation of saturation concentration for relevant heavy metals by Visual MINTEQ-software.....	26
Table 14: Saturation concentrations for cadmium and zinc for various pH-values for the system with anions and anion concentrations in Table 13	27
Table 15: Likelihood scale according to (IPCC 2010) for rough quantification of uncertainties	28
Table 16: Semi-quantitative overview of parameters, their uncertainties, their influence on PEC and their influence on exceeding the PNEC	29
Table 17: Current regulations for cadmium and zinc in fertilizers or sewage sludge by law in Germany and discussed limits on the European level	35
Table 18: Safety parameters for substances regarding human consumptions	43
Table 19: For calculations selected persistent organic pollutions and their specific parameter and calculated pseudo-first order rate constants according to (IHCP 2003)	44
Table 20: Equations for K _d -values of metals with the potential of mobilization, K _d -values for various pH-values and pseudo-first order rate constant for leaching	45
Table 21: Constant partition sorption constants defined by European Union risk assessment reports (for As and Hg from literature research) and calculated pseudo-first order rate constants for leaching	46
Table 22: Initial and atmospheric boundary conditions for organic substances.....	47
Table 23: Initial conditions, past and current/future atmospheric boundary conditions for heavy metals..	48
Table 24: Maximal risk characterization ratios regarding endpoint soil organisms.....	66

D 9.1

Table 25: Maximal risk characterization ratios regarding endpoint humans	67
Table 26: Maximal risk characterization ratios regarding endpoint groundwater.....	68

1 Introduction

In recent years several ways of recovering phosphorous from municipal wastewater have been developed. Depending on the applied technology the recovered products as well as the quality of sewage sludge vary significantly concerning the concentrations of heavy metals and organic residues.

Within WA 4 “environmental, economic and risk assessment of P recovery options” of the P-REX project a quantitative risk assessment of substances in phosphorus products for humans and environment is intended. In this deliverable risk assessment is done as a relative risk ranking for PCDD/F, dl-PCB, PAH, As, Cd, Cr, Cu, Hg, Ni, Pb and Zn between seven secondary phosphate fertilizers from wastewater stream, sewage sludge, mono-incinerated ash from sewage treatment and conventional phosphorus fertilizers.

2 Background on Risk Assessment

In chemical risk assessment “risk” is defined as “the probability of an adverse effect on man or the environment occurring as a result of a given exposure to a chemical or mixture” (van Leeuwen & Vermeire 2007 p.2 Table 1.1).

For an estimation of risk, the method of risk assessment has been developed. Risk assessment is the first and more objective/scientific part of the whole risk management process. The scope of risk assessment ranges widely: assessments can be done for specific sites (e.g. a landfill or specific pollution incidents) or more general for example with relation to registration of new chemicals. Therefore, the risk assessment process is a central theme in the control of chemicals and their registration (e.g. important part in EU-REACH-legislation). (van Leeuwen & Vermeire 2007)

The second part in the risk management process is risk management itself. In contrast to risk assessment, risk management is about measures and has to consider issues of acceptability as well as the feasibility of risk reduction measures. Thus, it goes beyond the scientific assessment of risk and has to include legal, social and economic issues, too. In conclusion, the whole risk management process involves eight steps, with the first four steps (hazard identification, exposure assessment, hazard characterization and risk characterization) being part of the risk assessment (see Figure 1). (van Leeuwen & Vermeire 2007)

In hazard identification, the capacity of substances to cause harm is identified. According to (EU 2002 p.8 Chapt.1 Art.3 (14)) “[...] hazard means a biological, chemical or physical agent [...] with the potential to cause an adverse health effect”. In reference to risk assessment of chemicals (van Leeuwen & Vermeire 2007 p.2 Table 1.1) defined hazard as “[...] the inherent capacity of a chemical or mixture to cause adverse effects in man or the environment under the conditions of exposure”. The definitions are slightly contradictory on the point whether a hazard is a substance or the capacity of a substance. Nevertheless, identification of adverse effect had to be assigned to a substance for identifying a hazard. According to these definitions, a substance which does not cause adverse effects under the conditions of exposure is not a hazard.

Hazard characterization correlates the dose of a hazard and the corresponding effect on human health and/or the environment. This quantification is the main task of toxicology. For risk characterization

the Predicted No-Effect Concentration (PNEC), “[...] a concentration below which an unacceptable effect will most likely not occur.” (IHCP 2003 p. 93, sect. 3.1), is derived from the result of toxicological testing like No Observed Effect Concentrations (NOEC), Lethal Concentration 50 (LC50) or Effective Concentration 50 (EC50). Depending on the amount of available information assessment factors are applied in order to cope with present uncertainty (Klöpffer 2012). PNECs are specific for substances and endpoints.

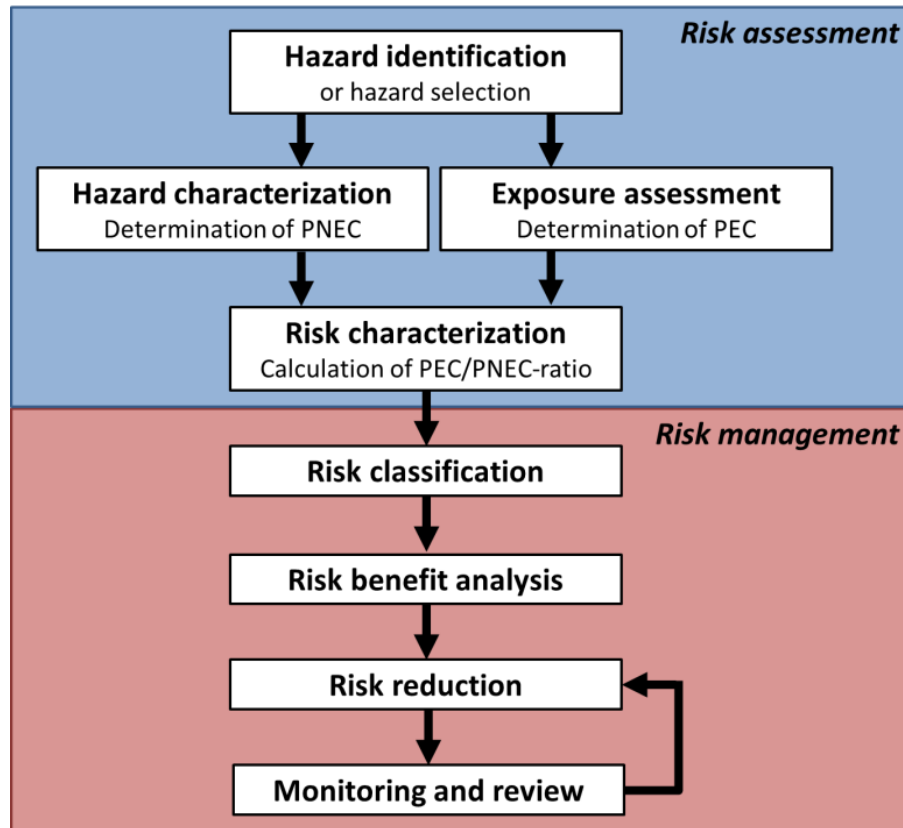


Figure 1: Steps of risk management process according to (van Leeuwen & Vermeire 2007)

In the exposure assessment models are used to estimate the Predicted Environmental Concentration (PEC) to which humans or the environmental endpoints are likely to be exposed. For exposure assessment assumptions are needed to quantify the expected concentrations as simple as possible but as accurate as needed. For general estimations in environmental media, several assumptions and models are suggested by the European “Technical Guidance Document on Risk Assessment (TGD)” (IHCP 2003)

In risk characterization PNECs from hazard characterization and PECs from exposure assessment are compared. Risk is expressed as the quotient of PEC and the PNEC, the “Risk Characterization Ratio (RCR)” (Klöpffer 2012) ” or “Risk Quotient (RQ)” (van Leeuwen & Vermeire 2007). However, these ratios are no absolute measure of risk. In fact, the absolute value of risk stays unknown. The only conclusion which can be drawn is that the probability of an adverse effect increases with an increasing RCR. Once a risk is determined, more detailed information must be collected to refine the PNEC in hazard characterization or the PEC in exposure assessment. Thus, risk assessment is an iterative process.

It has to be underlined that even if the RCR exceeds the value of “1” it does not mean that an adverse effect will actually happen, but that by applying a precautionary approach negative effects cannot be excluded. It should also be noted, that “[...] there is no such thing as a precise risk assessment and scientists will always differ in the conclusions they draw from the same set of data [...]” (van Leeuwen & Vermeire 2007 p.5 sect. 1.2.4)

In contrast to the whole risk assessment method using the $RCR = PEC/PNEC$ calculation, the often by insurance business used formula for risk out of the product of extent of damage and probability of occurrence (Klöpffer 2012) is not applicable for chemical or environmental risk assessment. Neither the extent of damage, nor the probability of occurrence can be described with sufficient accuracy when it comes to exposition of chemicals in environment. (Klöpffer 2012)

3 General system characteristics and scope

3.1 Hazard selection

Within the P-REX-project different secondary phosphate products were analysed for heavy metals, persistent organic pollutions and pharmaceuticals. For risk assessment the following measured substances or sums of substances are selected:

- Sum of WHO-PCDD/F-TEQ + WHO-dl-PCB-TEQ according to (WHO 2005a) - measurement of 7 dioxins, 10 furans and 12 polychlorinated biphenyls (PCBs)
- Sum of poly aromatic hydrocarbons (PAH) – measurement of 6 PAHs¹
 - Fluoranthene, Benz(b)fluoranthene, Benz(k)fluoranthene, Benz(a)pyrene, Benz(ghi)perylene, Indeno(1,2,3)pyrene
- Arsenic (As)²
- Cadmium (Cd)
- Chromium (Cr)
- Copper (Cu)
- Mercury (Hg)
- Nickel (Ni)
- Lead (Pb)
- Zinc (Zn)

3.2 Product definition

In this study a product is defined, as any primary or secondary phosphate fertilizer or raw material from wastewater treatment, which contains hazards as by-products. The selected products in this study are:

¹ For PAH, the sum of PAH is objected hazard, as well as the single substances Fluoranthene, Benz(b)fluoranthene, Benz(k)fluoranthene, Benz(a)pyrene, Benz(ghi)perylene and Indeno(1,2,3)pyrene for model refinement

² Arsen is numbered among heavy metals in this study, although Arsen is a metalloid

- dewatered digested sludge from enhanced biological phosphorus removal (EBPR) (**Bio-P sludge**) from the wastewater treatment plant Braunschweig-Steinhof, Germany
- dewatered digested sludge from chemical phosphorus removal by Fe-salts (**Fe sludge**) from the wastewater treatment plant Berlin-Münchehofe, Germany
- dewatered digested **generic sludge**, used in calculation by the Umberto software for Life-Cycle-Assessment within the P-REX project from averaged mono-incinerated raw ash of 13 selected municipal sewage treatment plants in Germany (Remy 2014)
- averaged mono-incinerated **raw ash** from 13 German municipal sewage treatment plants (Krüger & Adam 2014)
- Struvite from **Pearl/ Struvia** process (crystallization in sludge liquor)
- Struvite from **AirPrex** process (crystallization in sludge)
- Struvite from **Stuttgart** process (acidic chemical extraction in sludge and crystallization in sludge liquor)
- Struvite/ Calciumphosphate from **Gifhorn** process (acidic chemical extraction in sludge and crystallization in sludge liquor)
- P-mineral from **AshDec** process (thermal chemical extraction of sludge ash)
- P-slag form **Mephrec** process (thermal metallurgical phase separation of sludge or ash)
- P-mineral/ Calciumphosphate form **Leachphos** process (acidic chemical extraction of sludge ash)
- Conventional TSP fertilizer (**TSP Pot-trails**) from Van Loon Hoeven B.V. (NL) which has been used in growing experiments in the P-REX project with low heavy metal concentration regarding cadmium and chromium
- Conventional TSP fertilizer (**average TSP**), calculated by world-market shares in 2010 (Remy 2010) with higher heavy metal concentrations than the fertilizer from Van Loon Hoeven B.V. (NL)

The measured and calculated phosphate- and hazard- contents in these products are shown in Table 1 and Table 2.

Table 1: Phosphorus-and hazard concentrations in dry matter of products

product	Source/ Measurement	No. ³	P ₂ O ₅ total	PCDD/F & dl- PCB ⁴	PAH ⁵	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
			g/kg DM	mg WHO- TEQ/kg DM	mg/kg DM	mg/kg DM	mg/kg DM	mg/kg DM	mg/kg DM	mg/kg DM	mg/kg DM	mg/kg DM	mg/kg DM
Bio-P Sludge	FHNW/LUFA	1 (2)	102.6	5.70·10 ⁻⁶	0.97	3.5	1.20	27.7	220.2	1.05	22.6	29.3	902.3
Fe Sludge	FHNW/LUFA	1 (2)	93.7	4.01·10 ⁻⁶	0.62	4.7	1.02	17.6	831.7	1.10	17.6	35.7	949.6
Generic Sludge	(Remy 2014)	Calc.	100.8	-	-	7.7	1.10	71.5	482.0	0.90	26.5	57.0	1124.5
raw ash	(Krüger & Adam 2014)	13 (4-18)	221.1	-	-	17.5	2.45	161.5	1090.0	0.54	60.5	129.0	2544.0
Pearl/Struvia	Average ⁶	3 (2)	299.8	1.53·10 ⁻⁶	0.00	2.7	0.10	2.7	2.6	0.39	2.5	1.3	14.9
AirPrex	Average ⁶	3 (2)	262.0	1.61·10 ⁻⁶	0.60	1.0	0.25	16.4	42.4	0.23	15.9	12.5	89.8
Stuttgart	Average ⁶	2 (2)	230.0	1.91·10 ⁻⁶	0.08	1.6	0.43	4.2	30.4	0.32	4.7	6.5	47.2
Gifhorn	(Hermanussen et al. 2012)	1 (>5)	252.1	-	-	-	0.20	1.5	11.5	0.20	1.7	1.0	23.7
AshDec	(Herzel et al. 2014)	1 (7)	176.6	-	-	4.0	0.37	127.0	601.0	0.70	56.0	59.8	1737.0
Mephrec	Average ⁶	2 (2)	100.3	-	-	4.7	0.28	109.5	115.0	0.67	17.0	4.2	85.1
Leachphos	(Stemann et al. 2014)	1 (3)	300.2	-	-	10.1	3.80	34.0	851.0	0.20	13.8	25.0	1390.0
TSP Pot-trails	FHNW/LUFA	1 (2)	510.0	-	-	7.5	4.19	121.2	13.0	0.20	41.2	3.1	182.9
Average TSP	(Remy 2010)	Calc.	485.0	-	-	3.7	26.80	288.0	27.3	0.04	36.3	12.0	489.0

3 Number of sources/ plants (No. of measurement repetitions)

4 WHO-PCDD/F-TEQ + WHO-dl-PCB-TEQ of 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD, OCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCDF, OCDF, PCB 77, PCB 81, PCB 105, PCB 114, PCB 118, PCB 123, PCB 126, PCB 156, PCB 157, PCB 167, PCB 169 and PCB 189; including limits of quantification

5 Sum of Fluoranthene, Benz(b)fluoranthene, Benz(k)fluoranthene, Benz(a)pyrene, Benz(ghi)perylene and Indeno(1,2,3)pyrene

6 Averaged value from FHNW/LUFA, Ostara and Veolia Water for Pearl©/Struvia; from FHNW/LUFA, BWB and Niersverband for AirPrex; from FHNW/LUFA and AVZ Offenburg for Stuttgart; from FHNW/LUFA and Ingitec for Mephrec

Table 2: Concentrations of singular poly aromatic hydrocarbons in products for model refinement regarding PAH

product	Source/ Measurement	No. ⁷	P ₂ O ₅ total	PAH total	Flour-anthene	Benzo(a)-pyrene	Benzo(b)-flour-anthene	Benzo(k)-flour-anthene	Benzo(ghi)-perylene	Indeno-(1,2,3,-cd)-pyrene
			g/kg DM	mg/kg DM	mg/kg DM	mg/kg DM	mg/kg DM	mg/kg DM	mg/kg DM	mg/kg DM
Bio-P-Sludge	LUFA	1 (2)	102.6	0.97	0.38	0.12	0.17	0.07	0.10	0.13
Fe-Sludge	LUFA	1 (2)	93.7	0.62	0.30	0.08	0.10	0.00	0.07	0.07
Pearl/Struvia	LUFA	1 (2)	299.8	0.00	0.00	0.00	0.00	0.00	0.00	0.00
AirPrex	Averaged ⁸	2 (2)	262.0	0.60	0.26	0.08	0.10	0.05	0.06	0.06
Stuttgart	LUFA	1 (2)	230.0	0.08	0.08	0.00	0.00	0.00	0.00	0.00

⁷ Number of sources/ plants (No. of measurement per source/ product/ plant)

⁸ Overall PAH-value for AirPrex measured by Niersverband, recalculated on single PAH by measurements of LUFA

3.3 Endpoint definition and “standard environment”

After emission into the environment several pathways for effects on humans or ecosystem can be identified for hazards through fertilizer application. The most important pathways are (see Figure 2):

- Hazard application – soil – soil organisms
- Hazard application – soil – plants – humans by plant consumption
- Hazard application – soil – groundwater

For these three pathways the endpoints soil organisms, humans and groundwater are identified. Risk is assessed at two midpoints of the modelling chain (see also Figure 2):

- Topsoil (for soil organisms and for humans)
- Leachate (for groundwater)

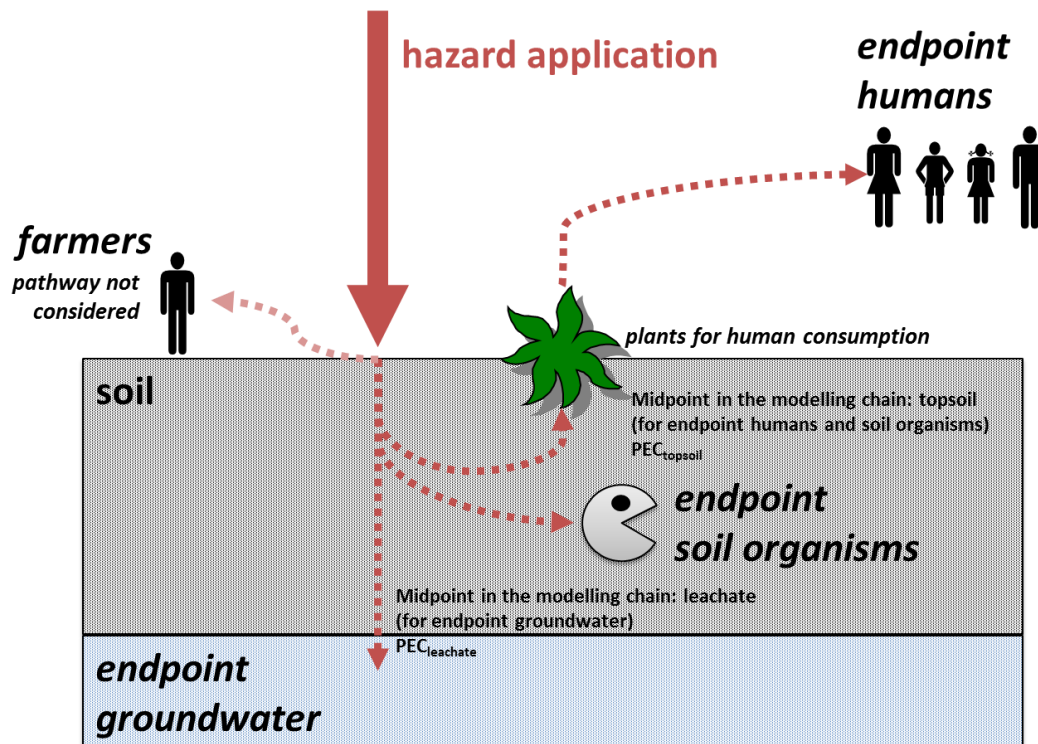


Figure 2: Pathways for exposure, endpoints and midpoints in the risk assessment

Hazard characterization is done twice for topsoil, whereby two $PNEC_{topsoil}$ are derived, one for endpoint soil organisms and one for human consumption. For the endpoint groundwater hazard characterization and exposure assessment is done once for leachate. Some general characteristics defining a “standard environment” for model assumptions are needed for agricultural soil. These basic assumptions are shown in Table 3.

Table 3: General characteristics for “standard environment”

Characteristic	Assumption	Source
Soil type	No differentiation; only for model refinement requested: sandy soil, since the highest potential of leaching is given.	(BGR 2014)
Content of organic carbon	2 % for topsoil, only for model refinement requested: 0.2 % for subsoil	(IHCP 2003), (Scheffer & Schachtschabel 2010)
Soil-pH value	5-7	(Kerschberger et al. 2000), (Scheffer & Schachtschabel 2002)
Rain and infiltration rate	700 mm rain/year, 175 mm infiltrated water/year	(IHCP 2003)
Soil depth	20 cm topsoil, only for model refinement requested: 130 cm for subsoil	(IHCP 2003), (Scheffer & Schachtschabel 2010)

3.4 Scope

In this study a kinetic model according to the Technical Guidance Document (TGD) on risk assessment (IHCP 2003) is used to estimate the exposure to topsoil and leachate to quantify potential risks for the endpoints humans, soil organisms and groundwater. For topsoil this model considers the input of hazards by fertilizer application and atmospheric deposition and the outputs volatilization, biodegradation and leaching for organic substances (see Figure 3). Since chemical analysis was done on many organic substances the risk assessment is done on the WHO-TEQ for PCDD/F and dl-PCB and on the sum parameters for PAH. If an exceeding of the PNEC-value is achieved, a single substance assessment is done as model refinement (see Figure 4 on the left side).

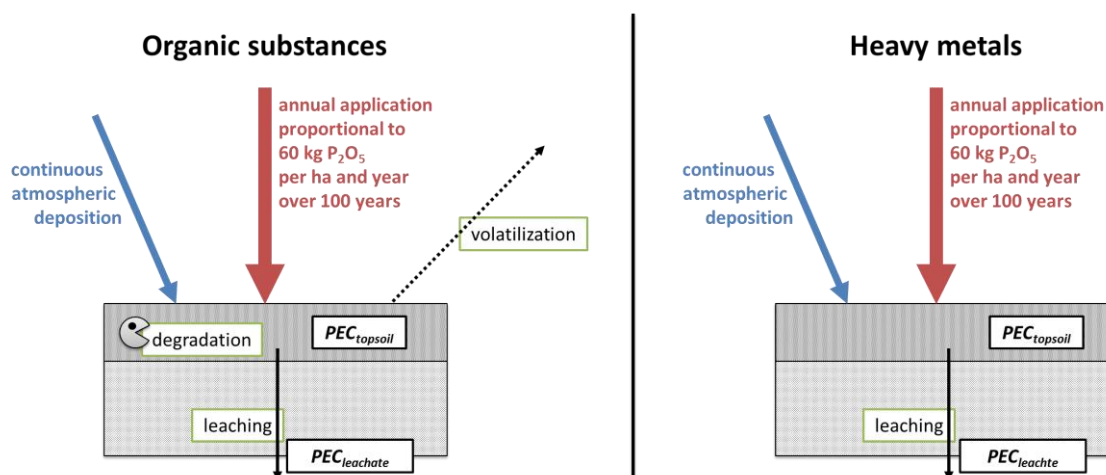


Figure 3: Inputs (upper boundary conditions) and outputs in the kinetic model according to (IHCP 2003) for organic substances (left), and modified for heavy metals (right), The solute transport model in refinement for heavy metals consider the same boundary conditions and processes

For heavy metals the model has been modified, so leaching is the only output (see Figure 3). Leaching is thereby described by soil hydraulic properties and the retardation of metals by their behaviour to adsorb on soil material. Concerning exposure to groundwater via leachate, (IHCP 2003) suggests to equal soil-water concentration with groundwater-concentration. This suggestion does not consider the dislocation through subsoil to groundwater and probably underestimates the influence of subsoil. Therefore, a solute transport model using more soil-physical knowledge for mobile substances by the HYDRUS 1D-software is used for refinement of substances exceeding the PNEC value. In both models precipitation and complex formation is neglected and reversible adsorption is the only process

regarded. If there is still PNEC-exceeding expected, the calculation of these hazards is evaluated by estimation with the Visual MINTEQ-software, in regard to whether precipitation might be a relevant process (see Figure 4 on the right side).

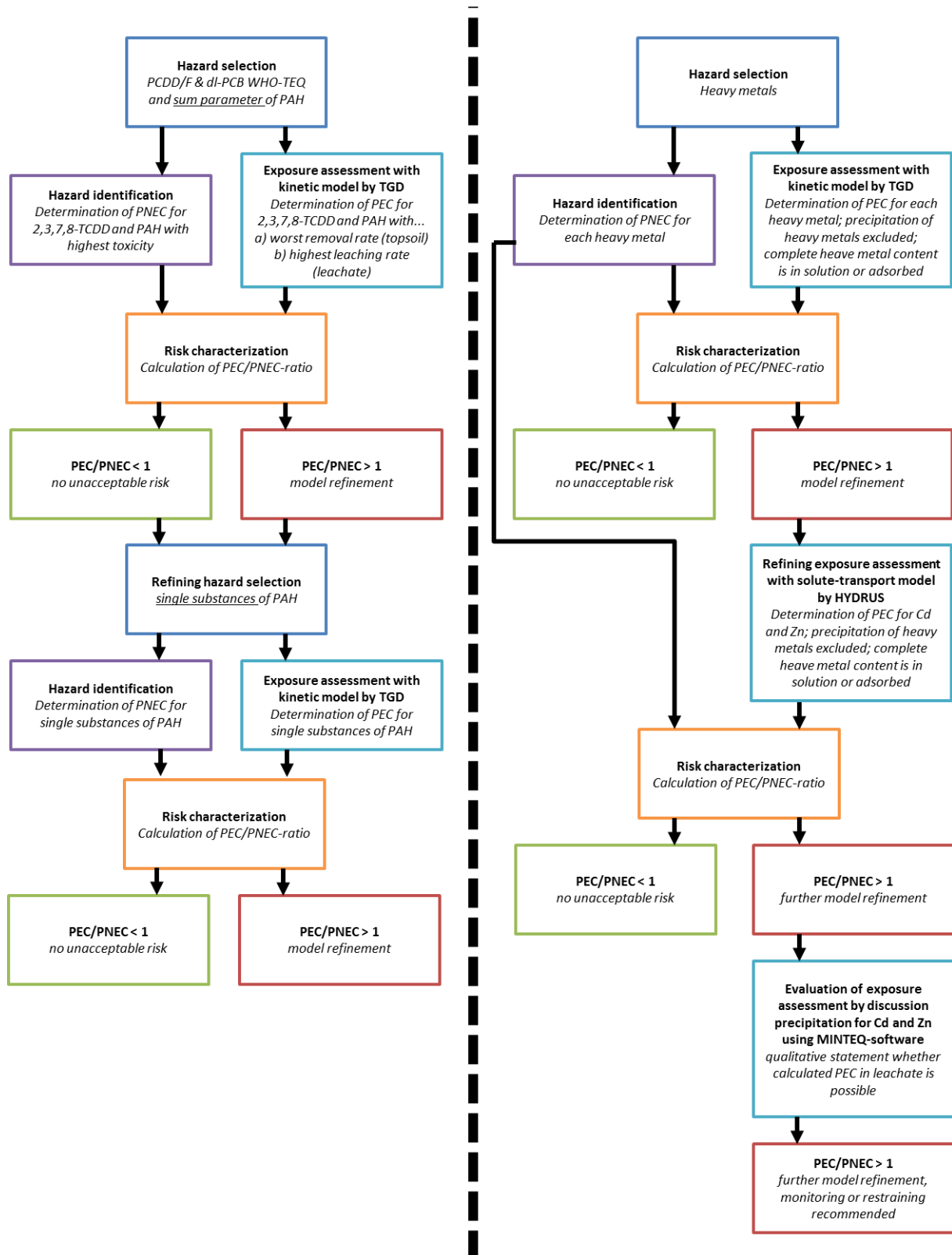


Figure 4: Iterations of risk assessment in this study (left for organic substances, right for heavy metals). Adjusted according to (IHCP 2003 p.174 Fig.17)

4 Hazard characterization

4.1 Endpoint soil organisms

Regarding negative effects on soil organisms and their food chain, the $PNEC_{\text{topsoil (soil organisms)}}$ were adopted from several risk assessment reports by the Institute for Health and Consumer Protection of the European Union. Regarding PAH for each of the six measured single substances PNEC-values were collected to refine hazard characterization. The PNEC-values are shown in Table 4. For PCDD/F and arsenic NOEC-values divided to an assessment factor of 10 (IHCP 2003 p. 118 Table 20) were used as PNEC-values, since no PNEC-values were available.

Table 4: PNEC in mg per kg topsoil for hazards regarding soil organisms

Substance	$PNEC_{\text{topsoil-(organisms)}}$ [mg/kg]	Source
PCDD/F & dl-PCB	$2 \cdot 10^{-5}$ WHO-TEQ	(Herter & Külling 2001), (LUBW 2003)
PAH (Benz(a)pyrene)	0.053	(IHCP 2008a)
Flouranthene	1.5	(IHCP 2008a)
Benzo(a)pyrene	0.053	(IHCP 2008a)
Benzo(b)flouranthene	0.28	(IHCP 2008a)
Benzo(k)flouranthene	0.27	(IHCP 2008a)
Benzo(ghi)perylene	0.17	(IHCP 2008a)
Indeno(1,2,3,-cd)pyrene	0.13	(IHCP 2008a)
As	7	(Scheffer & Schachtschabel 2010)
Cd	1.15	(IHCP 2007)
Cr	62	(IHCP 2005)
Cu	89.6	(ECI 2009)
Hg	0.3	(van Wijk 2004)
Ni	50	(IHCP 2008d)
Pb	166	(IHCP 2008b)
Zn	26	(IHCP 2010)

For PAHs regarding the endpoint soil organisms the PNEC for Benz(a)pyrene was chosen, since this is the lowest PNEC of all six regarded PAH. The PEC exceeds the PNEC in the beginning of simulation as a result of high initial concentration (see chapter 6 or Figure 10 in the annex). The hardly degradable substance Indeno(1,2,3,-cd)pyrene is selected as reference substance. As consequence the concentration in topsoil increases especially through input by atmospheric deposition.

Regarding the PNEC of zinc for endpoint soil organisms various refinements regarding PEC and PNEC are suggested in (IHCP 2010). Background is an observed adoption of organisms or plants with respect to high zinc concentrations. If the parent rock material has high loads of zinc, naturally there are also higher concentrations in soil compared to soil with parent rock material, which is poor in zinc. As consequence of adoption to this environment, higher zinc loads in soil and soil water are tolerable. (IHCP 2010) suggests methods, where either a PEC_{add} or a $PNEC_{\text{add}}$ is used for refining the PEC/PNEC-ratio. To reduce the PEC which is overestimated through the lithogenic background concentration, PEC is divided through an assessment factor and the reduced PEC_{add} is used instead of

the PEC. Regarding $PNEC_{add}$ the lithogenic background concentration is added to the NOEC of 26 mg Zn/ kg dry weight soil. Since in this study no lithogenic zinc is assumed and only anthropogenic zinc is selected as hazard, (IHCP 2010) suggests to use the NOEC as PNEC. (IHCP 2010)

4.2 Endpoint humans

Regarding human consumption, there is no direct $PNEC_{humans}$ for agricultural soil available. According to (de Vries et al. 2005) the cadmium content in wheat is “[...] an appropriate indicator for critical load calculations addressing human health effects via food intake [...]” (de Vries et al. 2005 p.15 sect.2.1). To approach negative effects on humans by consumption of wheat from concentrations in soil, estimations according to (Schütze et al. 2002) and (VKM 2009) are used.

According to (Schütze et al. 2002) the following two empirical transfer-functions from soil to wheat are given for wheat concerning the heavy metals cadmium and lead (see eq. 1 and eq. 2). In the case of lead, there is no clear-cut correlation given ($R^2 = 0.24$). Furthermore quality criteria for the tolerable concentration of cadmium and lead in wheat is given by (Schütze et al. 2002). Regarding these tolerable wheat concentrations, the tolerable concentration in soil can be calculated (see Table 5).

	$\log(Cd_{wheat}) = 0.35 - 0.15 \cdot pH - 0.39 \cdot \log(\% OM) + 0.76 \cdot \log(Cd_{soil})$ with $R^2 = 0.72$			eq. 1
and	$\log(Pb_{wheat}) = 0.25 \cdot pH - 1.42 \cdot \log(\% OM) + 1.14 \cdot \log(Pb_{soil})$ with $R^2 = 0.24$			eq. 2
<i>pH</i>	pH-Value		[-]	5-7
<i>OM</i>	Content of organic matter		[%]	4
<i>HM_{soil}</i>	Concentration of heavy metal in soil		[mg/kg]	
<i>HM_{wheat}</i>	Concentration of heavy metal in plant		[mg/kg]	

Table 5: Calculated tolerable concentrations in soil for cadmium and lead according to pH-value (Schütze et al. 2002)

Heavy Metal	HM _{plant} [mg/kg]	HM _{soil} [mg/kg]				
		pH 5	pH 5.5	pH 6	pH 6.5	pH 7
Cd	0.12	0.42	0.53	0.66	0.83	1.04
Pb	0.24	20.1	25.8	33.3	42.8	55.1

For all other substances no comparable transfer-functions to the formulas in eq. 1 and eq. 2 are given. According to (VKM 2009) the tolerable concentration in soil is approached by a safety parameter (e.g. Tolerable daily intake (TDI)) and bio-concentration factor (BCF) for the equilibrium between soil and plant.

The researched values for safety parameters (see in the annex in Table 18) are calculated into a daily basis to determine which concentration is tolerable for a person with a bodyweight of 70 kg per day (Schütze et al. 2002). The daily wheat consumption for a person with a bodyweight of 70 kg is maximal 600 g wheat per day (MRI 2008). Also it is assumed, that the tolerable fraction via food is set to 50 % (Schütze et al. 2002). The fraction which is resorbed in the human body is set to 15 %

(Schütze et al. 2002), so an effective consumption of 90 g wheat per day is used to assess the tolerable risk. The calculation of the tolerable wheat concentration is shown in eq. 3.

$c_{wheat} = \frac{TDI \text{ via food}}{eff. cons.} = \frac{TDI \cdot 50 \%}{tot. cons. \cdot 15 \%}$				eq. 3
<i>TDI</i>	Tolerable Daily Intake for a Person with a bodyweight of 70 kg	[$\mu\text{g}/\text{d}$]		Table 6; Table 18
<i>eff. cons.</i>	effective consumption of wheat	[g/d]		90
<i>tot. cons.</i>	total consumption of wheat	[g/d]		600
<i>c_{wheat}</i>	Tolerable concentration in wheat	[mg/kg]		

The equation in (VKM 2009 sect. 5.3.3.3, p. 92, eq. 21A) published by (Travis & Arms 1988) is evaluated for above-ground plants. To approach the tolerable topsoil concentration from plant concentration eq. 4 is used.

$c_{soil} = \frac{c_{wheat}}{BCF}$				eq. 4
<i>c_{wheat}</i>	Tolerable concentration in wheat	[mg/kg]		eq. 3; Table 6
<i>BCF</i>	bio-concentration factor for above-ground plant parts	$[(\mu\text{g}/\text{kg})_{plant} \cdot (\mu\text{g}/\text{kg})_{soil}^{-1}]$		Table 18
<i>c_{soil}</i>	Tolerable concentration in soil	[mg/kg]		

Summarizing, the calculated tolerable daily intake via food for a person of 70 kg bodyweight, the calculated tolerable wheat concentration and the calculated tolerable soil concentration regarding human consumption are shown in Table 6.

Table 6: Tolerable daily intake via food for a person of 70 kg bodyweight, tolerable wheat and soil concentration

Substance	TDI [$\mu\text{g}/\text{d}$]	<i>c_{wheat}</i> [$\text{mg}/\text{kg}_{plant}$]	<i>c_{soil}</i> [$\text{mg}/\text{kg}_{soil}$]
PCDD/F & dl-PCB	$3.5 \cdot 10^{-5}$ WHO-TEQ	$3.89 \cdot 10^{-7}$ WHO-TEQ	$5.44 \cdot 10^{-5}$ WHO-TEQ
PAH	11.900	132	3109
As	10.5	0.12	8.39
Cd	12.5	0.14	1.07
Cr	500	5.56	327
Cu	2500	27.8	107
Hg	20	0.22	17.1
Ni	770	8.56	143
Pb	125	1.39	1543
Zn	12500	138	817

Regarding cadmium and lead various tolerable concentrations in soil are derived. The approached PNEC for cadmium by this TDI-method is 1.07 mg Cd/kg soil. In contrast, the PNEC from wheat to soil transfer-function is within a range from 0.42 to 1.04 mg Cd/kg soil depending on pH-value. Assuming a worse-case scenario the PNEC of cadmium was set to 0.42 mg Cd/kg soil. Since this worse-case PNEC was always above the PEC for any product, no model-refinement was necessary.

The approached PNEC for lead by TDI-method is 1543 mg Pb/ kg soil. The PNEC by the transfer-function from (Schütze et al. 2002) is within a range from 20.1 to 55.1 mg Pb/ kg soil. The considerable difference results from three relevant factors:

- First of all the tolerable wheat concentrations differs: the value by (Schütze et al. 2002) is set to 0.24 mg Pb/ kg wheat, the value approached by TDI-method is 1,39 mg Pb/kg wheat.
- Secondly a bad correlation rate of 0.24 was found for the transfer-function (see eq. 2). So the results of the transfer-functions are not very reliable compared to the good correlation rate for cadmium.
- Thirdly, the assumed BCF for lead for the system soil-cereals in the TDI method is with 0.0009 the lowest of all hazards.

Assuming the lowest calculated concentration for pH 5 of 20.1 mg Pb/ kg soil as PNEC, negative effects on humans by plant consumption are probably overestimated. Concluding these results for overestimation of risks, the PNEC-values are shown in Table 7.

Table 7: PNEC in mg per kg topsoil for hazards regarding human consumption

Substance	Calculated PNEC _{topsoil (human consumption)} [mg/kg]
PCDD/F & dl-PCB	5.44·10 ⁻⁵ WHO-TEQ
PAH	3109
As	8.39
Cd	0.42
Cr	327
Cu	107
Hg	17.1
Ni	143
Pb	20.1
Zn	817

4.3 Endpoint groundwater

For risk assessment of groundwater minor threshold values for leachate according to (LAWA 2004) are used. These values are derived from eco and human toxicological data (see Table 8). For PCDD/F no value is given neither for the sum of dioxins and furans nor as WHO-TEQ. The minor threshold value for the sum of PCB is used instead and calculated into WHO-TEQ considering a (sludge) typical PCB-compound contribution.

Table 8: PNEC in µg per L leachate (minor threshold values) (LAWA 2004)

Substance	PNEC _{leachate} [µg/L]
PCDD/F & dl-PCB	- (sum of PCB: 0.01; approx. $3.25 \cdot 10^{-6}$ WHO-TEQ)
PAH	0.2
As	10
Cd	0.5
Cr	7
Cu	14
Hg	0.2
Ni	14
Pb	7
Zn	58

5 Exposure assessment

5.1 Substance-specific parameters for organic substances

5.1.1 Assumptions

According to the TGD model described in (IHCP 2003) the fate of organic substances in the environment is derived from the following chemical properties:

- K_{OC} -value
- Henry's law constant K_H

From these characteristics pseudo-first order rate constants for volatilisation, leaching and biodegradation are derived. All three processes are only possible, when the substance is dissolved in soil water. The water solubility is approached by the K_{OC} -value. For the dissolved substance, the Henry's law constant is used to approach volatilization. Degradation is estimated from the amount of the dissolved substance and water solubility. Leaching depends on rain rate and infiltration rate.

Assuming a worst-case scenario for the endpoint humans and soil organisms, the accumulation in topsoil has to be maximized. Therefore all three removal paths have to be minimized. Thus, the accumulation increases for high K_{OC} -values (lipophilic, less water soluble substances) and low Henry's law constants (reduced volatilization).

To estimate the K_{OC} -value from K_{OW} -value (n-octanol-water partition coefficient) an equation by (Di Toro 1985) with validation for nonionizing organic compounds is used. For a first estimation this study works with WHO-TEQ for PCDD/F and dl-PCB and with the sum parameters for PAH. For PCDD/F and dl-PCB the equivalent substance regarding toxicity (2,3,7,8-TCDD) is used for calculation. For PAH on the one hand a substance is selected as reference for calculation with high potential of accumulation (highest K_{OC} and lowest Henry's law constant) for topsoil (endpoints soil organisms and humans). On the other hand, a substance is selected with high leaching rate (lowest K_{OC} and optional low Henry's law constant) to approach a worst-case regarding leachate (endpoint groundwater). The reference substances and other PAH-compounds, their parameters and pseudo-first

order rate constants are shown in the annex in Table 19 are. The approach of pseudo-first order rate constants for organic substances is done according to (IHCP 2003 sect. 2.3.6.5, p. 56, Table 8 and sect. 2.3.6.5, p. 82, eq. 56-58).

Following this pseudo-first order rate constants a half-life in topsoil according to (IHCP 2003 sect. 2.3.6.5, p. 56, eq. 29) is calculated using the combined constant from volatilization, biodegradation and leaching. This half-life in soil is in approx. 610 years for 2,3,7,8-TCDD and in the range of 20-480 years for the six selected PAHs.

5.1.2 Discussion

For the half-life in soil of PCDD/Fs periods from 1 to 12 years are mentioned (Kearney et al. 1973), (Young 1981), (Di Domenico et al. 1982). In deeper soil layers half-life is up to 100 years (Nauman & Schaum 1987). For contaminated sites a half-life far higher than 10 years is expected (LUBW 1995). Measures for sanitation and their effectivity had been tested frequently for contaminated sites. The achieved half-life under specific conditions through sanitation of contaminated sites cannot be achieved by natural attenuation on agricultural soil. Similar to PCDD/Fs the approached half-life of PCBs is higher than in literature studies. Studies determined half-life in soil ranging from 7 to 25 years (Harner & Mackay 2002) up to about 200 years (Wania & Daly 2002) for some PCB congeners. Half-life increases with a mixture of different PCBs and magnitude of chlorination (Dąbrowska et al. 2004). Nevertheless the effect of PCB-accumulation in the selected time period is of minor importance.

The half-life of PAHs varies considerably with amount of benzene rings. PAHs with 5 rings or more are considered as hardly degradable. The half-life of the six regarded PAHs was measured in a range of 2 to 4 years according to (Coover & Sims 1987), (Thiele-Bruhn & Brümmer 2005). Comparing the experimental rates from the literature with the calculation in this study, the approached half-life in this study is minimum one scale higher. These differences in the half-life are caused by assuming a worse-case in the TGD. The conservative approach of the half-life for inherently biodegradable substances, leads to a worse-case accumulation in topsoil.

Leaching in soil-water of organic hazards (especially of PCDD/Fs) is negligible. Dislocation bounded to particles by translocation of organic matter is more relevant because of high K_{OC} -value of all organic hazards (LUBW 1995). Especially in case of PAHs this particle bounded translocation is more relevant, since PAH had been found in subsoil and dissolved translocation is only possible in small quantities (Scheffer & Schachtschabel 2010).

Referring to (U.S. EPA 2012), volatilization is as relevant sink in soil for PCDD/Fs and dl-PCBs and for PAHs with less than three rings because of a large Henry's law constant. As a matter of fact, the large K_{OC} -value and the calculated soil-water partition coefficient ($K_{soil-water}$) is dominant for all organic hazards in the TGD-model, so the constant for volatilization is about two scales smaller than the constant for biodegradation.

For sensitivity analysis, a pseudo-first order rate constant calculated from half-life in literature was used to evaluate the effect of this parameter. In case of PCDD/Fs and dl-PCB, degradation of the initial concentration is dominant even for sewage sludge application. For PAHs, the half-life according to several literature sources leads to an almost high degradation within 20-50 years of initial concentration, although annual product application and continuous atmospheric deposition are included. As a consequence of this low half-life, the validated literature values for actual

concentrations of PCDD/F, dl-PCB and especially PAH on arable soils could not be reached in the past or only if the input would be significantly higher than in any assumed scenario. Even though the approached half-life and pseudo-first order rate constants in this study overestimate accumulation in topsoil, they seem more realistic in reference to the initial concentration, than the half-life from literature.

5.2 Substance-specific parameters for heavy metals

5.2.1 Assumptions

In (IHCP 2003) suggestions are made for modifying the model for heavy metal accumulation and translocation. For regional exposure assessment “[...] it is assumed that all the individual metal compounds are changed to the ionic species” (IHCP 2003 App.VIII, sect. Regional exposure assessment, p.303). Furthermore, the model should consider an equilibrium partition coefficient between soil and water, which implies that in the case of presence of ionic species that the process of sorption has to be considered.

In this study only anthropogenic mobile heavy metals are regarded. A linear adsorption isotherm is assumed in the whole pH-range and precipitation above the critical pH-value⁹ of metals is neglected (assuming maximum solubility according to (IHCP 2003 App.VIII, sect. Local exposure assessment, p.303)). This worst case assumption that heavy metal can be mobilized in any pH-range is used in the kinetic TGD model. It is assumed that all anthropogenic heavy metals are exchangeable and equilibrium is between adsorbed and dissolved heavy metals. If the dissolved concentration exceeds the solubility equilibrium it is not revoked by precipitation in these models. Complex-formation and heavy metal uptake by plants or organisms are neglected, too.

Since adsorption is a more dynamic reversible process than precipitation, these assumptions potentially underestimate the concentration in topsoil. The concentration regarding leachate is partly overestimated. This overestimation may include any particular or complex bounded heavy metal which can translocate under specific conditions. Consequently, if there is no exceeding of PNEC regarding leachate by modelling only the sorption-process, risk to groundwater is very unlikely. In cases of exceeding of the PNEC, the results are validated with the same assumptions regarding heavy metal distribution on ionic species with the solute transport model. Finally, the results are evaluated against the background of precipitation-processes, discussing whether the calculated leachate-concentrations of these ionic species are possible.

The relationship between adsorbed and dissolved metal fraction is described by the K_d -value For heavy metals many regression-equations regarding mobility have been developed (Degryse et al. 2009), (IHCP 2007), (IHCP 2008d), (IHCP 2010). The regression-equations are validated above the

⁹ Concept of critical pH-value for heavy metals in soil e.g. described in DVWK (1998) Filter- und Puffereigenschaften von Böden un deren Ermittlung im Felde -Stand und Aussichten, In Blume, H.-P. et al. [eds.], DVWK-Schriften: Zukunftfähige Schutzstrategien der Wasserwirtschaft - Teil V. Bodenschutztagung " Böden und ihre Funktion als Filter und Puffer im Sinne des Grundwasserschutz. Kommissionsvertrieb Wirtschafts- und Verlagsgesellschaft Gas und Wasser mbH, Bonn: Deutscher Verband für Wasserwirtschaft und Kulturbau e.V. (DVWK)

critical pH-value, where besides sorption precipitation is a dominant process. Consequently, it is not certain that these K_d -values only describe the sorption-process.

For heavy metals with critical-pH-values below pH 5 a constant K_d -value can be assumed in the pH-range from 5 to 7. In contrast, for heavy metals with the potential of mobilization within the selected pH-range like cadmium, nickel and zinc empirical equations in dependence on pH-value are used. In (Degryse et al. 2009) separate regression functions are derived for total and labile fraction of solid. The labile fraction considers the fraction of heavy metal which can be adsorbed reversibly. The total fraction includes inert material from parent rock material, which cannot be allocated easily under native conditions. In this study only the anthropogenic heavy metals are considered, so regression functions for the labile fraction are regarded.

The calculation results for the pseudo-first order rate constant regarding leaching is done similar to the calculation for organic substances (IHCP 2003 sect. 2.3.8.5, p. 82, eq. 58) although a few adoptions are taken. The pseudo-first order rate constant for leaching of heavy metals from topsoil is defined in eq. 5. The results for this rate constant by various K_d -values of all selected heavy metals are also shown in the annex in Table 20 and Table 21.

$k := k_{leach} = \frac{Finf_{soil} \cdot RAINrate}{K_d \cdot DEPTH_{soil} \cdot RHO_{soil} \cdot 10^{-3} \frac{m^3}{L}}$				eq. 5
$Finf_{soil}$	fraction of rain water that infiltrates into soil	[-]		0,25
$RAINrate$	rate of wet precipitation (700 mm/year)	[m · d ⁻¹]		1,92 · 10 ⁻³
K_d	substance specific sorption constant	[L · kg ⁻¹]		Table 20; Table 21
$DEPTH_{soil}$	mixing depth of soil for agricultural use	[m]		0,2
RHO_{soil}	Bulk density of soil	[kg · m ⁻³]		(IHCP 2003 sect. 2.3.4., p. 44, eq. 18)
k_{leach}	pseudo-first order rate constant for leaching from topsoil	[d ⁻¹]		
k	pseudo-first order rate constant from topsoil	[d ⁻¹]		

Beside the three metals Cd, Ni and Zn, for the other heavy metals there is only negligible leaching suspected for the pH-range from 5 to 7. The K_d -values are assumed as fixed values for the whole pH-range, since the variability in K_d -values above 500 L/ kg hardly effects leaching according to the calculations. For K_d -values lower than 200 L/kg leaching is dominant and any change in K_d -value hardly effects leachate concentration.

According to several EU risk assessment reports the following constant K_d -values are assumed (see in the annex in Table 21). For cadmium, nickel and zinc, the different K_d -values influenced by a range in pH are considered as well as the K_d -values by EU risk assessment reports.

5.2.2 Discussion

Since not only the pH-value and fraction of organic matter are responsible for sorption of heavy metals, (Utermann et al. 2005) derived more complex equations considering soil texture (by content of

clay), as well as effective cation exchange capacity and content of iron- and aluminium-hydroxides. Assumptions for these parameters are not taken into consideration in this study. Furthermore, all parameters are site-specific and uncertainty of conclusions for European arable land increases the more detailed site-specific assumptions are included. This study uses the regression functions for the labile heavy metal fraction by (Degryse et al. 2009) given in the annex in Table 20 to estimate general risks. Also in Table 20 the calculated K_d -values are shown for these metals and various pH-values.

Comparing the defined K_d -values for cadmium, nickel and zinc in Table 21 from EU risk assessment reports and values from regression functions in Table 20 for a pH-range from 5 to 7 and 2 % organic carbon, the K_d -value for cadmium and zinc defined by European Union's risk assessment reports fits into the function quite well. Recalculating a pH-value with the regression functions in Table 20, the values from EU risk assessment reports would be in a range of pH 6 to 6.5. Regarding nickel, the EU risk assessment report exceeds the values from regression equation. Regarding precipitation of nickel above pH 5.5 and the smaller number of repetitions of measurements, the K_d -value from EU risk assessment report (IHCP 2008d) is more plausible. A general problem is the validation of all these K_d -values in the pH-range and dependency from other site specific influences on metal behaviour in soil.

5.3 Atmospheric boundary conditions and initial conditions

5.3.1 Assumptions

Regarding the atmospheric deposition, (IHCP 2003) suggests an estimation based on annual production of the chemicals. In this study, validated literature values are chosen for estimation of this input path (Böhm et al. 2001), (Fuchs et al. 2002), (Fuchs et al. 2007), (Gocht et al. 2005), (Lehmhaus et al. 2009), (Fuchs et al. 2010), (Ilyin et al. 2012). Considering the fact, that the emissions of some substances were limited by law in the last decades, atmospheric deposition declines for these substances. So for this study, if there were various values for atmospheric deposition, the lowest value which also implicates the value from the newest publication, is used for modelling of atmospheric deposition in the future. The results of literature research regarding the atmospheric deposition fluxes for the current time are shown in the annex Table 22 and Table 23.

As initial condition for organic substances a common background concentration value by literature research is used (see in the annex in Table 22).

In contrast, as initial condition for heavy metals 150 years (average time since beginning of industrialization) of constant continuous atmospheric deposition is assumed before the first application. Thereby, no current values for atmospheric deposition are reasonable for the past. So in distinction to the values used as boundary condition for the future, values from long-term studies over past decades are used (see in the annex in Table 23). This estimation is used, since only the heavy metals from anthropogenic sources are selected in this study. The calculation results for initial concentrations of heavy metals are also shown in the annex in Table 23 for the kinetic model by TGD and K_d -values in Table 21.

The kinetic model and for refinement the solute transport model are used to calculate the initial concentration of heavy metals in the year of first product application. Thereby the actual initial concentration is different for both models. The kinetic model calculates an averaged initial

concentration in topsoil, while in the solute transport model initial concentration is a function of soil depth.

5.3.2 Discussion

The most available data for atmospheric deposition were found for the heavy metals in EMEP-monitoring: cadmium, (mercury) and lead. In (Bultjes et al. 2011) critical loads for soil are discussed, mainly for cadmium and lead. For cadmium the maximal atmospheric deposition is assumed in the 1960s with 14 g Cd/ ha and year and has been reduced to 1 g Cd/ ha and year since 2000. For lead the highest atmospheric deposition is also assumed in the 1960s with approximately 450 g Pb/ ha and year. The prognosis since 2000 and for the future approaches 10-20 g Pb/ ha and year. (Bultjes et al. 2011 sect. 5.6.2, p. 85, Fig.28)

These modelled values were extensively higher in the past than the values from (Böhm et al. 2001) used in this study (see Table 23). Consequently the anthropogenic background concentration is probably underestimated. Especially the assumptions for zinc can be problematic against the background of calculated risk quotients (see chapter 6). In contrast to the assumed deposition rate of 250 g Zn/ha and year by (Böhm et al. 2001), (Fuchs et al. 2010) published an average deposition rate of 385 g Zn/ha and year (for Western Germany) and 730 g Zn/ha and year (for eastern Germany) for the 1980s. Assuming the maximal atmospheric deposition had been reached for zinc as well as for cadmium and lead in the 1960s, the average anthropogenic background concentration is higher and as a matter of fact the risk quotients either.

Since there is rare literature about the amount of anthropogenic (exchangeable) heavy metals in arable land, the following estimation is done to validate the scale of the calculated initial concentrations in the annex in Table 23. By data of (LABO 2003), (Fuchs et al. 2010) and (Destatis 2014) the average heavy metal content on arable land in Germany is estimated. In comparison to that the average geogenic heavy metal content in Germany is shown in Table 9.

Table 9: Average total heavy metal content on arable land and geogenic heavy metal content in Germany in comparison with calculated heavy metal content in Table 23

Heavy metal	Average heavy metal content on arable land in Germany (LABO 2003), (Destatis 2014) [mg/kg]	Average geogenic heavy metal content in Germany (Fuchs et al. 2010) [mg/kg]	Calculated initial concentration in Table 23 [mg/kg]
Cd	0.23	0.16	0.08
Cr	29.01	26.04	0.21
Cu	13.71	9.41	1.29
Hg	0.07	0.018	0.01
Ni	19.20	20.30	0.63
Pb	24.55	21.80	1.75
Zn	53.30	40.60	8.73

Even if differentiation of geogenic from total heavy metal content is invalid, since the total content is for arable land and the geogenic content is from general sites, most of the differences are in the same

scale as the calculated anthropogenic initial concentration. In most cases they are slightly higher than by calculation. Only in case of chromium the difference is one scale higher. For nickel the geogenic concentration exceeds the total content on arable land, since nickel is present in many parent rock materials of mountain districts.

Regarding the exceeding of PNEC in the model, no adaption of the initial concentration to these differences would exclude risks or create “additional” risks in risk characterization regarding the endpoint soil organisms or humans. Even though the anthropogenic initial concentration is probably underestimated in the model, a refinement would not lead to significant other results.

Regarding the assumption for the future the most current values from (Lehmhaus et al. 2009), (Fuchs et al. 2010) and (Ilyin et al. 2012) were assumed. It is debatable if by law regulation these values can be reduced even further in the future. According to (Bultjes et al. 2011) for cadmium and lead no additional reduction to current state is assumed in the future until 2050. However a reduction especially of zinc is necessary against the background of made assumptions to exclude risks for the endpoint groundwater even by atmospheric deposition only (see also Chapter 6ff.). The actual database for zinc and some other heavy metals are outdated, since EMEP-Monitoring is focusing on cadmium, mercury and lead.

Regarding organics, no validation of the chosen data are possible for PCDD/Fs and dl-PCBs since there are not many publications about atmospheric deposition of these organics. Regarding PAH validated data for Germany from (Fuchs et al. 2010) were chosen, which are exceeding site specific-data from (Gocht et al. 2005) by factor 5 to 10. Based on the data from (Fuchs et al. 2010) PAH are the only hazard where atmospheric deposition exceeds product application in a magnitude, whereas it is irrelevant which product is used as fertilizer. Nevertheless this high deposition-rate is plausible compared to the initial concentration in unpolluted soils of PAH at the current time.

Based on expected dominant accumulation or degradation the initial concentrations of organic substances can be evaluated. The concentrations of PAHs in soil are increasing against the background of made assumptions (see Figure 10 in the annex). For the initial concentration of PCDD/Fs and dl-PCBs, it can be stated that with the assumed pseudo-first order rate constant and the annual input an almost constant value is assumed. By variation the initial concentration of one magnitude similar results are achieved. Consequently, the annual input and the minor pseudo-first order rate constant are too small to have a significant effect. Regarding PAHs the initial concentration is plausible based on the accumulation by continuous atmospheric deposition within a simulation over 100 years.

5.4 Boundary condition for product application

Regarding the annual discharge of product, a hazard specific load proportional to phosphorus content of the product is fertilized. For this study it is assumed that the annual phosphorus output is 50-100 kg P₂O₅ per ha and year (KTBL 2005), (Winzler 2014). Due to the fact that fertilizer application of phosphorus in soil is not effective within the same year, an output orientated fertilizer application to restock the phosphorus storage in soil is used. In this study an annual application of 60 kg P₂O₅ per ha is assumed and a proportional contamination amount of hazards is modelled. The results of these calculations are shown in Table 10.

Table 10: Annual mass flow of hazards per ha soil by fertilizer application of 60 kg P₂O₅/ha·yr

product	PCDD/F & dl-PCB	PAH	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
	g WHO-TEQ/ha·yr	g/ha·yr	g/ha·yr	g/ha·yr	g/ha·yr	g/ha·yr	g/ha·yr	g/ha·yr	g/ha·yr	g/ha·yr
Bio-P Sludge	3.33·10 ⁻⁶	0.58	2.05	0.70	16.19	128.74	0.62	13.21	17.0	527.44
Fe Sludge	2.57·10 ⁻⁶	0.40	3.00	0.65	11.29	532.33	0.70	11.24	22.84	607.77
Generic Sludge	-	-	4.60	0.66	42.55	286.85	0.54	15.77	33.92	669.21
raw ash	-	-	4.74	0.67	43.82	295.77	0.15	16.42	35.00	690.31
Pearl/Struvia	3.06·10 ⁻⁷	0	0.54	2.09·10 ⁻²	0.54	0.53	7.80·10 ⁻²	0.50	0.27	2.98
AirPrex	3.69·10 ⁻⁷	0.14	0.22	5.81·10 ⁻²	3.76	9.71	5.38·10 ⁻²	3.65	2.86	20.51
Stuttgart	5.19·10 ⁻⁷	2.10·10 ⁻²	0.12	0.11	1.09	7.94	8.30·10 ⁻²	1.22	1.68	12.30
Gifhorn	-	-	-	4.76·10 ⁻²	0.36	2.73	4.76·10 ⁻²	0.39	0.24	5.65
AshDec	-	-	1.36	0.13	43.13	204.12	0.24	19.02	20.30	589.95
Mephrec	-	-	2.83	0.17	65.47	68.76	0.40	10.18	2.49	50.91
Leachphos	-	-	4.91	0.86	6.23	128.05	0.16	2.17	2.75	224.22
TSP Pot-trails	-	-	0.88	0.49	14.26	1.53	2.37·10 ⁻²	4.85	0.36	21.52
Average TSP	-	-	0.46	3.32	35.63	3.38	4.95·10 ⁻³	4.49	1.48	60.49

In the implementation of boundary conditions, the models differ from one another. In the kinetic model, the assumption immediately causes an average concentration in 20 cm of topsoil by atmospheric deposition and product application, although the concentration by diffuse inputs increases only at the soil surface (continuous plowing, topsoil as ideal mixed reactor). In the solute transport model, the input into the soil surface is by irrigation as concentration in rain water (no plowing). For the annual product application an excessive concentration in rain water for the day of fertilizer application is calculated from annual mass of the hazard and rain water of one day.

5.5 Data-quality of products

An overall problem is the small number of samples taken for hazard analysis. For an estimation of determined concentration of hazards and phosphorus the averaged concentration of minimum two measurements were taken, assuming that this average hazard concentration is to be determined in the product over 100 years. For three out of seven secondary fertilizers, no sufficient data were given for a mass balance of the process within the sewage treatment plant. Furthermore, additional to the hazard in product measurement, no source-sludge measurement was realized within the P-REX project, so no reliable “source-sludge-to-product-transfer-function” could be established.

It can be stated that the assumed concentrations of hazards for the struvite products (Pearl/ Struvia, AirPrex, Stuttgart and partly Gifhorn) are reliable, since many more measurements were done out of existing full-scale plants. Also the measurements of ash related products were realized on pilot-scale plants, since full-scale operations do not exist. In contrast to the measurements for struvite uncertainties concerning upscaling from pilot- to full-scale cannot be neglected for ash related products. Even though the struvite products have differences in hazard concentrations relatively to each other they are in the same order of magnitude.

By a combined source-sludge and product measurement or monitoring, these potential uncertainties can be removed. Furthermore, a monitoring through all seasons is needed, showing whether a process works with the same quality, when for example iron is used in winter to support the enhanced biological phosphorous removal during wastewater treatment. Additionally, it has to be evaluated if a process constantly develops a product with same product quality or if a product quality is dependent on local issues of wastewater and sludge quality or operational processes in a sewage treatment plant. For certain a distinction of hazard-ratios between struvite, sludge, several ash-related products and TSP can be established. Since the precipitation of struvite is a clean stoichiometric process, high hazard contaminations are most unlikely. The qualities of ash-related products are more dependent on the hazard contamination of the source material (sewage sludge / ash), since it is assumed that the processes deplete several heavy metals in a certain percentage related to the input material.

5.6 Exposure

5.6.1 Kinetic model by TGD

The analytical solution for basic equation of the kinetic model by TGD is given in eq. 6. (IHCP 2003 sect. 2.3.8.5, p. 79, eq. 51)

$C_{Soil} = \frac{D_{air}}{k} - \left(\frac{D_{air}}{k} - C_0 \right) \cdot e^{-k \cdot t}$				eq. 6
k	pseudo-first order rate constant for removal from topsoil	$[d^{-1}]$	(IHCP 2003 sect. 2.3.8.5, p. 82, eq. 56 ff.) or eq. 5	
C_{Soil}	concentration in soil	$[mg \cdot kg^{-1}]$		
D_{air}	atmospheric deposition flux per kg of soil	$[mg \cdot kg^{-1} \cdot d^{-1}]$	Table 22, Table 23	
t	time in days per year ($0 d < t \leq 365 d$)	$[d]$		
C_0	initial concentration for each year in soil	$[mg \cdot kg^{-1}]$		

The initial concentration (in eq. 7) for each year in soil is the sum of the concentration in soil of the 365th day of the previous year and the concentration in soil, which is annually discharged by product application.

$C_0(n) = \frac{m \cdot 10^{-1} \cdot mg \cdot g^{-1} \cdot ha \cdot m^{-2} \cdot d^{-1}}{DEPTH_{soil} \cdot RHO_{soil}} + C_{Soil}(n-1)$				eq. 7
m	Annual mass flow of a hazard in a product on ha soil by annual fertilizer application of 60 kg P2O5 per ha in one day	$[g \cdot ha^{-1} \cdot d^{-1}]$	Table 10	
$DEPTH_{soil}$	mixing depth of soil for agricultural use	$[m]$	0.2	
RHO_{soil}	Bulk density of soil	$[kg \cdot m^{-3}]$	(IHCP 2003 sect. 2.3.4., p. 44, eq. 18)	
$C_{Soil}(n-1)$	concentration in soil in year “n-1” on 365th day	$[mg \cdot kg^{-1}]$		
$C_0(n)$	initial concentration for year “n” in soil	$[mg \cdot kg^{-1}]$		

To estimate the $PEC_{topsoil}$ and to determine bio magnification effects on soil organisms an average concentration in soil over a time period of the first 30 days (toxicological tests) is calculated for each year. For human consumption an average concentration over a time period of the first 180 days (growing season) is calculated. The equation for this calculation is shown in (IHCP 2003 sect. 2.3.8.5, p. 81, eq. 54-55). In contrast to (IHCP 2003 sect. 2.3.8.5, p. 85, eq. 66) no regional background concentration is added afterwards. The background concentration is considered as initial condition C_0 ($n=0$) in calculation of C_{Soil} for the first year.

Regarding leachate, (IHCP 2003 sect. 2.3.8.6, p. 86, eq. 68) suggests to assume that groundwater concentration equals pore water concentration, following (IHCP 2003 sect. 2.3.8.5, p. 81, eq. 54-55) an averaging time of 30 days is also used. To avoid misunderstandings, this concentration is in leachate not in groundwater so in contrast to (IHCP 2003) $PEC_{leachate}$ is used instead. The equation for the concentration in leachate (IHCP 2003 sect. 2.3.8.6, p. 86, eq. 68) is modified for heavy metals in eq. 8.

$PEC_{leachate} = PEC_{pore\ water} = \frac{PEC_{soil}}{K_d}$			eq. 8
PEC_{soil}	Predicted environmental concentration in soil	$[mg \cdot kg^{-1}]$	(IHCP 2003 sect. 2.3.8.5, p. 81, eq. 54-55)
K_d	substance specific sorption constant	$[L \cdot kg^{-1}]$	Table 20; Table 21
$PEC_{leachate}$	Predicted environmental concentration in leachate	$[mg \cdot L^{-1}]$	

For model refinement regarding high soluble heavy metals Cd and Zn, the solute transport model is used. The detailed description and equations of this model are in chapter 9.5 in the annex.

5.6.2 Results and Discussion

The results of exposure assessment and the PNECs from hazard characterization are shown in the annex 9.5 and 9.7 in Figure 10 to Figure 23. Table 11 gives an overview on the figures in the annex in dependency on hazards, models and K_d -/pH-values.

Table 11: Overview on results of exposure assessment and PNECs from hazard characterization

Figure	Page	Hazards	Model	K_d -/pH-value
Figure 10	52	PCDD/Fs + dl-PCB, PAH (sum parameter)	Kinetic (TGD)	-
Figure 11	53	PAH (single substances, only for endpoint soil organisms)		-
Figure 12	54	As, Cr, Cu		-
Figure 13	55	Hg, Pb		-
Figure 14	56	Cd		pH 5; pH. 5.5; pH 6
Figure 15	57			pH 6.5; pH 7; K_d (RAR)
Figure 16	58	Ni		pH 5; pH. 5.5; pH 6
Figure 17	59			pH 6.5; pH 7; K_d (RAR)
Figure 18	60	Zn		pH 5; pH. 5.5; pH 6
Figure 19	61			pH 6.5; pH 7; K_d (RAR)
Figure 20	62	Cd	Solute transport (HYDRUS)	pH 5; pH. 5.5; pH 6
Figure 21	63			pH 6.5; pH 7; K_d (RAR)
Figure 22	64	Zn		pH 5; pH. 5.5; pH 6
Figure 23	65			pH 6.5; pH 7; K_d (RAR)

The graphs make obvious that the calculated concentrations in topsoil for both models (kinetic and solute transport model) show similar tendencies. Differences can be ascribed to various implementations of boundary conditions in both models. The simple and modified kinetic model by Technical Guidance Document is sufficiently enough for approaches of topsoil concentrations in this risk assessment.

Regarding the estimations of leachate concentrations a few critical notes could specify the approaches regarding the Technical Guidance Document. The PECs are in a magnitude that they will probably be reached, especially for low sorption rates. Depending on the K_d -value this PEC-magnitude will be reached at a future date but not in the observed time period the kinetic model calculates. Since retardation within the soil profile is not regarded in the kinetic model, the real PEC_{topsoil} is likely lower than the calculated PEC. For a general approach regarding risk assessment the calculation by TGD gives reliable results.

In case of reduced annual mass flows and low pH-values (e.g. Cd by Pearl/Struvia for pH 5 in the annex Figure 14 top), and consequently reduced topsoil and leachate concentrations, the results of the kinetic model are seen critically, due to the following points:

- High initial leachate concentration and following decrease in concentration is implausible
- Consequently to this decrease in concentration, the maximum concentration in the observed timespan calculated by TGD is in the beginning of simulation
- If this maximum concentration is considered in risk characterization, the calculated ratio will not characterize the product in any kind
- This means in terms of risk assessment the hazard concentration in the fertilizer is of minor importance because of high background concentrations, unless it does not exceed a certain level

For leachate concentrations the magnitude of PEC in both models is sufficient. By model refinement with HYDRUS-1D an additional spatial component is added compared to the just temporal modelling of the kinetic model. However, this hardly affects the risk characterization results.

The results of calculations for leachate¹⁰ (especially the calculated initial concentrations) were evaluated on measured values in literature. According to (Scheffer & Schachtschabel 2010) the cadmium and mercury flux for unpolluted agricultural sites was validated to 0.028 mg/m² and year. The zinc flux in leachate is listed with 3.8 mg/m² and year. The calculated initial fluxes by solute transport model are with a range of 0 to 0.1 mg/m² and year for cadmium (approximately 0,01 mg/m² and year for pH 5,5) and 0 to 25 mg/m² and year for zinc (approximately 2 mg/m² year for pH 6) in the same magnitude. For woodlands with lower pH-values than pH 5 (Scheffer & Schachtschabel 2010) cited measurements are at maximum 2 mg Cd/m² and year and 150 mg Zn/m² and year. None of these high fluxes is reached at any simulated pH-value for any product. Maximum for cadmium at pH 5 and average TSP application is about 0.3 mg/m² and year. For zinc the maximum at pH 5 and raw ash application is about 75 mg/m² and year. A comparison of leachate concentrations from literature with calculated concentrations is shown in Table 12.

According to Table 12 the calculated leachate concentrations for chromium and mercury and the initial concentrations of copper and nickel are significantly lower than values in literature. In comparison with the values from literature, lead is showing good accordance. Cadmium's and zinc's initial concentration is slightly higher in this study than in literature but in the same order of magnitude. By using different K_d -values for cadmium, nickel and zinc in the selected pH-range between pH 5 and pH

¹⁰ Discussion on topsoil concentrations see chapter 5.3.2

7, these values for initial concentration fit quite well with the values from literature. Nevertheless, there is a great level of uncertainty regarding leachate concentration prognoses and transferability of measured data to general agricultural ecosystems, since site-specific concentrations and parameters have a major influence.

Table 12: Average heavy metal discharge from agricultural ecosystems

Heavy metal	Leachate conc. [$\mu\text{g/L}$] according to (Bannick 2001)	Simulated initial leachate conc. [$\mu\text{g/L}$] by kinetic model for K_d -values from risk assessment reports	Range of maximal leachate conc. [$\mu\text{g/L}$] by kinetic model with including all used K_d -values
Cd	0.14	0.28	0.13...1.81
Cr	4.6	0.26	0.30...2.63
Cu	4	0.81	1.11...10.73
Hg	0.14	0.0014	0.0021...0.0053
Ni	8.9	0.87	1.00...11.77
Pb	0.28	0.27	0.33...0.49
Zn	19	55	33...440

5.7 Evaluation of results regarding Cd- and Zn-distributions between precipitated and ionic species (MINTEQ-software)

For evaluation of possible high leachate concentrations and an exceeding of the PNEC regarding leachate, the results by kinetic and solute transport model are evaluated with a precipitation model using the Visual MINTEQ-software. The saturation concentration is calculated for the relevant heavy metals for a system with anions and expected anion concentrations in agricultural soil in Table 13.

Table 13: Expected anions and concentrations (Lindsay 1979) in agricultural soil for calculation of saturation concentration for relevant heavy metals by Visual MINTEQ-software

Anion	Expected concentration (Lindsay 1979) in agricultural soil [mol/L]
Carbonate, hydrogen carbonate or carbon dioxide	$7.54 \cdot 10^{-3}$ (100-fold atmospheric partial pressure of carbon dioxide)
Chloride	$1.00 \cdot 10^{-3}$
Nitrate	$1.00 \cdot 10^{-3}$
Phosphate or hydrogen phosphates	$1.00 \cdot 10^{-5}$
Sulphate or hydrogen sulphate	$1.00 \cdot 10^{-3}$

For calculation of saturation concentration for various pH-values (pH 5 to 7 in 0.5-pH-steps) an extensive heavy metal concentration of 1 mol Cd or Zn/L is used. The cadmium or zinc concentrations, which are still soluble under this condition, are assumed as saturation concentration for this system.

This concentration is for each selected pH-value compared to the products and atmospheric boundary concentration in infiltration water. Since there is a dilution in additional soil-water expected, it is the highest possible liquid concentration.

- For the annual approach, the annual heavy metal mass flow per square meter soil by product application and annual atmospheric deposition are summed. This sum is divided through annual infiltration water of 175 L/m².
- Since the product application is realized on one day (like in the kinetic and in solute transport model), the annual heavy metal mass flow by product application in one day and the atmospheric deposition of one day are summed for the daily approach. This sum is divided through infiltration water of one day (similar the implementation of boundary conditions in solute transport model in eq. 10 and eq. 11).

By comparing saturation concentration to the annual or daily approached concentration in infiltration water, it can be clarified, whether precipitation takes place. In case the concentration in infiltration water is below saturation concentration, the total amount of heavy metal is expected to be dissolved. By exceeding of the saturation concentration, the heavy metal amount equal to saturation concentration is dissolved and the amount above this concentration is precipitated.

Since cadmium and zinc are the relevant hazards regarding leachate, calculation of saturation concentration is done for these two metals. The results for various pH-values are shown in Table 14.

Table 14: Saturation concentrations for cadmium and zinc for various pH-values for the system with anions and anion concentrations in Table 13

Metal	Saturation concentration	pH 5	pH 5.5	pH 6	pH 6.5	pH 7
Cd	[mol/L]	$6.60 \cdot 10^{-3}$	$5.84 \cdot 10^{-4}$	$5.87 \cdot 10^{-5}$	$6.15 \cdot 10^{-6}$	$7.14 \cdot 10^{-7}$
	[mg/L]	742.01	65.70	6.60	0.69	0.08
Zn	[mol/L]	$1.67 \cdot 10^{-1}$	$8.58 \cdot 10^{-3}$	$7.19 \cdot 10^{-4}$	$7.47 \cdot 10^{-5}$	$9.02 \cdot 10^{-6}$
	[mg/L]	10929.57	560.89	47.03	4.88	0.59

Comparing these saturation concentrations with “annual” and “daily” cadmium and zinc concentrations (mass flow per square meter in Table 23 and Table 10), there is no exceeding of saturation concentration on annual basis for cadmium or zinc for any pH-value. The maximal concentration for cadmium by average TSP is $1.89 \cdot 10^{-8}$ mol/L calculated on annual basis, for raw ash’s zinc it is $6.99 \cdot 10^{-6}$ mol/L. The excessive “daily” concentration in infiltration water partly precipitates (see Figure 5).

For cadmium precipitation only takes place for highly cadmium-contaminated products above pH 6.4. For zinc precipitation takes place for all products except “atmospheric deposition only”, whereby the first product precipitates above pH 5.7 calculated on daily basis.

Partly depending on pH-value precipitation is relevant within the first months of a year. After product application depending on product contamination, a bulk of cadmium or zinc can precipitate. Through dilution by rain over the year, this solid phase is dissolved. By this effect especially for contaminated products and only for high pH-values, retardation by precipitation can be added additionally to retardation by sorption. On a long-period-scale over 100 years, this effect is not significant to any major changes in diagrams of cadmium or zinc in the appendix Chapter 9.5 or 9.7. Regarding the initial cadmium or zinc concentration and their effect on precipitation it can be stated, that these concentrations are not relevant either, since there is no permanent exceeding of saturation

concentration concerning any product application or pH-value even for the surface concentrations in the solute-transport model.

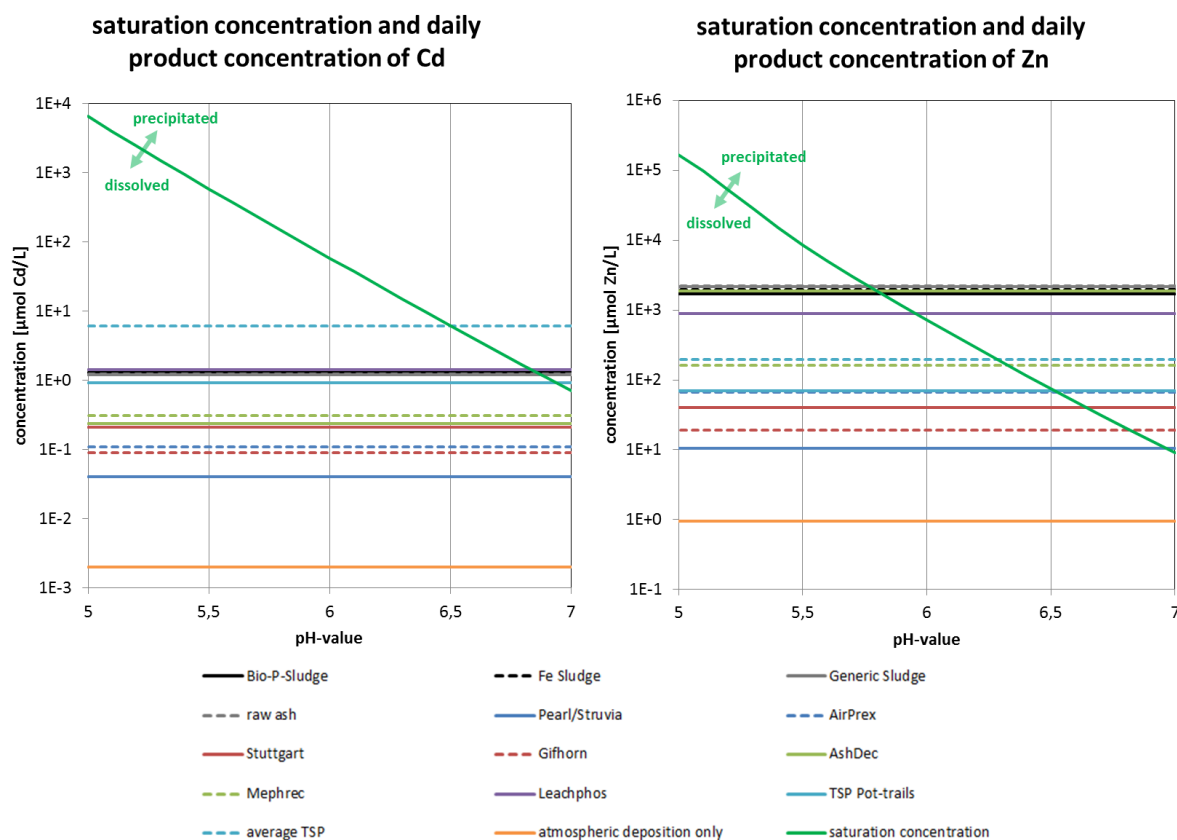


Figure 5: Saturation concentration and product concentration including daily atmospheric deposition calculated on infiltration water of one day in selected pH-range for cadmium and zinc

5.8 Sensitivity analysis on exposure assessment

Concluding the uncertainties mentioned above

Table 16 gives a qualitative overview of parameters and assumptions, their uncertainties, their influence on results. For a rough quantification of uncertainties a likelihood scale according to (IPCC 2010) is used, shown in Table 15.

Table 15: Likelihood scale according to (IPCC 2010) for rough quantification of uncertainties

Term	Likelihood of the Outcome according to (IPCC 2010) used in Chapter 6 and 7	Likelihood of the Outcome used in Table 16 reaching the calculated PEC, RCR
Very likely	90 – 100 % probability	< ± 10 %
Likely	66 – 100 % probability	< ± 33 %
About as likely as not	33 – 66 % probability	< ± 66 %
Unlikely	0-33 % probability	< ± 90 %
Very unlikely	0-10 % probability	-

Table 16: Semi-quantitative overview of parameters, their uncertainties, their influence on PEC and their influence on exceeding the PNEC

Parameter/ Assumption	Uncertainty/ Validation of data	Likelihood on reaching the PEC as calculated by parameter variation	Likelihood on reaching the RCR as calculated by parameter variation
Soil-hydraulic (Water flow) parameters	High variation <ul style="list-style-type: none"> • average data for sandy soil being used • site-specific influences had to be considered 	Likely	Very likely
Rain rate/ infiltration rate	High variation: <ul style="list-style-type: none"> • rain-rate in Europe approx. 400-1000 mm • infiltration rate depending on soil type 	Unlikely	About as likely as not
K_{OW}-/K_{OC}-value (organic substances)	Low variation in literature	Likely	Very likely
HENRY's law constant (organic substances)	Low variation in literature	Likely	Very likely
K_d-value (heavy metals)	High variation in literature <ul style="list-style-type: none"> • several dependencies • soil-specific influences 	Unlikely	About as likely as not
Quality of data for atmospheric deposition	High variation in literature <ul style="list-style-type: none"> • no accurate assumptions for the future are possible 	<ul style="list-style-type: none"> • Likely (for contaminated products and all hazards except for PAH) • Unlikely (for "clean" products e.g. struvites and most hazards) 	<ul style="list-style-type: none"> • Likely (all hazards except for Zn regarding groundwater) • About as likely as not (for Zn regarding groundwater)
Quality of product-data	<ul style="list-style-type: none"> • High variation in sewage sludge, its ashes (Krüger & Adam 2014) and partly in ash-related products • Low variation for struvite 	<ul style="list-style-type: none"> • Unlikely for sewage sludge, its ashes and partly ash related products • Likely for struvite 	<ul style="list-style-type: none"> • About as likely as not for sewage sludge, its ashes and partly ash related products, especially for Zn • Very likely for struvite
Initial concentrations	High variation between several sites, depending on natural weathering and parent rock material	Unlikely	<ul style="list-style-type: none"> • About as likely as not • Unlikely for Zn regarding soil-organisms
neglecting precipitation of heavy metals, assuming ionic species are dissolved or adsorbed	Not particularly relevant for Cd and Zn (see Chapter 5.7), relevant for non-mobile metals (e.g. As, Cr, Cu, Hg, Pb)	<ul style="list-style-type: none"> • Very likely for Cd, Zn • About as likely as not for As, Cr, Cu, Hg, Ni and Pb 	Likely
Halved fertilizer amount (30 kg P₂O₅/ha-yr instead of 60 kg P₂O₅/ha-yr)	Depending on output by harvesting and phosphorus storage in soil	Unlikely	About as likely as not

In summary the most important parameters regarding uncertainties regarding risk characterization are:

- K_d-values for exposure of heavy metals
- rain and infiltration rate (influence of soil type)
- atmospheric deposition of metals/ POP
- Range in quality of sewage sludge, its ashes and consequently ash related products
- exchangeable heavy metal contents in arable land
- fertilizer amount (demand-actuated fertilizer application)

6 Risk characterization

The risk characterization ratio is calculated from quotient PEC to PNEC for each endpoint, each hazard and product (IHCP 2003 sect. 5.1, p.172, Table 32). Approaching a worse case, the maximal PEC for each product and endpoint is used for risk characterization, the results of these calculations are shown in Table 24 to Table 26 (see annex).

Following the process of risk management, risk reduction measures are required especially when the ratio is above one. A risk quotient of 1 is according to (van Leeuwen & Vermeire 2007) the maximum permissible level. Below this value risk reduction is still recommended. Only if the PEC/PNEC-ratio is below 1 % the risk is at a negligible level (van Leeuwen & Vermeire 2007). Risk can be classified in “unacceptable risk” ($RQ > 1$), “risk reduction required” ($0.01 < RQ < 1$) and “negligible risk” ($RQ < 0.01$) (van Leeuwen & Vermeire 2007). Since this wording is sharp and may be misunderstand a classification into “risk reduction required/demand for action” ($RQ > 1$), “risk reduction recommended/ ALARA¹¹ principle” ($0.01 < RQ < 1$) is used. The ranges of hazard- and endpoint-specific ratios are shown in Figure 6 to Figure 8 and classified in “risk reduction required/demand for action”, “risk reduction recommended/ ALARA principle” and “negligible risk”.

1. Endpoint soil organisms (see Figure 6).

- a. The calculation for PAHs as sum parameter indicates a risk. By model refinement and calculation of single substances of PAHs, this concern turned out to be negligible.
- b. For zinc by application of the products Bio-P sludge, Fe sludge, generic sludge, raw ash or AshDec for pH-values above pH 6 an exceeding of the PNEC cannot be excluded. Below pH 6 the risk ratio for these products is below 1, but measures for risk reduction are still recommended.

2. Endpoint humans (see Figure 7)

- a. No exceeding of the PNEC was calculated.
- b. The highest risk characterization ratios are for PCDD/F and dl-PCB (0.3) regarding organic substances and for cadmium (0.5) regarding heavy metals by using worst-case assumptions for calculation.

3. Endpoint groundwater (see Figure 8)

- a. Significant higher risk characterization ratios for the heavy metals cadmium, copper, nickel and zinc are calculated compared to the other endpoints.
- b. Depending on metal and K_d -value the PNEC is considerably exceeded.
- c. Especially for zinc the PEC exceeds the PNEC for most of the products in the whole selected pH-range
- d. Regarding cadmium the PEC exceeds the PNEC for all product applications and low pH-values less than pH 6.

¹¹ ALARA: as low as reasonable achievable

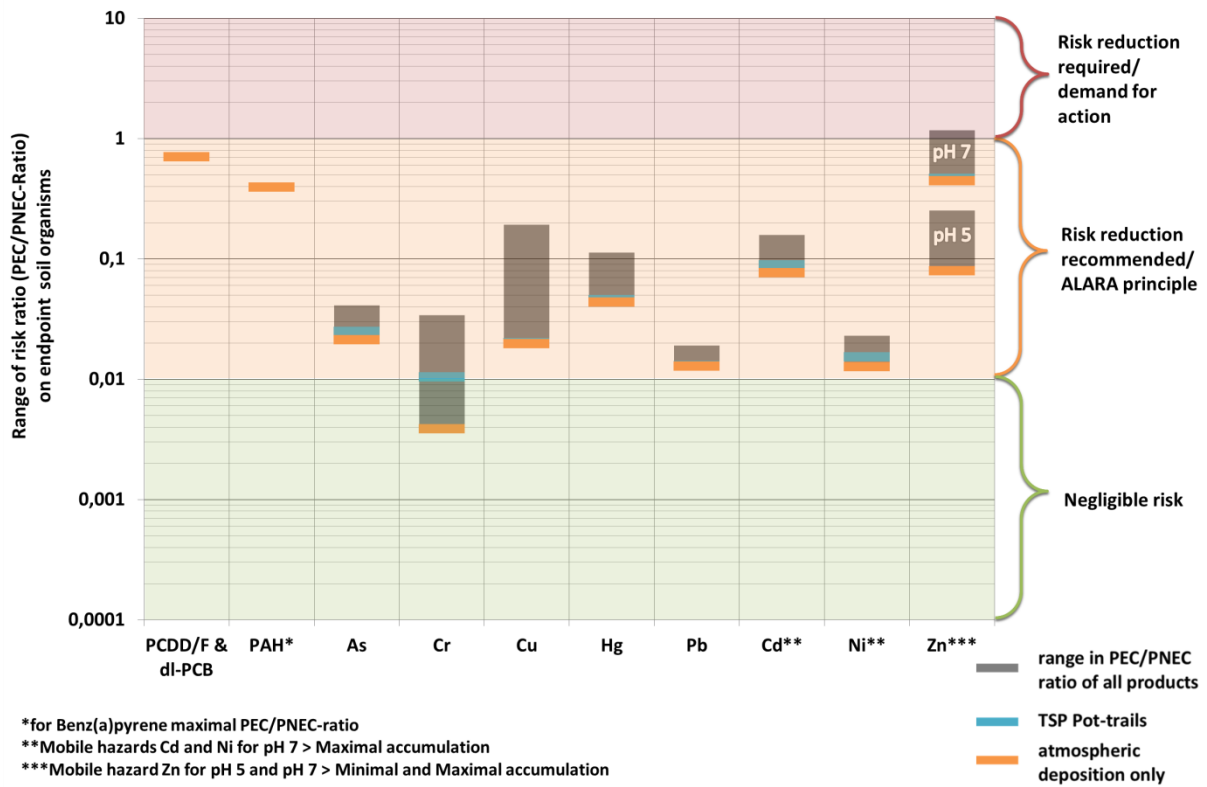


Figure 6: Range of Risk Characterization Ratio (PEC/PNEC-Ratio) on particular hazards for the endpoint soil organisms, TSP Pot-trails and atmospheric deposition for comparison

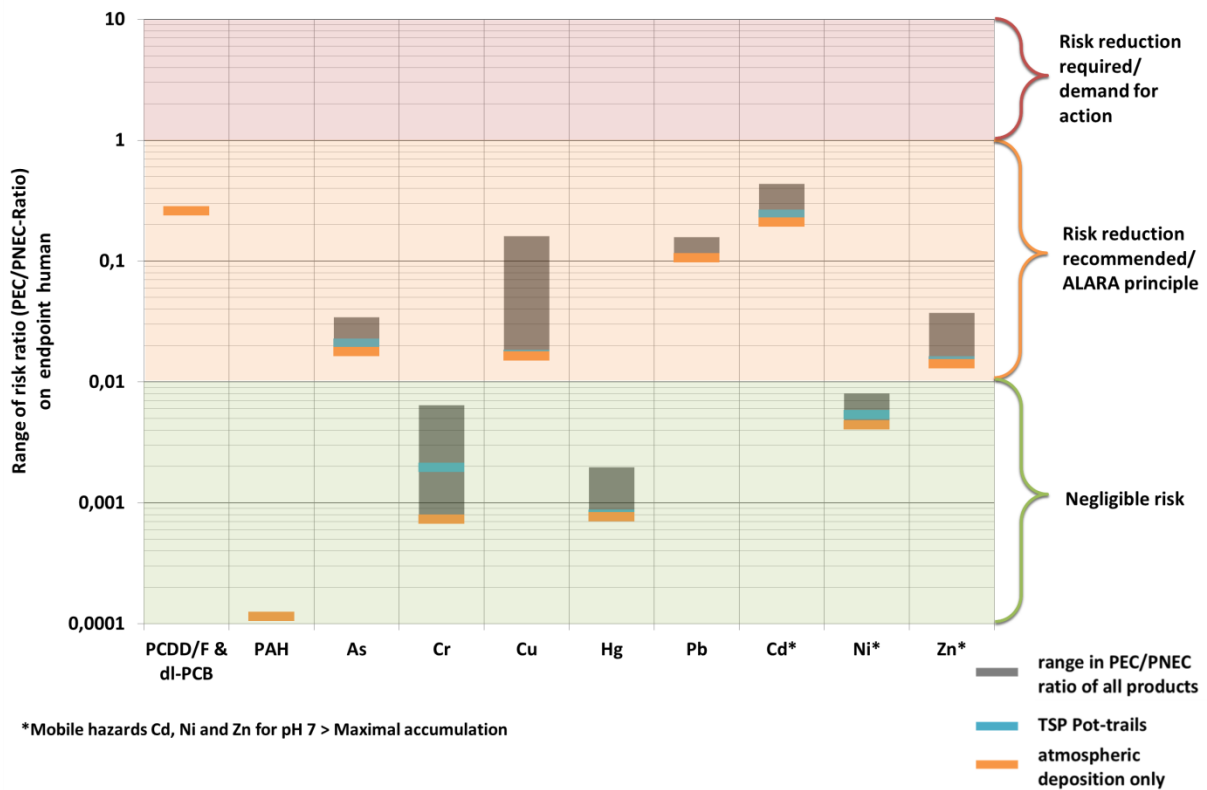


Figure 7: Range of Risk Characterization Ratio (PEC/PNEC-Ratio) on particular hazards for the endpoint human, TSP Pot-trails and atmospheric deposition for comparison

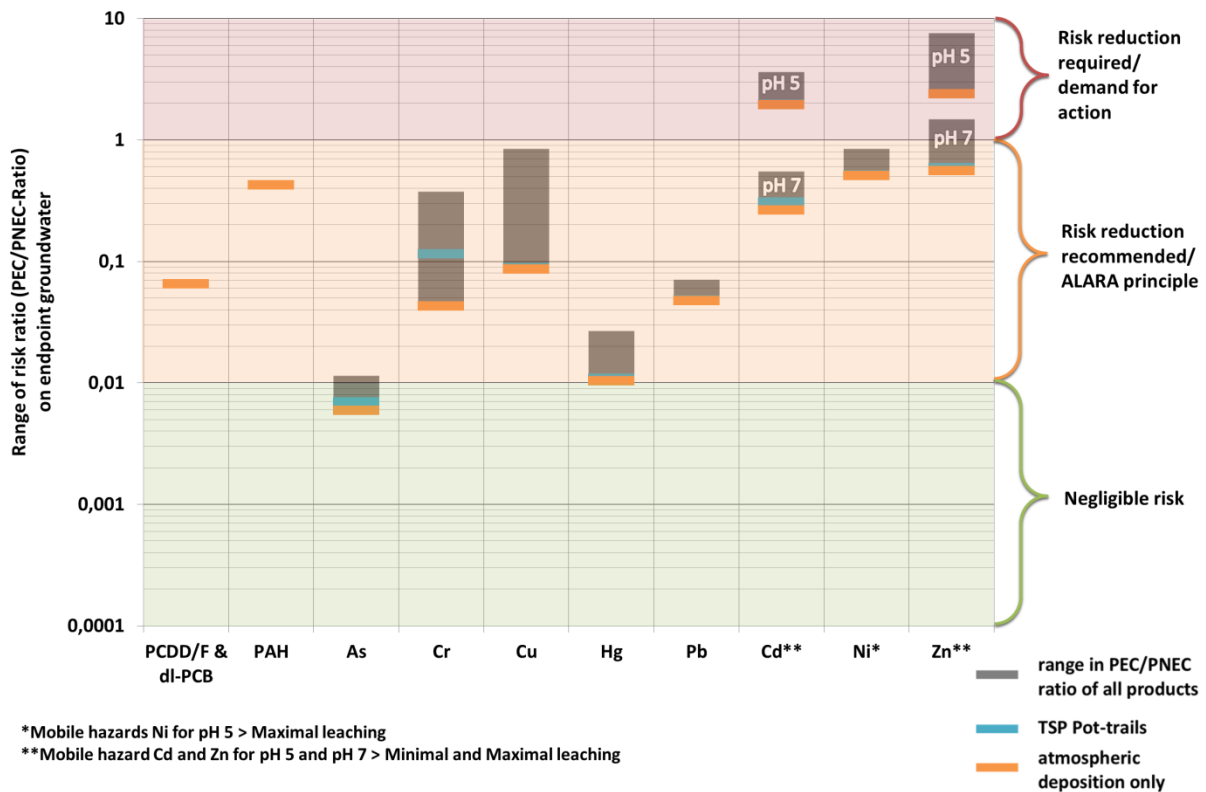


Figure 8: Range of Risk Characterization Ratio (PEC/PNEC-Ratio) on particular hazards for the endpoint groundwater, TSP Pot-trails and atmospheric deposition for comparison

The risk ratios of secondary phosphates are in the same magnitude as TSP. Against the background of made assumptions, there are no unacceptable risks caused by the organic substances, arsenic, chromium, copper, mercury, nickel or lead.

Besides cadmium and zinc, many hazards entail endpoint-specific risk quotients above the negligible level. Based on the made assumptions (e.g. worst-case assumptions for calculation $PNEC_{human}$ especially for lead or neglecting precipitation for heavy metals besides cadmium and zinc) the quotients could be reduced by further model refinements in many cases. Risk is on a negligible level concerning humans for PAHs, chromium and mercury.

For the endpoint groundwater all products exceed the PNEC for low pH-values regarding cadmium and zinc (see Figure 8) at some time point in simulation. Since in both models the concentration is reduced for uncontaminated products in the future (see Figure 14, Figure 18, Figure 20 and Figure 22 in the annex) a distinction between the products is reasonable. Regarding cadmium only average TSP application leads to significantly higher risk ratios. Regarding zinc a significantly higher risk ratio can be identified for all three types of sludge, raw ash, AshDec and Leachphos application.

In case of low-contaminated products, the exceeding of PNEC is often a result of high past or even present atmospheric deposition. In these cases a risk by product application cannot be excluded, although the product-quality is not responsible for exceeding the PNEC. For an effective minimization of risks a reduced diffuse discharge into the atmosphere would be necessary in contrast to any process development refining the product.

All secondary phosphates have a lower impact on groundwater risk ratio regarding cadmium compared to atmospheric deposition. For the Leachphos product the influence is approximately 9 % even low compared to average TSP with almost 50 %. For AshDec, Mephrec and struvite products, this impact is within the negligible amount of 1 %.

Regarding zinc conventional phosphorus fertilizer showed much lower concentrations. Especially the product all three types of sludge, raw ash and AshDec have a major impact (approximately 60 %) compared to atmospheric deposition. Similar to cadmium, the influence of struvite on the risk characterization ratio compared to atmospheric deposition is almost negligible for zinc and the other heavy metals (exception chromium).

6.1 Product comparison

Since there are many assumptions considered in the calculated risk ratios, the product quality regarding heavy metal and organic substance loads per phosphorus is not accurately shown in the risk ratios. Focusing on this product quality and in comparison to diffuse discharge by atmospheric deposition into the ecosystem, an assessment based on phosphorus specific hazard loads makes differences between single products more obvious. This is done in Figure 9, where the results of Table 10 are plotted normalized. The mass flow of each hazard is compared to hazard mass flow of atmospheric deposition. It is normalized to 1 for atmospheric deposition as status-quo.

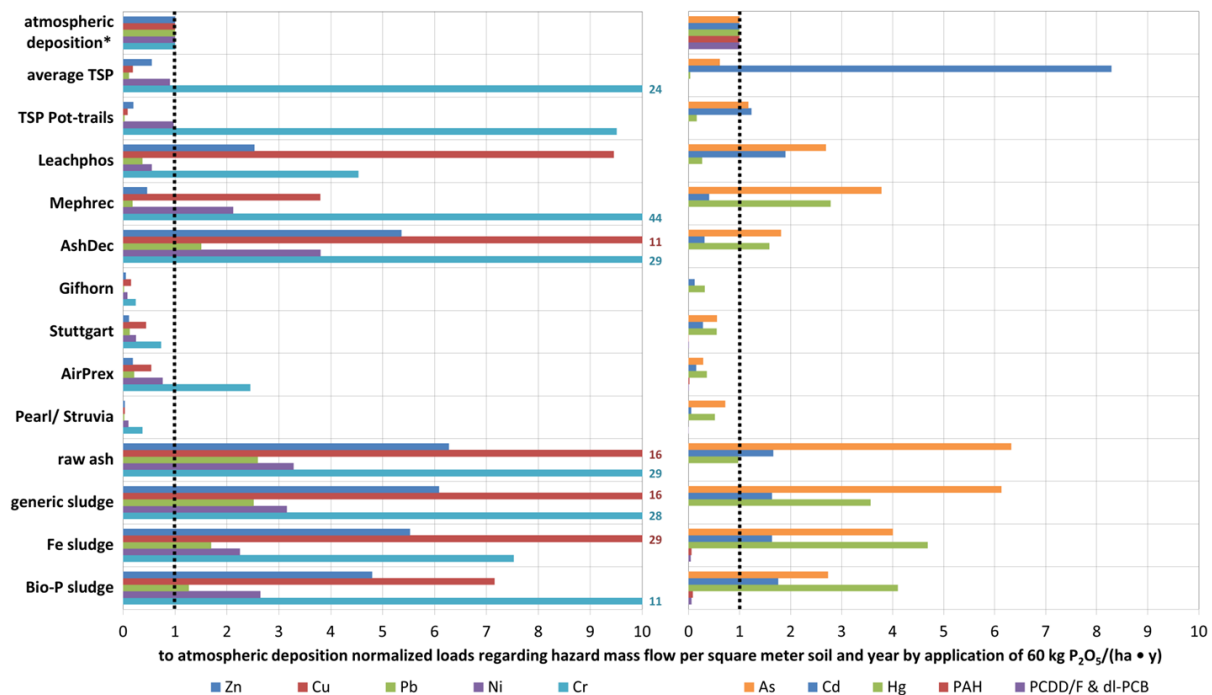


Figure 9: Ratio of average phosphorus related mass flow per square meter soil and year for hazards; for atmospheric deposition all mass flows set to 1; for products proportional ratio

- In comparison to the annual load of atmospheric deposition, almost all products have elevated chromium contents.
- In case of sludge and ash-related products copper seems a relevant hazard compared to atmospheric deposition.

- For average TSP, cadmium is the relevant hazard in comparison to atmospheric deposition. In contrast, the copper, mercury and lead concentrations in mineral phosphorus fertilizers are significantly lower than in sludge or any secondary fertilizer.
- Persistent organic pollutions (PCDD/F + dl-PCB and PAH) are very likely brought into soil by atmospheric deposition. The discharge by sludge or struvite fertilizer application is quite low compared to diffuse sources of persistent organic pollutions.

Struvite shows in general the lowest hazard concentrations. The annual input by struvite application is below the input by atmospheric deposition with exception of chromium in the AirPrex product. The higher heavy metal contents in the AirPrex product compared to the other struvites can be accredited to procedural manner. Crystallization in the Pearl/ Struvia, Stuttgart and Gifhorn processes takes place directly in the process water after dewatering; in contrast the AirPrex product recovery takes place in sludge after digestion and before dewatering. Although crystallization is a chemical clean stoichiometric process, it can be expected that by the over stoichiometric dosage of magnesium chloride for precipitation of struvite in the airlift reactor more hazards are transferred into the product. Beside the low hazard concentrations related to dry mass of all struvite products, the high phosphorus content of struvite affects the Figure 9. The content of total or mineral acid soluble phosphorus is with approximately 20-30 % P_2O_5 very high for secondary phosphorus fertilizers.

In comparison to struvite, all ash related processes have significantly higher heavy metal loads. The AshDec process significantly reduces arsenic, cadmium, mercury (if it is not removed in mono-incineration already) and lead. No or only minor reduction of chromium, copper, nickel or zinc is achieved. Especially the high zinc load within the product is problematic against the background regarding recycling in agriculture.

The Mephrec product has, compared with other ash related products, the lowest cadmium and zinc content. With focus on the expected risks regarding these two metals in leachate, it is the best ash related product examined in this study. Since the data in the inventory of this study are from a lab-plant of 2009 and the process is evaluated building a demonstration plant for 2015 in Nuremberg, the heavy metal concentrations of the process are probably changing in the future. Concerning the high chromium per phosphorus load (see Figure 9), it cannot be clarified if this is a result of the process, reactor or source material.

Regarding the product quality of Leachphos compared to other secondary phosphates an average overall heavy metal load was assessed in the inventory. Compared with other ash-related processes, Leachphos has a high phosphorus amount (comparable to the amount of phosphorus in struvite).

6.2 Derivation of critical concentrations in phosphorus fertilizers for cadmium and zinc

To reach the maximum permissible level in leachate ($PEC_{leachate} = PNEC_{leachate}$) risk reduction measures are required. Based on an infiltration rate of 175 mm/ yr an annual surface flux of maximum 0.8 g Cd/(ha · yr) and 100 g Zn/(ha · yr) is necessary to reduce risks for groundwater to the maximum permissible level. By input of this annual surface flux for cadmium and zinc the maximum permissible level would also be reached for soil organisms and humans within 100 (and even more) years of application.

In comparison to this “critical flux” of 0.8 g Cd/(ha · yr) and 100 g Zn/(ha · yr) the assumed atmospheric deposition in this study based on literature for the future accounts 0.4 g Cd/ (ha · yr) and 110 g Zn/(ha · yr). This comparison underlines the required reduction of zinc from atmospheric deposition. It should be noted, that the atmospheric flux for zinc is from a 3-year average from 2001 to 2003, whereby data more up to date should be generated and zinc should be included into the EMEP-Monitoring program.

Neglecting the diffuse sources, based on these fluxes critical concentration for phosphorus fertilizers can be calculated using the assumption of an annual restock of phosphorus storage of 60 kg P₂O₅/(ha · yr). This critical concentrations based on PNEC_{leachate} amounts for cadmium 15 mg Cd/kg P₂O₅ or 34 mg Cd/kg P and for zinc 1.7 g Zn/kg P₂O₅ or 3.9 g Zn/kg P.

For derivation of these critical concentrations neither the solubility of metals in the fertilizer or in soil nor cadmium or zinc by atmospheric deposition was considered. These concentrations give simplified toxicological limits for fertilizers depending on P₂O₅-content.

In comparison with limits by German law and current discussions on the European level, the derived critical concentrations are below current limits in German fertilizer ordinance (DüMV), German sewage sludge ordinance (AbfKlärV) or the currently discussed limits regarding European Union Fertilizer Regulation in Table 17 (BMELV 2012), (BMU 1992), (Embert 2014).

Table 17: Current regulations for cadmium and zinc in fertilizers or sewage sludge by law in Germany and discussed limits on the European level

Limits by law	Cadmium	Zinc
DüMV (BMELV 2012)	1.5 mg/kg for P ₂ O ₅ -content above 5 %: 50 mg/kg P ₂ O ₅	None Labelling value 1000 mg/kg
AbfKlärV (BMU 1992) Only if soil has limited heavy metal content sewage sludge application is allowed	10 mg/kg For soil-pH-value beneath pH 6: 5 mg/kg	2500 mg/kg For soil-pH-value beneath pH 6: 2000 mg/kg
EU Fertilizer Regulation (Embert 2014) in discussion Dependent on kind of fertilizer (mineral/organic e.g.)	1.5-3.0 mg/kg for P ₂ O ₅ -content above 5 %: 20-60 mg/kg P ₂ O ₅	None for mineral fertilizers 600 mg/kg for organic fertilizers

The limit value for cadmium in DüMV of 1.5 mg/kg is for phosphorus fertilizers irrelevant. In fact the limit of 50 mg/kg P₂O₅ obtains for phosphorus fertilizers. On European level a cadmium limit between 20-60 mg/kg P₂O₅ is discussed. Based on the critical limit derived in this study a concentration of 15 mg Cd/kg P₂O₅ would be reasonable.

In case of zinc, no “limit value” is set in DüMV. This is due to discussions whether zinc is apprehended as micronutrient or hazard. The on European level discussed limit for zinc of 600 mg/kg for organic fertilizers is a positive advancement against the background of the toxicological derived concentration. Based on assumptions in this study a phosphorus specific critical load for zinc in phosphorus fertilizers should be included in the discussion of limit values. Also a limit value for zinc has to be established for all phosphorus fertilizers, whereby it does not matter if it is a mineral or an organic fertilizer.

It should be noted, that even if there is a toxicological justification; derivation of limit values is part of the risk management process and besides potential risks, economic and practicable issues have to be considered.

7 Conclusion

7.1 Summary

The used models in exposure assessment (kinetic model by TGD and solute transport model by HYDRUS) differ slightly in results by using the same or similar assumptions. None of the model-refinements leads to a fundamental different conclusion regarding risk characterization ratios.

High uncertainties in assumptions are regarding assumed parameters for water flow and site-specific influences of soil-physical and –chemical parameters on partition sorption constants. These parameters can be refined by local exposure assessment on particular sites.

The boundary conditions regarding atmospheric deposition and hazard-to-phosphorus loads of products have major impact on the risk ratios and conclusions. To clear up uncertainties given by these boundary conditions an intensive monitoring for atmospheric deposition of substances and for the concentrations of hazardous substances in soil, sludge, primary and secondary phosphorus fertilizers are recommended. A reduction of atmospheric deposition of the selected hazards would be reasonable. In case of zinc this reduction is required to protect groundwater from potential risks. Furthermore, the inputs by atmospheric deposition exceed the annual input by struvite fertilizer application for almost all selected substances.

Against the background of the made assumptions cadmium and zinc are hazards which are of concern. No unacceptable risks had been calculated for PCDD/F and dl-PCB, PAH, As, Cr, Cu, Hg, Ni or Pb. Nevertheless for most of these substances risk reduction measures regarding at least one endpoint are recommended.

- Summarizing the assessment regarding the endpoint soil organisms, an exceeding of the PNEC for zinc and soils with a pH-value about 7 is about as likely as not for application of sewage sludge, its ash and ash-based products with worse Zn-depletion. For struvite and conventional fertilizers (e.g. TSP) an exceeding of the PNEC for zinc is unlikely. Furthermore an exceeding of the PNEC regarding the endpoint soil organism for the other observed hazards is unlikely.
- Summarizing the assessment regarding the endpoint human, an exceeding of the PNEC for any hazard and product is unlikely.
- Summarizing the assessment on the endpoint groundwater, an exceeding of the PNEC for cadmium and zinc for soils with a pH-value around 5 and all products is very likely. For cadmium and soils with a pH-value around 7 an exceeding of the PNEC for groundwater is unlikely. For application of sewage sludge, its ash and ash-based products with worse Zn-depletion, an exceeding of the PNEC for zinc and soils with a pH-value around 7 is likely, for the other products about as likely as not. Furthermore an exceeding of the PNEC regarding the endpoint groundwater and the other observed hazards is unlikely.

7.2 Recommendations and Outlook

From the selected hazard- and endpoint-specific risk characterization ratio a few recommendation regarding risk assessments for agricultural issues (especially the use of phosphorus fertilizers) in the future can be given:

- Regarding the ecological assessment for soil organisms, zinc is the relevant parameter to assess at first on background of zinc's lithogenic background concentration. Regarding organic substances 2,3,7,8-TCDD showed the highest potential to cause an ecological risk.
- For assessing health risks for humans, cadmium is the relevant heavy metal, since accumulation over the system soil-plant-human had been selected. Besides cadmium 2,3,7,8-TCDD can be seen as indicator of human health risks for the group of organic hazards.
- Regarding potential threats to groundwater, definitely the highly soluble heavy metals cadmium and zinc had to be considered as best indicators for an estimation of risks. Particularly on this endpoint the effect of atmospheric boundary condition seems relevant for long-term assessments. The potential of the observed organic hazards to cause risks can be assumed at least one magnitude lower. Out of the organics the PAH Flouranthene seems most problematic since this PAH has the highest water solubility of selected organic hazards.

By comparison of hazard concentrations a relative risk ranking of the products can be achieved. In principle lower concentrations reduces risk. In summary, struvite can be considered as high quality phosphate fertilizer, so an extensive struvite recovery and recycling in agriculture can be promoted. Considering sludge or TSP application as status-quo in agriculture, struvite application instead reduces risks regarding the selected hazards. Considering ash related processes an improvement regarding heavy metal depletion is in some cases advisable.

Regarding the issue of certification and implementation of secondary phosphate fertilizers into fertilizer legislation, not only the hazardous content is of importance. The product has to be classified according to fertilizer legislation (European Commission 2003 p.19 sect. A2). Beside TSP none of the observed products in this study is certified as a phosphorus fertilizer (European Commission 2003). This European Fertilizer Legislation is, as mentioned, amended in 2015. Thereby secondary phosphate fertilizers from sewage treatment will be included into the legislation. For products with high dependency on the raw materials a certification (also REACH-registration) will be difficult. For products with a defined composition, such as struvite or Ca-P out of technical phosphoric acid from sewage sludge ash, a certification and integration into fertilizer legislation is more likely.

Apart from the relative risk ranking and issues of certification and legislation a general measure for risk reduction in practice can be suggested: A demand-actuated (restock-orientated) fertilizer application may be advisable. There is no need for phosphorus fertilizer application, when the phosphorus storage in soil is sufficiently filled with plant available phosphorus or sufficiently enough phosphorus from soil is mineralizing within a short time-frame into a plant available form. As further consequence the input of hazards is reduced due to a demand-actuated fertilizer application. Stricter legislative limits for particular hazards and effective high quality fertilizers help to ensure fertilizer quality and reduce risks. Nevertheless, sufficiency of fertilizer-use in

agriculture is in terms of risk reduction and with respect to a responsible handling of limited resources the area needing the most improvement.

8 Literature

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9 Annex

9.1 Safety-parameters and BCF for approach of PNEC for endpoint humans

Table 18: Safety parameters for substances regarding human consumptions

Substance	Safety parameter					(Approach of) Bio-concentration-factors		
	Safety parameter	Value	Unit	Source	TDI via food = 1/2 TDI [µg/d]	log K _{ow}	BCF [(µg/kg) _{plant} · (µg/kg) _{soil} ⁻¹]	Source
PCDD/F & dl-PCB	Guideline level	1	pg WHO-TEQ/(kg bw·day)	(BfR 2012)	$3.5 \cdot 10^{-5}$ WHO-TEQ	6.46	0.007	(Becker et al. 2010)
PAH ¹²	BMDL-Benchmark	0.34	mg/(kg bw·day)	(EFSA 2008)	11900	5.12	0.04	(U.S. EPA n.y.)
As	BMDL-Benchmark	0.3	µg/(kg bw·day)	(EFSA 2009b)	10.5	-	0.014	(EFSA 2009b) ¹³
Cd	Tolerable Weekly Intake	2.5	µg/(kg bw·week)	(EFSA 2009a)	12.5	-	0.13	(VKM 2009)
Cr	Guideline level	1	mg/day	(EFSA 2006)	500	-	0.17	(VKM 2009)
Cu	Upper Intake level	5	mg/day	(SCF 2003a)	2500	-	0.26	(VKM 2009)
Hg	Tolerable Weekly Intake	4	µg/(kg bw·week)	(EFSA 2012)	20	-	0.013	(VKM 2009)
Ni	Tolerable Daily Intake	22	µg/(kg bw·day)	(WHO 2005b)	770	-	0.06	(VKM 2009)
Pb	Tolerable Weekly Intake	25	µg/(kg bw·week)	(VKM 2009)	125	-	0.0009	(VKM 2009)
Zn	Upper Intake level	25	mg/day	(SCF 2003b)	12500	-	0.17	(VKM 2009)

¹² Reference substances Flouranthene

¹³ No direct BCF for plants available. According to EFSA (2009b) Scientific Opinion on Arsenic in Food - EFSA Panel on Contaminants in the Food Chain (CONTAM). European Food Safety Authority a maximum value for BCF of $1,390 (\mu\text{g}/\text{kg})_{\text{plant}} \cdot (\mu\text{g}/\text{kg})_{\text{soil}}^{-1}$ for a not specified organism, furthermore if arsenic is accumulated in the plant only an amount of 1 % is transferred to the fruit.

9.2 Substance-specific parameters for organic substances

Table 19: For calculations selected persistent organic pollutions and their specific parameter and calculated pseudo-first order rate constants according to (IHCP 2003)

Hazard	log K _{OW} [10 ^(L/kg)]	log K _{OC} [10 ^(L/kg)]	HENRY [Pa*m ³ /mol]	Source	k _{volat} [1/d]	k _{bio} _{soil} [1/d]	k _{leach} [1/d]	k [1/d]
2,3,7,8-TCDD (reference for PCDD/F and dl-PCB according to WHO-TEQ)	6.69	6.58	2.79	(Becker et al. 2010)	2.71·10 ⁻⁰⁸	3.06·10 ⁻⁰⁶	2.12·10 ⁻⁰⁸	3.11·10 ⁻⁰⁶
Flouranthene (reference for PAH, total calculating PEC _{leachate})	5.20	5.11	1.63	(IHCP 2008a), (U.S. EPA n.y.)	4.88·10 ⁻⁰⁷	8.93·10 ⁻⁰⁵	6.18·10 ⁻⁰⁷	9.04·10 ⁻⁰⁵
Benzo(a)pyrene	6.13	6.03	0.11		1.12·10 ⁻⁰⁸	1.09·10 ⁻⁰⁵	7.59·10 ⁻⁰⁸	1.10·10 ⁻⁰⁵
Benzo(b)flouranthene	6.12	6.02	11.55		3.83·10 ⁻⁰⁷	1.11·10 ⁻⁰⁵	7.71·10 ⁻⁰⁸	1.16·10 ⁻⁰⁵
Benzo(k)flouranthene	6.11	6.01	0.08		1.07·10 ⁻⁰⁸	1.14·10 ⁻⁰⁵	7.88·10 ⁻⁰⁸	1.15·10 ⁻⁰⁵
Benzo(ghi)perylene	6.22	6.11	-		-	-	-	-
Indeno(1,2,3,-cd)pyrene (reference for PAH, total calculating PEC _{topsoil})	6.58	6.47	0.16		4.58·10 ⁻⁰⁹	3.93·10 ⁻⁰⁶	2.72·10 ⁻⁰⁸	3.96·10 ⁻⁰⁶

9.3 Substance-specific parameters for heavy metals

Table 20: Equations for K_d -values of metals with the potential of mobilization, K_d -values for various pH-values and pseudo-first order rate constant for leaching

Metal	Empirical regression equation	n	R ²	Source	Calculated parameter ¹⁴	pH 5	pH 5,5	pH 6	pH 6,5	pH 7
Cd ¹⁵	$\log K_d = -1.7 + 0.62 \cdot pH + 0.61 \cdot \log(\% OC)$	86	0.71	(Degryse et al. 2003)	K_d -value (topsoil, 2 % OC) [L/kg]	38	78	160	326	666
					k_{leach} (topsoil, 2 % OC) [1/d]	$3.68 \cdot 10^{-05}$	$1.80 \cdot 10^{-05}$	$8.83 \cdot 10^{-06}$	$4.33 \cdot 10^{-06}$	$2.12 \cdot 10^{-06}$
					K_d -value (subsoil 0.2 % OC) [L/kg]	9	19	39	80	164
Ni ¹⁶	$\log K_d = -0.58 + 0.44 \cdot pH$	16	0.71	(Oorts et al. 2006)	K_d -value (topsoil) [L/kg]	42	69	115	191	316
					k_{leach} (topsoil, 2 % OC) [1/d]	$3.39 \cdot 10^{-05}$	$2.04 \cdot 10^{-05}$	$1.23 \cdot 10^{-05}$	$7.41 \cdot 10^{-06}$	$4.46 \cdot 10^{-06}$
					K_d -value (subsoil 0.2 % OC) [L/kg]	-	-	-	-	-
Zn ¹⁵	$\log K_d = -2.48 + 0.69 \cdot pH + 0.67 \cdot \log(\% OC)$	97	0.71	(Degryse et al. 2003)	K_d -value (topsoil, 2 % OC) [L/kg]	15	33	73	161	356
					k_{leach} (topsoil, 2 % OC) [1/d]	$9.51 \cdot 10^{-05}$	$4.30 \cdot 10^{-05}$	$1.94 \cdot 10^{-05}$	$8.77 \cdot 10^{-06}$	$3.96 \cdot 10^{-06}$
					K_d -value (subsoil 0.2 % OC) [L/kg]	3	7	16	34	76

¹⁴ Calculated K_d -value by use of equation for various pH-values in the range from 5 to 7 for 2 % OC in topsoil and 0.2 % in subsoil (requested only for the model-refinement by the solute transport model using HYDRUS 1D-software), k_{leach} calculated only for topsoil according to eq. 5 (requested in kinetic model by TGD)

¹⁵ K_d -value for equilibrium between labile solid phase (isotopically exchangeable amount) and solution, extracted with pore water and isolated by centrifugation, measurement with ICP-AES

¹⁶ K_d -value for equilibrium between labile solid phase and solution based on partitioning of Ni in NiCl₂ amended soils, no dependency on content of organic carbon

Table 21: Constant partition sorption constants defined by European Union risk assessment reports (for As and Hg from literature research) and calculated pseudo-first order rate constants for leaching

Metal	K_d -value [L/kg] or equation	Source	K_d -value [L/kg]	k_{leach} [1/d]
As	$\log K_d = 3.4$	(Allison & Allison 2005)	2512	$5.62 \cdot 10^{-07}$
Cd	280	(IHCP 2007)	280	$5.04 \cdot 10^{-06}$
Cr ¹⁷	800	(IHCP 2005)	800	$1.76 \cdot 10^{-06}$
Cu ¹⁸	$\log K_d = 1.75 + 0.21 \cdot pH + 0.51 \cdot \log (\% OC)$	(ECI 2009), (Sauvé et al. 2000)	1600	$8.82 \cdot 10^{-07}$
Hg	$\log K_d = 3.8$	(Allison & Allison 2005)	6310	$2.24 \cdot 10^{-07}$
Ni	$\log K_d = 2.86$	(IHCP 2008d)	724	$1.95 \cdot 10^{-08}$
Pb	6400	(IHCP 2008c)	6400	$2.21 \cdot 10^{-07}$
Zn	$\log K_d = 2.2$	(IHCP 2010)	158	$8.91 \cdot 10^{-06}$

¹⁷ Fixed value for Cr (III) and acid conditions

¹⁸ Approached for pH 6.2 and 2 % OC

9.4 Initial and atmospheric boundary conditions

Table 22: Initial and atmospheric boundary conditions for organic substances

Substance	Initial conditions			Atmospheric boundary conditions				
	Range of concentration in unpolluted soil [mg/kg] ¹⁹	Source	Assumed initial concentration [mg/kg] ²⁰	Literature value for atmospheric deposition	Unit	Source	Assumed aerial deposition flux per kg of soil [mg/kg·d] ^{21 22}	Assumed annual average total deposition flux [g/ha·yr] ²²
PCDD/F & dl-PCB	$2.2 \cdot 10^{-6} \dots 2.5 \cdot 10^{-5}$ WHO-TEQ	(Scheffer & Schachtschabel 2002)	$1.4 \cdot 10^{-5}$ WHO-TEQ	16	WHO-TEQ pg/m ² ·d	(Akkan et al. 2004)	$4,71 \cdot 10^{-11}$ WHO-TEQ	$5,84 \cdot 10^{-5}$ WHO-TEQ
PAH, total	0.1...0.3		0.2	6.8	g/ha·yr	(Fuchs et al. 2010)	$5.48 \cdot 10^{-6}$	6.80
Flouranthene	$3.0 \cdot 10^{-3} \dots 0.23$	(IHCP 2008a), (Wilcke 2000)	$4.9 \cdot 10^{-2}$	-	-	-	$1.34 \cdot 10^{-6}$	1.67
Benzo(a)pyrene	$2.0 \cdot 10^{-3} \dots 8.5 \cdot 10^{-2}$		$1.4 \cdot 10^{-2}$	-	-	-	$3.84 \cdot 10^{-7}$	0.48
Benzo(b)flouranthene	$5.0 \cdot 10^{-3} \dots 0.1$		$3.0 \cdot 10^{-2}$	-	-	-	$8.22 \cdot 10^{-7}$	1.02
Benzo(k)flouranthene	$0.0 \dots 3.8 \cdot 10^{-2}$		$1.0 \cdot 10^{-2}$	-	-	-	$2.74 \cdot 10^{-7}$	0.34
Benzo(ghi)perylene	$5.0 \cdot 10^{-3} \dots 4.8 \cdot 10^{-2}$		$1.8 \cdot 10^{-2}$	-	-	-	$4.93 \cdot 10^{-7}$	0.61
Indeno(1,2,3,-cd)pyrene	$5.0 \cdot 10^{-3} \dots 3.5 \cdot 10^{-2}$		$8.0 \cdot 10^{-3}$	-	-	-	$2.19 \cdot 10^{-7}$	0.27

¹⁹ For PCDD/F & dl-PCB calculated value out of 0.16...15 ng WHO-TEQ/kg soil for PCDD/F and 2...10 ng WHO-TEQ/kg soil for PCB considering a (sludge) typical PCB-compound contribution and a summarized PCB-content of 1...20 µg/kg soil according Scheffer & Schachtschabel (2002) Lehrbuch der Bodenkunde, 15. Auflage. Spektrum Akademischer Verlag

²⁰ For single PAH, median in Wilcke, W. (2000) Polycyclic Aromatic Hydrocarbons (PAHs) in soil – a review. *Journal of Plant Nutrient and Soil Science* 163: 229-248

²¹ According to sect. 2.3.8.5, p. 80, eq. 52 in IHCP (2003) Technical Guidance Document on Risk Assessment - Part II: Environmental Risk Assessment. European Union - Institute for Health and Consumer Protection.

²² Based on single PAH concentrations in soil from Wilcke, W. (2000) Polycyclic Aromatic Hydrocarbons (PAHs) in soil – a review. *Journal of Plant Nutrient and Soil Science* 163: 229-248 calculated deposition rate, assuming that PAH in soil originate from air.

Table 23: Initial conditions, past and current/future atmospheric boundary conditions for heavy metals

Substance	Initial conditions/ past atmospheric boundary conditions			Current/future atmospheric boundary conditions				
	Assumed average total deposition flux [g/ha·yr]	Source	Calculated (anthropogenic) initial concentration [mg/kg] ²³	Literature value for atmospheric deposition [g/ha·yr]	Three year average from...	Source	Assumed aerial deposition flux per kg of soil [mg/kg·d] ²⁴	Assumed annual average total deposition flux [g/ha·yr]
As	3.0	(Scheffer & Schachtschabel 2010)	0.13	0.74	2007-2009	(Lehmhaus et al. 2009)	$6.04 \cdot 10^{-7}$	0.75
Cd	2.0	(Böhm et al. 2001)	0.08	0.41	2008-2010	(Ilyin et al. 2012)	$3.22 \cdot 10^{-7}$	0.40
Cr	5.0	(Böhm et al. 2001)	0.21	1.42	2001-2003	(Fuchs et al. 2010)	$1.21 \cdot 10^{-6}$	1.50
Cu	30	(Böhm et al. 2001)	1.29	18.16	2001-2003	(Fuchs et al. 2010)	$1.45 \cdot 10^{-5}$	18.00
Hg	0.2	(Böhm et al. 2001)	0.01	0.15	2008-2010	(Ilyin et al. 2012)	$1.21 \cdot 10^{-7}$	0.15
Ni	15	(Böhm et al. 2001)	0.63	4.33	2001-2003	(Fuchs et al. 2010)	$4.03 \cdot 10^{-6}$	5.00
Pb	40	(Böhm et al. 2001)	1.75	13.90	2008-2010	(Ilyin et al. 2012)	$1.09 \cdot 10^{-5}$	13.50
Zn	250	(Böhm et al. 2001)	8.73	112.91	2001-2003	(Fuchs et al. 2010)	$8.86 \cdot 10^{-5}$	110.00

²³ Anthropogenic (exchangeable) initial concentration of heavy metals in soil assuming 150 years of continuous atmospheric deposition by the use of the K_d -values from Table 21 (risk assessment reports) and kinetic model by TGD, the concentrations differ by the model and the K_d -value which is used in the particular case.

²⁴ According to sect. 2.3.8.5, p. 80, eq. 52 in IHCP (2003) Technical Guidance Document on Risk Assessment - Part II: Environmental Risk Assessment. European Union - Institute for Health and Consumer Protection.

9.5 Description of solute transport model (HYDRUS)

The rain and infiltration rate assumed by (IHCP 2003) leads to an effective water infiltration of 175 mm/ year. Evaporation and runoff are considered before modelling. Due to the fact that water does not accumulate in soil over ages, groundwater intake equals infiltration per year. This boundary condition keeps constant over the whole simulation time. The lower boundary condition regarding water flow: constant pressure head to groundwater is also constant over the simulation time. So a steady state for pressure head (matrix potential), water content, hydraulic conductivity, water flux, water velocity and other parameters regarding water flow is accomplished. The water flux is also constant within the soil profile due to the Richards's equation (Šimůnek et al. 2013 sect. 2.1.1, p. 11, eq. 2.1) since depressions (e.g. root water uptake) are neglected.

For solving the Darcy's equation (part of Richards' equation in (Šimůnek et al. 2013 sect. 2.1.1, p. 11, eq. 2.1)) Mualem's equation for hydraulic conductivity and the equation for van Genuchten's water-retention-model (Šimůnek et al. 2013 sect. 2.3.1, p. 23, eq. 2.30) are used. The hydraulic parameters for Mualem/van Genuchten are taken from the HYDRUS-1D software for sandy soil published in (Carsel & Parrish 1988).

The Conversion-Dispersion-Equation including retardation by sorption is given by eq. 9 (derivation according to (Durner & Fühler 2003 sect. 3.2-3.4.1, p. 17-24)).

$(\theta + F_{solid_{soil}} \cdot RHO_{solid} \cdot K_d) \cdot \frac{\partial C_{liquid}}{\partial t} = q \cdot \left(\lambda \cdot \frac{\partial^2 C_{liquid}}{\partial z^2} - \frac{\partial C_{liquid}}{\partial z} \right)$		eq. 9	
q	Water flux	$[m^3 \cdot m^{-2} \cdot yr^{-1}]$	
λ	Longitudinal dispersivity	$[m]$	0,1 in topsoil; 0,15 in subsoil
$\frac{\partial^2 C_{liquid}}{\partial z^2}$	Second derivation of liquid concentration with respect to soil depth	$[mg \cdot m^{-5}]$	
$\frac{\partial C_{liquid}}{\partial z}$	Derivation of liquid concentration with respect to soil depth	$[mg \cdot m^{-4}]$	
θ	Water content	$[-]$	
$\frac{\partial C_{liquid}}{\partial z}$	Derivation of liquid concentration with respect to soil depth	$[mg \cdot m^{-4}]$	
$F_{solid_{soil}}$	Volume fraction of solid phase in soil	$[-]$	0,6
RHO_{solid}	Density of solid phase	$[kg \cdot m^{-3}]$	2500
K_d	substance specific sorption constant	$[m^3 \cdot kg^{-1}]$	
$\frac{\partial C_{liquid}}{\partial t}$	Derivation of liquid concentration with respect to time	$[mg \cdot m^{-3} \cdot yr^{-1}]$	

Water flux and the product of volume fraction in solid phase in soil and density of solid phase are constant with respect to soil depth and time. The longitudinal dispersivity and the substance specific sorption constant for each metal and constant pH-value are fixed for each horizon. Longitudinal dispersivity is mainly dependent on soil type and length of flow distance and fixed by HYDRUS for topsoil (0.1 m) and subsoil (0.15 m) generally for all soil types. The substance specific sorption constant for one metal and a constant pH-value is dependent on content organic matter. This content

is, as mentioned, fixed for topsoil (2 % organic carbon) and subsoil (0.2 % organic carbon). The water content is the only parameter in equation eq. 9 which has a strong dependency on soil type, but is negligible especially for high pH-values and thereby high K_d -values.

The boundary conditions have an impact on surface concentration ($C(z=0) = C(z_0)$), since no plowing is considered in this model. Atmospheric deposition continuously increases the surface concentration (annual average total deposition flux in the annex in Table 23). The annual product application (annual mass flow in the annex in Table 10) also increases discontinuously the surface concentration. This concentration is calculated from heavy metal irrigation into soil surface, as continuous concentration in rain water for atmospheric deposition (see eq. 10) and as excessive concentration in rain water of one day for product application (see eq. 11). For the day of application the sum of liquid concentrations of eq. 10 and eq. 11 is used.

$\text{for atmospheric deposition: } C_{liquid}(t_{cont.}, z_0) = \frac{DEP_{total_{ann}} \cdot 10^{-1} \cdot mg \cdot g^{-1} \cdot ha \cdot m^{-2}}{Finf_{soil} \cdot RAINrate}$		eq. 10
$\text{for annual application: } C_{liquid}(t_{annual}, z_0) = \frac{m \cdot 10^{-1} \cdot mg \cdot g^{-1} \cdot ha \cdot m^{-2}}{Finf_{soil} \cdot RAINrate}$		eq. 11
$DEP_{total_{ann}}$	Annual average total deposition flux	$[g \cdot ha \cdot yr^{-1}]$ Table 23
m	Annual mass flow of a hazard in a product on ha soil by annual fertilizer application of 60 kg P ₂ O ₅ per ha in one day	$[g \cdot ha^{-1} \cdot d^{-1}]$ Table 10
$Finf_{soil}$	fraction of rain water that infiltrates into soil	$[-]$ 0,25
$RAINrate$	rate of wet precipitation (700 mm/year)	$[m \cdot yr^{-1}]$ 0,7
$C_{liquid}(t_{cont.}, z_0)$	Liquid concentration at soil surface by atmospheric deposition	$[mg \cdot m^{-3}]$
$C_{liquid}(t_{annual}, z_0)$	Liquid concentration at soil surface by product or raw material application	$[mg \cdot m^{-3}]$
$t_{cont.}$	Continuous time ($0 d \leq t_{cont.} \leq 36500 d$ (100 years))	$[d]$
t_{annual}	Annual discontinuous time ($0 \text{ years} \leq t_{annual} \leq 100 \text{ years}$)	$[yr]$

For a better comparability to the kinetic model the PEC is calculated from mean concentration in topsoil, although the HYDRUS-software calculates specific concentrations for each depth in soil profile. This mean is calculated for analogue to horizons in HYDRUS defined sub regions by integration of concentration from 0 to 20 cm of soil depth for a fixed time step (here: after 100 years of application) and dividing this integral through depth of 20 cm (eq. 12). The calculation of concentration from liquid to total concentration by using substance specific sorption constant is shown in eq. 13.

$$C_{liquid}(topsoil) = \frac{1}{DEPTH_{soil}} \int_0^{DEPTH_{soil}} C_{liquid}(z) dz \quad \text{eq. 12}$$

$$PEC_{soil} = (\theta \cdot + F_{solid_{soil}} \cdot RHO_{solid} \cdot K_d) \cdot \frac{C_{liquid}(topsoil)}{RHO_{soil}} \quad \text{eq. 13}$$

$DEPTH_{soil}$	mixing depth of soil for agricultural use	[m]	0.2
$C_{liquid}(z)$	Liquid concentration in dependency from soil depth	[mg · m ⁻³]	
$C_{liquid}(topsoil)$	Averaged liquid concentration	[mg · m ⁻³]	
θ	Water content, constant for topsoil	[-]	0,0802
$F_{solid_{soil}}$	Volume fraction of solid phase in soil	[-]	0.6
RHO_{solid}	Density of solid phase	[kg · m ⁻³]	2500
K_d	substance specific sorption constant	[m ³ · kg ⁻¹]	
RHO_{soil}	Bulk density of soil	[kg · m ⁻³]	(IHCP 2003 sect. 2.3.4., p. 44, eq. 18)
PEC_{soil}	Predicted environmental concentration in soil	[mg · kg ⁻¹]	

Regarding leachate an assumption according to Technical Guidance Document is adopted: leachate concentration equals pore water concentration. Contrary to the kinetic model pore water concentration at the bottom of soil $z = 150$ cm is used (eq. 14). Since HYDRUS calculates with liquid concentration a translation is not needed. In consideration of water flux the solute flux to groundwater can be calculated according to eq. 15 if solute breakdown is neglected.

$$PEC_{leachate} = C_{liquid}(z_{1,5m}) \quad \text{eq. 14}$$

$$FLUX_{groundwater} = C_{liquid}(z_{1,5m}) \cdot q \quad \text{eq. 15}$$

$C_{liquid}(z_{1,5m})$	Liquid concentration in a depth of 150 cm	[mg · m ⁻³]	
$PEC_{leachate}$	Predicted environmental concentration in leachate	[μg · L ⁻¹]	
q	Water flux (constant over soil profile)	[m ³ · m ⁻² · year ⁻¹]	0.175
$FLUX_{groundwater}$	Solute flux to groundwater	[mg · m ⁻² · year ⁻¹]	

9.6 Results of exposure assessment by kinetic model (TGD)

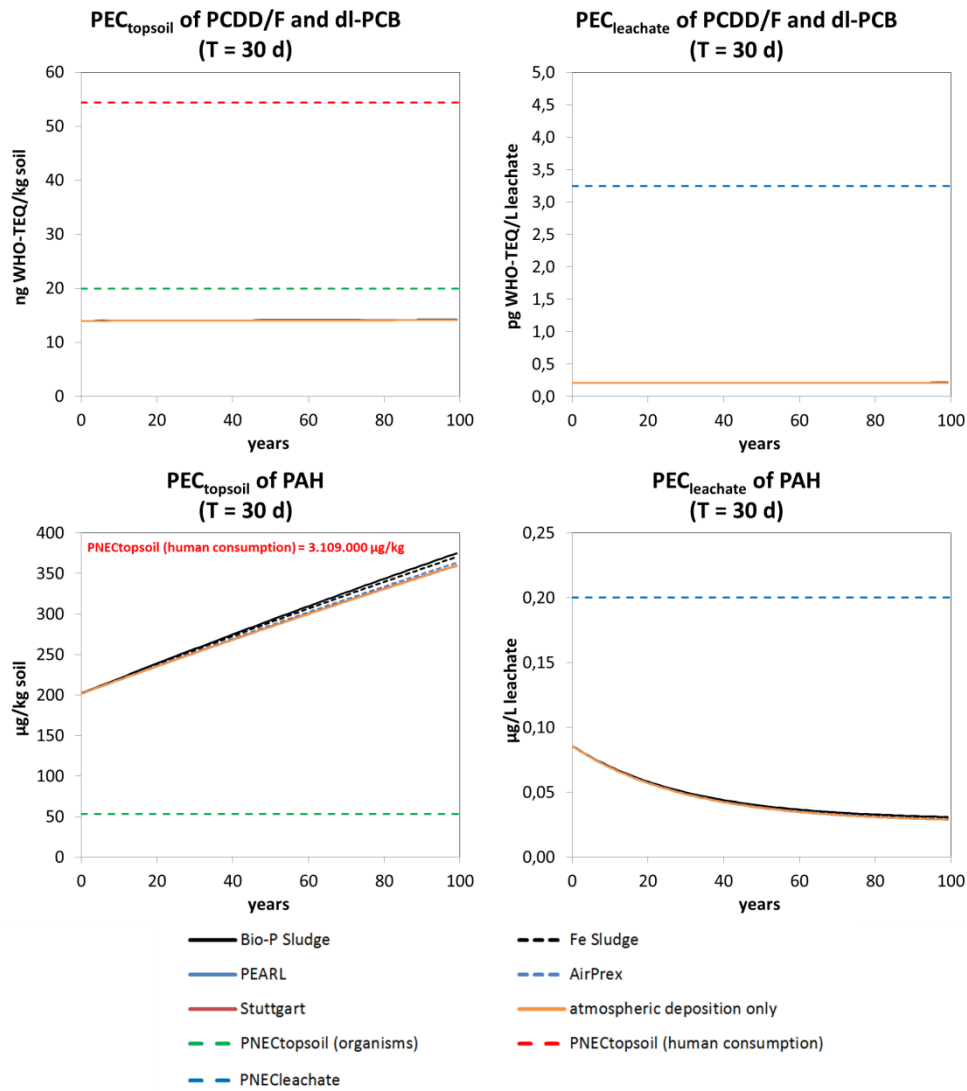


Figure 10: $PEC_{topsoil}$ and $PEC_{leachate}$ for PCDD/F and dl-PCB and PAH over 100 years of application averaged for the first 30 days after application in due consideration of initial concentrations and PNEC from hazard characterization

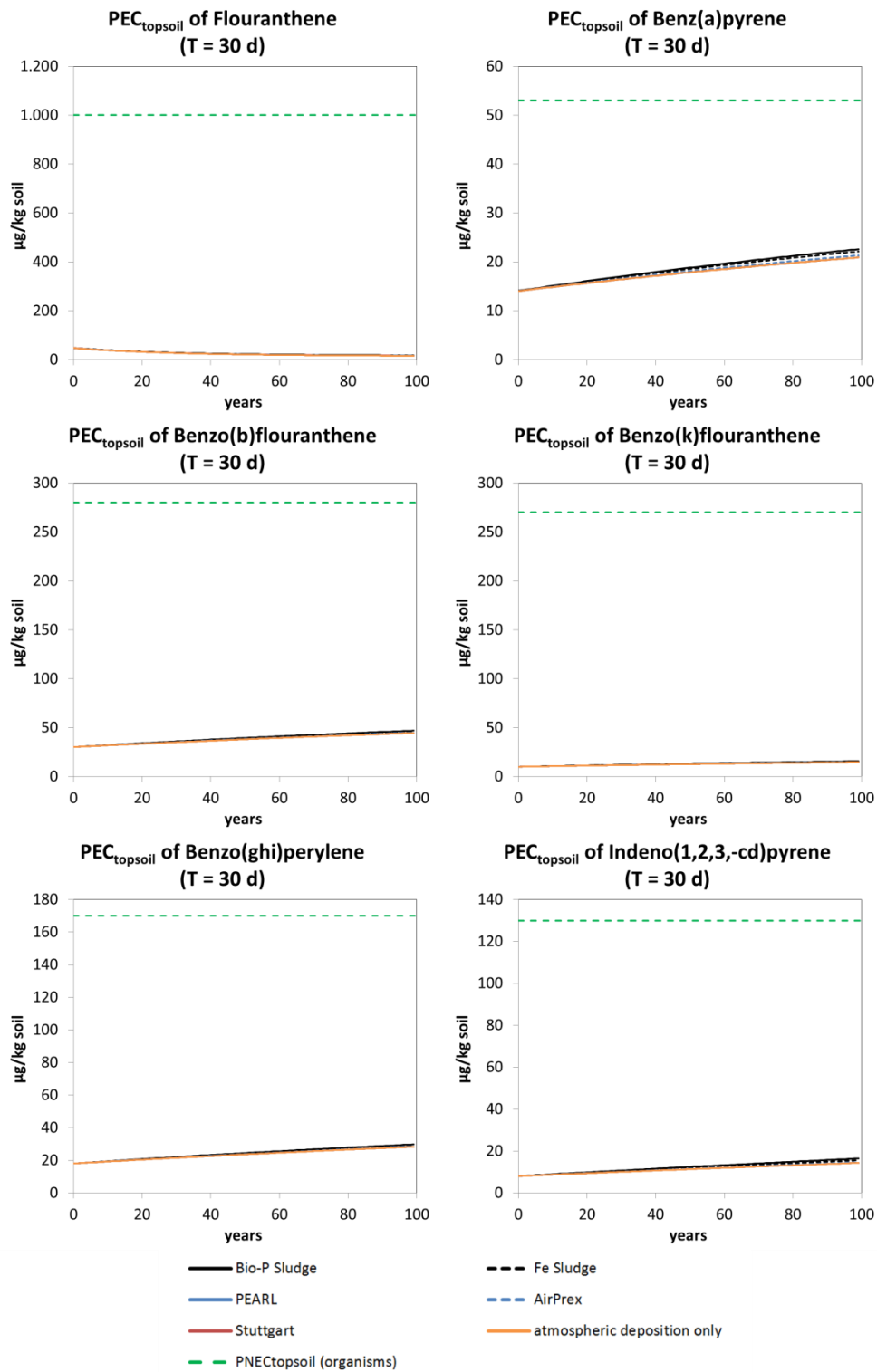


Figure 11: PEC_{topsoil} for single-substance of PAH (model refinement) over 100 years of application averaged for the first 30 days after application in due consideration of initial concentrations and PNEC from hazard characterization

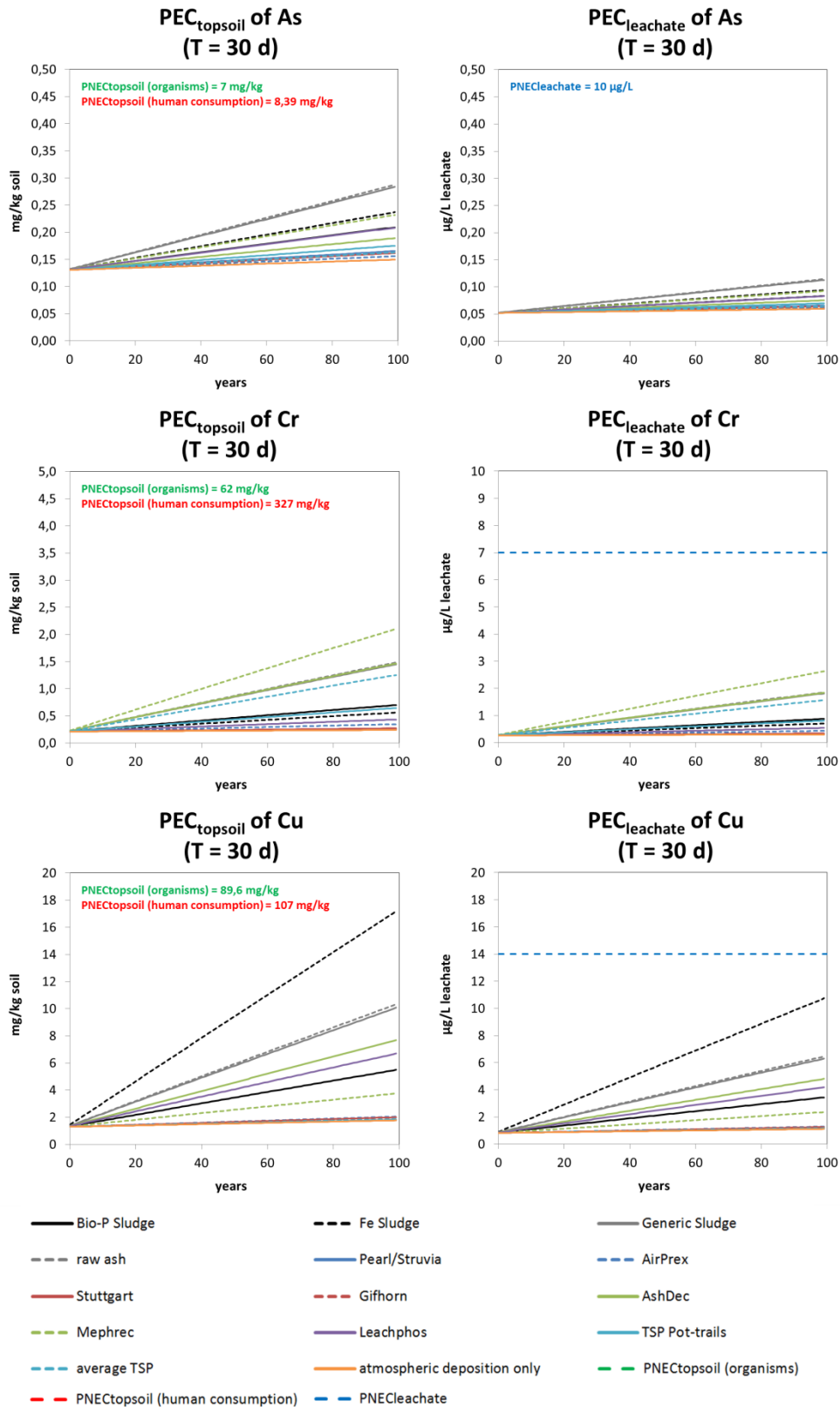


Figure 12: PEC_{topsoil} and PEC_{leachate} for As, Cr and Cu over 100 years of application averaged for the first 30 days after application in due consideration of initial concentrations and K_d-value from risk assessment reports and PNEC from hazard characterization

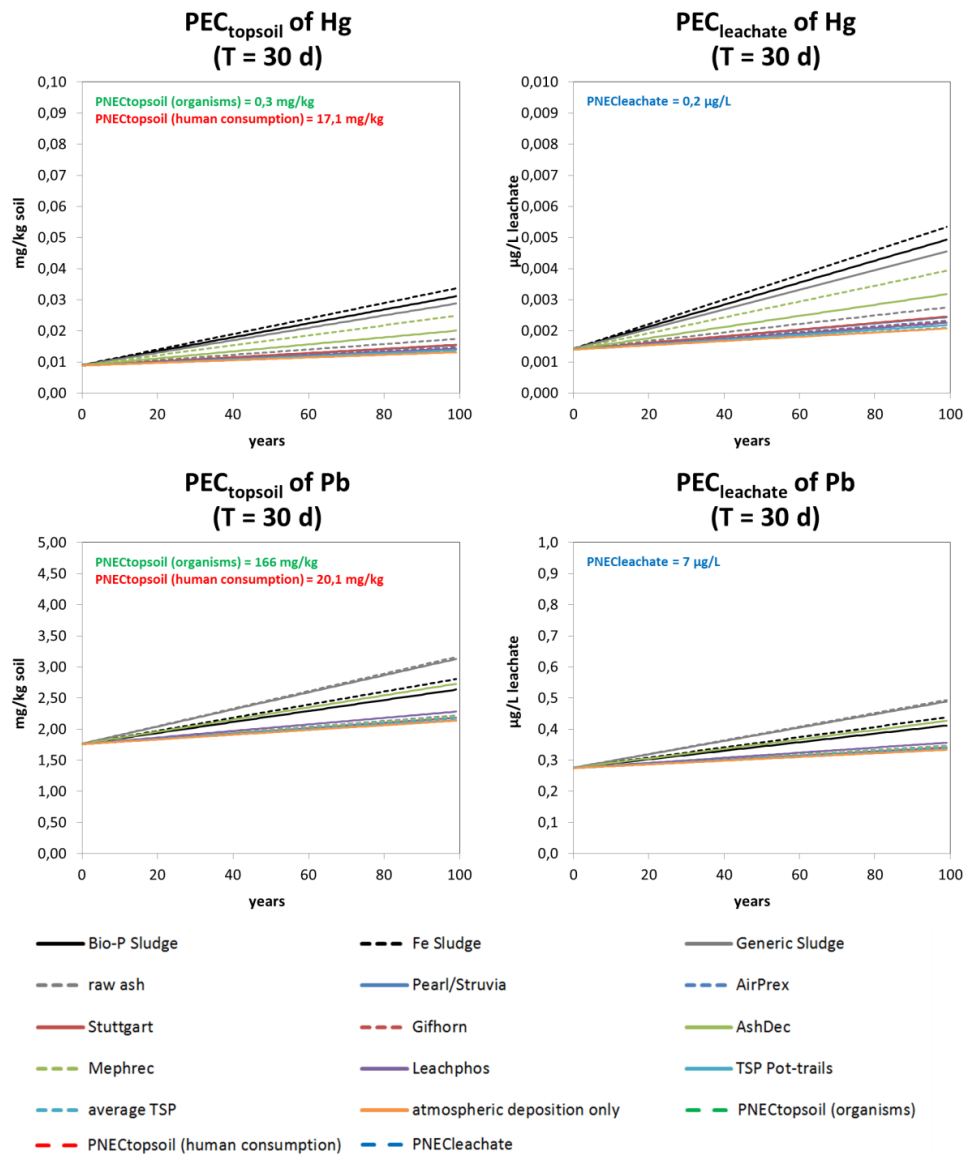


Figure 13: PEC_{topsoil} and PEC_{leachate} for Hg and Pb over 100 years of application averaged for the first 30 days after application in due consideration of initial concentrations and K_d-value from risk assessment reports and PNEC from hazard characterization

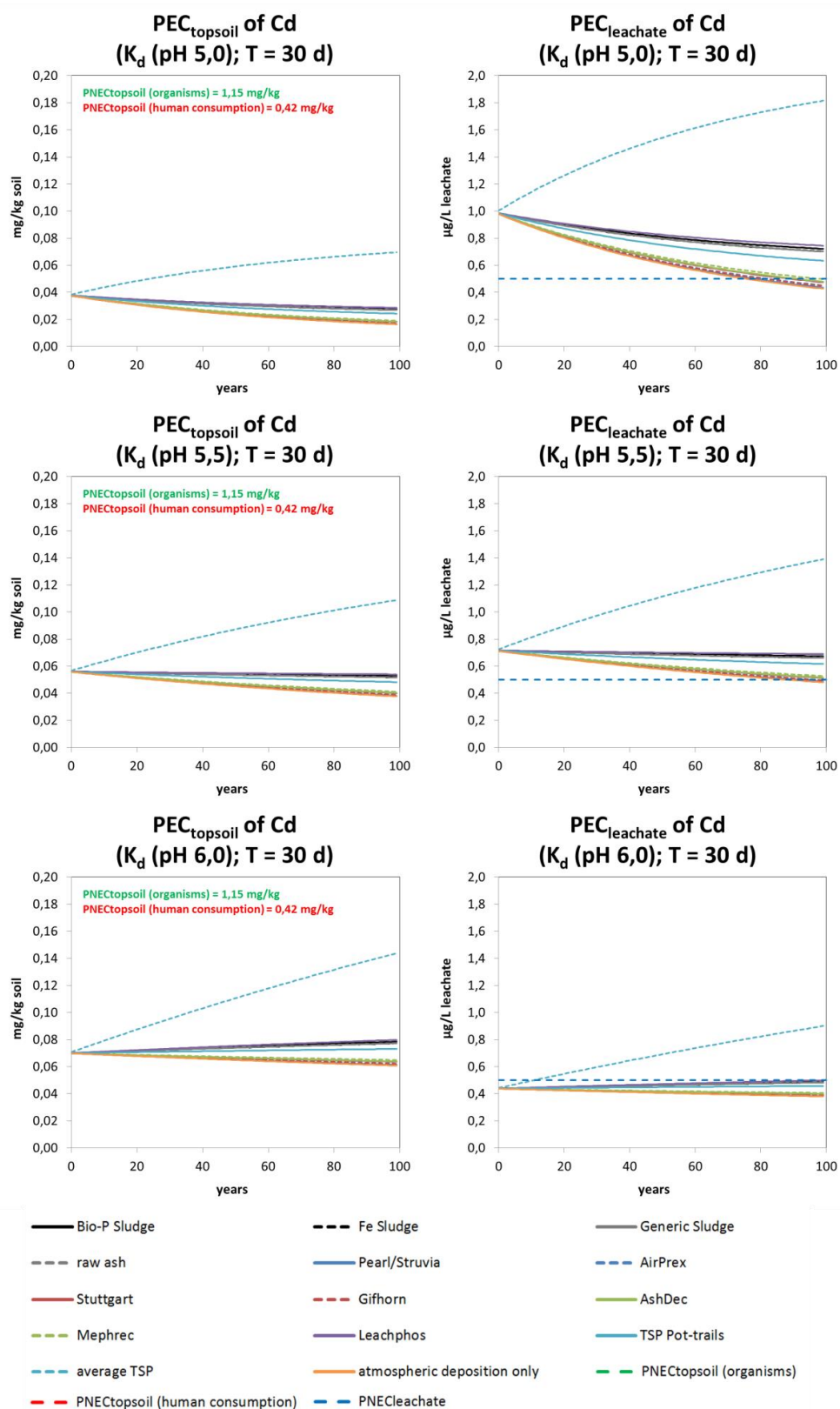


Figure 14: $PEC_{topsoil}$ and $PEC_{leachate}$ for Cd over 100 years of application averaged for the first 30 days after application in due consideration of initial concentrations and variable K_d -values in dependency from soil-pH-value for pH 5,0; pH 5,5 and pH 6,0 in Table 20 and PNEC from hazard characterization

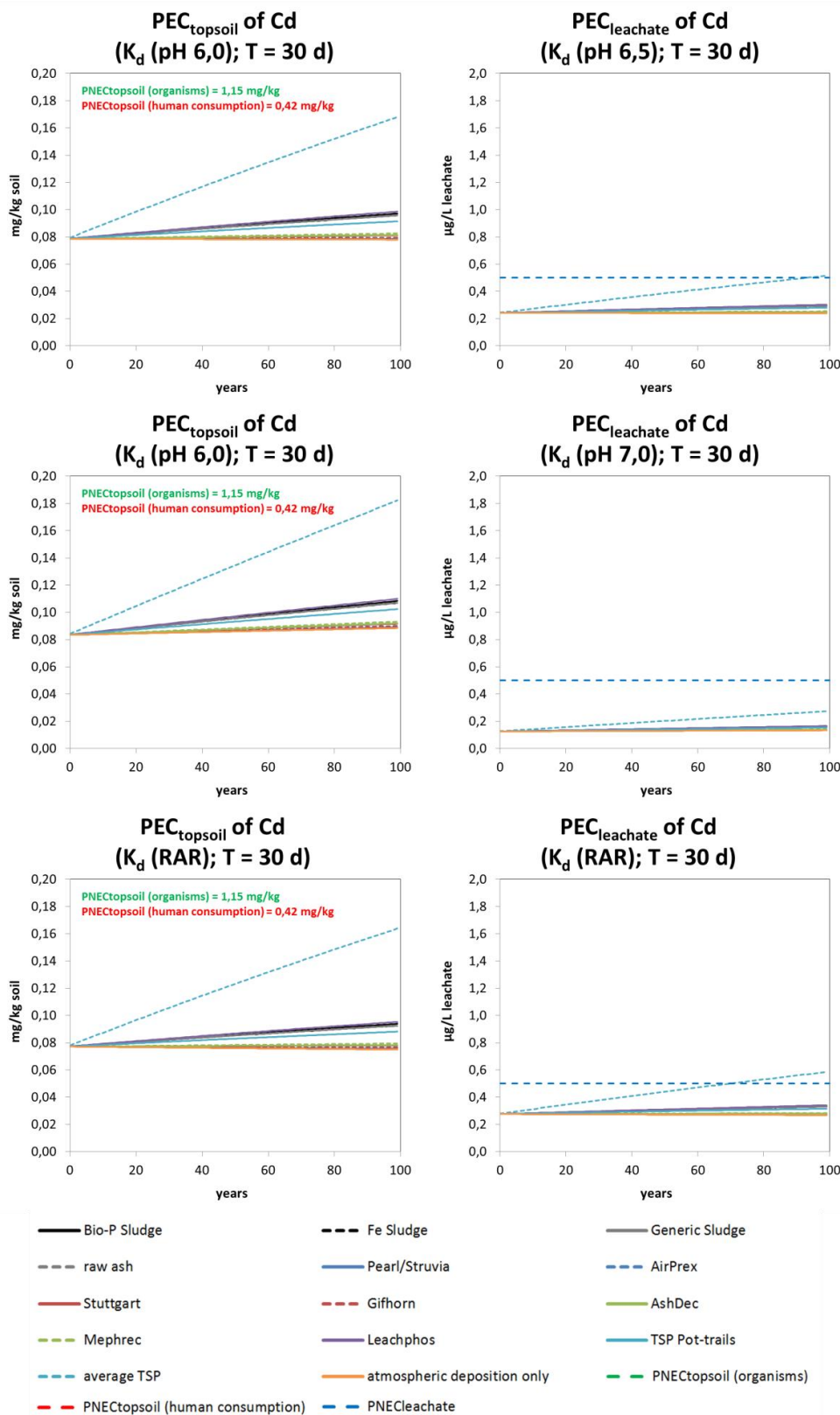


Figure 15: $PEC_{topsoil}$ and $PEC_{leachate}$ for Cd over 100 years of application averaged for the first 30 days after application in due consideration of initial concentrations and variable K_d -values in dependency from soil-pH-value for pH 6,5 and pH 7,0 in Table 20 and K_d -value from risk assessment report in Table 21 and PNEC from hazard characterization

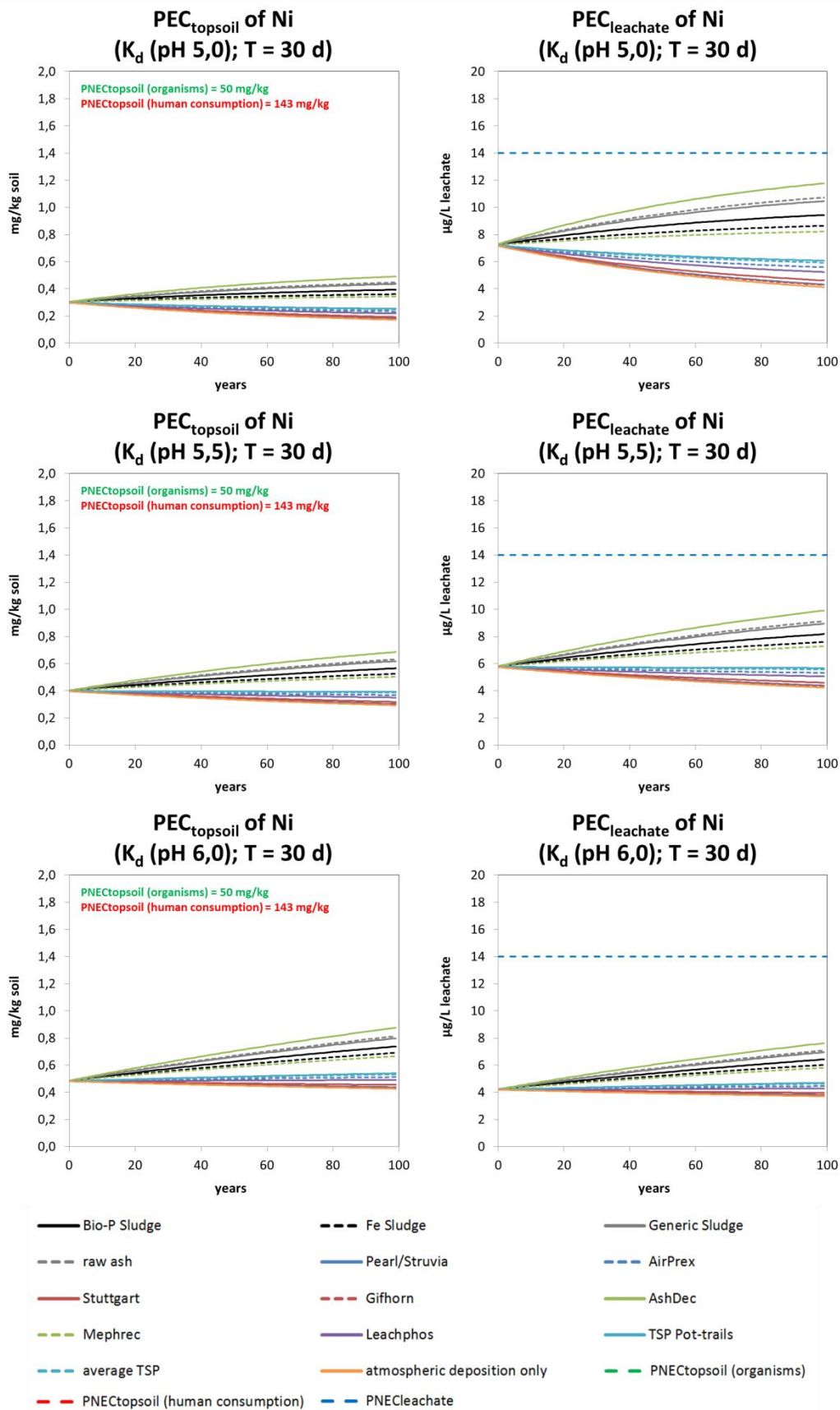


Figure 16: $PEC_{topsoil}$ and $PEC_{leachate}$ for Ni over 100 years of application averaged for the first 30 days after application in due consideration of initial concentrations and variable K_d -values in dependency from soil-pH-value for pH 5,0; pH 5,5 and pH 6,0 in Table 20 and PNEC from hazard characterization

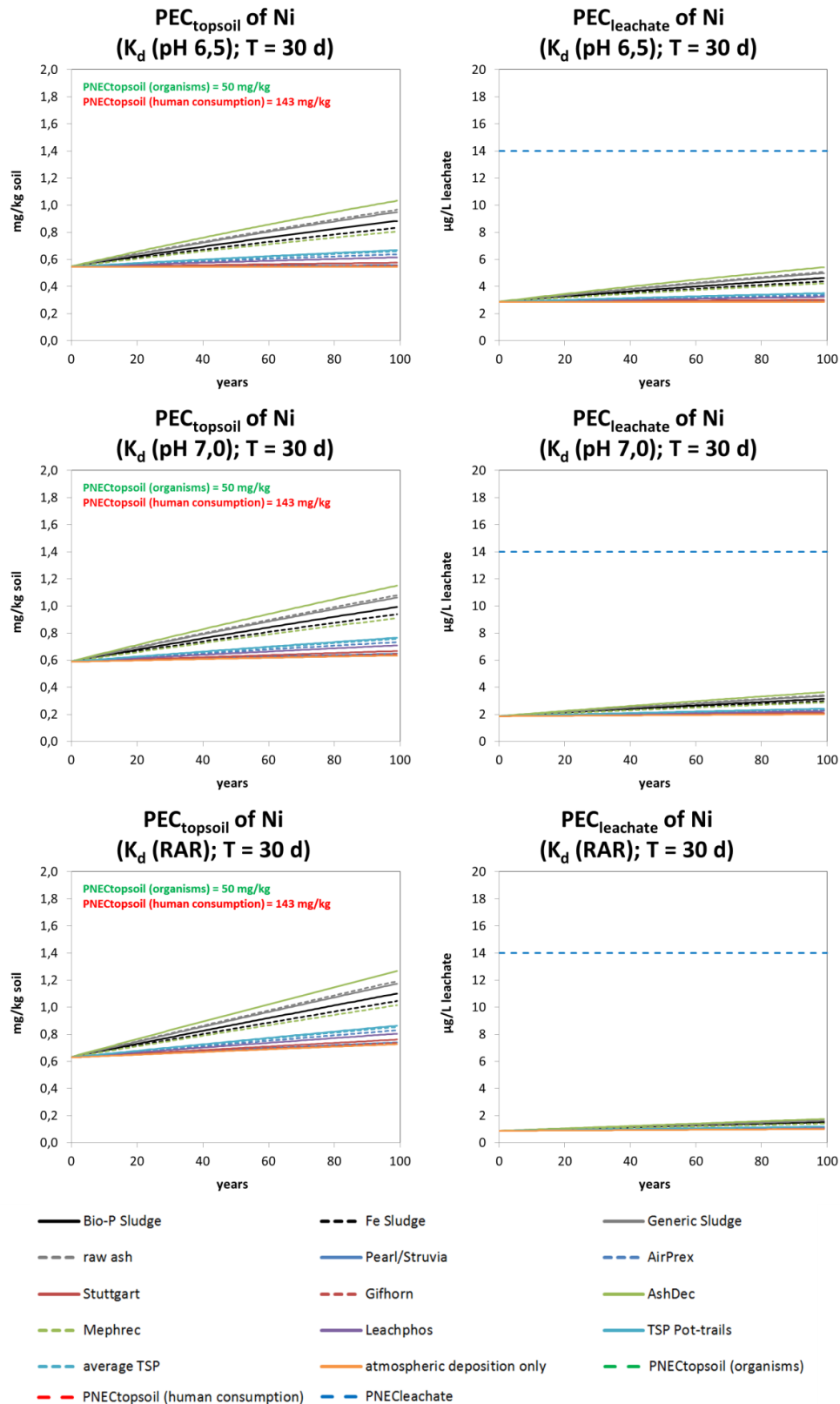


Figure 17: $PEC_{topsoil}$ and $PEC_{leachate}$ for Ni over 100 years of application averaged for the first 30 days after application in due consideration of initial concentrations and variable K_d -values in dependency from soil-pH-value for pH 6,5 and pH 7,0 in Table 20 and K_d -value from risk assessment report in Table 21 and PNEC from hazard characterization

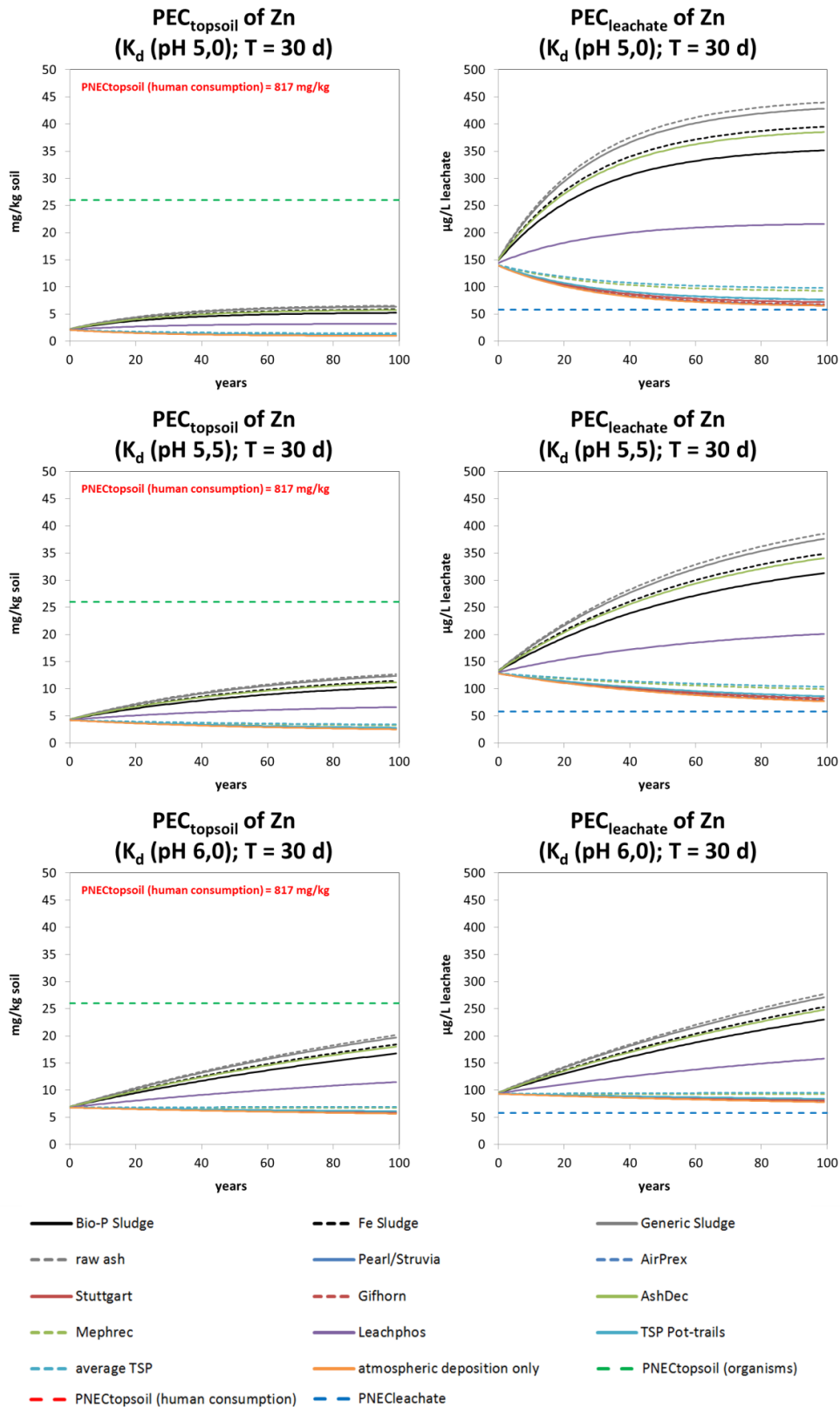


Figure 18: $PEC_{topsoil}$ and $PEC_{leachate}$ for Zn over 100 years of application averaged for the first 30 days after application in due consideration of initial concentrations and variable K_d -values in dependency from soil-pH-value for pH 5,0; pH 5,5 and pH 6,0 in Table 20 and PNEC from hazard characterization

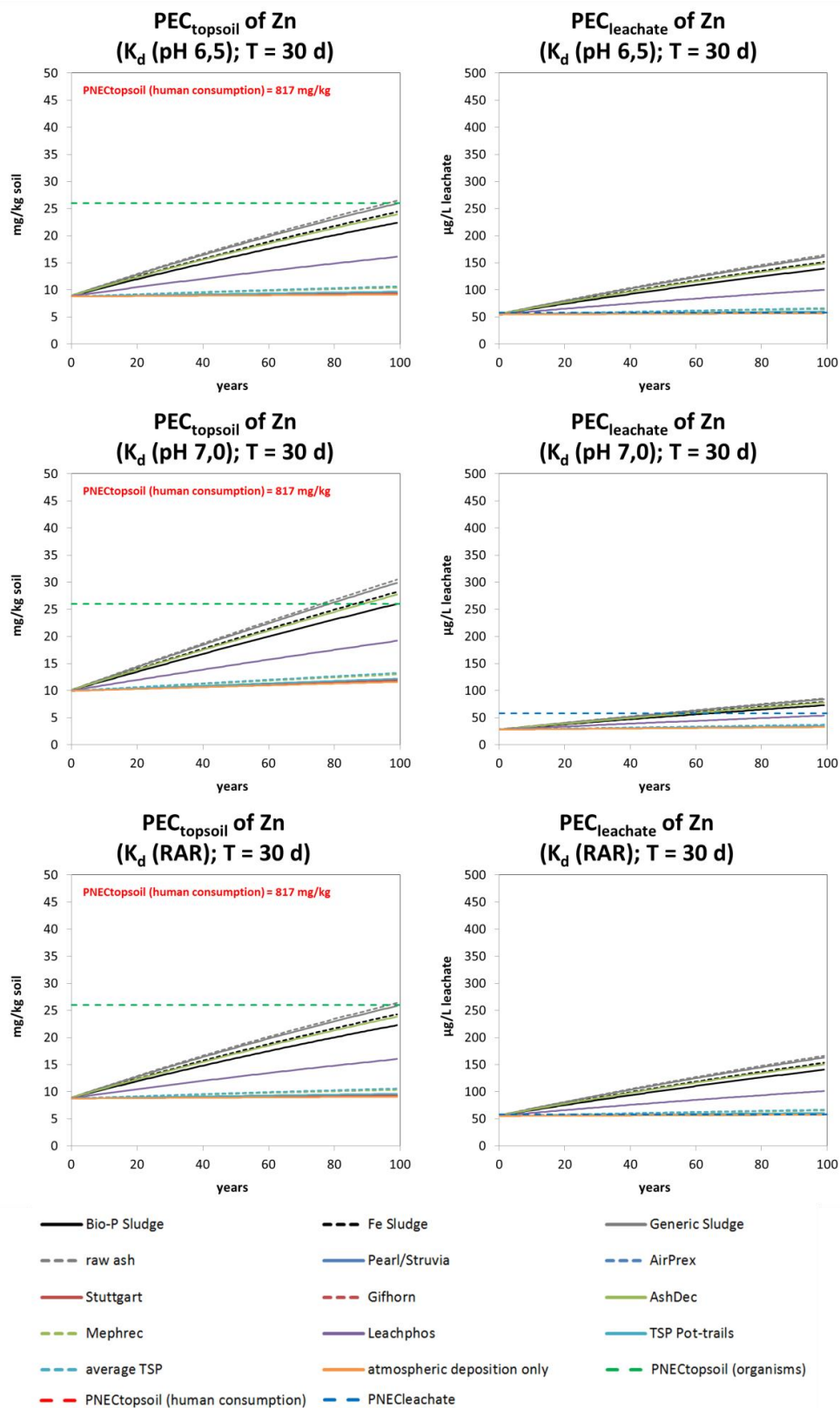


Figure 19: PEC_{topsoil} and PEC_{leachate} for Zn over 100 years of application averaged for the first 30 days after application in due consideration of initial concentrations and variable K_d-values in dependency from soil-pH-value for pH 6,5 and pH 7,0 in Table 20 and K_d-value from risk assessment report in Table 21 and PNEC from hazard characterization

9.7 Results of exposure assessment by solute transport model (HYDRUS)

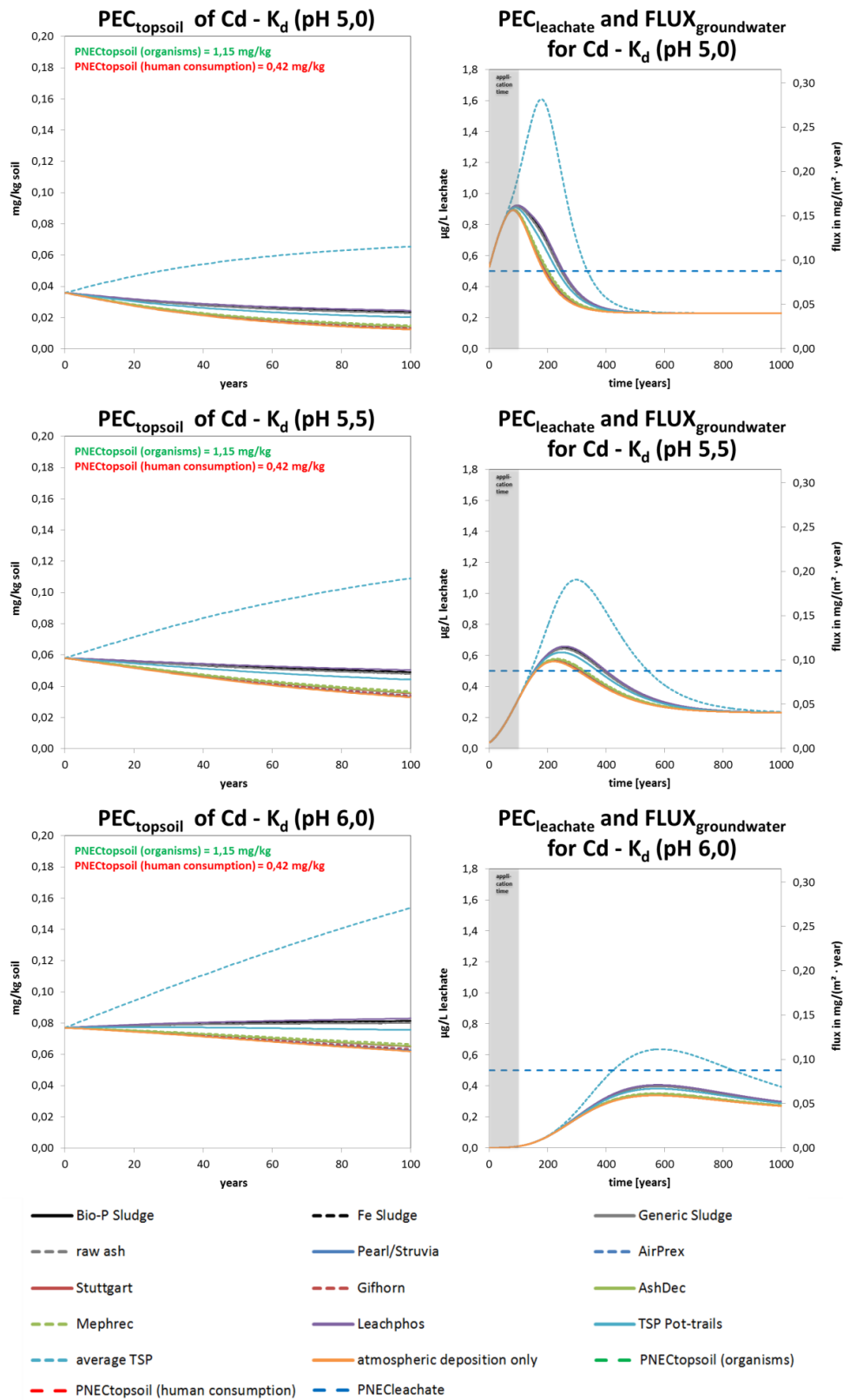


Figure 20: PEC_{topsoil} over 100 years and PEC_{leachate} and flux to groundwater over 1000 years for Cd in due consideration of initial concentrations and variable K_d-values in dependency from soil-pH-value for pH 5,0; pH 5,5 and pH 6,0 in Table 20 and PNEC from hazard characterization

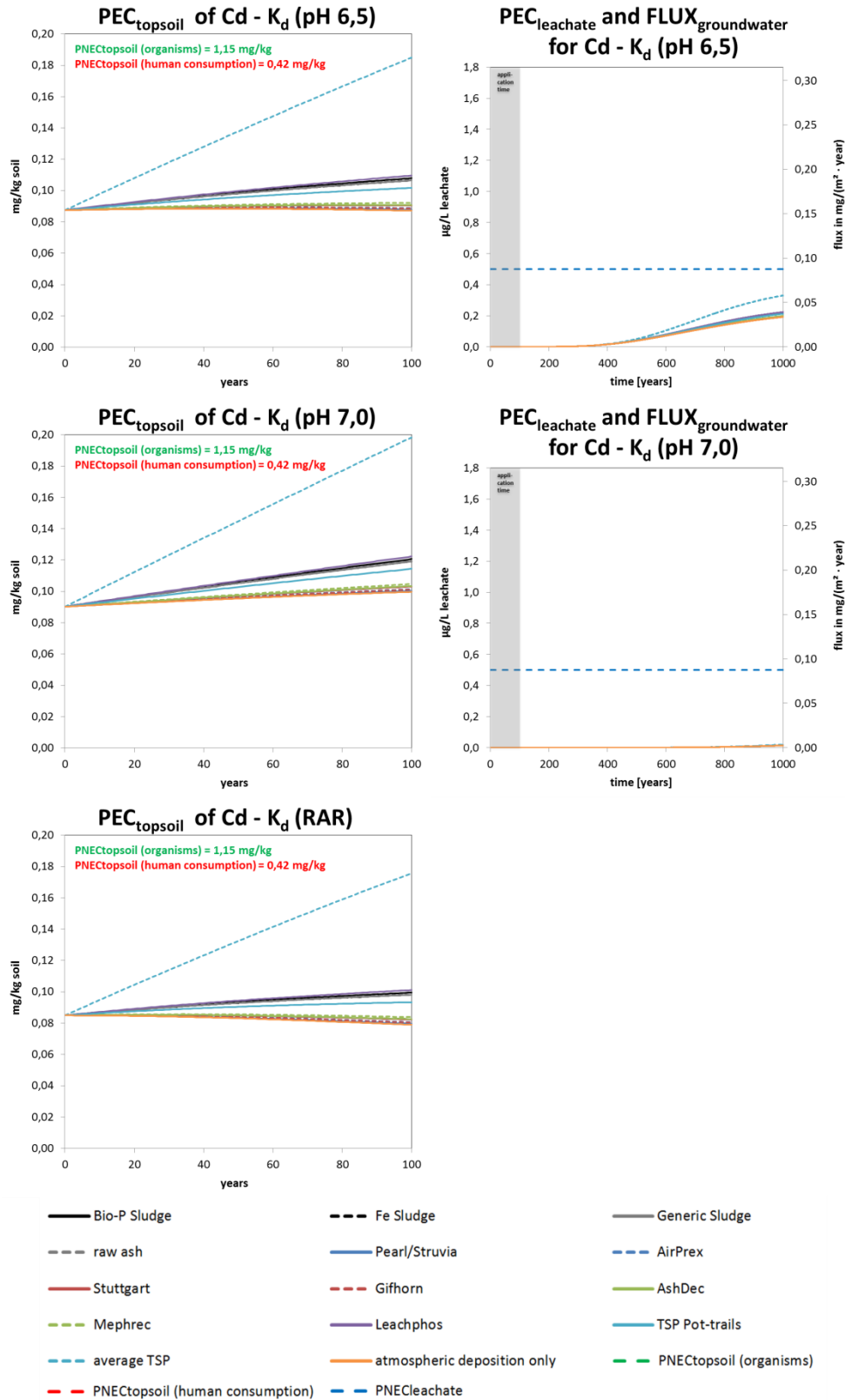


Figure 21: PEC_{topsoil} over 100 years and PEC_{leachate} and flux to groundwater over 1000 years for Cd in due consideration of initial concentrations and variable K_d-values in dependency from soil-pH-value for pH 6,5 and pH 7,0 in Table 20 and K_d-value from risk assessment report in Table 21 and PNEC from hazard characterization

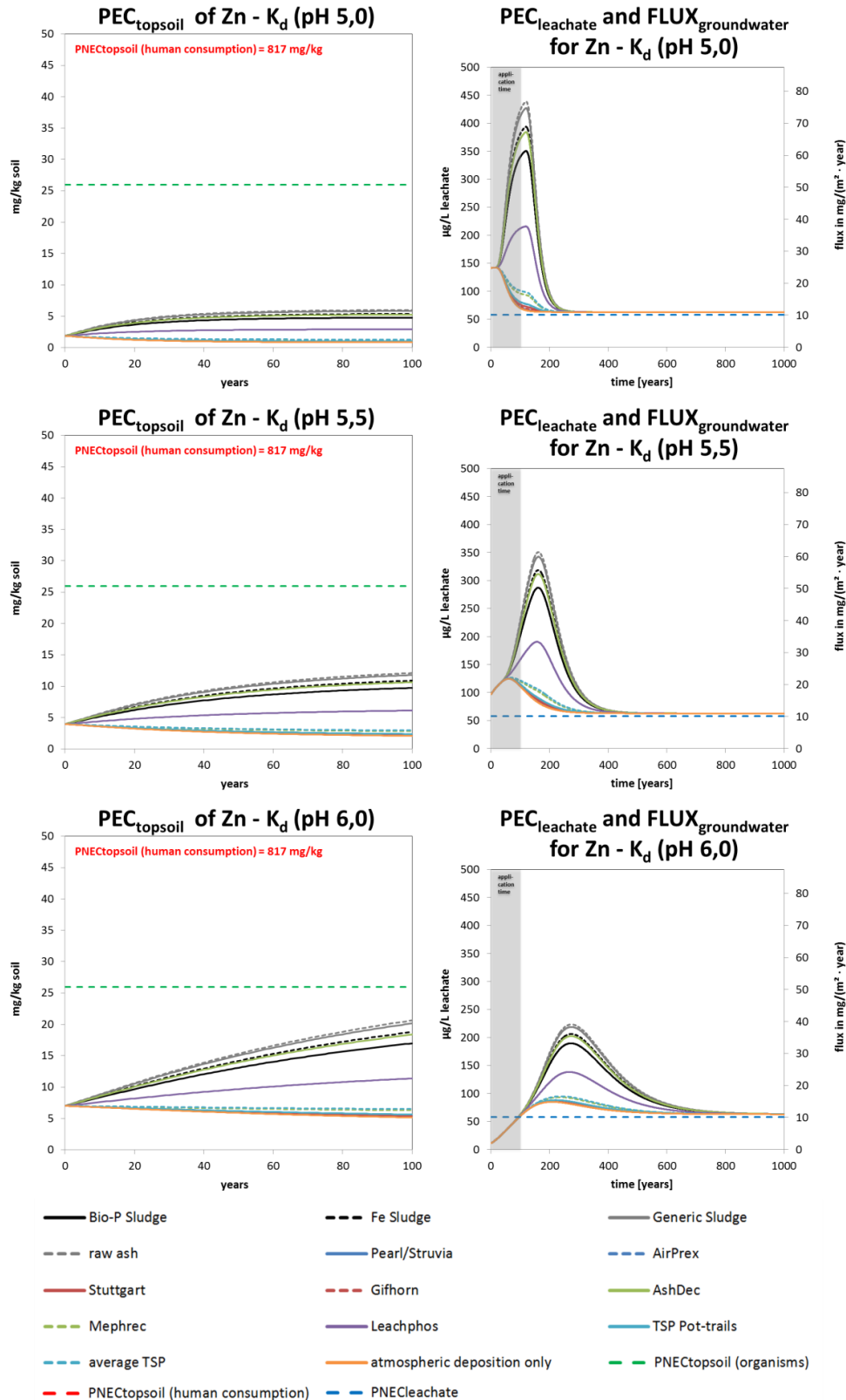


Figure 22: $PEC_{topsoil}$ over 100 years and $PEC_{leachate}$ and flux to groundwater over 1000 years for Zn in due consideration of initial concentrations and variable K_d -values in dependency from soil-pH-value for pH 5,0; pH 5,5 and pH 6,0 in Table 20 and $PNEC$ from hazard characterization

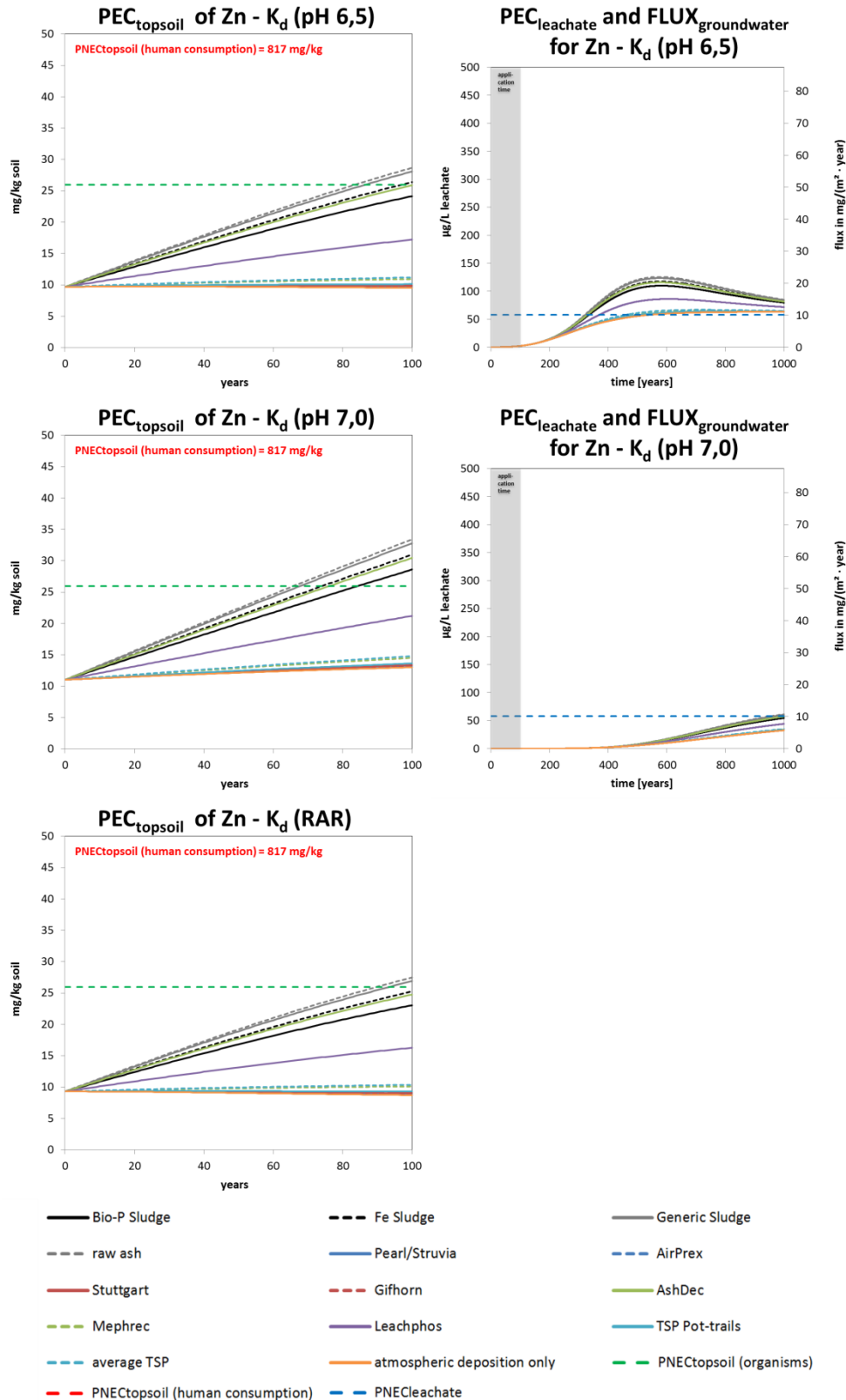


Figure 23: PEC_{topsoil} over 100 years and PEC_{leachate} and flux to groundwater over 1000 years for Zn in due consideration of initial concentrations and variable K_d-values in dependency from soil-pH-value for pH 6,5 and pH 7,0 in Table 21 and K_d-value from risk assessment report in Table 21 and PNEC from hazard characterization

9.8 Results of risk characterization

Table 24: Maximal risk characterization ratios regarding endpoint soil organisms

Hazard	Model (Parameter)	Bio-P sludge	Fe sludge	generic sludge	raw ash	Pearl/ Struvia	AirPrex	Stuttgart	Gifhorn	AshDec	Mephrec	Leachphos	TSP Pot-trails	average TSP	atmospheric deposition only
PCDD/F & dl-PCB	TGD	0,71	0,71	-	-	0,71	0,71	0,71	-	-	-	-	-	-	0,71
PAH	TGD	7,1	7,0	-	-	6,8	6,9	6,8	-	-	-	-	-	-	6,8
Flouranthene	TGD	0,05	0,05	-	-	0,05	0,05	0,05	-	-	-	-	-	-	0,05
Benzo(a)pyrene	TGD	0,427	0,42	-	-	0,39	0,40	0,39	-	-	-	-	-	-	0,39
Benzo(b)flouranthene	TGD	0,2	0,2	-	-	0,2	0,2	0,2	-	-	-	-	-	-	0,2
Benzo(k)flouranthene	TGD	0,06	0,05	-	-	0,05	0,06	0,05	-	-	-	-	-	-	0,05
Benzo(ghi)perylene	TGD	0,2	0,2	-	-	0,2	0,2	0,2	-	-	-	-	-	-	0,2
Indeno(1,2,3-cd)pyrene	TGD	0,1	0,1	-	-	0,1	0,1	0,1	-	-	-	-	-	-	0,1
As	TGD	0,03	0,03	0,04	0,02	0,02	0,02	0,02	0,04	0,03	0,03	0,03	0,03	0,02	0,02
Cr	TGD	0,01	0,01	0,02	0,02	0,00	0,01	0,00	0,00	0,02	0,03	0,01	0,01	0,02	0,00
Cu	TGD	0,06	0,2	0,1	0,1	0,02	0,02	0,02	0,02	0,09	0,04	0,07	0,02	0,02	0,02
Hg	TGD	0,1	0,1	0,1	0,06	0,05	0,05	0,05	0,05	0,07	0,08	0,05	0,05	0,04	0,04
Pb	TGD	0,02	0,02	0,02	0,02	0,01	0,01	0,01	0,01	0,02	0,01	0,01	0,01	0,01	0,01
Cd	TGD (K _d RAR)	0,08	0,08	0,08	0,08	0,07	0,07	0,07	0,07	0,07	0,07	0,08	0,08	0,1	0,07
	HYDRUS (K _d RAR)	0,09	0,09	0,09	0,09	0,07	0,07	0,07	0,07	0,07	0,07	0,09	0,08	0,2	0,07
	TGD (K _d pH 5,0)	0,03	0,03	0,03	0,03	0,03	0,03	0,03	0,03	0,03	0,03	0,03	0,03	0,06	0,03
	HYDRUS (K _d pH 5,0)	0,03	0,03	0,03	0,03	0,03	0,03	0,03	0,03	0,03	0,03	0,03	0,03	0,06	0,03
	TGD (K _d pH 5,5)	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,09	0,05
	HYDRUS (K _d pH 5,5)	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,09	0,05
	TGD (K _d pH 6,0)	0,07	0,07	0,07	0,07	0,06	0,06	0,06	0,06	0,06	0,06	0,06	0,07	0,06	0,1
	HYDRUS (K _d pH 6,0)	0,07	0,07	0,07	0,07	0,07	0,07	0,07	0,07	0,07	0,07	0,07	0,07	0,1	0,07
	TGD (K _d pH 6,5)	0,08	0,08	0,08	0,08	0,07	0,07	0,07	0,07	0,07	0,07	0,07	0,09	0,08	0,1
	HYDRUS (K _d pH 6,5)	0,09	0,09	0,09	0,09	0,08	0,08	0,08	0,08	0,08	0,08	0,08	0,1	0,09	0,2
	TGD (K _d pH 7,0)	0,09	0,09	0,09	0,09	0,08	0,08	0,08	0,08	0,08	0,08	0,08	0,1	0,09	0,2
	HYDRUS (K _d pH 7,0)	0,1	0,1	0,1	0,1	0,09	0,09	0,09	0,09	0,09	0,09	0,09	0,1	0,1	0,2
Ni	TGD (K _d RAR)	0,02	0,02	0,02	0,02	0,01	0,02	0,02	0,01	0,03	0,02	0,02	0,02	0,02	0,01
	TGD (K _d pH 5,0)	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01
	TGD (K _d pH 5,5)	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01
	TGD (K _d pH 6,0)	0,01	0,01	0,02	0,02	0,01	0,01	0,01	0,01	0,02	0,01	0,01	0,01	0,01	0,01
	TGD (K _d pH 6,5)	0,02	0,02	0,02	0,02	0,01	0,01	0,01	0,01	0,02	0,02	0,01	0,01	0,01	0,01
	TGD (K _d pH 7,0)	0,02	0,02	0,02	0,02	0,01	0,01	0,01	0,01	0,02	0,02	0,01	0,01	0,02	0,01
Zn	TGD (K _d RAR)	0,9	0,9	1,0	1,0	0,4	0,4	0,4	0,4	0,9	0,4	0,6	0,4	0,4	0,3
	HYDRUS (K _d RAR)	0,9	1,0	1,0	1,1	0,4	0,4	0,4	0,4	1,0	0,4	0,6	0,4	0,4	0,4
	TGD (K _d pH 5,0)	0,2	0,2	0,2	0,3	0,08	0,08	0,08	0,08	0,2	0,08	0,1	0,08	0,08	0,08
	HYDRUS (K _d pH 5,0)	0,2	0,2	0,2	0,2	0,07	0,07	0,07	0,07	0,2	0,07	0,1	0,07	0,07	0,07
	TGD (K _d pH 5,5)	0,4	0,4	0,5	0,5	0,2	0,2	0,2	0,2	0,4	0,2	0,3	0,2	0,2	0,2
	HYDRUS (K _d pH 5,5)	0,4	0,4	0,5	0,5	0,2	0,2	0,2	0,2	0,4	0,2	0,2	0,2	0,2	0,2
	TGD (K _d pH 6,0)	0,6	0,7	0,8	0,8	0,3	0,3	0,3	0,3	0,7	0,3	0,4	0,3	0,3	0,3
	HYDRUS (K _d pH 6,0)	0,7	0,7	0,8	0,8	0,3	0,3	0,3	0,3	0,7	0,3	0,4	0,3	0,3	0,3
	TGD (K _d pH 6,5)	0,9	0,9	1,0	1,0	0,4	0,4	0,4	0,4	0,9	0,4	0,6	0,4	0,4	0,4
	HYDRUS (K _d pH 6,5)	0,9	1,0	1,1	1,1	0,4	0,4	0,4	0,4	1,0	0,4	0,7	0,4	0,4	0,4
	TGD (K _d pH 7,0)	1,0	1,1	1,1	1,2	0,4	0,5	0,5	0,5	1,1	0,5	0,7	0,5	0,5	0,4
	HYDRUS (K _d pH 7,0)	1,1	1,2	1,3	1,3	0,5	0,5	0,5	0,5	1,2	0,6	0,8	0,5	0,6	0,5

negligible risk
 risk reduction recommended/ ALARA principle
 risk reduction required/ demand for action

Table 25: Maximal risk characterization ratios regarding endpoint human

Hazard	Model (Parameter)	Bio-P sludge	Fe sludge	generic sludge	raw ash	Pearl/ Struvia	AirPrex	Stuttgart	Gifhorn	AshDec	Mephrec	Leadphos	TSP Pot-trails	average TSP	atmospheric deposition only
PCDD/F & dl-PCB	TGD	0,3	0,3	-	-	0,3	0,3	0,3	-	-	-	-	-	-	0,3
PAH	TGD	0,00	0,00	-	-	0,00	0,00	0,00	-	-	-	-	-	-	0,00
As	TGD	0,02	0,03	0,03	0,03	0,02	0,02	0,02	0,02	0,02	0,03	0,02	0,02	0,02	0,02
Cr	TGD	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,01	0,00	0,00	0,00	0,00
Cu	TGD	0,05	0,2	0,09	0,1	0,02	0,02	0,02	0,02	0,07	0,04	0,06	0,02	0,02	0,02
Hg	TGD	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Pb	TGD	0,1	0,1	0,2	0,2	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1
Cd	TGD (K _d RAR)	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,4	0,2
	HYDRUS (K _d RAR)	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,4	0,2
	TGD (K _d pH 5,0)	0,09	0,09	0,09	0,09	0,09	0,09	0,09	0,09	0,09	0,09	0,09	0,09	0,2	0,09
	HYDRUS (K _d pH 5,0)	0,09	0,09	0,09	0,09	0,09	0,09	0,09	0,09	0,09	0,09	0,09	0,09	0,2	0,09
	TGD (K _d pH 5,5)	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,3	0,1
	HYDRUS (K _d pH 5,5)	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,3	0,1
	TGD (K _d pH 6,0)	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,3	0,2
	HYDRUS (K _d pH 6,0)	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,4	0,2
	TGD (K _d pH 6,5)	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,4	0,2
	HYDRUS (K _d pH 6,5)	0,3	0,3	0,3	0,3	0,2	0,2	0,2	0,2	0,2	0,2	0,3	0,2	0,4	0,2
	TGD (K _d pH 7,0)	0,3	0,3	0,3	0,3	0,2	0,2	0,2	0,2	0,2	0,2	0,3	0,2	0,4	0,2
HYDRUS (K _d pH 7,0)	0,3	0,3	0,3	0,3	0,2	0,2	0,2	0,2	0,2	0,2	0,3	0,3	0,5	0,2	
Ni	TGD (K _d RAR)	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01
	TGD (K _d pH 5,0)	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
	TGD (K _d pH 5,5)	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
	TGD (K _d pH 6,0)	0,01	0,00	0,01	0,01	0,00	0,00	0,00	0,00	0,01	0,00	0,00	0,00	0,00	0,00
	TGD (K _d pH 6,5)	0,01	0,01	0,01	0,01	0,00	0,00	0,00	0,00	0,01	0,01	0,00	0,00	0,00	0,00
	TGD (K _d pH 7,0)	0,01	0,01	0,01	0,01	0,00	0,01	0,00	0,00	0,01	0,01	0,00	0,01	0,01	0,00
Zn	TGD (K _d RAR)	0,03	0,03	0,03	0,03	0,01	0,01	0,01	0,01	0,03	0,01	0,02	0,01	0,01	0,01
	HYDRUS (K _d RAR)	0,03	0,03	0,03	0,03	0,01	0,01	0,01	0,01	0,03	0,01	0,02	0,01	0,01	0,01
	TGD (K _d pH 5,0)	0,01	0,01	0,01	0,01	0,00	0,00	0,00	0,00	0,01	0,00	0,00	0,00	0,00	0,00
	HYDRUS (K _d pH 5,0)	0,01	0,01	0,01	0,01	0,00	0,00	0,00	0,00	0,01	0,00	0,00	0,00	0,00	0,00
	TGD (K _d pH 5,5)	0,01	0,01	0,02	0,02	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01
	HYDRUS (K _d pH 5,5)	0,01	0,01	0,01	0,01	0,00	0,00	0,00	0,00	0,01	0,00	0,01	0,00	0,00	0,00
	TGD (K _d pH 6,0)	0,02	0,02	0,02	0,02	0,01	0,01	0,01	0,01	0,02	0,01	0,01	0,01	0,01	0,01
	HYDRUS (K _d pH 6,0)	0,02	0,02	0,02	0,03	0,01	0,01	0,01	0,01	0,02	0,01	0,01	0,01	0,01	0,01
	TGD (K _d pH 6,5)	0,03	0,03	0,03	0,03	0,01	0,01	0,01	0,01	0,03	0,01	0,02	0,01	0,01	0,01
	HYDRUS (K _d pH 6,5)	0,03	0,03	0,03	0,04	0,01	0,01	0,01	0,01	0,03	0,01	0,02	0,01	0,01	0,01
	TGD (K _d pH 7,0)	0,03	0,03	0,04	0,04	0,01	0,01	0,01	0,01	0,03	0,02	0,02	0,01	0,02	0,01
HYDRUS (K _d pH 7,0)	0,04	0,04	0,04	0,04	0,02	0,02	0,02	0,02	0,04	0,02	0,03	0,02	0,02	0,02	

negligible risk
 risk reduction recommended/ ALARA principle
 risk reduction required/ demand for action

Table 26: Maximal risk characterization ratios regarding endpoint groundwater

Hazard	Model (Parameter)	Bio-P sludge	Fe sludge	generic sludge	raw ash	Pearl/ Struvia	AirPrex	Stuttgart	Gifhorn	AshDec	Mephrec	Leadphos	TSP Pot-trails	average TSP	atmospheric deposition only
PCDD/F & dl-PCB	TGD	0,07	0,07	-	-	0,07	0,07	0,07	-	-	-	-	-	-	0,07
PAH	TGD	0,428	0,43	-	-	0,43	0,43	0,43	-	-	-	-	-	-	0,43
As	TGD	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01
Cr	TGD	0,1	0,1	0,3	0,3	0,05	0,06	0,05	0,04	0,3	0,4	0,1	0,1	0,2	0,04
Cu	TGD	0,3	0,8	0,5	0,5	0,09	0,1	0,1	0,09	0,4	0,2	0,3	0,09	0,09	0,09
Hg	TGD	0,02	0,03	0,02	0,01	0,01	0,01	0,01	0,01	0,02	0,02	0,01	0,01	0,01	0,01
Pb	TGD	0,06	0,06	0,07	0,07	0,05	0,05	0,05	0,05	0,06	0,05	0,05	0,05	0,05	0,05
Cd	TGD (K _d RAR)	0,7	0,7	0,7	0,7	0,6	0,6	0,6	0,6	0,6	0,6	0,7	0,6	1,2	0,6
	TGD (K _d pH 5,0)	2,0	2,0	2,0	2,0	2,0	2,0	2,0	2,0	2,0	2,0	2,0	2,0	3,6	2,0
	HYDRUS (K _d pH 5,0)	1,8	1,8	1,8	1,8	1,8	1,8	1,8	1,8	1,8	1,8	1,8	1,8	3,2	1,8
	TGD (K _d pH 5,5)	1,4	1,4	1,4	1,4	1,4	1,4	1,4	1,4	1,4	1,4	1,4	1,4	2,8	1,4
	HYDRUS (K _d pH 5,5)	1,3	1,3	1,3	1,3	1,1	1,1	1,1	1,1	1,1	1,2	1,3	1,2	2,2	1,1
	TGD (K _d pH 6,0)	1,0	1,0	1,0	1,0	0,9	0,9	0,9	0,9	0,9	0,9	1,0	0,9	1,8	0,9
	HYDRUS (K _d pH 6,0)	0,8	0,8	0,8	0,8	0,7	0,7	0,7	0,7	0,7	0,7	0,8	0,8	1,3	0,7
	TGD (K _d pH 6,5)	0,6	0,6	0,6	0,6	0,5	0,5	0,5	0,5	0,5	0,5	0,6	0,6	1,0	0,5
	HYDRUS (K _d pH 6,5)	0,4	0,4	0,4	0,4	0,4	0,4	0,4	0,4	0,4	0,4	0,4	0,4	0,7	0,4
	TGD (K _d pH 7,0)	0,3	0,3	0,3	0,3	0,3	0,3	0,3	0,3	0,3	0,3	0,3	0,3	0,5	0,3
HYDRUS (K _d pH 7,0)	0,03	0,03	0,03	0,03	0,03	0,03	0,03	0,03	0,03	0,03	0,03	0,03	0,03	0,04	0,03
Ni	TGD (K _d RAR)	0,1	0,1	0,1	0,1	0,07	0,08	0,08	0,07	0,1	0,1	0,08	0,09	0,08	0,07
	TGD (K _d pH 5,0)	0,7	0,6	0,7	0,8	0,5	0,5	0,5	0,5	0,8	0,6	0,5	0,5	0,5	0,5
	TGD (K _d pH 5,5)	0,6	0,5	0,6	0,7	0,4	0,4	0,4	0,4	0,7	0,5	0,4	0,4	0,4	0,4
	TGD (K _d pH 6,0)	0,5	0,4	0,5	0,5	0,3	0,3	0,3	0,3	0,5	0,4	0,3	0,3	0,3	0,3
	TGD (K _d pH 6,5)	0,3	0,3	0,4	0,4	0,2	0,2	0,2	0,2	0,4	0,3	0,2	0,3	0,2	0,2
	TGD (K _d pH 7,0)	0,2	0,2	0,2	0,2	0,1	0,2	0,2	0,2	0,1	0,3	0,2	0,2	0,2	0,1
Zn	TGD (K _d RAR)	2,4	2,6	2,8	2,9	1,0	1,0	1,0	1,0	2,6	1,1	1,7	1,0	1,2	1,0
	TGD (K _d pH 5,0)	6,1	6,8	7,4	7,6	2,4	2,4	2,4	2,4	6,6	2,4	3,7	2,4	2,4	2,4
	HYDRUS (K _d pH 5,0)	6,0	6,8	7,4	7,6	2,4	2,4	2,4	2,4	6,6	2,4	3,7	2,4	2,4	2,4
	TGD (K _d pH 5,5)	5,4	6,0	6,5	6,7	2,2	2,2	2,2	2,2	5,9	2,2	3,5	2,2	2,2	2,2
	HYDRUS (K _d pH 5,5)	5,0	5,5	5,9	6,0	2,1	2,2	2,2	2,2	5,4	2,2	3,3	2,2	2,2	2,1
	TGD (K _d pH 6,0)	4,0	4,4	4,7	4,8	1,6	1,6	1,6	1,6	4,3	1,6	2,7	1,6	1,6	1,6
	HYDRUS (K _d pH 6,0)	3,3	3,6	3,8	3,8	1,5	1,5	1,5	1,5	3,5	1,6	2,4	1,5	1,6	1,5
	TGD (K _d pH 6,5)	2,4	2,6	2,8	2,8	1,0	1,0	1,0	1,0	2,6	1,1	1,7	1,0	1,1	1,0
	HYDRUS (K _d pH 6,5)	1,9	2,0	2,1	2,2	1,1	1,1	1,1	1,1	2,0	1,1	1,5	1,1	1,2	1,1
	TGD (K _d pH 7,0)	1,3	1,4	1,4	1,5	0,6	0,6	0,6	0,6	1,3	0,6	0,9	0,6	0,6	0,6
HYDRUS (K _d pH 7,0)	0,9	1,0	1,0	1,1	0,6	0,6	0,6	0,6	1,0	0,6	0,8	0,6	0,6	0,6	

negligible risk
 risk reduction recommended/ ALARA principle
 risk reduction required/ demand for action