Risk Assessment and Fertilizer regulation –
A valuation with respect to recycled phosphorus materials from wastewater

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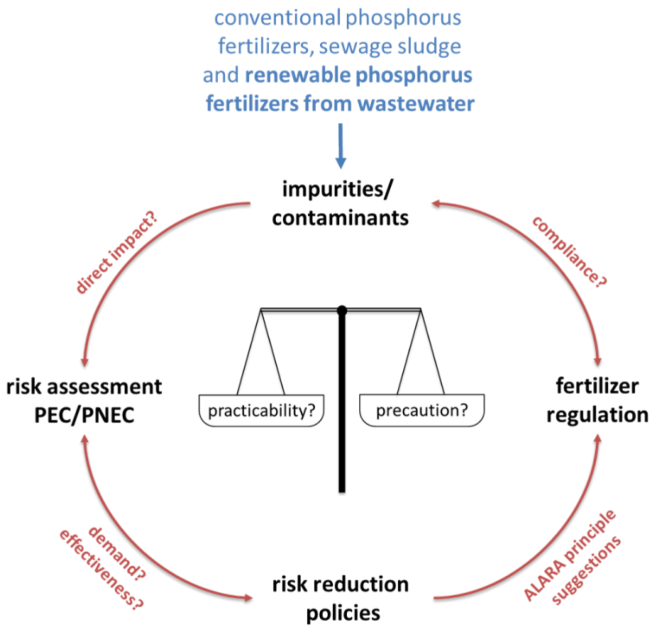
This paper had been prepared within the EU-FP7 Project P-REX. It is a brief version of "Deliverable D 9.1-Quantitative risk assessment of potential hazards for humans and the environment: quantification of potential hazards resulting from agricultural use of the manufactured fertilizers" and the presentation on risk assessment from the 11.06.2015 at the P-REX Final Workshop in Amsterdam. This paper provides a further discussion regarding limit values for fertilizer regulation. It should be noted that this work is based on a quantitative risk assessment with qualitative sensitivity analysis based on a data-set compiled in 2014. Many uncertainties are not entirely addressed in this paper. An enhanced version with better consideration of these uncertainties and a quantitative sensitivity analysis is planned for mid-2018.

Abstract

In recent years several ways of recovering phosphorous from municipal wastewater have been developed. Depending on the applied technology the recovered materials as well as the quality of sewage sludge vary significantly concerning the concentrations of heavy metals and organic residues. A comparative risk assessment of seven renewable and not certified phosphorus fertilizers, sewage sludge, raw ash and triple super phosphates has been conducted for PCDD/Fs + dl-PCBs, PAHs, As, Cd, Cr, Cu, Hg, Ni, Pb and Zn. Results indicate that Cd and Zn are of concern under specific conditions for some endpoints. Additional risk reduction measures are recommended for many observed substances and endpoints to reduce risks to a negligible level. The use of limit values as one instrument in fertilizer regulations is one possible measure for risk reduction. Considering the results of this risk assessment, substance-contents in materials and current fertilizer policies; the effectiveness of stricter limit values to reduce the input of hazardous substances into the ecosystem is assessed and risk-based values are proposed.



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1 Introduction

On European level, it is expected that the Commission's proposal for a new fertilizer regulation enters the legislative process in 2015 [1]. Recycled phosphorus materials will be included in this regulation. Conventional P-fertilizers as well as renewable/recycled fertilizers contain various by-products/impurities, which are emitted into environment together with fertilizers applied in agriculture. The present study intends to evaluate the environmental risks of those impurities. Moreover, the method of environmental risk assessment is used to assess the effectiveness of stricter limit values for risk reduction in fertilizer regulation.

The limit values of the German Fertilizer Ordinance (DüMV) and the drafted novel of the Sewage Sludge Ordinance (AbfKlärV) of Germany are arbitrarily chosen to illustrate this approach, but could be replaced by any other benchmark or national regulation (in comparison to other EU member states Germany has rather strict limit values).

The drafted fertilizer regulation of the EU was not taken into account, since suggested fertilizer-category-specific limit values raises questions regarding the quality criteria for certification into a specific fertilizer-category. Although this is roughly possible for the investigated materials of this study, the current approach by EU has to be rethought on categorization of fertilizers and consequently on varying limit values of several fertilizer-categories.

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" [2 p.2 Table 1.1]. Risk assessment involves four steps: hazard identification, hazard characterization, exposure assessment and risk characterization. [2]

In hazard identification, the capacity of substances to cause harm is identified. "[…] Hazard means a biological, chemical or physical agent […] with the potential to cause an adverse health effect" [3 p.8 Chapt.1 Art.3 (14)].

Hazard characterization correlates the dose of a hazard and the corresponding effect on human health and/or the environment. The Predicted No-Effect Concentration (PNEC), "[…] a concentration below which an unacceptable effect will most likely not occur." [4 p. 93, sect. 3.1], is derived from the result of toxicological testing and assessment factors in order to cope with present uncertainties.

Exposure assessment models are used to estimate the Predicted Environmental Concentration (PEC) to which humans or environmental endpoints are likely to be exposed. For this part of risk assessment assumptions are needed to quantify the expected concentrations as simple as possible but as accurate as needed.

Risk is expressed as the quotient of PEC and the PNEC in risk characterization. This risk quotient (RQ) is no absolute measure of risk. In fact, the absolute value of risk remains unknown. The only conclusion which can be drawn is that the probability of an adverse effect increases with an increasing RQ. Once a risk was 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. [2]

It has to be understood that even if the risk ratio 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 has been shown that on the one hand stricter limit values for heavy metals as precautionary measure of risk reduction may reduce environmental risks effectively, while on the other hand they fail as other (diffuse) sources are more important than the inputs on arable land via fertilizers or recycled materials. The study emphasizes the added value and the need of a sound and competitive scientific evaluation of all relevant inputs before limit value setting and the advantages of the systematic and transparent method of environmental risk assessment.

2 Methods

2.1 Scope

The scope of this assessment is compartmentalized in hazards, materials and endpoints:

Hazards: PCDD/F & dl-PCB as WHO-TEQ, PAH, As, Cr, Cu, Hg, Pb, Cd, Ni and Zn

Materials: 13 materials

- types of sludge: samples for **Bio-P sludge** and **Fe sludge** from Germany; **generic sludge** based on measurements of ashes of 13 municipal sewage sludge mono-incineration plants in Germany
- **raw ash** based on measurements of ashes of 13 municipal sewage sludge mono-incineration plants in Germany
- 4 struvite/CaP from sludge/liquor: struvite from **Pearl/Struvia** and **AirPrex** without acidification of sludge and struvite/CaP from **Stuttgart** and **Gifhorn** process with acidification of sludge
- 3 phosphorus materials from ash/thermal treatment: thermochemical **AshDec** material, **Mephrec** material by metallurgic sludge or ash treatment, **Leachphos** material by acidification of ash
- 2 conventional TSP fertilizers: **TSP Pot-tests** as sample TSP for the European market and more polluted **average TSP** calculated by world-market shares in 2010

Endpoints: human via plant consumption, soil organisms, groundwater

2.2 General Methodology

The risk assessment is conducted for each combination of hazard, material and endpoint. Following the process of risk management, risk reduction measures are required when the ratio is higher than one. According to [2] risk can be classified in “unacceptable risk” ($RQ > 1$), “risk reduction required” ($0.01 < RQ < 1$) and “negligible risk” ($RQ < 0.01$). Since this wording is sharp and may be misunderstand a classification into “risk reduction required/ need for action” ($RQ > 1$), “risk reduction recommended/ *ALARA* principle” ($0.01 < RQ < 1$) is used. This classification is adopted in this study (see Figure 1, results see chapter 3.1) to quantify the urgency of risk reduction measures for specific hazards in combination with endpoints. If a hazard showed a $RQ < 0.01$ for all three endpoints (human, soil organisms and groundwater), there is no need for action. However, the limit value in the fertilizer ordinance is compared with the contamination of materials (chapter 3.3) to estimate a by legislation permitted PEC_{max}/PNEC quotient.

If the RQs exceed 0.01, measures for risk reduction are recommended [2]. The size of RQ describes the urgency for proper measures. Therefore, the relevance of hazardous loads on arable land by materials application is assessed (see Figure 1). Within risk assessment diffuse sources for hazardous inputs, such as atmospheric deposition have to be considered too. The comparison of annual loads by fertilizer application and atmospheric deposition illustrates if stricter limit values would show an effect on risk reduction at all. A proportion of maximal 20 % hazardous input by material application compared to atmospheric deposition is taken into account to approach the effectiveness of stricter limit values in the context of risk reduction. If this comparison points out that diffuse sources are of higher relevance, risk reduction measures were more successful by stricter limitations regarding emissions to air.

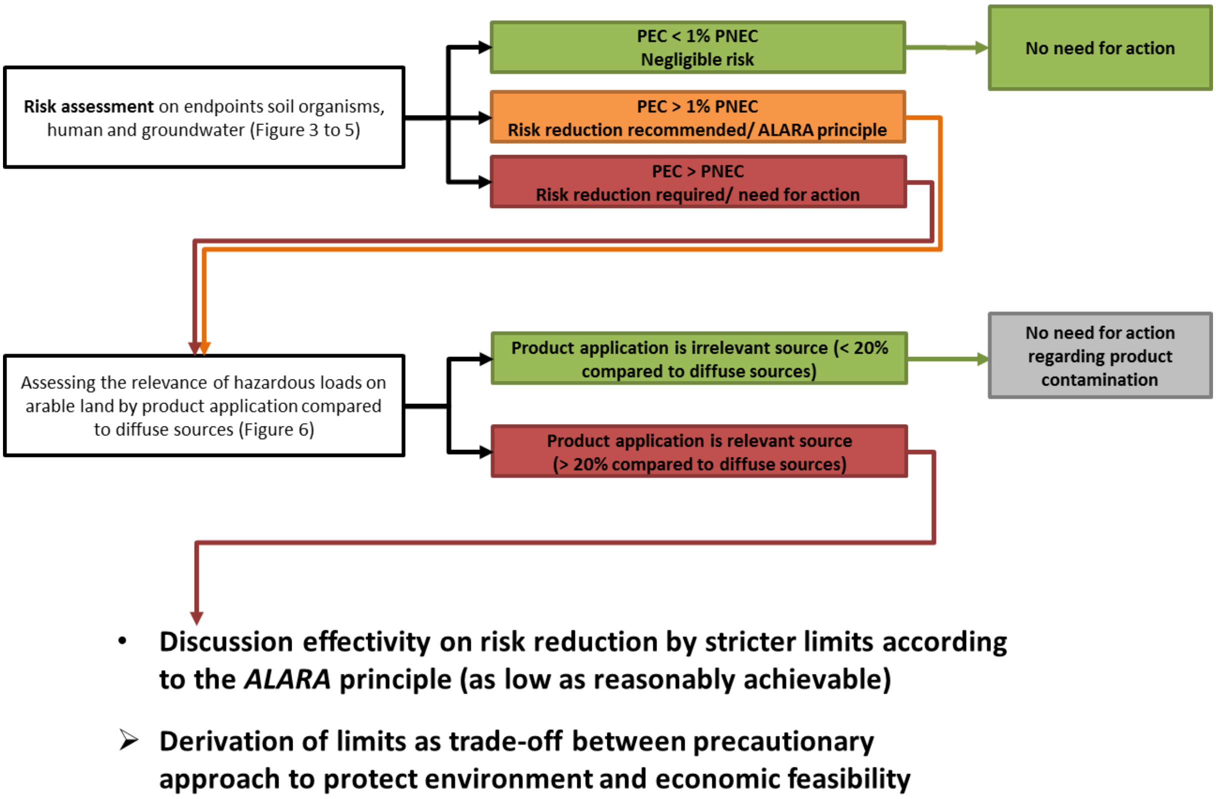


Figure 1: Approach for derivation of limit values suggested in Chapter 4 for ordinances

Finally a number of crucial issues are taken into account to derive limits as trade-off between precautionary approach to protect both environment and economic feasibility. This so called *ALARA* principle (as low as reasonably achievable) includes:

- Discussion of limit and labeling values in ordinances in reference to material contamination
- Discussion of different limits in ordinances regarding aspects of harmonization
- Discussion whether risk reduction to PEC = PNEC or even PEC = 1% PNEC is possible with stricter limit values in legislation
- Discussion whether model refinements reduce calculated PEC/PNEC ratios
- Discussing the issue of micro-nutrients and target values in soil (Cu, Zn)

The following points provide two possible examples:

- For a certain hazard the RQ exceed 0.01 for at least one endpoint, so risk reduction is recommended; the comparison with atmospheric deposition indicates that the hazardous input by fertilizer application is way below 20 % of annual atmospheric deposition and stricter limit values for fertilizers would not have an effect on risk reduction: consequently the limit value for fertilizers is sufficiently strict in terms of environmental protection
- For a certain hazard the RQ exceed 0.01 for at least one endpoint, so risk reduction is recommended; the comparison with atmospheric deposition indicates that the hazardous input by fertilizer application exceeds 20 % of annual atmospheric deposition although the limit value in fertilizer ordinance is met by the materials: consequently a stricter limit value has to be considered as one option of risk reduction. It may be that even without fertilizer application the negligible level is exceeded. Consequently very strict limit values for fertilizers would not conclude in an RQ below 0.01 but risk reduction still can be achieved by stricter limit values. Considering a number of crucial issues according to the *ALARA* principle a stricter limit value for this hazard is eventually suggested in terms of risk reduction and feasibility.

2.3 Approach for risk assessment

Based on the potential accumulation of hazards in soil, a time span of 100 years of fertilizer application is modelled in exposure assessment. An annual fertilizer equivalent to 60 kg P_2O_5/ ha × year is assumed. Average atmospheric deposition of hazards in Germany is considered as well as the initial concentrations of the hazardous substances in soil based on literature values and pre-modelling

In exposure assessment model refinements additional to the proposed model by EU Technical Guidance Document [4] were realized with a solute transport and a precipitation model for the hazards of concern (Cd and Zn). Generally, the assumption for an “European standard environment” [4] was applied for modelling. A number of sensitivity analyses were conducted on the different input parameters: water flow parameters, rain and infiltration rate, substance-specific parameters, soil-pH (for hazards Cd, Ni and Zn with high potential of mobilization in acidic soils), initial and boundary fluxes and quantity of fertilizer application. Figure 2 illustrates the exposure routes considered in the risk assessment.

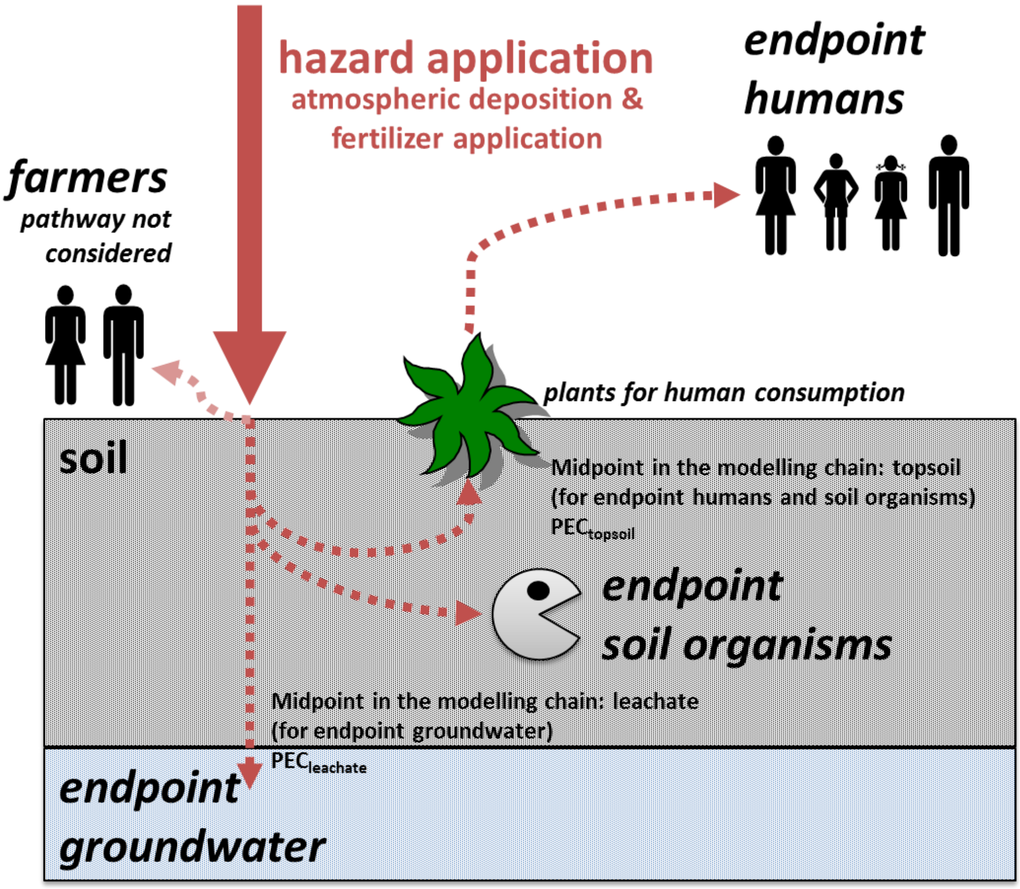


Figure 2: Pathways for exposure, endpoints and midpoints in the risk assessment

For topsoil the model [4] considers the input of hazards by fertilizer application and atmospheric deposition and the outputs volatilization, biodegradation and leaching for organic substances. For heavy metals the model has been modified, so leaching is the only output. Leaching is thereby described by soil hydraulic properties and the retardation of metals by their behaviour to adsorb on soil particles. Hazard uptake by plants or organisms is only considered for risk characterization regarding the endpoint human and soil organisms, so an equivalent load is not reduced in topsoil. This worst-case assumption is common practice in risk assessments [4].

Risk characterization is realized for two midpoints: topsoil and leachate. Thereby the PNEC is described as a concentration in topsoil or leachate which is tolerable for humans, soil organisms or groundwater due to inverse modelling. For humans this inverse modelling is founded on safety parameters, like the Tolerable Daily Intake, for each hazard. Assumptions to derive a tolerable concentration in topsoil for humans regarding wheat consumption were applied [5], [6], [7]. The precise description for derivation of PNEC$_{human}$ is described in in the Deliverable D 9.1 of the EU FP7 project P-REX [8]. The hazard- and endpoint-specific PNECs are shown in Table 1.

Table 1: Hazard- and Endpoint-specific PNECs for assessment

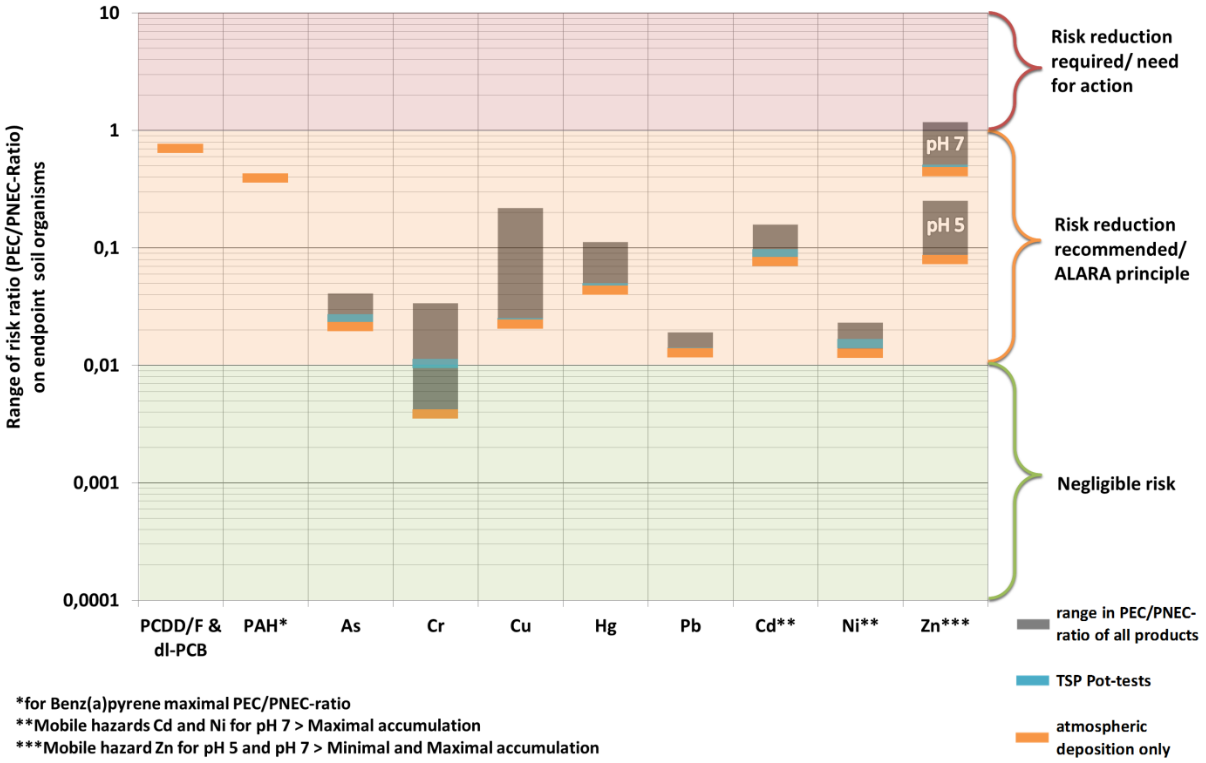
Substance	**Endpoint soil organisms Midpoint topsoil**		**Endpoint humans Midpoint topsoil**		**Endpoint groundwater Midpoint leachate**	
	PNEC [mg/kg topsoil]	**Source**	**PNEC [mg/kg topsoil]**	**Source for safety parameter**	**PNEC [µg/L leachate]**	**Source**
PCDD/F & dl-PCB	$2 \cdot 10^{-5}$ WHO-TEQ	From NOEC: [9], [10]	$5.44 \cdot 10^{-5}$ WHO-TEQ	[11]	PCB approx. $3.25 \cdot 10^{-6}$ WHO-TEQ	Minor threeshold value [12]
PAH (BaP)	BaP: 0.053	[13]	PAH: 3109	[14]	PAH: 0.2	
As	7	From NOEC: [15]	8.39	[16]	10	
Cr	62	[17]	327	[18]	7	
Cu	78.9	[19]	107	[20]	14	
Hg	0.3	[21]	17.1	[22]	0.2	
Pb	166	[23]	20.1	[6]	7	
Cd	1.15	[24]	0.42	[25]	0.5	
Ni	50	[26]	143	[27]	14	
Zn	26	[28]	817	[29]	58	

3 Results

3.1 Risk assessment and classification

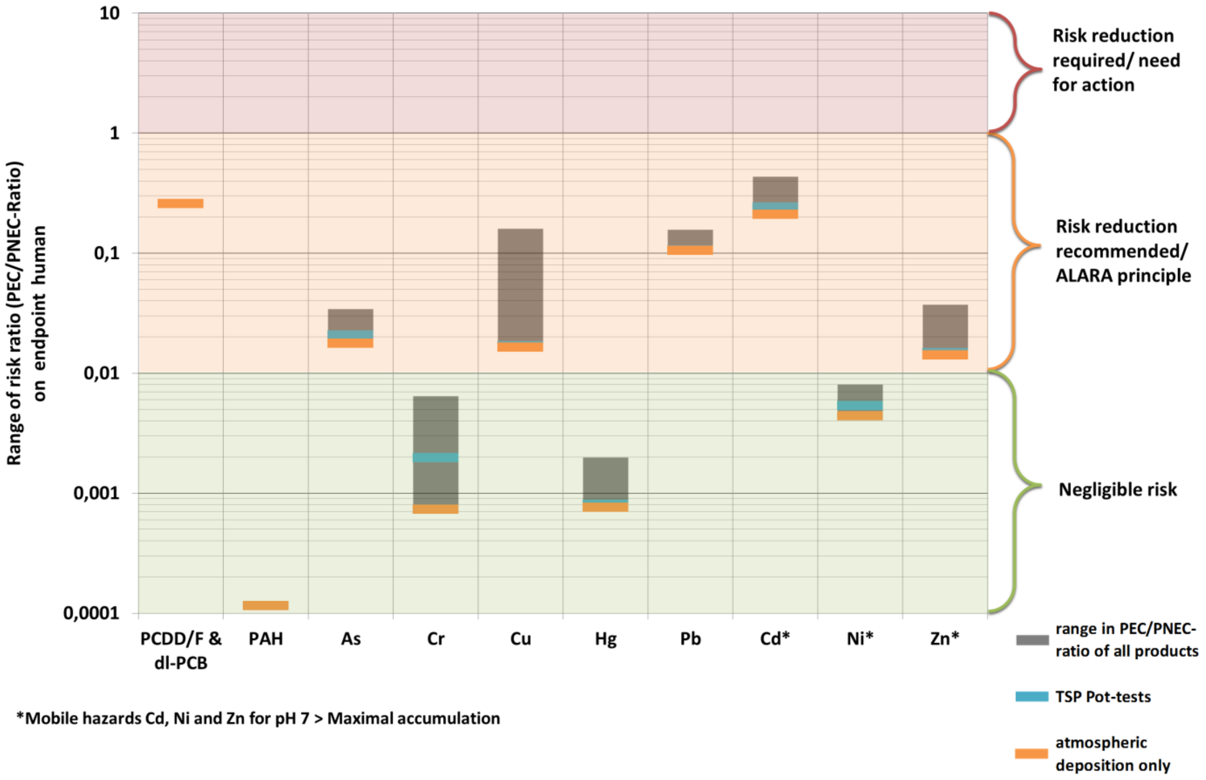
The RQ is calculated from quotient PEC to PNEC for each endpoint, each hazard and product [4 sect. 5.1, p.172, Table 32]. The ranges of hazard- and endpoint-specific ratios are shown in Figure 3 to Figure 5.

1. **Endpoint soil organisms (see Figure 3).**
    a. 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 4)**
    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 5)**
    a. High 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 (in dependency form soil-pH) the PNEC for Cd and Zn 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 below pH 6.



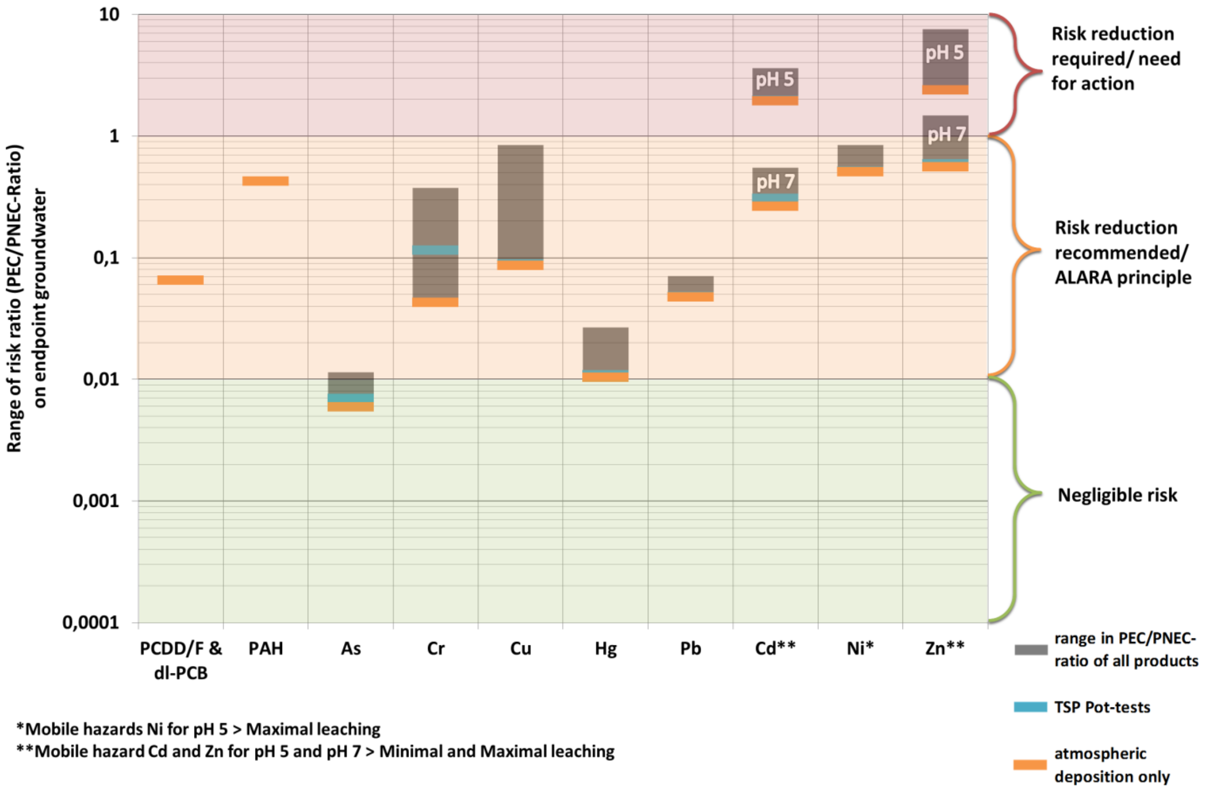
*for Benz(a)pyrene maximal PEC/PNEC-ratio
**Mobile hazards Cd and Ni for pH 7 > Maximal accumulation
***Mobile hazard Zn for pH 5 and pH 7 > Minimal and Maximal accumulation

Figure 3: Range of risk ratio (PEC/PNEC-Ratio) on particular hazards for the endpoint soil organisms, TSP Pot-tests and atmospheric deposition for comparison



*Mobile hazards Cd, Ni and Zn for pH 7 > Maximal accumulation

Figure 4: Range of risk ratio (PEC/PNEC-Ratio) on particular hazards for the endpoint human, TSP Pot-tests and atmospheric deposition for comparison



*Mobile hazards Ni for pH 5 > Maximal leaching
**Mobile hazard Cd and Zn for pH 5 and pH 7 > Minimal and Maximal leaching

Figure 5: Range of risk ratio (PEC/PNEC-Ratio) on particular hazards for the endpoint groundwater, TSP Pot-tests and atmospheric deposition for comparison

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

Besides cadmium and zinc, many hazards lead to endpoint-specific risk quotients above the negligible level. Based on the worst-case assumptions made 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.

In case of low-contaminated products, the exceeding of PNEC for Cd and Zn regarding groundwater is often a result of high previous or present rates of atmospheric deposition of these substances. In these cases a risk cannot be excluded, although the product-quality is not responsible. For an effective minimization of risks a reduced diffuse discharge into the atmosphere would be necessary instead to any process development refining the product.

3.2 Relevance of product contamination compared to diffuse sources

Figure 6 illustrates the relevance of the hazards in the products compared to the input via diffuse sources, such as atmospheric deposition. It becomes apparent that…

- …in comparison to the annual load of atmospheric deposition, almost all products have elevated chromium contents. In case of sludge, raw ash and ash products additionally copper appears to be a relevant hazard compared to atmospheric deposition.

- …for sludge and raw ash, the input via product application exceeds the input via atmospheric deposition for all heavy metals. For ash products this is partly depended on the selected metal, the input material and the depletion rate of the process.
- …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 these persistent organic pollutions.
- …struvite generally shows 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.

3.3 Contamination of products and legal classification

The concentrations of hazards per dry matter of product and the limit values of DüMV [34] and amendment to AbfKlärV [35] are shown in Figure 7. Additionally, the phosphorus specific concentrations per kg P_2O_5 and the phosphorus specific limit for Cd according to DüMV are shown in Figure 8. A few notes are given for legal classification:

- **Cu**: raw ash exceeds the maximum content of DüMV (Table 4.1.1)
- **Cd:** raw ash, Leachphos, TSP Pot-tests and average TSP exceed the limit value for Cd of 1.5 mg/kg DM (Dry matter) (Figure 7**)**. Since these products contain > 5 % P_2O_5 FM (Fresh matter) the limit of 50 mg Cd/kg P_2O_5 applies: so only average TSP exceeds the limit of Cd according to DüMV; the tolerance span of 50 % for Cd in DüMV is not exceeded, so no product is prohibited by their Cd-content (Figure 8).
- **Hg:** Bio-P and Fe sludge exceed the limit of DüMV marginal; the tolerance span of 50 % for Hg in DüMV is not exceeded, so no product is prohibited by their Hg-content

A correlation between the limit values in DüMV for certain substances and the calculated risk ratios is undistinguishable for the endpoints soil organism and groundwater. Furthermore, for substances like Zn (but also Cr and Cu), where high risk ratios are observed a proper limit value is missing in DüMV. Since no risk is expected for the endpoint human, the limits in DüMV are primary founded on ensuring food safety and human health protection, not particular on protecting multiple environmental compartments.

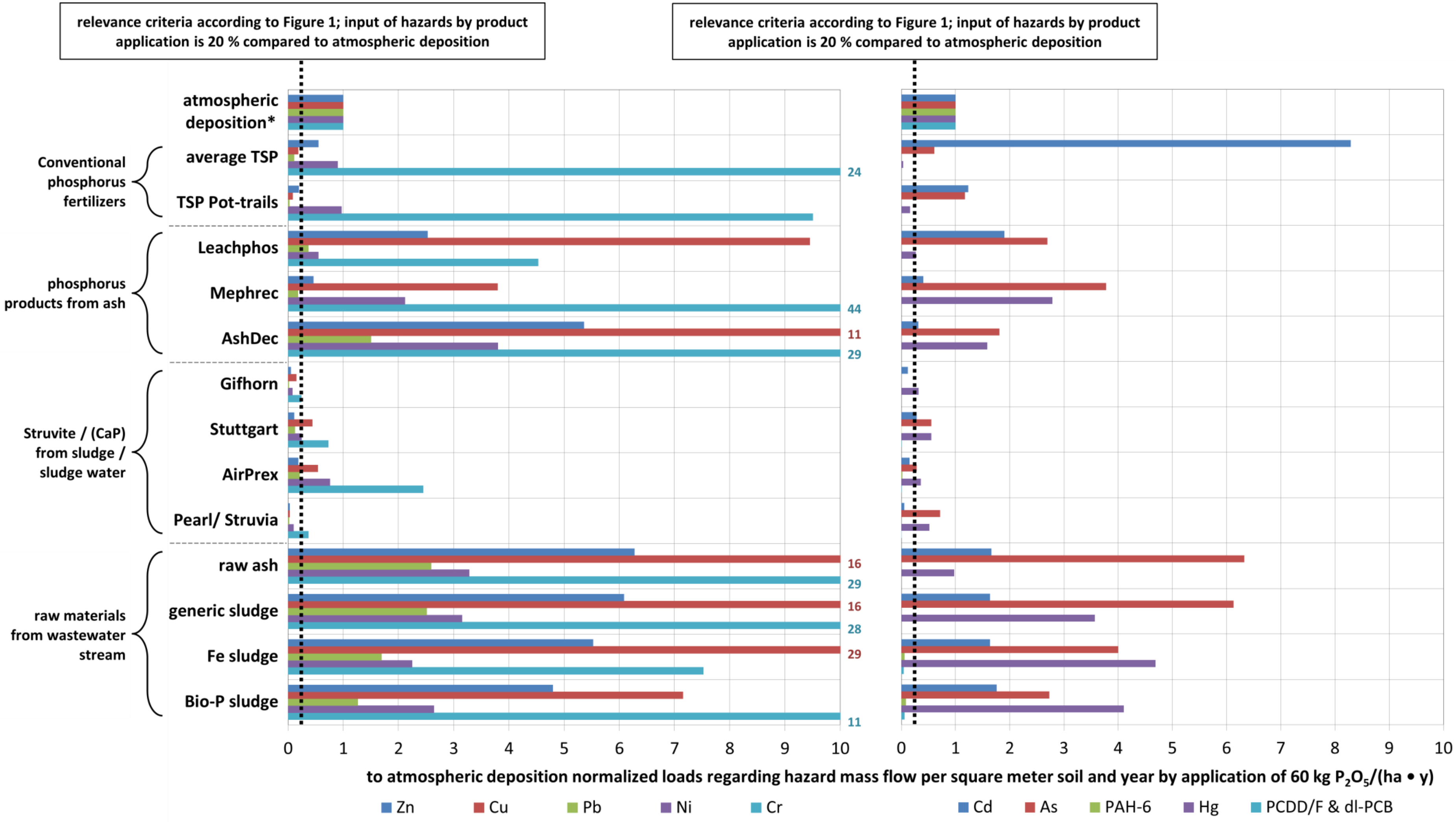


Figure 6: Ratio of average phosphorus related mass flow per square meter soil and year for hazards in the model; for atmospheric deposition all mass flows set to 1; for products proportional ratio; *atmospheric deposition in Germany for Cr, Cu, Ni, Zn (2001-2003) [30]; PCDD/F & dl-PCB (2004) [31]; As (2007-2009) [32]; Cd, Hg, Pb (2008-2010) [33]; PAH (2010) [30]

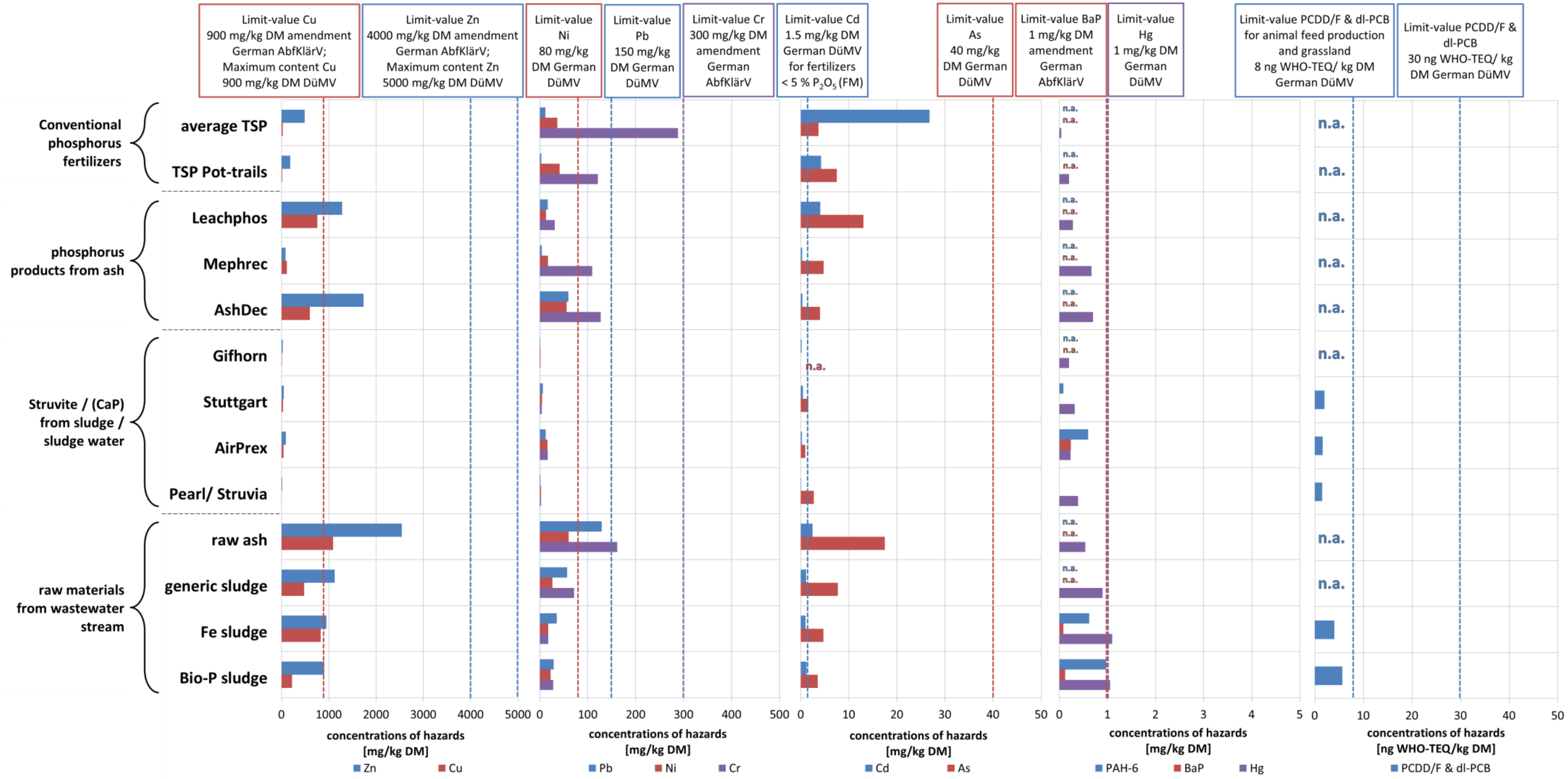


Figure 7: Concentration of hazards per dry matter of product for sludge, sludge ash, secondary phosphate and conventional phosphate fertilizers and German limits values according to amendment of AbfKlärV and current DüMV

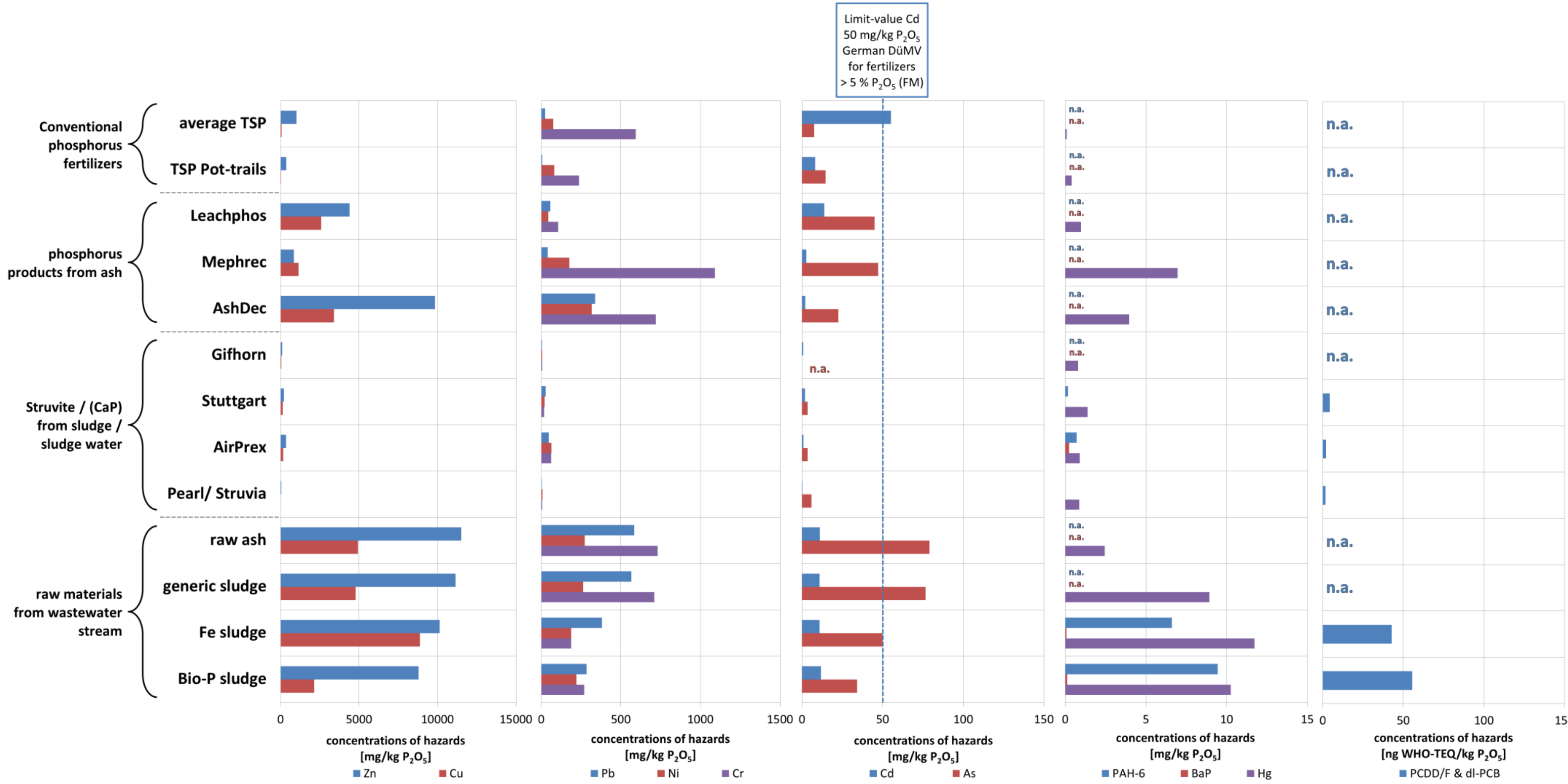


Figure 8: Phosphate specific concentrations of hazards per dry matter of product for sludge, sludge ash, secondary phosphate and conventional phosphate fertilizers and German limit values according to current DüMV

4 Discussion and derivation of limit values

Considering the uncertainties of the used models, input parameters and data quality, limit values are discussed concerning their effectiveness to reduce environmental risks. The overall target is to derive consistent limit values for (mineral and organic; conventional and renewable) fertilizers under the aspects of risk reduction and practicability. As a result of distinctions in P_2O_5-contents and different output quantities a precise hazard-content per dry matter content fertilizer to reach the maximum permissible level or the negligible level cannot be easily suggested. Further distinctions regarding nutrient-contents are considered by fertilizer-categorization in the drafted EU Fertilizer regulation. This study suggests limit values for P-fertilizers with a minimum content of 10 % P_2O_5 per dry matter. Aspects of reactivity, solubility and fertilizer effectivity of P_2O_5 had to be considered and have to be evaluated separately. Table 2 gives an overview on hazards towards classification of the methodology described in Chapter 2.2 and Figure 1.

Table 2: Hazard classification towards methodology

Substance	**Risk reduction recommended[1] (worst case assumptions)**	**Relevance of product application (Figure 6)**	**legal product classification (exceeding of limit values)**	**Most sensitive endpoint on substance**	**Maximal permissible concentration[2] PEC = PNEC**	**Negligible concentration PEC = 1% PNEC**
PCDD/F & dl-PCB	soil organisms, human, groundwater	No	-	-	-	-
PAH (BaP)	soil organisms, groundwater	No	-	-	-	-
As	soil organisms, human, (groundwater)	Yes (exceptions)	No exceeding of limit values	soil organisms	≈ 350 mg/kg	- the negligible level is exceeded for the most sensitive endpoint by background system
Cr	(soil organisms), groundwater	Yes (exceptions)	No limit value in DüMV	groundwater	≈ 300 mg/kg	
Cu	soil organisms, human, groundwater	Yes (exceptions)	No limit value in DüMV	groundwater	≈ 1100 mg/kg	
Hg	soil organisms, groundwater	Yes (exceptions)	No exceeding of limit values or tolerance span	soil organisms	≈ 15 mg/kg	
Pb	soil organisms, human, groundwater	Yes (exceptions)	No exceeding of limit values	human	≈ 950 mg/kg	
Cd	soil organisms, human, **groundwater**	Yes (exceptions)	No exceeding of limit values or tolerance span	groundwater	Depending on pH; ≈ 3-150 mg/kg P_2O_5	
Ni	soil organisms, groundwater	Yes (exceptions)	No exceeding of limit values	groundwater	Depending on pH; ≈ 40-220 mg/kg	
Zn	**soil organisms**, human, **groundwater**	Yes (exceptions)	No limit value in DüMV	groundwater	Depending on pH; ≈ 0-500 mg/kg	

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[1] According to Figure 3 to Figure 5; in brackets: partly PEC > 1 % PNEC, depending on product contamination; bold print: PEC > PNEC

[2] Assumed minimum P_2O_5-content of 10 % for derived maximal permissible concentration

- **PCDD/F & dl-PCB** and **PAH**: Figure 6 as well as Figure 3 to Figure 5 underline the negligible effect on the overall immissions due to fertilizer application. The risk ratio is either a result of the background concentration in soil or due to high rates of atmospheric deposition. Stricter limit values in DüMV will not have any effect on risk reduction.
- **As:** According to Figure 3 and Figure 4 risk reduction is recommended regarding the endpoints soil organisms and humans. The current limit value of 40 mg/kg in DüMV is totally sufficient to deceed the maximal permissible concentration (see Table 2). A stricter limit value e.g. the labelling value according to DüMV of 20 mg/kg will not reduce the risk ratios to the negligible level, but can be considered as reasonable measure of risk reduction. None of the observed fertilizers exceeds 20 mg/kg. Hence other measures of risk reduction may achieve similar results by lower efforts a risk-benefit analysis can be conducted.
- **Cr:** There is currently no limit value for total Cr in DüMV. Figure 4 confirms the low relevance of Cr (III) regarding human health. Leaching of chromium depends on pH-value because of a low saturation concentration of Cr in neutral soils. In current fertilizer regulations often a limit value for Cr (VI) of 2 mg/kg is set or discussed instead of a limit for total chromium. [36] Although Cr (VI) has a considerably higher toxicity compared to Cr (III), this discussion should not underestimate toxicity to organisms of Cr (III)/ total Cr especially under acidic conditions [17]. Furthermore Cr (VI) is likely to be reduced to Cr (III) under environmental conditions [17]. Under aspects of precaution the limit value from AbfKlärV and the labelling value from DüMV of 300 mg/kg (total Cr) should be considered as one possible limit value for an upcoming fertilizer regulation. This limit achieves the maximal permissible level of risk for groundwater considering worst-case assumptions according to this risk assessment.
- **Cu:** Cu is on the one hand an essential micro-nutrient and on the other hand a hazard depending on concentration in soil. Figure 3 to Figure 5 indicate a recommendation of risk reduction measures regarding Cu for all endpoints. This is still the case, although precipitation of Cu takes place in neutral soils and the real PEC/PNEC ratio is reduced in this case for the endpoint groundwater. The maximum content for Cu in DüMV in fertilizers and the limit value in AbfKlärV is fixed at 900 mg/kg. Considering both, risk reduction measures and the essentiality of Cu, a limit value with exceptions is suggested: for soils with content of exchangeable Cu above 2-4 mg/kg soil [37], a limit value in fertilizer ordinance of 900 mg/kg is sufficient, so the maximum permissible level is not exceed (see Table 2). Below this level no limit value should be applied, to ensure the Cu-supply of the soil. A limit value of 900 mg/kg would prohibit valorization on arable land of some sewage sludge incineration ashes.
- **Hg:** Risks on human health by Hg are on a negligible level due its high immobility in soil (Figure 4). For risk reduction regarding soil organisms the limit value of 1 mg/kg in DüMV is totally sufficient to deceed the maximum permissible concentration (see Table 2). For groundwater the calculated risk ratio (Figure 5) can be reduced by model refinement, since Hg is likely to precipitate in a pH-range between 5 and 7. A Stricter limit value would result only minor effects on risk reduction but would correspond with an almost complete prohibition of sewage sludge valorization on arable land and is as a result not a reasonable option reflecting the current situation in Germany or Europe.

- **Pb:** Risk reduction is recommended regarding all three endpoints. By model-refinement of the worst-case assumptions the risks regarding the endpoints human and groundwater could be reduced (refining of transfer-rate for plant-uptake and precipitation of Pb). The current limit value of 150 mg/kg in DüMV is totally sufficient to deceed the maximum permissible concentration (see Table 2). A stricter limit value e.g. the labelling value according to DüMV of 100 mg/kg will not reduce the risk ratios to the negligible level, but can be considered as useful measure of risk reduction. Hence other measures of risk reduction may achieve similar results by lower efforts a risk-benefit analysis can be conducted. A limit value of 100 mg/kg would prohibit valorization on arable land of many sewage sludge incineration ashes.
- **Cd:** Cd is often seen as most problematic hazard, due to high toxicity, ascertained transfer-rate regarding accumulation in plants, mobile behavior even in neutral soils and elevated Cd-concentrations in conventional fertilizers as a result of high concentrations in sedimentary phosphate rock. Against the background of assumptions made the risk for the endpoint groundwater cannot be excluded on acidic soils (Figure 5). An exceeding of the $PNEC_{groundwater}$ is not necessarily the result of fertilizer application, but is likely to be already reached by background-concentrations and atmospheric deposition. In DüMV two limit values are applied for Cd. For P_2O_5-poor fertilizers (< 5 % P_2O_5 FM) the limit value can be sufficiently protective dependent on the quantity of fertilizer, that is been used. In contrast, for P_2O_5-rich fertilizers (> 5 % P_2O_5 FM), the limit value is too high regarding sustainable groundwater protection. A limit value of 3 mg/kg P_2O_5 DM would reduce risks based on the assumptions to the maximum permissible level on acidic soils. This limit value would exclude all commonly produced conventional phosphorus fertilizers. Therefore a limit value of 30 mg/kg P_2O_5 DM is suggested, since this value also meets the other limit value of 1.5 mg/kg for Cd at a P_2O_5-content of 5 % DM. Concerning the endpoints soil organisms and humans, risk reduction is included by this proceeding.
- **Ni:** Primary because of the solubility of Ni in acid soils, risk reduction is recommended (Figure 5). Against the background of Figure 7 a reduction of the limit value to the current labelling of 40 mg/kg seems not possible concerning conventional fertilizers. Nevertheless this value can be debated as target under the aspect of risk reduction, so the maximum permissible level is not exceeded (see Table 2) on acid soils. A limit value of 40 mg/kg would also prohibit valorization on arable land for many sewage sludge incineration ashes and recent ash-based products. Hence other measures of risk reduction may achieve similar results by lower efforts a risk-benefit analysis can be conducted.
- **Zn:** Zn seems one of the most problematic hazards especially in context with the missing limit-value in DüMV. On neutral soil risks regarding the endpoint soil organisms and groundwater cannot partly be excluded, dependent on the Zn-load of the products. On acidic soils an exceeding of the $PNEC_{groundwater}$ is very likely. This is the consequence of the high mobility and the high Zn-concentrations especially in sewage sludge, ashes and partly ash-products. Zn is an essential micro-nutrient. Therefore, a similar proceeding like for Cu is suggested. A limit value in fertilizer legislation of 1000-1500 mg/kg is meaningful for soils with content of exchangeable Zn above 3 mg/kg [37]. Below this level no limit value should be applied, to ensure the Zn-supply of the soil. Depending on the strictness of the limit value

for Zn, a corresponding prohibition of sewage sludge incineration ash is intended; but also for recent ash-based products and partly sewage sludge this measure would intend new challenges. It should also be noted that even a limit value of 1000 mg/kg is not sufficient to deceed the maximum permissible level (see Table 2) for all conditions.

Table 3 gives a summary on the suggested limit values. 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.

Table 3: Summary of limit values in current legislation and suggested limit values

Substance	**Limit value in current legislation according to DüMV**	**Toxicologically derived limit to reach the maximal permissible level (PEC=PNEC)**	**Suggested limit value according to ALARA principle**
PCDD/F & dl-PCB	30 ng WHO-TEQ/kg	-	30 ng WHO-TEQ/kg
BaP	-; AbfKlärV 1 mg/kg	-	1 mg/kg
As	40 mg/kg	≈ 350 mg/kg	40 mg/kg (evaluate 20 mg/kg)
Cd	1.5 mg/kg; 50 mg/kg P_2O_5	≈ 3-150 mg/kg P_2O_5 (soil pH-dependency)	1.5 mg/kg; **30 mg/kg P_2O_5**
Cr	none for total Cr in DüMV; AbfKlärV: 300 mg/kg DüMV: 2 mg/kg (Cr VI)	≈ 300 mg/kg	**300 mg/kg (total Cr);** 2 mg/kg (Cr VI)
Cu	Maximum Content in DüMV: 900 mg/kg AbfKlärV: 900 mg/kg	≈ 1100 mg/kg	**900 mg/kg** for soils above 2-4 mg exch. Cu/ kg soil
Hg	1 mg/kg	≈ 15 mg/kg	1 mg/kg
Ni	80 mg/kg	≈ 40-220 mg/kg (soil pH-dependency)	80 mg/kg (evaluate 40 mg/kg)
Pb	150 mg/kg	≈ 950 mg/kg	150 mg/kg (evaluate 100 mg/kg)
Zn	Maximum Content in DüMV: 5000 mg/kg AbfKlärV: 4000 mg/kg	≈ 0-500 mg/kg (soil pH-dependency)	**1000-1500 mg/kg** for soils above 3 mg exch. Zn/ kg soil

5 Conclusion

In summary, 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. Against the background of the made assumptions cadmium and zinc are hazards of concern.

- Summarizing the assessment for the endpoint soil organisms, an exceeding of the PNEC for zinc and neutral soils is as likely as not for application of sewage sludge, its ash and ash-based products with low 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 for the endpoint human, an exceeding of the PNEC for any hazard and product is unlikely.
- Summarizing the assessment for the endpoint groundwater, an exceeding of the PNEC for cadmium and zinc for soils with a pH-value around 5 is very likely for all assessed products. For cadmium, an exceeding of the PNEC for groundwater is unlikely for soils with a pH-value around 7. For application of sewage sludge, its ash and ash-based products with low Zn-depletion, an exceeding of the PNEC for zinc and soils with a pH-value around 7 is likely. For all other products it is about as likely as not. Furthermore, an exceeding of the PNEC regarding the endpoint groundwater and the other observed hazards is unlikely.

By comparison of the hazard contents in fertilizers a relative risk ranking of the products can be derived. In principle lower concentrations will reduce the risk. Thus, struvite can be considered a high quality phosphate fertilizer and an extensive struvite recovery and recycling in agriculture can be recommended. Considering sludge or TSP application as status-quo in agriculture, struvite application even reduces risks regarding the selected hazards. Considering ash related processes an improvement regarding heavy metal depletion is in some cases necessary.

The comparison of risk assessment results with regulated limit values revealed a lack in regulation for Cr, Cu and Zn, which are not strictly limited by DüMV. Especially in case of Zn a limit value is necessary to reduce potential risks to environment. It becomes apparent that this ordinance is focussed on protecting the endpoint human; risks for environment are not completely covered.

The present study also showed that:

1. Risk assessment is appropriate method to support political decisions regarding limit values (here for fertilizer regulation) and to reveal and communicate present knowledge and uncertainties in a transparent way.
2. Stricter limit values for fertilizers are not in all cases a suitable measure for risk reduction because other routes of exposure are far more important than fertilizer application.
3. Limit values can be used as an instrument to exclude certain product groups from the market. If the political decision for excluding a product (e.g. sewage sludge) from the market a stricter limit value for a certain substance can be used to do so, without actually banning it.
4. In many cases common fertilizers are in compliance with toxicologically derived limits, but there are also exceptions (e.g. Cd and Cr for some products and especially Zn). In the latter cases, the ALARA principle has to be applied. When toxicologically derived limits are not suitable as limit values in fertilizer regulations, since several materials would be excluded from the market, other political measures may be considered to reduce the possibility of negative effects on the environment. One idea might be a “contamination tax” in dependency on hazardous content per nutrients in fertilizers.

Regarding the issue of certification and implementation of renewable phosphate fertilizers into fertilizer legislation, not only the hazardous content is of importance. The product has to be classified according to fertilizer legislation [38 p.19 sect. A2]. This European Fertilizer Legislation is, as mentioned, currently recast. Thereby renewable phosphate fertilizers from sewage treatment are intended to be included into the legislation. For products, like AshDec and Leachphos, whose quality depends highly on the quality of the raw materials a certification (also REACH-registration) will be difficult. In contrast, for products with a defined composition, such as struvite or fertilizers with defined composition 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 mineralized 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 can additionally help to ensure fertilizer quality and to reduce risks. Nevertheless, sufficiency of fertilizer-use in agriculture, in terms of risk reduction and with respect to responsible handling of limited resources, is the area which requires the highest attention.

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Reports (also full report of this risk assessment [8]), technical factsheets and publications of the P-REX Project are available on the website www.p-rex.eu.

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