Chapter 3

Soil Contamination Health Risks in Czech Proposal of Soil Protection Legislation

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Additional information is available at the end of the chapter

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Abstract

A new system of soil contamination limit values proposed for Czech legislation is described. The system is based on the hierarchical limit values system with two levels. The first one—prevention limit—defined background values of risk elements (REs) and persistent organic pollutants (POPs) in Czech agricultural soils supported by the data from soil monitoring system. The second one—indication limit—is defined for human health protection by two principles, the protection of food chain and the protection of direct human health risks by inhalation, dermal and oral intake of RE and POPs in soil particles on the field. The practical application of limit values proposal was applied in the project focused on soil contamination influence on health and environmental risks in fluvial zones of Czech important river basins. The floodplain soils belong to the most contaminated soils in Europe generally and the project defined the potential fluvial areas with increased human health risks.

Keywords: soil contamination, health risks, risk elements, persistent organic pollutants, soil protection legislation

1. Introduction

The one of the important way of contamination risk elimination is the existence of legislative norms of contaminants in the environment. The soil is medium where the load from other environments can concentrate and interact. The limit values of main contaminants (risk elements (REs) and persistent organic pollutants (POPs) predominantly) were set in most of developed countries worldwide including the Czech Republic. The limits of REs and POPs concentrations in agricultural soil are set by the Decree No. 13/1994 Coll. in the Czech legislation [1]. These limit values have a status of maximum tolerable values in agricultural soils. The criteria were derived from available data in the Czech Republic at the beginning of 90th and the data were corresponding with the load of Czech agricultural soils and also of some European countries. The REs limit values stated in the decree were derived as rounded 90 percentile of the background values in soil (pseudototal content in extract of Aqua regia). Some authors [2, 3] published the data concerning the total content of REs in the Czech soils before the proposal of background values of REs in Czech agricultural soils [4] was given. The history of POPs limit values assessment was different. The POPs limits were derived from available external data (especially from the Netherlands) since no relevant data for the Czech soils were available in 1994. As a result, limit values of some individual polycyclic aromatic hydrocarbons in the Decree No. 13/1994 Coll. are lower than their real background values in Czech agricultural soils proposed later [5]. This situation is misapplied by subjects demanding appropriation of agricultural land for construction purposes because there are assessed lower levies for the appropriation in the cases where the limit values are exceeded.

The described limit values were derived statistically and do not represent any specific risk in fact. The delimitation of soil suitability for agricultural use by the existence of one value of risk substance concentration is very questionable. For these reasons, the presented version of limit values can be considered as behind the time. The new version of limit values was proposed [6] and it is based on the principle of hierarchical limit values, differentiated in three levels. These individual levels present specific risks. The first one is derived from the background values of RE (POPs, respectively) in agricultural soils and the principles of limit construction follow German experiences [7], Regulation BGBl I, No. 36/1999 [8]. The principles of the assessment of nationals' soil background values of REs presented by [9] include following steps: The assessment of natural background given by the geology—REs contents in rocks and parent materials and REs contents in organic matter of soils; the assessment of diffusion load given by atmospheric deposition especially (determined the background values of organic pollutants) and the definition of practical questions connected with soil use and its relationship to environmental protection level. The suitable statistical methods for the assessment of element background levels in soils (defined as the first level) and of the higher levels of soil limits were described in detail in previous study [10].

The second level of limit values can be defined for specific risks (transfer into plants, transfer into ground water, or microbial activity inhibition for example). Considering the limits for transfer into plants, the Czech legislation proposal follows the German approach [11] using single extraction methods (1 mol/L NH_4NO_3, 0.01mol/L $CaCl_2$) which were scientifically verified by several studies [12–15].

The third level of limit values is directly connected with an impact on human health (Maximum Permissible Concentrations—MPC in the Netherlands, Contaminated Land Exposure Assessment in Great Britain) or the threat of ground water contamination (US EPA) generally. The applications of soil decontamination technologies must be used when these limit values are exceeded. The limit for Czech legislation was based on the US EPA methodology [16]. The protection of direct human health risk by inhalation, dermal, and oral intake is based on the fact that zootoxic RE and POPs can cause the kind of mentioned risks to farmers spending the time on the field during agro technical activities. The zootoxic RE (As, Cd, Hg, Pb, and Tl) and POPs substances (sum of PAHs, benzo(a)pyrene, sum of 7 PCBs, sum of DDTs, HCB, HCH, and PCDDs/Fs) were chosen for their known negative impact on human health. The EPA methodology was applied for limit values calculation based on the toxicity of individual RE or POP substance (defined carcinogenic risk by WHO), the general soil properties and expected time period spending by the farmer on the field.

The limit values system is in legislative process in current days and validity is presumed since 2016. The practical application of limit values proposal was verified in the project focused on soil contamination influence on health and environmental risks in fluvial zones of Czech important river basins. The floodplain soils belong to the most contaminated soils in Europe generally and the project defined the potential fluvial areas with increased human health risks by the methodology described above. The results of project are presented as the practical application of proposed limit values in the methodology of selected risks in fluvial zones. The Fluvisols are soil group with specific soil properties and soil vulnerability by contamination (the sources of soil contamination) developed on fluvial sediments. The floods are the most serious way of soil contamination and soil properties show a high heterogeneity and variability. The heterogeneity is influenced by nature water stream dynamic (the gradient of erosion-deposition properties) with increased influence of neolitisation, it means acceleration of erosion-accumulation processes as the result of vegetation cover change and husbandry development in the landscape. The Fluvisols belong to fertile soils that has been used in agriculture historically. The husbandry in contaminated fluvial zones could cause increased risk and our study defines the risks on the most important fluvial zones in the Czech Republic.

2. Material and methods

Two levels of soil limit values were proposed for the Czech legislation, so-called prevention and indication limit. Their general characterisation is as follows:

Prevention limit was derived from the background values of REs and POPs in Czech agricultural soils when real data were calculated. The indication limits reflect two kinds of the risks. The first one is focused on increased REs transfer from soil into agricultural plants (POPs transfer was not calculated). The second one calculates direct impact on human health via their inhalation, dermal or oral intake on contaminated land for selected POPs and REs.

2.1. The prevention limits of RE and POPs

The prevention limit was derived from background values of RE and POPs in Czech agricultural soils proposed by [4] and [5]. REs background values are depending strongly on geochemical properties of the soil substrates and were proposed for 13 soil-lithological groups originally. The reduction into two groups was realised for pragmatic reasons. The background values are not valid for geochemically anomalous soils (mafic rocks, metallogenic zones of acid rocks, etc.). The RE background values were calculated for pseudototal REs contents (Aqua regia extract, ČSN EN 13346 [17]) finally.

The POPs background values were calculated by [5]. The research of 560 soil samples of agricultural soils from the area of the Czech Republic was utilised. The background values were statistically calculated as two multiples of the standard deviation of geometric means or 90% percentiles—$GM.GD^2$) for both groups (RE and POPs). The background values were set for every individual substance of observed POPs groups. Clearly, the simplification of limit values for legislative process was necessary in result of which summary limits were calculated for some POPs groups.

The sum of PAHs—calculated as the sum of 12 substances concentration (anthracene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, phenanthrene, fluoranthene, chrysene, indeno(1,2,3-cd)pyrene, naphthalene, pyrene).

The polychlorinated hydrocarbons—limits for sum of seven indication congeners of polychlorinated biphenyls—PCB_7 (28 + 52 + 101 + 118 + 138 + 153 + 180) and sum of DDTs (DDT, DDE, and DDD).

The hexachlorbenzene and hexachlorcyclohexane ((Σ $\alpha + \beta + \gamma$) and polychlorinated dibenzo-p-dioxines and dibenzofurans (PCDDs/Fs) should be analysed only in the case of suspicion of their contents in soil.

The background value of PCCDs/Fs was calculated separately because of different collection of soil samples. The used statistic was identical and 102 soil samples taken in the areas of the Czech Republic with different source of the load [18] were taken into account. The value of International Toxic Equivalent (I-TEQ PCCDs/Fs) of 17 toxic congeners was calculated [19].

2.2. The indication limit values of food chain contamination and plant growth inhibition

The separation on phytotoxic and zootoxic REs should be accepted. The limits for plant growth inhibition were proposed for this reason. The limits for food chain contamination regulate the transfer of zootoxic elements from the soil into plant production. The limits were supported by the research of RE transfer from the soil into selected plants (triticale, radish) in experimental conditions and into fodder plants (clover, alfalfa, and grass species) in field conditions [20–23]) and the dependency of REs mobile contents and selected soil conditions (pH, Cox, soil texture) was evaluated by multidimensional statistical methods (factor analysis). The comparison of the selected RE total contents (As, Cd, Cu, Hg, Ni, Pb, Th, Zn) and the content in the extract of 1 mol/L NH_4NO_3 (As, Cd, Cu, Ni, Pb, Th, Zn) characterised as RE mobile fraction (ISO DIS 19730 [24]) was the principle of RE indication values assessment. The limit values were referred to RE critical values in eatable and fodder plants (the Decree No. 305/2004 Coll. [25]). The other legislative norms for plant contamination (European legislation) are shown in our practical study focused on the husbandry in fluvial zones.

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2.3. The indication limit values of human health protection

The limit values were derived from the direct risk of increased POPs and RE (As, Cd, Hg, and Pb) contents on human health by their inhalation, dermal, and oral intake on contaminated fields. The calculation corresponds with the US EPA methodology (US EPA 2002) and respects the toxicity of the selected substances or elements and the movement duration of farmers on the contaminated land (standard exposition scenario was applied). It is also supported by the experience following from the activities provided in Czech conditions [26].

2.4. The case study of human health risks assessment from soil pollution in flood affected areas in the Czech Republic

The evaluation of health risk was realised and verified in the research project focused on soil contamination of flood affected areas in the Czech Republic. The human health risk assessment is becoming relevant when the -proposed indication limit values are exceeded, because they are derived as "effect based" for worst-case scenario. The screening evaluation of exposition by Soil Screening Level (SSL) method was applied (see 3.3 of the chapter). The calculation approach is based on the application of exposition models of chemical substances inputs into human bodies followed by the comparison of this predicted chronical dose with referenced "effect-based" dose. This approach allows to assign individual exposition parameters to every locality and then calculate site-specific SSL values and risks following from the exposition. The calculation of human risk ($RISK_{HUMAN}$) has been done for individual chemical substances first and there has been calculated total sum of all evaluated substances including the calculation of percentage of individual substances contributions to total sum. The $RISK_{HUMAN}$ values should not be higher than 1. The values higher than 2 indicate the possible risk and in the dependency on detail evaluation of exposition scenarios up to significant. The other cases can be evaluated as non-significant considering selected exposition scenario.

The next step for the evaluation of contamination level in floodplain soils was a rigorous statistical evaluation of the results. The dataset for soil contamination of 100 floodplain soils in the Czech Republic was used to estimate the human health risks by presented methodology (Equations 1–3).[1] Relative contributions of each risky element/substance to an overall hazard index ($RISK_{HUMAN}$) were calculated. A matrix transformation of relative contribution of each analyte to total $RISK_{HUMAN}$ on each locality was undertaken before the statistical analysis. The similarity of the soil pollution profiles in individual floodplain samples was assessed by a hierarchical cluster analysis using the average linkage clustering. The results of hierarchical cluster analyses are presented using technique of heatmap, where the similarity among the objects in a cluster dendrogram is visualised by the colour intensity in a square matrix of coloured pixels (R Core Team, Library Gplot).

[1] There were sampled 100 floodplain soils in various catchments of the Czech Republic. For each sampling site, a mixed sample consisting of 10 individual samples from the area of 100 × 100 m was used. Samples are separated and homogenised by quartation. The sample depth was 0–10 cm for pastures and 0–30 cm for arable land. In the soil samples there was analysed a wide range of risky substances including seven indicator PCBs (28, 52, 101, 118, 138, 153, 180), 7 risky elements (As, Cd, Cu, Hg, Ni, Pb, and Zn), polycyclic aromatic hydrocarbons (29 PAHs compounds), and pesticides (DDT and metabolites; hexachlorcyclohexane isomers, HCHs; pentachlorbenzene, PeCB; hexachlorbenzene, HCB). The basic soil properties (e.g. total organic carbon, soil texture characteristics) were determined.

3. Results and discussion

3.1. Proposal of legislative limit values

3.1.2. Prevention limit

The prevention limits of the RE for two soil texture units are presented in **Table 1**. This separation includes light texture soils (loamy-sandy soils and gravel-sandy soils) and standard soils (all the other soil). The values show REs contents in the extract of Aqua regia (pseudototal contents). These values were derived from the background values of REs in Czech agricultural soils—the soil geochemical background plus the average diffuse anthropogenic load [4]. The prevention limits were derived from the soils developed on different soil substrates of the Czech Republic except of the soils developed on geochemically anomalous substrates. These causes including the substrates with increased REs contents of lithogenic or chalcogenic origin [27] must be under an individual evaluation.

	Prevention value (mg/kg of d.m.)												
Soil category	As	Be	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	V	Zn	Tl
Standard texture soils[1]	20	2.0	0.5	30	90	60	0,3	1200	50	60	130	120	0.5
Light texture soils[2]	15	1.5	0.4	20	55	45	0,3	1000	45	55	120	105	0.5

[1]Soils except light texture soils.
[2]Sandy soils, loamy-sandy soils, gravel-sandy soils.

Table 1. Proposed RE prevention limits in agricultural soils.

The POPs prevention limits are shown in **Table 2**. The differentiation of the soil texture units has no relevant reason for POPs and was not done. The POPs limit values are given in the form of total POPs contents in the soil. The background values of POPs in soil were derived from the average diffuse anthropogenic load (the dependency of POPs soil contents on nature background values is marginal). The real Czech background values [5] were adopted for legislative proposal.

POPs	Prevention value (mg/kg of d.m.)
Polycyclic aromatic hydrocarbons	
Σ PAHs[1]	1.0
Chlorinated hydrocarbons	
Σ PCB[2]	0.02
Σ DDT[3]	0.075
HCB[4]	0.02
HCH[4] ($\Sigma\ \alpha + \beta + \gamma$)	0.01

POPs	Prevention value (mg/kg of d.m.)
PCDDs/Fs[5]	1.0*
Petroleum hydrocarbons	
Hydrocarbons C10–C40	100

[1]Σ PAHS—polycyclic aromatic hydrocarbons (anthracene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, phenanthrene, fluoranthene, chrysene, indeno(1,2,3-cd)pyrene, naphthalene, pyrene).
[2]Σ PCB congeners—28 + 52 + 101 + 118 + 138 + 153 + 180.
[3]Σ DDT, DDE, DDD.
[4]HCB and HCH ($\Sigma\ \alpha + \beta + \gamma$)—analysed only by suspicion of their contents in soil.
[5]International toxic equivalent value (I-TEQ PCDDs/Fs) (ng/kg)—analysed only by suspicion of increased PCDDs/Fs contents in soil.

Table 2. Proposed POPs prevention limits in agricultural soils.

The exceeding of RE or POPs prevention limits signalises the increased anthropogenic soil load (over the background values). In the cases of prevention limits exceeding, the precaution measure is proposed: the use of sludge, dredged sediments, or biosolids on the field will be forbidden. This level of limit values has already been partially implemented in the Czech legislation, namely in the Decrees No. 382/2001 Coll. [28] and No. 257/2009 Coll. [29] for sewage sludge and dredged sediments [30] application on agricultural soils. The proposed prevention limits should be valid for all types of substances applied on the agricultural land generally.

The system of so-called background values is not absolutely unified and can be partially different in individual EU countries. The Czech one is derived from German methodology where the background values are characterised as the concentration resulting from geological and pedological processes and including diffuse source inputs. This method is described in ISO 19258 (2005) [31] for RE and POPs and has international relevance. This methodology is used for the background value assessment in France and United Kingdom. Belgium, Luxembourg, and Netherlands derive the REs and POPS background values only from clean reference areas without any anthropogenic inputs (concentrations found in soil unaffected by any human activity, respectively, soils possibly contaminated by line/point source are exceeded). Nevertheless, the approaches can be different not only between the member countries but between the regions of individual countries in some of them (LABO 1995 [32]) because of different geological and pedological processes and anthropogenic inputs influencing the values and the differences in legislation systems.

3.2. Indication limits

3.2.1. Indication limit of food chain contamination and plant growth inhibition

The indication limit values reflect the mobility of REs. The comparison of RE (pseudo) total contents and their mobile fraction analysed in the extract of 1 mol/L NH_4NO_3 are the principle of indication limits. The limits of zootoxic REs (As, Cd, Pb, Tl, Hg) were proposed for the food chain protection purpose (**Table 3**). The mobility of REs dependency on soil properties complicates the limit values when indication values for Cd are most complicated because of Cd mobility dependency on soil texture and soil pH. The evaluation of REs pseudototal and mobile form must be done if the limit values are available. The exceeding of limit value of pseudototal or of mobile form means exceeding of indication limit. The proposal of this level of limit value was based on the testing of selected plant species (fodder plants, vegetables, and corns) in experimental and field conditions and general validity of proposed values was derived. The statistical probabilities of critical values exceeding in eatable or fodder plants can be resulted when RE indication limits in the soil are exceeded. The real exceeding of indication limit value in local field conditions must be confirmed by the testing on individual crop.

Element	Soil texture	pH/$CaCl_2$	Indication value (mg/kg of d.m.)	
			Aqua regia	1mol/L NH_4NO_3
As	–	–	–	1.0
Cd		<5	1	–
		5–6.5	1.5	–
	Standard texture	>6.5	2.0	0.1
	Light texture	>6.5	2.0	0.04
Ni		<5	90	–
		5–6.5	150	–
		>6.5	200	–
		–	–	1.0
Pb		–	300	1.5
Tl		–	10	0.2
Hg*		–	1.5	–

*Total content by AMA technique.
The exceeding of limit value is valid in the case of any exceeding, a) Aqua regia extraction, b) 1mol/L NH_4NO_3 extraction when both analyses must be done if the limit values are available.

Table 3. Proposed indication limits of food chain contamination.

The indication limit values of plant growth inhibition (**Table 4**) were proposed for phytotoxic REs (Ni, Cu, and Zn) because the phytotoxicity can result into significant yield reduction. The limit values proposal was supported by the testing on plant species identical with previous indication limit value and the exceeding of indication limit values must be confirmed by the testing on individual crop in field conditions as well. In the cases of exceeding of both indication limit values the suitable remediation techniques for REs immobilisation (the liming, the application of inorganic or organic additives [33] are recommended).

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Element	Soil texture	$pH/CaCl_2$	Indication value (mg/kg of d.m.)	
			Aqua regia	1mol/L NH_4NO_3
Cu		<5	150	–
		5–6.5	200	–
		>6.5	300	–
		–	–	1.0
Ni		<5	90	–
		5–6.5	150	–
		>6.5	200	–
		–	–	1.0
Zn			400	–
			–	20

The exceeding of limit value is valid in the case of any exceeding, a) Aqua regia extraction, b) 1 mol/L NH_4NO_3 extraction when both analyses must be done if the limit values are available.

Table 4. Proposed indication limits of plant growth inhibition.

3.2.2. The indication limit values of human health protection

The limit was proposed for zootoxic REs (**Table 5**) and selected POPs (**Table 6**). The model calculation of exposition scenario (method US EPA [16] was used as the principle for limit values assessment. The scenario calculates the effect of individual element/substance, the input into human bodies by inhalation, dermal, and oral inputs and the time period of exposition (estimated number of days per year). The calculated value is maximum tolerable value and the exceeding of this level of limit values could cause human health risk. The precaution defined in the legislation is based on the risk analysis of the site confirmed or excluded human health risk. The similar approach is applied in some EU countries, for example, limit value for human health protection is defined as decontamination limit for chlorinated substances in the soils of Germany (Federal Ministry of Justice and Consumer Protection of Germany).

Element	Indication value (mg/kg of d.m.)
As[1]	40
Cd[1]	20
Hg[2]	20
Pb[1]	400
Tl	60

[1]Aqua regia extract—valid for all soil texture categories
[2]Total content by AMA method

Table 5. Proposed RE indication limits of human health protection.

Substance	Indication value (mg/kg of d.m.)
Σ PAHs[1]	30
Benzo(a)pyrene	0.5
Σ PCB[2)]	1.5
Σ DDT[3]	8.0
HCB[4]	1
HCH[4] (Σ α + β + γ)	1
PCDDs/Fs[5]	100*

[1]Σ PAHs—polycyclic aromatic hydrocarbons (anthracene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, phenanthrene, fluoranthene, chrysene, indeno(1,2,3-cd)pyrene, naphthalene, pyrene).
[2]Σ PCB congeners—28 + 52 + 101 + 118 + 138 + 153 + 180.
[3]Σ DDT, DDE, DDD.
[4]HCB and HCH (Σ α + β + γ)—analysed only by suspicion of their contents in soil.
[5]International toxic equivalent value (I-TEQ PCDDs/Fs) (ng/kg)—analysed only by suspicion of increased PCDDs/Fs contents in soil.

Table 6. Proposed POPs indication limits of human health protection.

3.3. The evaluation of health risks in floodplain soils in the Czech Republic

The project proposed the methodology for evaluation of health risks in contaminated flood-affected soils useful in practical conditions [34]. The method of SSL was proposed for first screening evaluation. The method is based on the approaches of risk evaluation by US EPA [35] and EPA [36]. The methodology uses the exposition models of chemical inputs into human body. The predicted chronic daily doses are then compared with reference "effect-based" doses mathematically. The partial values of chemical substances concentrations and parameters of chosen exposition scenario (used in limit values assessment) for the main three exposition ways together are used in calculation:

Dust particles inhalation entering into air as secondary dust in the vicinity of evaluated localities.

- Soil ingestion (by consumption of insufficiently washed crops/eatables).
- Dermal contact with soil.

The SSL model was adopted for estimation of the human intake of soil contaminants and consequent risks. This method is based on the risk assessment procedure developed by US EPA. SSLs represent the risk-based soil concentrations derived for the individual chemicals of concern from equations combining exposure assumptions with toxicity criteria.

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For each chemical, SSL is back-calculated from the target risk level, whereas an excess lifetime cancer risk (ELCR) is 1×10^{-6} for the soil exposure. Following equations are used to calculate SSL values for a residential population exposed to hazardous chemicals via all three exposure pathways. Default exposure parameters are provided whenever site-specific data are not available. The site specific exposure parameters were set out according to typical conditions of an intensive agriculture (arable land in alluvial areas). The detailed methodology is also described [37].

A. SSL based on non-carcinogenic risks

$$C = \frac{THQ \cdot BW_c \cdot AT_n}{EF_r \cdot ED_c \left[\left(\frac{1}{RfD_o} \cdot \frac{IRS_c}{10^6 mg / kg} \right) + \left(\frac{1}{RfD_o} \cdot \frac{SA_c \cdot AF_c \cdot ABS}{10^6 mg / kg} \right) + \left(\frac{1}{RfD_i} \cdot \frac{IRA_c}{VF_s or PEF} \right) \right]} \quad (1)$$

where

C Contaminant concentration (SSL) (mg kg^{-1}) Chemical-specific

THQ Target hazard quotient 1

BWc Body weight, child (kg) 15

ATn Averaging time, non-carcinogens (days) ED × 365

EFr Exposure frequency, resident (day yr^{-1}) 250 (8 h/day)

EDc Exposure duration, child (years) 25

IRSc Soil ingestion rate, child (mg day^{-1}) 100

RfDo Oral reference dose (mg kg^{-1} day^{-1}) Chemical-specific

SA Dermal surface area, child (cm^2 day^{-1}) 3470

AF Soil adherence factor, child (mg cm^{-2}) 0.12

ABS Skin absorption factor (unitless) Chemical-specific

IRAc Inhalation rate, child (m^3 day^{-1}) 20

RfDI Inhalation reference dose (mg kg^{-1} day^{-1}) Chemical-specific

VFs Volatilisation factor for soil (m^3 kg^{-1}) Chemical-specific

PEF Particulate emission factor (m^3 kg^{-1}) Chemical-specific

B SSL based on carcinogenic risks

$$C = \frac{TR \cdot AT_c}{EF_r \left[\left(\frac{IFS_{adj} \cdot CSF_o}{10^6 mg / kg} \right) + \left(\frac{SFS_{adj} \cdot ABS \cdot CSF_o}{10^6 mg / kg} \right) + \left(\frac{InhF_{adj} \cdot CSF_i}{VF_s or PEF} \right) \right]} \quad (2)$$

where

C Contaminant concentration (SSL) (mg kg^{-1}) Chemical-specific

TR Target cancer risk 1E-06

ATc Averaging time, carcinogens (days) 25,550

EFr Exposure frequency, resident (day yr^{-1}) 250 (8 h/day)

IFSadj Age-adjusted soil ingest. factor ([mg yr^{-1}]/[kg day])$^{-1}$ 100

CSFo Oral cancer slope factor (mg kg^{-1} day^{-1}) Chemical-specific

SFSadj Age-adjusted dermal factor ([mg yr^{-1}]/[kg day^{-1}]) 361

ABS Skin absorption factor (unitless) Chemical-specific

InhFadj Age-adjusted inhalation factor ([m3 yr^{-1}]/[kg day^{-1}]) 11

CSFi Inhalation cancer slope factor (mg kg day)$^{-1}$ Chemical-specific

VFs Volatilisation factor for soil (m3 kg^{-1}) Chemical-specific

PEF Particulate emission factor (m3 kg^{-1}) Chemical-specific

In case of the exposure to multiple chemicals, total risk is calculated as an additive value according to following equation:

$$RISK_{HUMAN} = \frac{c_1}{SSL_1} + \frac{c_2}{SSL_2} + ... + \frac{c_i}{SSL_i} \quad (3)$$

Resulting ratio smaller than 1 indicates that the POP concentrations measured at the site are unlikely to result in an adverse health impact.

Following uncertainties must be taken into account in final result assessment:

- Other non-analysed substances can influence the real risk.
- Toxicological data of some substances are estimated from in vivo tests on animals or in vitro. Therefore, extrapolation for humans must be done; however, for some chemical substances, the indexes are not set out yet.
- The exposure coefficient can be a serious source of uncertainties.

4. The results of health risks assessment in floodplain soils in the Czech Republic

Since the magnitude of the total estimation for human health risks on individual sampling localities was calculated (Equations 1–3) and cartographically represented (see **Figure 2**), the regional differentiation of potential human health impacts of complex soil pollution can be determined for floodplains soils in the Czech Republic. An increase of human health risk estimation was recorded for the Elbe River below the industrial centres (Opatovice, Pardubice, Neratovice, the Ohře River inflow) confirming the spatial patterns of pollution of various environmental compartments in the Elbe basin reported by previous studies [38, 39]. The high PAHs contributions together with an above-average $RISK_{HUMAN}$ were surprisingly found in the upper reaches of the Elbe River and Morava River. This could only be explained by a high propensity of PAHs to atmospheric transport resulting in high concentration of airborne POPs in remote and unpolluted freshwater ecosystems [40]. The higher magnitude of $RISK_{HUMAN}$ was recorded in a consequence of some well-known hot spots in the Berounka catchment (the Litavka stream inflow [41, 42] or the influence of Ag-Pb-Zn deposit in Stříbro). Similarly, the elevated $RISK_{HUMAN}$ followed the Odra River with the regional rising near the Ostrava agglomeration where the long-term airborne pollution resulted in a higher PAHs and Cd contamination of agricultural soils [43]. The elevated level of quantified human risks was also recorded in soil samples near the confluence of the Morava and Dřevnice River below the Otrokovice-Zlín agglomeration as a regional centre of industry that involves especially plastic and rubber manufacturing and historically established chemical industries for secondary manufacturing (shoemaking tradition). Several local contamination rising were detected in a consequence of spatially confined pollution sources (industrial centre of Mladá Boleslav or the Svitava River near Boskovice). A cluster analysis was processed for the transformed data matrix of relative contributions of each analyte to the total estimation of human health risk to reveal patterns of pollution profiles of floodplain samples in the Czech Republic. The results proved high cophenetic correlation coefficient ($r = 0.92$) with the optimal number of 11 clusters in the cluster analysis. One substantial cluster (covered 71 from 100 sampling localities) and several regional pollution abnormalities were detected in our analysis (see **Figure 1**). The dominant cluster was formed by the localities characteristic in a high contribution of polycyclic aromatic hydrocarbons (and especially benzo(a)pyrene, benzo(a)anthracene and benzo(b)fluoranthene) and in an elevated contribution of lead to total estimation of health risks. Some regional pollution abnormalities were connected to higher contribution of organochlorine pesticides (the Berounka and Ohře River), elevated contribution of PCBs (the Elbe River), or geochemical anomalies connected to local metallogenic zones (deposits). When combining both the magnitude of estimated $RISK_{HUMAN}$ and structural characteristics of pollution profiles (the cluster analysis results), the highest estimated humanotoxicological risks proved only several localities with a high content of polycyclic aromatic hydrocarbons accompanied by higher lead contents (there are depicted the predominant pollution profiles for the localities with the elevated total $RISK_{HUMAN}$ hazard index in **Table 7**). The results of human risk assessment well correspond with the exceedance of indication limit values for human protection. The indication limits of human health protection for PAHs and Pb contents were exceeded for several localities of floodplain soils in our study.

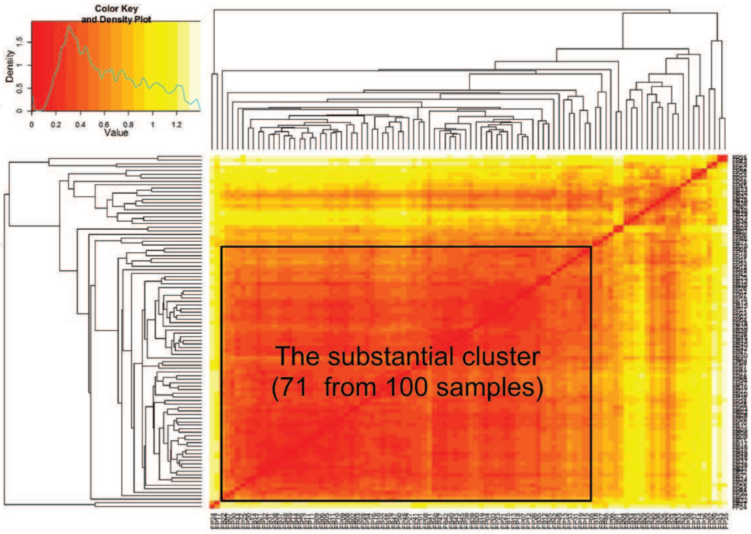

Figure 1. Similarity of the soil pollution profiles (relative contribution of pollutants to overall estimation of human risks—$RISK_{HUMAN}$) of individual floodplain samples in a cluster analysis presented by the heatmap and a projection of dominant cluster in our dataset. *Note—the more intense red color the more similar samples.*

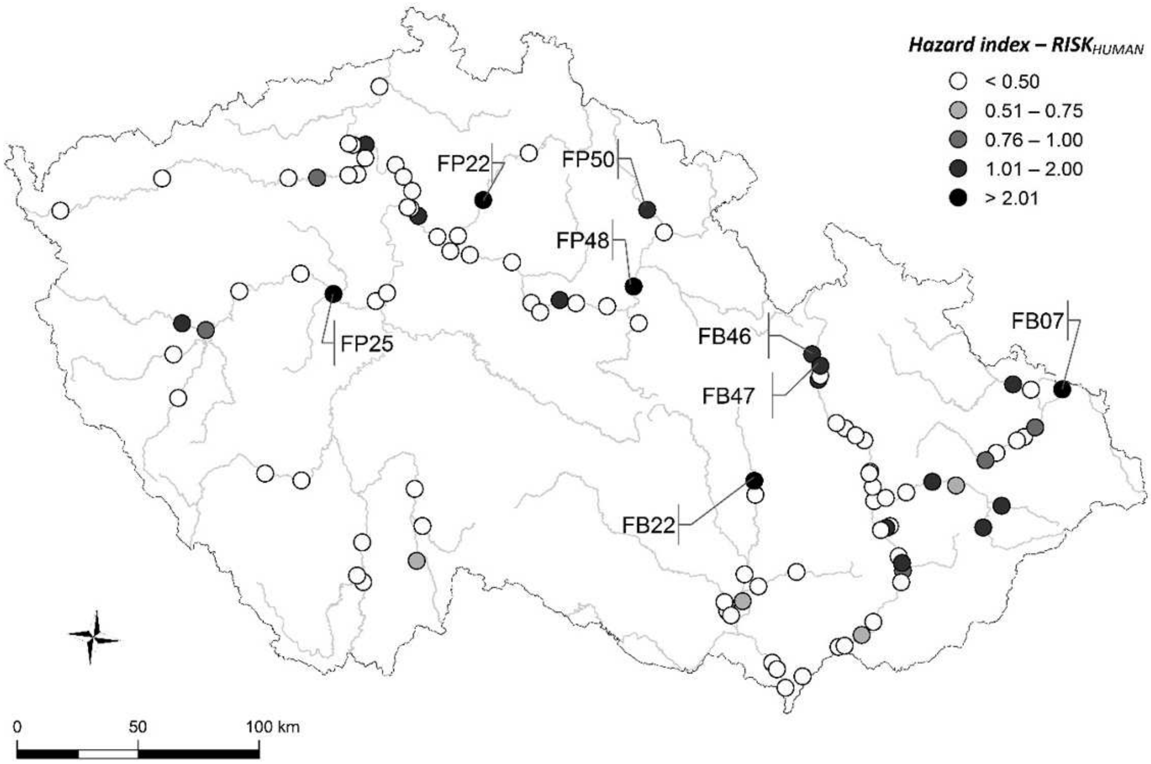

Figure 2. Spatial differentiation of magnitude of human health risks quantified using total $RISK_{HUMAN}$ (Equations 1–3) and visualisation of the regional hot spots (where $RISK_{HUMAN} > 1.5$).

Sample	$RISK_{HUMAN}$	Priority pollutants (relative contribution—%) [measured concentration—mg/kg]				
		1.	2.	3.	4.	5.
FB07	3.76	***B(a)P (74)[0.8]****	B(*a*)A (7.5) [0.82]	B(*b*)F (7.0) [0.77]	In(*cd*)P (4.9) [0.53]	DiB(*ah*)A (3.5) [0.04]
FB22	6.92	***B(a)P (74)[1.47]****	B(*b*)F (9.1) [1.82]	B(*a*)A (8.3) [1.67]	In(*cd*)P (4.8) [0.97]	DiB(*ah*)A (2.9) [0.06]
FB46	1.96	B(*a*)P (72) [0.41]	B(*b*)F (7.7) [0.44]	B(*a*)A (6.6) [0.38]	DiB(*ah*)A (5.3) [0.03]	In(*123*)P (4.9) [0.28]
FB47	1.61	B(*a*)P (71) [0.33]	B(*b*)F (8.2) [0.38]	B(*a*)A (7.9) [0.37]	In(*cd*)P (5.3) [0.25]	DiB(*ah*)A (5.1) [0.02]
FP22	2.15	B(*a*)P (75) [0.47]	B(*a*)A (6.9) [0.43]	B(*b*)F (5) [0.31]	DiB(*ah*)A (4.8) [0.03]	In(*cd*)P (4.4) [0.27]
FP25	2.03	B(*a*)P (52) [0.3]	***Pb (31.8) [516]****	B(*b*)F (4.4) [0.26]	B(*a*)A (4.1) [0.24]	In(cd)P (3.9) [0.23]
FP48	3.56	***B(a)P (78)[0.81]****	B(*a*)A (6.8) [0.7]	B(*b*)F (6.4) [0.66]	In(*cd*)P (4.6) [0.48]	DiB(*ah*)A (2.6) [0.03]
FP50	1.72	B(*a*)P (74) [0.37]	B(*a*)A (7.0) [0.35]	B(*b*)F (6.7) [0.33]	In(*cd*)P (4.9) [0.24]	Pb (3.4) [47]

Notes
B(a)P—benzo(a)pyrene; B(a)A—benz(a)anthracene; B(b)F—benzo(b)fluoranthene; In(cd)P—Indeno(1,2,3-cd)pyrene; DiB(ah)A – Dibenz(a,h)anthracene, Pb – lead.
*Exceeding of indication limit of human health protection for particular pollutant and locality.

Table 7. Priority pollutants for floodplain samples with topmost estimation of human health risks ($RISK_{HUMAN} > 1.5$) and their pollution profiles (predominant pollutant concentrations and their relative contribution to $RISK_{HUMAN}$).

5. Conclusion

The proposed system of hierarchical limit values helps to protect soil environment, food chain, and human health against the contamination and will improve the current version fundamentally. The currently valid principle of maximally tolerable values presenting no actual risk (but selected agricultural soils on two categories—useful and non-useful by the existence of one limit value level) will be replaced by the system of hierarchical limit values referred to an individual level of the risks and followed by appropriate measures in the cases of limit exceeding. The case study of floodplains research proved the operability of the established methodology and verified relevancy of the human health limits (indication limits of human health protection) in Czech proposal of soil protection legislation. The established methodology helped to reveal the areas where the soil does not meet the soil quality standards and where the human health risks were elevated. The characteristic pollution profiles of floodplain soils with elevated human health risks were defined on the basis of the results.

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