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The Inputs of POPs into Soils by Sewage Sludge and Dredged Sediments Application

Radim Vácha
Research Institute for Soil and Water Conservation, Prague
Czech Republic

1. Introduction

The use of sewage sludge and dredged sediments in agriculture belong to the most important ways of possible pollutants inputs into agricultural soils in many countries including Czech Republic.

The application of sewage sludge on agricultural soils is connected with following facts:

- increasing amounts of sewage sludge thanks to intensive waste water treatment
- the characteristic of sludge as the material with increased content of organic matter and nutrients

The application of sludge into soil could lead to an increase of the contents of organic matter or macro elements, but the contamination by potentially risky elements and persistent organic pollutants could be relevant also. The problems connecting with increased persistent organic pollutants (POPs) contents in sewage sludge were confirmed by many authors (Markard, 1988; Melcer et al., 1988; Starke, 1992; Oleszczuk, 2007; Clarke et al., 2008; Natal-da-Luz et al., 2009). The load of soil by POPs after sludge application can influence their transfer into food chains (Passuello et al., 2010). Increased contents of polycyclic aromatic hydrocarbons (PAHs) limit not only direct application of sewage sludge on the soil but also the use of sludge in composting processes for example (Rosik-Dulewska et al., 2009). The inputs of POPs into agricultural soils by biosolids use in agriculture plays an important role. This problematic is documented on the example of following study realised in the Czech Republic where the contents of POPs in the soil and plants after sewage sludge and sediments application were observed.

The number of waste water factories increased after implementation of Czech Republic into European Union when the obligation of waste water factory existence in every settlement over 10 000 inhabitants till 2010 year had to be fulfilled. The necessity of legislative regulation existence controlling this process was obvious since the beginning of ninetieth years and the Directive No. 382/2001 was the first version of legislative adaptation. The Directive was modified under the No. 504/2004 Sb. in 2004 year.

The directive of Czech Ministry of Environment No. 504/2004 Sb. regulates the application of the sludge on agricultural soils. The directive determines the conditions of sludge application on agricultural soils, including limit values of potentially risk elements and some persistent organic pollutants (sum of halogenated organically bound substances - AOX, sum of six congeners of polychlorinated biphenyls - PCB6) in sludge. The directive 86/278/EEC regulates the sludge application in EU legislation. Only the contents of 6 potentially risk elements in sludge (Cd, Cu, Hg, Pb, Ni and Zn) are limited in the directive. The proposal of limit values of potentially risk elements and persistent organic pollutants was presented in Working Document on Sludge that was available for professional community, too. This proposal altered existing criteria and installed new criteria for persistent organic pollutants especially. The contents of seven POPs groups were regulated, the sum of halogenated organic compounds (AOX), linear alkylbenzene sulphonates (LAS), di(2-ethylhexyl)phtalate (DEHP), nonylphenol and nonylphenoletoxylates substances with 1 or 2 ethoxy groups (NPE), sum of polycyclic aromatic hydrocarbons (PAHs), the sum of seven congeners of PCB (28+52+101+118+138+153+180) and polychlorinated dibenzo-p-dioxins and dibenzofuranes (PCDD/F). The acceptance of Working Document on Sludge for the legislation was complicated by the lobbies and by economical needs for the determination of the pollutants. The proposal was refused and the directive 86/278/EEC is valid in original form.

The second group of problematic materials including into our research are the sediments dredged from river or pond bottoms. The volumes of dredged river and pond sediments reach huge amounts because of the necessity of periodical maintenance of river channels and water reservoirs. The existence of 97 millions m3 of ponds sediments and 5 millions m3 of river and irrigation channel sediments was reported in Czech Republic (Gergel, 1995). The problem of the liquidation or suitable use of extracted sediments of these amounts is evident. In spit of the traditional use of the sediments as the fertilizers on agricultural soils till to first halve of 20th century is not current approach unified, especially thanks to misgivings of their hygienic standards and environmental merits.

The elaboration of complex methodological approach including the assessment and testing of sediment conditions, the contamination and possible negative effects and the evaluation of positives and negatives of their application is highly needed. This approach must follow current EU politics of soil protection, sewage sludge application and the use of the other wastes (European Parliament, 2003; ISO 15799, 2003; EN 14735, 2006). The complex system should use chemical and biological methods concluded by risk assessment where contact ecotoxicity tests cannot be missing (Domene et al., 2007; Pandard et al., 2006).

The sedimentation of soil particles originated from agricultural soil erosion seems to be the most important way of sediments inputs into water systems. This process is described in Czech Republic also where about 50% of soil fund is endangered by water erosion (Janeček et al., 2005). The accumulation of nutrients and organic matter especially in pond and downstream sediments belongs to the positives of sediment application. The sediment could be valuable substrate useful in soil and landscape reclamation for example (Santin et al., 2009).

The other hand must be accepted that eroded soil particles are under the influence of many factors in water environment resulting to the changeover of their quality especially from the viewpoint of elements and substances sorption. The sediment characteristics are changing by particles sedimentation process in different parts of the stream and this process influences sorption of risky substances (Tripathy & Praharaj, 2006; Fuentes et al., 2008). It could lead to the problems of water eutrofization or sediment contamination. The sediments are known as the “chemical time bomb” thanks to their function of final deposits of pollutants in the river basins (Hilscherová et al., 2007; Holoubek et al., 1998). The sediment load by risky substances is connected with the presence of pollution sources like industrial or urban zones or wastes outputs from mining activities. The negative impact of these sources can be confirmed by chemical methods (Gomez-Alvarez et al., 2007) or by toxicity tests (Riba et al., 2006). The inputs of risky elements into sediments from geochemical anomalous substrates or from the other natural sources respectively can play an important role (Liu et al., 2008). The increased loads of risky substances lead to the complications of sediment use in the same way as the use of sewage sludge and the other organically reach materials (Vácha et al., 2005a).

The potential contamination of the sediments by wide spectrum of hazardous substances could not be eliminated. We accept the fact that fluvisols developed on alluvial sediments in river fluvial zones belong to the most loaded soils in our conditions by risky elements Cd>Hg>Zn>Cu>Pb and Cr (Podlešáková et al., 1994) and by persistent organic pollutants (POPs). Increased contents of polycyclic aromatic hydrocarbons (PAHs), chlorinated pesticides (sum of DDT), petroleum hydrocarbons and polychlorinated biphenyls (PCBs) on some localities were observed (Podlešáková et al., 1994; Vácha et al., 2003). The monitoring of fluvisols load by polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/Fs) resulted into similar trends (Podlešáková et al., 2000; Vácha et al., 2005b). The contamination of sediments from water reservoirs by PCDDs/Fs was confirmed (Urbaniak et al., 2009). At the same time, POPs degradation is strongly influenced by sediment conditions, oxygenation conditions belong to the most important (Devault et al., 2009). The sediment quality was monitored in Labe river basin by germen researchers. They observed increasing water quality in Labe River after collapsing of communist regime in central Europe thanks to increasing number of wastewater factories and the other modern pollution-controlling technologies (Netzband et al., 2002). In spit of this fact the concentrations of several contaminants are still remaining in sediments of Labe River and their use for agriculture is questionable (Heininger et al., 2004). The most problematic are the contents of Cd, Hg, As, Zn, HCB, PCBs and PCDDs/Fs in the sediments (Heise et al., 2005).

The other hand, realised monitoring of pond sediments load by risky elements in the Czech Republic confirmed relatively low contamination (Benešová & Gergel, 2003). The authors did not find the exceeding of risky elements limit values in the Czech Direction for soil protection No. 13/1994 Sb. The database of sediment load by risky elements and some POPs separated into groups following sediment origin (field ponds, village ponds, forest ponds and rivers) is available in the Central Institute for Supervising of Testing of Czech Republic (Čermák et al., 2009). The results of this monitoring show only sporadically increased values of risky elements (Cd and Zn usually) in the sediments but these load can reach extremely increased contents namely in village ponds (1660 mg/kg for Cd or 1630 mg/kg for Zn) in some cases. The contents of risky elements and observed POPs (AOX, PCB_7) were under background values of agricultural soils in the most observed sediment samples.

Long-term prepared legislative regulation (Direction No. 257/2009 Sb.) for sediment application on agricultural soils is valid in the Czech Republic since 2009 year. The Direction regulates selected characteristics and conditions for the application of extracted sediments. The limits of potentially risky elements (As, Be, Cd, Co, Cr, Cu, Hg, Ni, Pb, V and Zn) and persistent organic pollutants (BTEX, sum of PAHs, PCB_7, sum of DDT and C_{10} – C_{40} hydrocarbons) in the sediment and soil of the locality for the application are defined. The limits of risky elements and substances in the soil were derived from the background values of Czech agricultural soils proposed originally (Podlešáková et al., 1996; Němeček et al., 1996). The limits in the Direction use total contents of risky elements only.

The paper shows the results of the research of risky substances contents in the set of sediment samples collected in 2008 year. These contents are compared with sediment characteristics depending on sediment origin and the way of sediment processing. The experiences following from real use of Czech legislative on the field of sediments use in agriculture can contribute to the process of European legislative formulation.

2. Materials and methods

2.1 Sewage sludge analyses

The research focused on the contents of POPs in sewage sludge resulting in the proposal of their recommended maximum contents in the sludge for application on agricultural soils was based on:
The POPs monitoring in 45 wastewater factories in Czech Republic,
the realisation of pot and micro field trial,
the synthesis of the results and their comparison with the proposal of EU directive amendment (EU 2000, Working Document on Sludge), table 1.
The monitoring of POPs in sewage sludge covered the area of the Czech Republic. The waste-water factories were separated into following groups:

- Areas of regional and district towns (including capital city of Prague),
- areas of towns with the presence of industrial activities,
- areas of settlements under 15 000 inhabitants.

The waste-water factories with comparable technologies of wastewater treatment were collected. The contents of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/Fs) were analysed in the samples from 16 wastewater factories. The example of wastewater characteristics for sludge sampling show table 2.
The list of POPs analyses realised in sludge samples shows table 3.
Two sludge samples form Nord-Moravian region with increased contents of PAHs and PCB6 (table 4) were used in pot and field trials. The application of sludge followed the criteria of Czech directive 382/2001 Sb. and the dose of sludge in trials was derived from the dose of 5 t/ha of dry matter.

2.2 Sewage sludge experiments

Three soil types (typic Chernozem, typic Cambisol and arenic Cambisol) were used in the pot trial (6 kg of soil in Mitscherlich pots). The pot trial was run in three replications.
The field trial was set up on typic Cambisol in the area of Bohemian and Moravian highlands. The field trial was realised in four variants (ploughed and not ploughed, two sludge samples) each in three replications. Ploughed and not ploughed variants were focused on the influence of soil treatment on the decomposition of POPs in the soil (photo degradation, increased input of the air, stimulation of microbial activity). The ploughed variant was treated every two weeks in the layer of humic horizon (cca 20 cm). The characteristics of all used soils are presented in table 5.
The mustard (*Brassica alba*) was used in both (pot and field) trials in first year. The pot trial was sowed by radish (*Raphanus sativus*) and the field trial by parsnip (*Pastinaca sativa*) in the second year. The samples of soil and plants were taken after the harvest, the yield was measured and the contents of POPs in soil and plant samples were analysed. The list of POPs substances and analytical methods for POPs determination in sludge and soil is identical with table 2, except of PCDDs/Fs. The identical analytical methods were used for POPs determination in digested plant samples. The standard elementary statistic methods (file characteristics) were used for the evaluation of the results.

2.3 Sediment sampling

The pond sediment samples from 29 locations were collected in 2008. The samples from pond bottoms and from sediment heaps were used. Field ponds, village ponds and forest ponds were observed. Probe poles with a length of 50 cm for the sampling of bottom sediments and 100 cm for the sampling of heap sediments were used. The individual samples consist of 10 partial samples. The samples were stored in plastic bags and closed jars (for POPs analyse). Closed jars were stored in a deep-freeze condition before chemical analysis. The summary of collected samples is presented (Table 6).

2.4 Sediment analysis

The following characteristics were analysed in sediment samples by the Research Institute for Soil and Water Conservation (RISWC):

- Dry matter content (%)
- Organic matter content (%) – 550^{o}, (CSN EN 12879, 2001)
- pH (H2O), pH (KCl) (CSN ISO 10390, 1996)
- Indicators of the cation exchange capacity CEC (CSN ISO, 13536), BS – the rate of complex saturation adsorption (%)
- Al-exchangeable – titration method (Hraško et al., 1962)

The content and quality of primary organic matter and humus substances were analysed in RISWC using the following approach:

- C_{ox} – organic carbon indicative of the carbon content in primary soil organic matter (SOM). The determination procedure is based on the chromic acid oxidation of organic carbon under the abundance of sulphuric acid and at elevated temperature. Unexpended chromic acid is determined by the iodometric method. This method is a modification of CSN ISO, 14235. The assay of loosely and tightly bound humus materials includes the determination of the humic acid carbon (C-HA), fulvic acid carbon (C-FA), humus matter carbon (C-FA+C-HA) and the assessment of the colour coefficient (Q4/6) indicating the humus quality. The determination procedure is based on the sample extraction method using a mixed solution of sodium diphosphate and sodium hydroxide (Zbíral et al. 2004). Carbon contents (C-FA, C-HA) are determined by titration and the coefficient Q4/6 results from the photometry.
- C_{ws} – water-soluble carbon, indicating the quality of primary SOM (bio available carbon for soil microorganism). Laboratory determination consists of an hour sample extraction using 0.01mol/L CaCl2 solution (1:5 w/V) and the determination of oxidizable carbon in the filtrate evaporation residue by heating the filtrate with chromium sulphuric acid and subsequent titration with Mohr's salt.
- C_{hws} – hot water-soluble carbon, being similar for the assessment purpose to water-soluble carbon. After the soil sample was boild for 1 hour in 0.01mol/L CaCl2 solution (1:5 w/V), the oxidizable carbon in the filtrate evaporation residue through the heating of filtrate with chromium sulphuric acid and subsequent titration with Mohr's salt is determined.

The contents of potentially potentially toxic elements were analysed in sediment samples in RISWC:

- As, Cd, Co, Cr, Cu, Hg, Ni, Pb a Zn in the extract of Aqua regia (ČSN EN, 13346), Hg was analysed by AMA 254 method (Advanced mercury analyser, total content).
- As, Cd, Cu, Pb and Zn in the extract of 1mol/L NH4NO3 (mobile contents). The samples were prepared according to ISO, 11464.

The analysis of the elements in the samples were conducted by the AAS method (AAS Varian), flame and hydride technique.
Persistent organic pollutants were analysed in commercial accredited laboratories Aquatest a.s.:

- BTEX (benzene, toluene, e-benzene and xylene), gas chromatography with mass spectrometry (GS/MS), EPA Method, 8260 B.
- PAHs – polycyclic aromatic hydrocarbons, the contents of 16 substances following EPA, liquid chromatography with fluorescence detector (HPLC), methodology TNV, 75 8055.
- PCB_7 – polychlorinated biphenyls, seven indicator congeners (28, 52, 101, 118, 138, 153, 180), gas chromatography with ECD detector (GC/ECD), EPA Method, 8082.
- DDT sum – sum of DDT, DDE and DDD, gas chromatography with ECD detector (GC/ECD), EPA Method, 8082.
- C_{10} – C_{40} hydrocarbons, gas chromatography with flame-ionisation detector (GC/FID), CSN EN, 14039.

The evaluation of sediment characteristics and the contents of potentially potentially toxic elements and persistent organic pollutants in the sediments separating on the base of their origin and type were done by the use of elementary statistics where median, maximum, minimum, average, standard deviation are presented (Excel). The correlations (Pearson correlation coefficients) between selected sediment properties (pH, CEC, content and quality of soil organic matter) significant at the 0.01 and 0.05 level were processed (SPSS Statistics 17.0).

3. Results and discussion

3.1 Sewage sludge results

The values of POPs (Polycyclic aromatic hydrocarbons – PAHs, monocyclic aromatic hydrocarbons – MAHs, Chlorinated hydrocarbons – ClHs and Petroleum hydrocarbons – PHs) contents are demonstrated in table 7. The sludge samples differentiation follows the type and range of studied area. The overview of POPs contents in sludge in individual years presented table 8.

On the example of tested set of sludge samples it was concluded that fluoranthene reaches the highest average concentrations among PAHs. This finding corresponds with the fact that fluoranthene concentrations in the environment belong to the highest from PAHs group (Holoubek et al., 2003). The phenanthrene concentration with highest maximum values follows fluoranthene. The variability of the values of concentrations of these two substances is the highest among PAHs group. Opposite naphtalene reaches the lowest values of all investigated substances.

The highest average and maximum values from the monocyclic aromatic hydrocarbons (MAHs) were detected in the case of toluene. Contents of toluene in the set of sludge samples were characterised by the highest variability, too. Toluene concentrations influenced predominantly the contents of the sum of MAHs because of very low concentrations of all the other substances.

The contents of chlorinated substances reach relatively low level. The values of PCBs concentrations are characterised by maximum variability. The concentrations of DDE are increased in comparison with DDD and DDT. The persistence of decomposition products of DDT in the environment is still detected (Holoubek et al., 2003; Poláková et al., 2003; Vácha et al., 2003).

Generally the highest contents were found in the case of petroleum hydrocarbons (PHs). The evaluation of the contents is complicated by difficult resolution of substances originated from petroleum contamination and of the substances from the decomposition of organic matter in the sludge.

The comparison between the values of sum of PAHs and values of sum of their toxic equivalent factors (TEF) in 25 samples presents figure 1. Good agreement between these values is evident. It could be concluded increased rate of more nuclei substances respectively substances with higher carcinogenic risk (table 9). This findings confirm the need of PAHs monitoring in sludge used for application on agricultural soils.

The data of the contents of POPs in the set of sewage sludge were processed for the assessment of their "background values". The 90% percentile was used after elimination of outlying values. These background values (table 10) are compared with background values of POPs in agricultural soils (Němeček et al., 1996) in table 11. If we compare obtained "background values" of the content of POPs in the set of sewage sludge with the limit values of POPs in sludge in Czech and European legislative norms we get following results.

The value of the sum of 6 congeners of PCBs is suitable from the viewpoint of Czech (0.6 mg/kg) and European (0.8 mg/kg for 7 congeners) legislation. More problematic seems to be content of the sum of PAHs (9.37 mg/kg) where the overcome of proposed limit of EU directive (6 mg/kg) was observed. No limit value regarding PAHs is included in Czech directive No. 382/2001.

On the base of comparison of background values of POPs in sewage sludge and soil (table 5) emerged following findings. Toluene (MAHs group) shows the maximum difference between the content in the soil and in the sludge from all POPs substances. The concentration in the sludge is cca 243-fold higher than the concentration in the soil. The difference of these contents is significantly lower in the group of PAHs with the maximal difference in the case of benzo(ghi)perylene where sludge content represented 13.7-fold higher value as compared to soil. The contents of PCBs in the sludge are cca 10-fold higher in sludge compared to soil while the contents of DDT (including DDD, DDE) are comparable with the contents in the soil.

The values of I-TEQ PCDD/F fluctuated in the range from 9.2 to 280.2 ng/kg. The value of 280.2 ng/kg was eliminated as outlying by statistic procedure. Resulting average I-TEQ PCDD/F is than 22.5 ng/kg in the set of sludge samples. For 90% percentile I-TEQ PCDD/F reaches the value 37.7 ng/kg. The values of I-TEQ PCDD/F fulfil safely the proposed limit of EU order (100 ng/kg I-TEQ PCDD/F).

The assessment of sludge load on the base of congener analysis of PCDD/F indicates regional differences (with the dominance of octo-chlorinated dibenzodioxins in sludge), which are depending on the wastewater load from the different sources very probably (the rate of communal and industrial wastewater of different type). The data are according with the finding that octo-chlorinated (OCDD) and hepta-chlorinated (HpCDDs) congeners are dominant in the sewage sludge (Holoubek et al., 2002). In spite of this fact the definition of typical general congener pattern of the load of set of sludge samples seems to be complicated considering to regional differences. Congener patterns of individual sludge samples could be used for the localisation of sources of wastewater contamination by PCDD/F (Holoubek et al., 2002).

The proposal of recommended limit values of elected POPs in sludge for the application on agricultural soils (table 12) was derived from the following:

- The background values of selected POPs in set of sludge samples from the wastewater factories of the areas of regional, district and industrial towns and smaller settlements were determined.
- Vegetation experiments did not confirm that sludge application in the dose of 5t/ha of dry matter on the soil influenced POPs contents in the soil and tested plants. Together with these findings we respect the results of the other authors following from long-term experiments about the accumulation of some POPs substances in the soil.
- The proposed limit values in "Working Document on Sludge" were observed.
- The substances from POPs group included in Czech Directive of Soil Protection No. 13/1994 Sb. were selected for the observation.
- Theoretical and simplified balance sheet of the input of POPs into soil by sludge application resulted that the background values of most selected POPs in the soil will be multiplied two times after period of 300 years by sludge application. This balance was not used for PCDD/F.
- Increased limit value was proposed for PAHs in comparison with primary proposal in "Working Document on Sludge". EU primary proposal seems to be not relevant in view of load by Czech sludge by PAHs and from the viewpoint of the strictness of PAHs limit against the other limits of the substances (PCDD/F, PCB_7) in EU primary proposal. The presence of PAHs in the environment in Czech conditions does not correspond with primary EU proposal of PAHs in the sludge and majority of sludge production will be excluded respecting the limit 6 mg/kg. We could not find the explanation for the respecting of this limit by the comparison of limit values of PAHs and PCDDs/Fs in the sludge and their background values in the soil for example. The content of PAHs in sludge is 6 times higher as in the soil but the content of PCDDs/Fs is 100 times higher as in the soil regarding the primary EU proposal.
- The extent of selected POPs substances was adapted for Czech legislative for soil protection (Directive No.13/1994 Sb.). The use of results of the research for the Czech legislation is depending on the confrontation of soil protection and sludge application needs respecting economical site of the problem. The difficulty of this process was documented by the refusal of "Working Document on Sludge" for EU legislation.

The results were derived from the set of sludge samples collected in the territory of the Czech Republic. The international validity could be assumed for European countries thanks to connected markets resulting to similar load of municipal waste waters by potentially toxic substances.

3.2 Dredged sediments results

The limit values of POPs in soil for sediment use in Czech legislation (No. 257/2009 Sb.) shows table 13 where only two POPs groups are limited.

The limit values of POPs in sediments in Czech legislation (No. 257/2009 Sb.) shows table 14 where six POPs groups are limited. The existence of national limits of pollutants in sediments for agricultural use in European countries is recommended

The basic physio-chemical properties of dredged sediments are presented in table 15. The content of dry matter, organic matter, sediment reaction, exchangeable H+ content and adsorption characteristics are defined for the set of sediment samples. The wide range of values of observed parameters is clearly visible in table 15. The differences between individual sediment groups can be observed when the separation of sediments with respect to their origin (the sediments of field, forest and village pounds) is carried out. The differences between sediment acidity were detected primarily. Forest sediments are characterised by higher acidity than the others. The lower values of the saturation of adsorption complex by basic ions (S value) and the values of the rate of adsorption complex saturation (V value) consecutively display an increase in sediment acidity.

The sediments were separated based on the sediment storage method (bottom, heap) due to the tendency to increase acidity during storage, and the comparison of the acidity of separated sediments and adsorption characteristics were observed. The prevailing separate sources (field, village and forest) were accepted also but village sediments were not calculated using this procedure due to missing data (only 1 sample of heap sediment was from a village pond). The results are presented in table 16. The storage of sediments on the heaps before application on agricultural soils is generally used methods in many countries.

The results confirm the trend of sediment acidification during sediment storage in the category of both sediment groups (field, forest). The forest sediments show sharper differences between the reaction of bottom and heap sediments. It was surprising to see, however, that the bottom forest sediments reached the highest pH value. The results demonstrate that decreasing pH value influences the values of adsorption characteristics markedly (S and V values).

The values of content and quality of sediment organic matter are presented in table 17.

The wide range of organic matter content in the set of sediment samples is evident; the sediment application with minimal C_{ox} content seems to not provide economical benefit from the viewpoint of organic matter inputs into agricultural soils. Conversely, the application of sediments with maximal C_{ox} content in a set of sediment samples will lead to increased organic matter input into soils. The lower values of organic matter contents are displayed in village pond sediments. Some countries (Slovakia for example) use minimal limit values of organic matter for sediment use in agriculture.

The quality of primary organic matter (the carbon ability for microbial utilization) when compared by water-soluble and hot-water soluble carbon contents (C_{ws} and C_{hws} values that characterise easily available carbon) reached the highest values in forest pond sediments following by field pond sediments. The lowest values in these parameters were observed in village pond sediments again. The same order can be observed by the evaluation of the content of humus substances where the rise of carbon content of total humus substances in forest pond sediments is distinctly increased. The quality of humus substances compared with the ratio of the carbon of humic and fulvic acid is higher in the field pond sediments compared with forest pond sediments. The lowest values of humus substances quality were observed in village pond sediments. From the comparison of carbon contents of primary organic matter and humus substances it follows that the highest humification degree in organic matter is observed in forest pond sediments. This parameter is comparable in field and village pond sediments. It could be generally resulted that forest sediments are very suitable for application on agricultural soils from the viewpoint of their organic matter quality.

The medians and maximums of POPs contents in field, village and forest sediments are presented in table 18 where the comparison with the Direction No. 257/2009 Sb. is available also.

The median values of PAHs indicate an increased load of village pond sediments and a similar trend can be found in the case of DDT. The contents of the others POPs are comparable between individual sediment types. The maximum limits of PAHs were exceeded in all three sediment types. Very probably, PAHs will be the most problematic of the observed POPs group in the sediments. This trend could be expected generally and the proposed limits for sludge in European proposal (Working Document of Sludge) confirm this fact. From the comparison of sediment load by PAHs with the proposal of PAHs limit values in Czech agricultural soils (Němeček et al., 1996) it was concluded that increased persistence of more nuclei compounds in the sediments was found. The tendency of the substances to accumulate in the sediments was observed in the order benzo(ghi)perylene>benzo(b)fluoranthene, benzo(k)fluoranthene, pyrene>benzo(a)pyrene, benzo(a)anthracene, fluoranthene and chrysene. The order was assessed on the basis of the rate between the individual PAHs substances content in the sediment and proposed soil limit value, and the comparison of the sum of PAHs in the sediments and soil limit value.

Despite the findings of DDT it remains that the increased contents in agricultural soils (Vácha et al., 2001; Čupr et al., 2009) did not exceed limits in sediment samples. The existence of the limit for BTEX in the sediments in Direction No. 257/2009 Sb. must be supported with more data collected, especially from river sediments. The limit for C_{10} – C_{40} hydrocarbons will eliminate their increased contents in sediments for agricultural use from local leaks of petroleum hydrocarbons.

The correlation between the contents of observed POPs groups (except of C_{10} – C_{40} hydrocarbons where a dominant number of values were under detection limit) and content and quality of organic matter was assessed. The data in table 19 confirm only sporadic correlation surprisingly.

The trend of PCB and BTEX accumulation in the dependency on content and quality of humus substances is presented. The PAHs groups did not show any trend of accumulation regarding their properties and affinity to organic carbon. Some authors (Cave et al., 2010) measured bioaccessible PAHs fraction in the soil (varied from 10 – 60%) and the multiple regression showed that the PAHs bioaccessible fraction could be explained using the PAHs compound, the soil type and the total PAHs to soil organic carbon content.

It could be assumed that the sources of the contamination by POPs determined in most POPs groups, except for BTEX, influenced the sediments load stronger than the selected sediment properties in an observed set of sediment samples.

The inputs of potentially toxic substances by sludge and sediment application can play important role in soil hygiene. The easy balance of POPs inputs into soil by sludge and sediments application in accordance with Czech legislative is presented in table 20. It must be accepted that the application of sewage sludge and dredged sediments runs under different conditions. The sludge can be applied once in 3 years in maximal dose of 5 tons of dry matter per hectare. The sediments can be applied once in 10 years in maximal dose of 750 tons of dry matter per hectare. The table presented the dose of sludge and sediments in 10 years. This balance could differ between individual countries following national legislative standards.

The maximum possible increase of POPs content in the soil after sludge and sediment application was derived from their possible maximum inputs (table 21). The values are only tentative because no process of POPs decomposition and migration in the soil was reflected.

4. Conclusion

It is evident that legislative regulation of sewage sludge and dredged sediment application on agricultural soils limits the inputs of risky substances into soils and the other parts of the environment. The uncontrolled application of these materials as well as the other biosolids could lead to serious damage of the soils and their functions. The problem with the limiting of POPs in sewage sludge is still continuing not only in the Czech Republic where only PCB_7 and AOX are limited but in European context especially. The refusal of Working Document on Sludge extended the validity of EU directive 86/278 with the absence for limit values of any POPs substances. At the same time it is known that sludge application significantly increased inputs of PAHs and chlorinated substances (PCBs, PCDDs/Fs) into agricultural soils.

The comparison of POPs inputs by sediment and sludge application demonstrated that the application of dredged sediments loads the agricultural soils more by POPs inputs thanks to use of high possible sediment doses. The European legislative is not available on the field of sediment use in agriculture in present time and the existence of national legislative regulations for sediment application can be highly recommended. The experiences of the practical use of limits application in individual countries can be utilized in the process of European legislative assessment.

5. Annex

5.1 Tables

Organic substances	The value (mg/kg dm)
AOX	500
LAS	2600
DEHP	100
NPE	50
PAHs	6
PCB_7	0,8
Dioxins	The value (ng TE/kg dm)
PCDDs/Fs	100

AOX - Sum of halogenated organic compounds
LAS - Linear alkylbenzene sulphonates
DEHP - Di(2-ethylhexyl)phthalate
NPE - Nonylphenol and nonylphenolethoxylates
PAHs - Sum of polycyclic aromatic hydrocarbons
PCB_7 - Sum of seven indication PCB congeners (28, 52, 101, 118, 138, 153, 180)
PCDDs/Fs - Polychlorinated dibenzodioxins/dibenzofurans

Table 1. The proposed limit values of EU directive 86/278.

Anaerobic and aerobic stabilisation (microbial activity stimulation), sludge dehydration and pressing		
No.	Potential use in agriculture	Characterisation
1	yes	agglomeration, different wastewaters, high technological level of wastewater factory - WF
2	yes	Small area, municipal wastewater, lower technological level of WF
3	yes	Small area, municipal wastewater, lower technological level of WF
4	yes (in use)	Regional town up to 35 000 inhabitants., municipal wastewater predominantly, good technological level of WF
8	yes	Regional town up to 55 000 inhabitants, municipal and industrial wastewater (glass, ceramic), high technological level of WF
9	-	Regional town up to 100 000 inhabitants, municipal and industrial wastewater (food production, chemistry – pre-treatment of wastewater), high technological level of WF
10	yes	Regional town up to 100 000 inhabitants, municipal and industrial wastewater (food and paper production), high technological level of WF
11	yes	settlement up to 7 000 inhabitants, municipal wastewater, good technological level of WF
12	yes	Regional town up to 40 000 inhabitants, municipal and industrial wastewater (food production), high technological level of WF
13	yes	Town up to 15 000 inhabitants, municipal wastewater, lower technological level of WF
14	yes	Regional town up to 170 000 inhabitants, municipal and industrial wastewater (food production), high technological level of WF
15	yes	Regional town up to 20 000 inhabitants, municipal wastewater predominantly, high technological level of WF
16	yes (in use)	Regional town up to 50 000 inhabitants, municipal and industrial wastewater (car production), high technological level of WF
17	yes	Regional town up to 50 000 inhabitants, municipal and industrial wastewater (car production), high technological level of WF
18	yes	Industrial town up to 20 000 inhabitants, municipal and industrial wastewater 50/50 (chemistry), high technological level of WF
19	yes	Regional town up to 80 000 inhabitants, municipal wastewater only, high technological level of WF
20	yes	Town up to 20 000 inhabitants, municipal wastewater, high technological level of WF

21	yes	Town up to 20 000 inhabitants, municipal and industrial wastewater, good technological level of WF
22	no	Regional town up to 100 000 inhabitants, industrial WF, high technological level
23	yes	Regional town up to 100 000 inhabitants, municipal and industrial (lower rate) wastewater, high technological level of WF
24	yes	Settlement up to 5 000 inhabitants, municipal wastewater, lower technological level of WF
25	no	Industrial town up to 20 000 inhabitants, increased rate of industrial wastewater (chemistry), high technological level of WF
Mechanical filtration, cold sludge maturation		
5	yes	Spa town up to 15 000 inhabitants, municipal wastewater
6	yes	Settlement up to 5 000 inhabitants, municipal wastewater
7	yes	Central WF for few small settlements, municipal wastewater

Table 2. The characteristics of selected wastewater factories.

Analyse	Samples
pH, Cox,Ca,Mg, P, K	45 samples
As, Be, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, V, Zn (extract of aqua regia)	45 samples
Monocyclic aromatic hydrocarbons benzene, toluene, xylene, ethylbenzene Polycyclic aromatic hydrocarbons naphtalene, anthracene, pyrene, phluoranthene, phenanthrene, chrysen, benzo(b)phluoranthene, benzo(k)phluoranthene, benzo(a)anthracene, benzo(a)pyrene, indeno(c,d)pyrene, benzo(ghi)perylene chlorinated hydrocarbons PCB, HCB, α-HCH, β-HCH, γ-HCH Pesticides DDT, DDD, DDE styrene, petroleum hydrocarbons	45 samples
PCDF 2,3,7,8 TeCDF, 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 189, PCB 170, PCB 180 PCDD 2,3,7,8 TeCDD, 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 PCB PCB 77, PCB 126, PCB 169, PCB 105, PCB 114, PCB 118+123, PCB 156, PCB 157, PCB 167	16 samples

Table 3. The analyses in sludge samples.

	PAHs												
	A	N	P	Ch	Ph	F	B(a)P	B(b)F	B(k)F	B(a)A	B(ghi)P	I(cd)P	PAHs
S 1	1440	3400	2520	1420	8340	7990	3630	4190	1820	1890	1930	1740	40310
S 2	851	50	2950	2590	7220	9520	6640	7490	3360	3150	3690	2830	50341
	MAHs						ChHs						
	B	T	X	Eb	MAHs	PCB6	αHCH	βHCH	γHCH	HCB	DDT	DDD	DDE
S 1	120	830	7	2300	1043	1090	1.00	1.00	1.00	1.00	1.00	1.00	1.00
S 2	14	90	3	3800	111	57	1.00	1.00	1.00	1.25	1.26	2.08	21.5

S 1 – sludge 1, S 2 – sludge 2
A – anthracene, N – naphthalene, P – pyrene, Ch – chrysene, Ph – phenanthrene, F – fluoranthene, B(a)P – benzo(a)pyrene, B(b)F – benzo(k)fluoranthene, B(a)A – benzo(a)anthracene, B(ghi)P – benzo(ghi)pyrene, I(cd)P – indeno(c,d)pyrene, PAHs – polycyclic aromatic hydrocarbons, B – benzene, T – toluene, X – xylene, EB – ethylbenzene, MAHs – monocyclic aromatic hydrocarbons, PCB6 – sum of 6 polychlorinated biphenyls congeners, HCH – hexachlorcyclohexane, HCB – hexachlorbenzene, DDT – dichlordiphenyltrichloethane, DDD – dichlordiphenyldichlorethane, DDE – dichlordiphenylethane, ChHs – chlorinated hydrocarbons

Table 4. POPs contents in sewage sludge used in pot trial (μg/kg).

Soil type	District of origin	pH (KCl)	Cox (%)	Trial
Arenic Cambisol	Melnik	7.05	1.02	pot
Modal Cambisol	Benesov	6.15	1.29	pot
Modal Chernozem	Nymburk	6.93	2.18	pot
Modal Cambisol	Jihlava	5.85	0.8	field

Table 5. The characteristics of soils used in the experiments.

	Field ponds	Forest ponds	Village ponds	Total
Bottom	6	4	3	13
Heap	7	7	2	16
Total	13	11	5	29

Table 6. The numbers and types of sediment samples.

		PAHs												
		A	N	P	Ch	Ph	Fl	B(a)P	B(b)F	B(k)F	B(a)A	B(ghi)P	I(cd)P	PAHs
Industrial towns	AM	299	279	1176	659	1748	941	316	290	168	481	202	158	6718
	GM	245	110	976	526	1484	783	238	222	129	375	154	124	5580
	std.	144	383	506	301	760	451	165	149	80	223	139	76	2851
	max.	477	1185	1870	984	2570	1500	539	463	245	754	506	254	9714
	min.	49	15	169	75	337	168	28	29	15	45	29	17	976
	med.	343	147	1100	791	2100	851	291	289	191	486	154	189	6771
Regional towns	AM	501	77	1706	1026	2280	1821	606	650	316	802	413	367	10564
	GM	282	26	1338	844	1599	1296	454	486	238	648	324	264	7970
	std.	551	67	1241	676	2074	1588	494	528	254	547	302	306	8454
	max.	1710	203	3850	2190	6700	4880	1410	1500	724	1670	940	918	26528
	min.	96	1	507	371	502	464	216	233	114	310	132	113	3071
	med.	165	64	1130	676	1260	1010	334	342	176	532	260	233	6165
Settlements	AM	215	20	1768	826	1399	1187	415	393	201	685	346	207	7662
	GM	181	5	1394	761	1159	1025	360	353	179	624	268	191	6624
	std.	134	25	1616	338	938	658	218	174	89	317	314	91	4705
	max.	548	69	6490	1570	3810	2810	900	732	368	1460	1240	434	20431
	min.	88	1	638	352	453	345	120	133	59	329	110	113	2741
	med.	188	1	1395	736	1100	1085	338	352	183	631	212	181	6328

PAHs – polycyclic aromatic hydrocarbon

Table 7a. The POPs contents in individual groups of sludge samples - PAHs (μg/kg).

		MAHs (μg/kg)					ChlH (μg/kg)								Sty-rene	PHs	Te
		B	T	X	Eb	MAU	PCB	α-HCH	β-HCH	γ-HCH	HCB	DDT	DDD	DDE			
Industrial towns	AM	39.6	494.9	154.5	856.4	1545.3	336	2.5	62.5	1.0	30.6	25.6	27.6	26.5	12.6	14571	2.6
	GM	10.8	138.0	93.0	79.6	481.9	240	1.8	5.7	1.0	16.0	21.9	5.4	24.9	2.1	11043	1.9
	std.	62.4	603.2	125.7	1977.6	2173.4	254	2.6	98.4	0.0	44.2	13.3	57.8	9.4	12.7	9322	1.6
	max.	191.0	1860.0	370.0	5700.0	6548.1	738	8.7	254.0	1.0	138.0	43.4	169.0	43.9	32.5	29000	6.1
	min.	0.1	5.1	19.9	16.1	61.1	98	1.0	1.0	1.0	4.3	10.6	1.0	14.2	0.1	2200	0.2
	med.	17.9	392.0	164.0	70.8	644.7	183	1.0	1.0	1.0	16.6	25.4	4.6	24.9	8.7	11000	2.3
Regional towns	AM	17.9	1543.8	38.2	25.3	1625.1	144	2.0	1.0	1.2	4.1	10.3	2.7	15.2	0.1	8943	2.3
	GM	7.7	452.6	2.6	6.1	630.5	119	1.7	1.0	1.1	2.5	9.5	2.2	10.6	0.1	8616	2.2
	std.	14.5	2804.5	57.3	22.5	2794.1	99	1.3	0.0	0.6	3.9	4.8	2.0	10.0	0.0	2496	0.7
	max.	44.1	8380.0	154.0	70.7	8437.4	358	4.5	1.0	2.7	11.6	21.6	7.1	35.3	0.1	13000	3.2
	min.	0.1	48.4	0.1	0.1	168.3	64	1.0	1.0	1.0	1.0	6.3	1.0	1.0	0.1	6200	1.1
	med.	13.6	314.0	5.7	20.9	369.9	99	1.5	1.0	1.0	1.7	9.2	2.1	14.6	0.1	7700	2.4
Settle-ments	AM	14.3	2784.4	13.4	20.5	2832.6	1566	15.1	1.6	1.0	11.4	21.2	11.4	35.9	0.1	11810	3.4
	GM	2.3	878.1	0.7	2.9	1141.6	170	2.4	1.2	1.0	7.1	15.2	6.5	25.1	0.1	10517	2.2
	std.	15.2	3463.8	30.7	22.6	3452.0	4345	40.0	1.9	0.0	7.5	16.9	12.3	34.8	0.0	5700	2.5
	max.	38.8	9330.0	104.0	59.8	9369.0	14600	135.0	7.2	1.0	20.1	58.6	43.0	134.0	0.1	21000	8.4
	min.	0.1	55.8	0.1	0.1	151.1	31	1.0	1.0	1.0	1.0	3.4	1.0	4.7	0.1	6000	0.2
	med.	8.3	800.0	0.1	14.2	830.0	123	1.6	1.0	1.0	13.9	16.5	7.3	25.3	0.1	9050	3.2

MAHs – mococyclic aromatic hydrocarbons; ClHs – chlorinated hydrocarbons
PHs – petroleum hydrocarbons Te – tenzides

Table 7b. The POPs contents in individual groups of sludge samples - MAHs, ClHs (μg/kg), Te and PHs (mg/kg)

		PAHs												
		A	N	P	Ch	Ph	Fl	B(a)P	B(b)F	B(k)F	B(a)A	B(ghi)P	I(cd)P	PAHs
2002 (20 sampl.)	AM	164	47	1442	616	1131	2499	709	906	409	595	508	398	9930
	GM	122	26	1219	527	940	2131	634	810	368	517	453	355	8488
	std.	120	43	814	363	704	1511	333	435	187	368	255	190	5964
	max	484	140	3330	1490	2880	6860	1440	1930	806	1900	1210	762	26434
	min.	16	2	363	189	240	596	206	334	141	193	161	156	2631
	med	160	30	1250	552	947	2115	635	798	370	560	413	333	8516
2001 (25 sampl.)	AM	252	45	1096	692	1479	904	316	329	173	504	216	165	5912
	GM	173	11	852	535	1067	709	241	250	133	392	163	123	4646
	std.	188	55	474	333	977	427	156	166	85	223	118	73	2571
	max	791	203	1870	1570	3910	1710	596	732	368	927	506	305	9714
	min.	3	1	14	11	17	18	7	6	4	10	3	1	95
	med	199	23	1115	676	1230	889	319	322	176	497	201	172	6170
Sum (45 sampl.)	AM	201	50	1159	685	1330	1405	540	617	294	508	352	283	6566
	GM	143	17	949	547	1010	1088	400	438	217	425	264	205	5497
	std.	144	55	536	383	887	815	364	454	200	205	229	192	2632
	max	548	207	2550	1750	3910	3630	1440	1930	806	927	940	762	11218
	min.	3	1	14	11	17	18	7	6	4	10	3	1	95
	med	164	30	1170	632	1070	1220	467	455	240	518	311	213	6525

PAHs – polycyclic aromatic hydrocarbons

Table 8a. Elementary statistic of the POPs in sludge samples – PAHs (μg/kg)

		MAHs					ChlHs					PHs
		B	T	X	Eb	MAU	PCB	HCB	DDT	DDD	DDE	(mg/kg)
2002 (20 sampl.)	AM	37.9	3815.3	39.8	12.5	3950	110	6.96	3.72	6.11	17.15	5845
	GM	27.6	1431.3	13.5	7.3	1680	98	5.54	3.13	4.94	13.75	5303
	std.	33.8	4315.9	47.8	10.6	4366	49	4.00	1.97	3.38	9.24	2310
	max.	120.0	16400.0	170.0	40.0	16820	201	15.40	7.85	11.50	36.30	8800
	min.	12.0	70.0	0.1	0.1	111	33	1.00	1.00	1.00	1.00	2300
	med.	20.5	2900.0	26.0	8.0	2974	103	6.70	3.51	6.18	15.50	6450
2001 (25 sampl.)	AM	14.8	498.8	36.5	28.2	608	122	9.13	16.91	4.24	21.54	11309
	GM	3.8	163.1	2.6	6.0	288	98	5.44	12.43	2.98	15.87	7848
	std.	13.8	553.0	59.0	27.3	614	75	7.13	12.56	3.74	12.38	6987
	max.	44.1	2040.0	192.0	82.1	2324	358	20.10	45.00	16.60	45.80	29000
	min.	0.1	0.1	0.1	0.1	0	7	1.00	1.00	1.00	1.00	20
	med.	11.1	350.0	5.7	20.2	360	104	8.23	11.40	3.24	20.75	9100
together (45 sampl.)	AM	22.4	2209.1	38.0	16.5	2293	110	8.17	8.00	5.13	20.33	6827
	GM	8.3	522.4	5.3	5.4	739	95	5.49	5.62	3.79	15.32	6219
	std.	22.8	2998.3	54.4	16.1	2998	52	6.05	6.54	3.69	12.17	2631
	max.	120.0	10200.0	192.0	59.8	10355	234	20.10	25.40	16.60	51.80	13000
	min.	0.1	0.1	0.1	0.1	0	7	1.00	1.00	1.00	1.00	2200
	med.	17.0	617.0	13.0	9.5	675	103	7.53	6.24	4.13	19.80	7000

MAHs – mococyclic aromatic hydrocarbons; ClHs – chlorinated hydrocarbons
PHs – Petroleum hydrocarbons

Table 8b. Elementary statistic of the POPs in sludge samples – MAHs, ClHs (μg/kg) and PHs (mg/kg)

Compound	The toxic equivalent value	Compound	The toxic equivalent value
Benzo(a)pyrene	1	Benzo(k)fluoranthene	0.01
Benzo(a)anthracene	0.1	Dibenzo(a,h)anthracene	1
Benzo(b)fluoranthene	0.1	Indeno(1,2,3-cd)pyrene	0.1

Table 9. The overview regarding the toxic equivalent value for individual PAHs compounds

	PAHs (µg/kg)												
	Fl	P	Ph	B(b)F	B(a)A	A	B(a)P	I(cd)P	B(k)F	B(ghi)P	Ch	N	ΣPAU
90 percentil	2412	1626	2407	1316	759	433	949	535	572	686	1148	132	9371

	MAHs (µg.kg-1)					ChlHs (µg/kg)					PHs mg/kg
	B	T	X	Eb	ΣMAU	PCB	HCB	DDT	DDE	DDD	
90 percentil	50	7300	150	37	7342	183	17.8	19.6	36.1	9.8	9440

Table 10. Background values of POPs in sludge collection, 90 percentil = backgroun value

	PAHs (µg/kg)											
	Fl	P	Ph	B(b)F	B(a)A	A	B(a)P	I(cd)P	B(k)F	B(ghi)P	Ch	N
Background - soil	300	200	150	100	100	50	100	100	50	50	100	50
Background - sludge	2412	1626	2407	1316	759	433	949	535	572	686	1148	132
difference in %	804	813	1605	1316	759	866	949	535	1144	1372	1148	264

	MAHs (µg/kg)				ChlHs (µg/kg)					PHs(mg/kg)
	B	T	X	Eb	PCB	HCB	DDT	DDE	DDD	
Background - soil	30	30	30	40	20	20	15	10	10	100
Background - sludge	50	7300	150	37	183	18	20	36	10	9440
difference in %	167	24333	500	92	917	89	130	361	98	9440

Table 11. The comparison of background values of POPs in sludge and soils.

	Content (µg/kg)							
Parameter	Sum MAHs	Sum PAHs	PCB_7	HCB	DDT	DDE	DDD	I-TEQ* PCDDs/Fs
Recommended limit	10 000	10 000	600	60	60	60	30	80
EU proposal	6000	-	800	-	-	-	-	100
Soil reference value (Czech)	1000	130	20	20	30	25	20	1

PAHs- polyaromatic hydrocarbons,
MAHs-monoaromatic hydrocarbons,
PCB7-sum of 7 congeners of polychlorinated biphenyls,
HCB-hexachlorbenzene,
DDT-dichlordiphenyltrichlorethane,
DDD-dichlordiphenyldichlorethane,
DDE-dichlordifenyldichlorethen,
I-TEQ PCDD/F-toxic equivalent of polychlorinated dibenzo-p-dioxins and dibenzofurans
I-TEQ PCDDs/Fs (ng/kg)

Table. 12. Recommended limit values of elected POPs in sludge, primary EU proposal and reference values in soils of the Czech Republic.

	Content (mg/kg)	
Limited substance	Middle and heavy texture soils	Light texture soils
PAHs	1.0	1.0
PCB_7	0.02	0.02

PAHs – polycyclic aromatic hydrocarbons
PCB7 – seven indication congeners of polychlorinated biphenyls

Table 13. Directive No. 257/2009, sediment use on agricultural soils, POPs limit values in soil.

Limited substance	Content (mg/kg)
PAHs	6
PCB_7	0.2
BTEX	0.4
DDT	1
C_{10}-C_{40}	300

PAHs – polycyclic aromatic hydrocarbons
PCB7 – seven indication congeners of polychlorinated biphenyls (28, 52, 101, 118, 138, 153, 180)
BTEX – sum of benzene, toluene, ethylbenzene and xylene
DDT – sum of DDT, DDD and DDE;
C10-C40 – sum of hydrocarbons - indication of petroleum hydrocarbons

Table 14. Directive No. 257/2009, sediment use on agricultural soils, POPs limit values in sediments (mg/kg).

	Dry matter %	Organic matter %	pH H_2O	pH KCl	Exchangeable H+ (mmol/100g)	CEC (mmol/100g)	BS %
Field (medians, 13 samples)	85.73	8.40	5.22	5.04	8.0	20.01	52.5
Village (medians, 5 samples)	98.06	7.07	5.42	5.23	6.5	18.91	63.5
Forest (medians, 11 samples)	80.08	8.44	4.09	3.82	16	20.88	48
Together (medians, 29 samples)	81.24	8.68	5.13	4.91	11.0	20.9	57.0
Together (A. means)	79.27	9.89	5.17	4.91	13.12	21.33	56.12
Together (St. deviation)	17.1	4.71	1.01	1.06	9.66	7.05	16.41
Maximum	99.06	22.5	7.1	6.95	42.0	41.19	100
Minimum	46.05	2.73	2.86	2.84	<0.5	8.81	28

CEC – cation exchange capacity
pH H2O – sediment pH measured in the extract of H2O
BS – the rate of complex saturation adsorption
pH KCl - sediment pH measured in the extract of 1M KCl

Table 15. Sediment characteristics in the set of 29 samples

	pH H_2O	pH KCl	Exchangeable H+ (mmol/100g)	CEC (mmol/100g)	BS %
Field-bottom	5.26	5.12	5.5	17.99	55.5
Field-heap	5.21	4.94	9.5	22.19	52.5
Forest-bottom	6.28	6.13	10	17.95	71
Forest-heap	3.81	3.63	26.5	25.24	31

CEC – cation exchange capacity
pH H2O – sediment pH measured in the extract of H2O
BS – the rate of complex saturation adsorption
pH KCl - sediment pH measured in the extract of 1M KCl

Table 16. The medians of sediment characteristics separated into sediment groups based on sediment type and storage method.

	C_{ox} %	C_{ws} mg.kg-1	C_{hws} mg.kg-1	HA %	FA %	HS %	Q4/6	HA:FA	HS:C_{ox}
Field	2.54	167.5	404.5	0.41	0.25	0.61	5.50	1.44	0.25
Village	1.72	108.5	324	0.21	0.23	0.47	6.1	0.92	0.27
Forest	2.53	199	558	0.49	0.61	0.97	5.4	1.18	0.39
Together	2.67	175	458.5	0.41	0.29	0.77	5.35	1.1	0.29
Maximum	8.29	515.0	1738.0	2.33	1.67	3.27	24.8	4.04	0.49
Minimum	0.52	72.0	76.0	0.07	0.04	0.11	3.4	0.23	0.16

Cox- organic carbon HA- carbon of humic acids
Cws- water-soluble carbon FA- carbon of fulvic acids
Chws- hot-water-soluble carbon HS- carbon of humus substances Q4/6- colour quotient

Table 17. The medians, maximum and minimum of organic matter content and quality in the sediments

		PAHs 2n	PAHs 3-4n	PAHs 5-6n	PAHs sum	PCB_7	DDT sum	BTEX	C_{10}-C_{40}*
Field	median	48	494	147	694	15.1	9.19	31.2	100
	max	210	4762	1290	6143	40.8	14.5	71.5	580
Village	median	77	2396	780	3386	14.2	15	30.35	105
	max	210	6842	2133	9052	36.9	32.3	43.2	110
Forest	median	41	326	54	517	15.4	8.83	66.3	100
	max	228	10347	2961	13536	1010	16.7	96.2	200
Limit 257/2009		-	-	-	6000	200	100	400	300
Limits exceeded. Field/Village/Forest					1/2/1	0/0/1	0/0/0	0/0/0	1/0/0

* C10-C40 – sum of hydrocarbons, content in mg/kg
PAHs 3-4n - the sum of PAHs with 3 and 4 rings
PAHs 2n - the sum of PAHs with 2 rings
PAHs 5-6n - the sum of PAHs with 5 and 6 rings
PCB7 – sum of seven indication congeners
BTEX – sum of benzene, toluene, ethylbenzene and xylene
DDT sum – sum of DDT, DDD and DDE

Table 18. The medians and maximums of POPs contents in the sediments (μg/kg) and values exceeding limits (Direction No. 257/2009 Sb.)

	PAHs 2n	PAHs 3-4n	PAHs 5-6n	PAHs sum	PCB_7	DDT	BTEX	C_{10}-C_{40}
C_{ox}	0.209	-0.194	-0.196	-0.187	0.347	0.085	**0.749***	0.287
C_{hws}	0.196	0.071	0.069	0.075	0.246	0.183	**0.468***	-0.015
C_{ws}	**0.418**	0.225	0.235	0.237	0.06	0.148	0.268	**0.419**
HS	0.170	-0.151	-0.165	-0.148	**0.462**	0.067	**0.727***	0.180
FA	0.351	-0.041	-0.51	-0.034	0.286	0.064	**0.723***	0.163
HA	0.051	-0.202	-0.217	-0.202	**0.524***	0.063	**0.632***	0.196
HA/FA	-0.299	-0.199	-0.203	-0.202	0.186	0.045	0.298	-0.034
C_{ox}/HS	0.121	0.092	0.083	0.091	**0.414**	0.094	0.268	-0.088

Cox - organic carbon HA - carbon of humic acids PCB7 – sum of seven indication congeners
Cws - water-soluble carbon FA - carbon of fulvic acids DDT – sum of DDT, DDD and DDD
Chws - hot-water-soluble carbon HS - carbon of humus substances PAHs 2n - the sum of PAHs with 2 rings PAHs 3-4n - the sum of PAHs with 3 and 4 rings PAHs 5-6n - the sum of PAHs with 5 and 6 rings C10-C40 – sum of hydrocarbons, content in mg/kg

Table 19. Pearson correlation coefficients between the contents of individual POPs groups and content and quality of organic matter, correlation significant at the 0,01 level (bold*) and 0,05 level (bold).

	POPs inputs (g/ha)	
Limited substance	Sewage sludge, application of 15t d.m. once in 10 years	sediments, application of 750t d.m. once in 10 years
PCB_7	9	150
PAHs	non limited	4500
BTEX	non limited	300
DDT	non limited	75
C_{10}-C_{40}	non limited	225000

(g/ha) PAHs – polycyclic aromatic hydrocarbons PCB7 – seven indication congeners of polychlorinated biphenyls BTEX – sum of benzene, toluene, e-benzene and xylene DDT – sum of DDT, DDD and DDE C10-C40 – sum of hydrocarbons - indication of petroleum hydrocarbons

Table 20. The comparison of POPs inputs by sewage sludge and dredged sediments application into agricultural soils.

	Sewage sludge		Dredged sediments	
Limited substance	Concentration increase (mg/kg)	% of soil background values CR	Concentration increase (mg/kg)	% of soil background values CR
PCB_7	0.002	10	0.03	150
PAHs	-	-	1	100
BTEX	-	-	0.07	54
DDT	-	-	0.02	27
C_{10}-C_{40}	-	-	50	50

PAHs – polycyclic aromatic hydrocarbons PCB_7 – seven indication congeners of polychlorinated biphenyls BTEX – sum of benzene, toluene, e-benzene and xylene DDT – sum of DDT, DDD and DDE C_{10}-C_{40} – sum of hydrocarbons - indication of petroleum hydrocarbons

Table 21. Maximum possible increase of POPs in soil after sewage sludge and dredged sediments application.

5.2 Figures

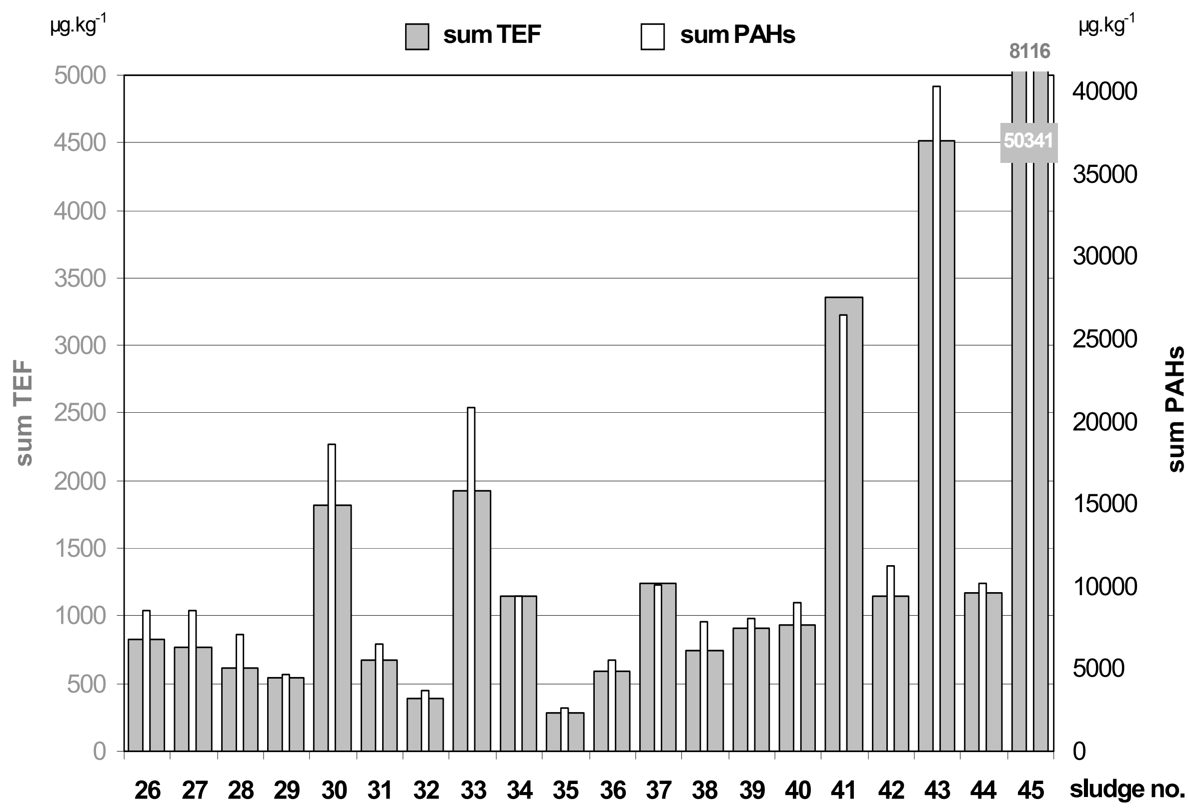

Fig. 1. The comparison of sum TEF PAHs and sum PAHs in sludge (µg/kg).

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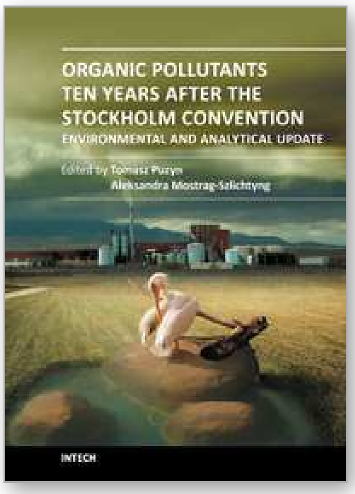

Organic Pollutants Ten Years After the Stockholm Convention - Environmental and Analytical Update
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Ten years after coming into force of the Stockholm Convention on Persistent Organic Pollutants (POPs), a wide range of organic chemicals (industrial formulations, plant protection products, pharmaceuticals and personal care products, etc.) still poses the highest priority environmental hazard. The broadening of knowledge of organic pollutants (OPs) environmental fate and effects, as well as the decontamination techniques, is accompanied by an increase in significance of certain pollution sources (e.g. sewage sludge and dredged sediments application, textile industry), associated with a potential generation of new dangers for humans and natural ecosystems. The present book addresses these aspects, especially in the light of Organic Pollutants risk assessment as well as the practical application of novel analytical methods and techniques for removing OPs from the environment. Providing analytical and environmental update, this contribution can be particularly valuable for engineers and environmental scientists.