Recommended maximum contents of persistent organic pollutants in sewage sludge for application on agricultural soils

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ABSTRACT

The recommended maximum contents of the substances from the group of persistent organic pollutants (POPs) in sludge for the application on agricultural soils were proposed. The list of the substances follows Czech legislative norms for soil protection (Directive of the Ministry of Environment No. 13/1994 Sb.). The list includes the groups of polycyclic aromatic hydrocarbons (PAHs), monocyclic aromatic hydrocarbons (MAHs), the amount of six congeners of polychlorinated biphenyls (PCB_6), DDT and residues, polychlorinated dibenzo-p-dioxins and dibenzofuranes (PCDDs/Fs). Recommended maximum contents were proposed on the basis of the determination of background values of POPs in the set of 45 sludge samples from the wastewater factories in the territory of the Czech Republic. The results of vegetation experiments focused on the POPs in soil and plants after sludge application were used and the proposal of EU legislation Working Document on Sludge was investigated.

Keywords: sewage sludge; persistent organic pollutants; recommended limit contents; agricultural soil

Many authors documented the positive effects of the sludge application on the yield and soil organic mater and the problem of potentially risk elements (Melcer et al. 1988, Balík et al. 1999, Hanč et al. 2005). In his previous article, Vácha et al. (2005a) documented that some foreign institutes deal with long-term research of persistent organic pollutants in sludge (Markard 1988, Witte 1988, Starke et al. 1991, Webber and Singh 2001). The contents of individual substances from POPs group were determined in the soil after sludge application and the transfer of some substances from soil into plants was observed. It was resulted that sludge could be an important source of POPs, and long-term and unregulated sludge application on agricultural soil could lead to a significant increase of POPs contents in the soil. The legislative limitation of POPs contents in sludge seems to be inevitable in future perspective. The research of POPs determination (the indicative methods) that could reduce economical needs is the most important way for practical use of these methods.

At present, the application of the sludge on agricultural soils is regulated by the directive of the Czech Ministry of Environment No. 504/2004 Sb. This directive was developed on the basis of the directive 382/2001 Sb. and contains only minor changes. The directive determines the conditions of sludge application on agricultural soils, including limit values of potentially risk elements and some persistent organic pollutants (AOX, PCB_6) in sludge. The sum of PCB_6 includes congeners 28 + 52 + 101 + 138 + 153 + 180. The directive 86/278/EEC regulates the sludge application in the 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 included in the Working Document on Sludge that was also available for the professional community. This proposal altered existing criteria and installed new criteria especially for the persistent organic pollutants. The contents of following seven POPs groups were regulated: the volume 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), volume of polycyclic aromatic hydrocarbons (PAHs), volume of seven congeners of PCB (28 + 52 + 101 + 118 + 138 + 153 + 180) and polychlorinated

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Table 1. The comparison of the Czech (MŽP ČR 504/2004) and EU (86/278/EU) legislation, including the EU proposal

Parameter	MŽP ČR 504/2004 (mg/kg d.m.)	86/278/EU (mg/kg d.m.)	EU Proposal (mg/kg d.m.)
AOX	500	–	500
PCB_6	0.6	–	–
PCB_7	–	–	0.8
LAS	–	–	2600
DEHP	–	–	100
NPE	–	–	50
PAHs	–	–	6
PCDDs/Fs (ng TE/kg dw.)	–	–	100

dibenzo-p-dioxins and dibenzofuranes (PCDDs/Fs). The ratification of the Working Document on Sludge for the legislation was complicated by lobbies and by economical needs for the determination of pollutants. The proposal was refused and the directive 86/278/EEC is still valid in its original form. The comparison of the Czech and EU legislation, including the proposal (Working Document on Sludge) is presented in Table 1.

This paper is the continuation of the work by Vácha et al. (2005a) and brings new information resulting from the project that was terminated in 2004.

MATERIAL AND METHODS

The proposal of recommended limit values of POPs in sludge was realised on the basis of:

– the research of POPs contents in the set of 45 sludge samples from the water factories in the Czech Republic,
– the results of pot and field trials focused on the contents of POPs in soil and plants after sludge application,
– the use of limit values of POPs in Working document on sludge.

Content of POPs in the set of 45 sludge samples

The wastewater factories were chosen at:

– areas of regional and district towns (including the capital city of Prague),
– areas of industrial towns,
– areas of settlements smaller than 15 000 inhabitants.

The contents of PCDDs/Fs were analysed in sixteen sludge samples. Detailed information about this research was published in the previous article by Vácha et al. (2005b).

Pot and field trial

The experiments were set up in spring 2003 and were realised in the vegetation periods 2003 and 2004. Two sludge samples form the North Moravia region with increased contents of PAHs and PCB_6 (Table 2) were used in both trials. The application of sludge followed the criteria of the Czech directive 382/2001 Sb. and the dose of sludge in trials was derived from the dose of 5 t/ha of dry matter.

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-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 (circa 20 cm). The characteristics of all used soils are presented in Table 3.

The mustard (*Brassica alba*) was used in both (pot and field) trials in 2003. The pot trial was sowed by radish (*Raphanus sativus*) and the field trial by parsnip (*Pastinaca sativa*) in 2004. 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 was presented in Vácha et al. (2005a). 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.

RESULTS AND DISCUSSION

The background values of POPs in the set of sludge samples were calculated as 90% of their

Table 2. Contents of POPs in sludge samples used in field and pot trials

	PAHs (μg/kg)												
	A	N	P	Ch	Ph	F	B(a)P	B(b)F	B(k)F	B(a)A	B(ghi)P	I(cd)P	Σ PAHs
Sludge 1	1440	3400	2520	1420	8340	7990	3630	4190	1820	1890	1930	1740	40 310
Sludge 2	851	50	2950	2590	7220	9520	6640	7490	3360	3150	3690	2830	50 341
	MAHs (μg/kg)						ChHs (μg/kg)						
	B	T	X	Eb	Σ MAHs	PCB_6	α-HCH	β-HCH	γ-HCH	HCB	DDT	DDD	DDE
Sludge 1	120	830	7	2300	1043	1090	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Sludge 2	14	90	3	3800	111	57	1.00	1.00	1.00	1.25	1.26	2.08	21.5

A – anthracene, N – naphthalene, P – pyrene, Ch – chrysene, Ph – phenanthrene, F – fluoranthene, B(a)P – benzo(a)pyrene, B(b)F – benzo(b)fluoranthene, B(k)F – benzo(k)fluoranthene, B(a)A – benzo(a)anthracene, B(ghi)P – benzo(ghi)pyrene, I(cd)P – indeno(c,d)pyrene, PAHs – polyaromatic hydrocarbons, B – benzene, T – toluene, X – xylene, Eb – ethylbenzene, MAHs – monoaromatic hydrocarbons, PCB_6 – amount of 6 congeners of polychlorinated biphenyls, HCH – hexachlorcyclohexane, HCB – hexachlorbenzene, DDT – dichlordiphenyltrichlorethane, DDD – dichlordiphenyldichlorethane, DDE – dichlordifenyldichlorethen, ChHs – chlorinated hydrocarbons

contents after the exclusion of outlying values (one sample of PCDDs/Fs was excluded by the use of the analysis of outlying values – software Unistat 5.1). The results are presented in Table 4, where the resulted background values in sludge are compared with reference values of POPs in the agricultural soils of the Czech Republic (Němeček et al. 1996). The differences between the contents of POPs in the sludge and soil are shown in percents in the third line of the Table 4. It could be concluded that the highest increase of the content of POPs in the sludge in comparison with the content in the soil was found in the case of toluene from MAHs group, phenantren and benzo(g,h,i)perylen from PAHs group and PCB_6 from chlorinated substances group (ChHs). DDE reached the highest contents within the group of DDT residues.

The comparison of the background values of POPs in the set of sludge samples with the Czech Directive 504/2004 Sb. allows only the evaluation of PCB_6, where the contents in sludge safely fulfils the limit value. Considering the proposal of the EU Directive Working Document on Sludge, the same result was observed in the case of PCB_6. The less advantageous result brought the comparison of PAHs because the background value in the set of sludge samples (9.37 mg/kg) overcomes proposed limit in the Working Document on Sludge (6 mg/kg). The background value of I-TEQ PCDDs/Fs (toxic equivalents of polychlorinated dibenzo-*p*-dioxins and dibenzofuranes) in the set of sludge samples (37.7 ng/kg) fulfils safely primary limit proposed by EU (100 ng/kg). Only one sample of sludge reached the value of I-TEQ PCDDs/Fs (280 ng/kg) and the increased content of PCDDs/Fs was substantiated by the presence of the industry focused on cardboard production. This sample was excluded by analysis of outlying values from the set of sludge samples (as noticed before).

On the basis of the data from the pot and field trial it was resulted that the application of sludge in the dose of 5 t/ha of dry matter did not influence the contents of POPs in soil and plants significantly. The differences of the content of PAHs, MAHs and PCB_6 in the soil between the control variants and variants with sludge application were not statisti-

Table 3. The characteristics of soils used in all experiments

Soil	District	Soil type	pH	C_{ox} (%)	Trial
Červená Píska	Mělník	arenic Cambisol	7.05	1.02	pot
Benešov	Benešov	typic Cambisol	6.15	1.29	pot
Úmyslovice	Nymburk	typic Chernozem	6.93	2.18	pot
Dudín	Jihlava	typic Cambisol	5.85	0.8	field

Table 4. The comparison of background values of POPs contents in sludge samples and their reference values in soils (for abbreviations see Table 2, PCDDs/Fs-polychlorinated dibenzo-p-dioxins and dibenzofuranes)

	PAHs (μg/kg)												
	F	P	Ph	B(b)F	B(a)A	A	B(a)P	I(cd)P	B(k)F	B(ghi)P	Ch	N	Σ PAHs
Reference value (soil)	300	200	150	100	100	50	100	100	50	50	100	50	1000
Background value (sludge)	2412	1626	2407	1316	759	433	949	535	572	686	1148	132	9371
Difference (%)	804	813	1605	1316	759	866	949	535	1144	1372	1148	264	937

	MAHs (μg/kg)				ChHs (μg/kg)					I-TEQ PCDDs/Fs (ng/kg)
	B	T	X	Eb	PCB_6	HCB	DDT	DDE	DDD	
Reference value (soil)	30	30	30	40	20	20	15	10	10	1
Background value (sludge)	50	7300	150	37	183	18	20	36	10	37.7
Difference (%)	167	24 333	500	92	917	89	130	361	98	3770

cally significant. The same results were obtained for the content of named POPs in identical plant samples between the variants. Moreover, marked differences between POPs contents in root and shoot of plants were observed. Especially MAHs, PAHs and PCB_6 contents reached significantly higher values in shoot in comparison with root of all tested plants. The hypothesis of superficial contamination of plants (imission fall-outs, soil dust) was confirmed by the comparison of POPs contents in washed and unwashed plants. Differences of the amount of TEF PAHs (toxic equivalents of PAHs) were found (Vácha et al. 2005a): 19% between washed and unwashed *Brassica alba* harvested from control variant; for sludge 1 application 30%; and for sludge 2 application even 86%. The superficial contamination of plants plays the most important role in comparison with the transfer of POPs from the soil into the plants via root of plants. Only in the case of MAHs the contents in the soil and the plants on the variant with sludge application increased slightly in the experiments in the first year. The differences between the variants of the trials were the lowest in the second year because of a probable decomposition or volatilisation of MAHs. The differences of PAHs, PCB_6 and DDT contents in soil and plants between variants of the trials were influenced by external impacts more than by sludge application and no significant differences were found between ploughed and unploughed variants of field trial. On the other hand, the trend of slight changes was observed by the use of congener analyses of PCDDs/Fs in the soil after sludge application (Figure 1). This trend is in accordance with the results of some authors (Schulz 1993) about PCDDs/Fs accumulation in the soil with long-term sludge application. This result could not be confirmed in our short-term experiment but the similar findings were observed by the monitoring of soil at our workplace (Vácha et al. 2005b).

The proposal of recommended limit values of elected POPs in sludge for the application on agricultural soils (Table 5) was derived from the following:

The background values of selected POPs in the 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 the sludge application in the dose of 5 t/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 other authors obtained in long-term experiments about the accumulation of some POPs substances in the soil.

The proposed limit values in the Working Document on Sludge were observed.

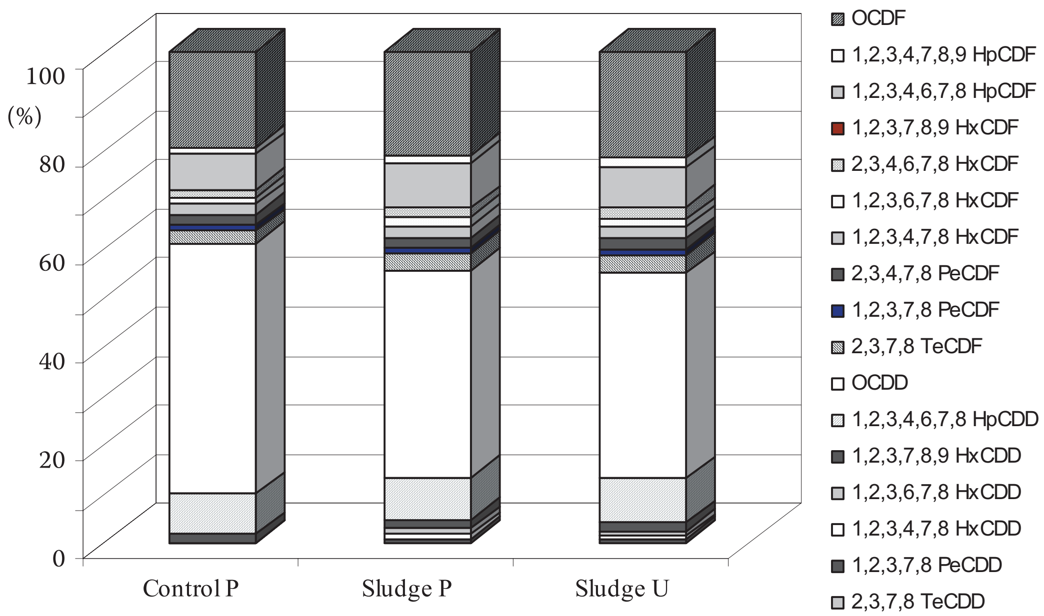

Figure 1. Congener analysis of PCDDs/Fs in the soil after sludge application for ploughed (P) and unploughed (U) variants

The substances from POPs group included in the Czech Directive of Soil Protection No. 13/1994 Sb. were selected for the observation.

Results of the theoretical and simplified balance sheet of the input of POPs into soil by sludge application show that the background values of most selected POPs in soil will be multiplied two times in a period of 300 years after the sludge application. This balance was not used for PCDDs/Fs.

Increased limit value was proposed for PAHs in comparison with the primary proposal in the Working Document on Sludge. EU primary proposal seems not to be relevant in view of the load of Czech sludge by PAHs and for its strictness of PAHs limit compared to the limits of other substances (PCDDs/Fs, PCB_6). The presence of PAHs in the Czech environment does not correspond with primary EU proposal of PAHs limits in the sludge and the majority of sludge production will thus be excluded if respecting the limit 6 mg/kg. For instance, we could not find the reason for respecting this limit comparing the limit PAHs and PCDDs/Fs values in the sludge and their background values in soils. Regarding the primary EU proposal the content of PAHs in sludge is 6 times higher than in the soil but the content of PCDDs/Fs is 100 times higher than in the soil. Does this fact correspond to the differences of potential toxicity between PAHs and PCDDs/Fs?

The extent of selected POPs substances was adapted for Czech legislation for soil protection (Directive No. 13/1994 Sb.). The research activities focused on other substances from POPs group in soil and biosolids will continue in Europe as well

Table 5. Recommended limit values of selected POPs in sludge, primary EU proposal and reference values in soils of the Czech Republic

Parameter	Σ PAHs	Σ MAHs	PCB_6	HCB	DDT	DDE	DDD	I-TEQ PCDDs/Fs
	μg/kg							ng/kg
Recommended limit	10 000	10 000	600	60	60	60	30	80
Proposal EU	6000	–	800 (PCB_7)	–	–	–	–	100
Reference value – soil	1000	130	20	20	15	10	10	1

PAHs – polyaromatic hydrocarbons, MAHs – monoaromatic hydrocarbons, $PCB_{6(7)}$ – amount of 6 (7) congeners of polychlorinated biphenyls, HCB – hexachlorbenzene, DDT – dichlordiphenyltrichlorethane, DDD – dichlordiphenyldichlorethane, DDE – dichlordifenyldichlorethen, I-TEQ PCDDs/Fs – toxic equivalent of polychlorinated dibenzo-*p*-dioxins and dibenzofuranes) as in the Czech Republic in future. The use of the results of the research for the Czech legislation depends on the confrontation of soil protection and sludge application needs respecting the economical site of the problem. The controversy of this process was reflected by the refusal of the Working Document on Sludge.

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