The application of sludge on agriculturally used soils and the problem of persistent organic pollutants

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ABSTRACT

A set of 45 samples of the sludge from wastewater factories in the area of the Czech Republic was completed. The selection of wastewater factories reflected the extent of observed area as well as the occurrence of the industrial wastewater. The contents of persistent organic pollutants (POPs) were determined in the samples. Moreover, the contents of polychlorinated dibenzo-p-dioxins and dibenzofuranes (PCDD/F) were detected in 16 samples. The set of analytical data summarises the level of sewage sludge contamination by POPs within Czech wastewater factories. The results were compared with the directive of Czech Ministry of Environment, No. 382/2001 Sb. and with the proposed limit values of the EU directive, No. 86/278. Among all the determined substances only the value of the sum of polycyclic aromatic hydrocarbons (PAHs) content exceeded the threshold value given by the proposed EU directive.

Keywords: sludge; persistent organic pollutants; polycyclic aromatic hydrocarbons; polychlorinated dibenzo-p-dioxins and dibenzofuranes

The problem with the disposal of sewage sludge is topical with the increasing number of wastewater factories. The use of sewage sludge for fertilization of agriculturally used soils seems to be economically favourable in comparison with the combustion or storage of the material. The positive effects of sewage sludge on production parameters of soils are already known and the input of organic matter into soils is very beneficial in the present time. The conditions and methodological approach of the application of the sludge on agricultural soils are defined in the directive of the Ministry of the Environment of Czech Republic, No. 382/2001. The contents of potentially risky elements, sum of PCBs and sum of halogenated organic compounds (AOX) are the limiting factors of sludge application in agriculture.

Persistent organic pollutants (POPs) belong to the most important environmental contaminants requiring intensive investigation. The innovation of EU order No. 86/278 concerning the use of sludge presents the limit values of polycyclic aromatic hydrocarbons, phthalate, nonylphenol and nonylphenolethoxylates or polychlorinated dibezo-p-dioxins and dibenzofuranes as mentioned in Table 1.

Significant levels of POPs in sewage sludge were reported in the last two decades. Detailed investigation was provided in Germany (Markard 1988, Melcer et al. 1988, Witte 1988, Schaecke and

Table 1. The proposed limit values of EU directive No. 86/278 for agricultural application of sewage sludge

Analytes	mg/kg dry matter
AOX[1]	500
LAS[2]	2600
DEHP[3]	100
NPE[4]	50
PAH[5]	6
PCB[6]	0.8
Dioxins	ng TE/kg dry matter
PCDD/F[7]	100

[1]sum of halogenated organic compounds, [2]linear alkylbenzene sulphonates, [3]di(2-ethylhexyl)phthalate, [4]nonylphenol and nonylphenolethoxylates, [5]sum of polycyclic aromatic hydrocarbons, [6]sum of seven PCB congeners, [7]polychlorinated dibenzodioxins/dibenzofuranes

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Pöplan 2000, Norbert and Krohne 2001) and USA (Shainberg 2000) for example. In these papers the contents of a wide scale of POPs including halogenated substances, polycyclic aromatic hydrocarbons (PAHs), and nonylphenole in sewage sludge were reported. Polychlorinated dibenzo-p-dioxins and dibenzofuranes (PCDD/F) belong to the most dangerous organic pollutants and high variability of their contents in different sludge samples was observed. The range of the values 20–177 ng/kg I-TEQ presents Hagenmaier et al. (1992) from the set of 13 samples of sludge in Germany. The concentrations from 6 to 4100 ng/kg I-TEQ PCDD/F (median 54 and average 357) were detected in the sludge in Sweden.

Some analyses of German soils amended by long-term sludge application showed increased concentrations of POPs. Similar results were found in the Czech Republic (Podlešáková et al. 2001). The input of PCDD/F into agricultural soils seems to be higher via sludge application than via emission fall-outs. Recommended compost processing of the sludge leads to significantly increasing the contents of most persistent congeners of PCDD/F in these samples (Jones and Sewart 1995).

This article presents the results of the measurement of POPs concentrations in a set of 45 sewage sludge samples.

MATERIAL AND METHODS

A set of 45 sludge samples was sampled during the years 2001 and 2002. The selected wastewater factories were situated in areas of district towns, towns with an increased percentage of industry and in the areas of middle and small settlements. The identification of the wastewater cleaners is numerical in the paper because of the anonymity guarantee.

The samples of fresh sludge (dehydrogenated and pressed) were transported in closed glass jars and frozen after the transport. The contents of POPs (monocyclic aromatic hydrocarbons, polycyclic aromatic hydrocarbons, chlorinated hydrocarbons, pesticides residua and petroleum hydrocarbons) were determined in the samples. The contents of PCDD/F were analysed in 16 sludge samples. The list of the analyses is presented in Table 2. The methods of POPs analyses are reported in the articles of Němeček et al. (1994), Jech et al. (1999) and Podlešáková et al. (2000).

The results of the laboratory analyses were processed by the use of basic statistical methods and the data was compared with Czech and EU legislative norms. The dependencies of the POPs concentrations on the origin of the sludge and the technology of sludge production were observed.

Table 2. The survey of analyses determined in sewage sludge

Analytes		No. of samples
Monocyclic aromatic hydrocarbons	benzene, toluene, xylene, ethylbenzene	45
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	
Others	styrene, petroleum hydrocarbons	
PCDF	2,3,7,8 TeCDF, 1,2,3,7,8 PeCDF, 2,3,4,7,8 PeCDF, 1,2,3,4,7,8 H_xCDF, 1,2,3,6,7,8 H_xCDF, 1,2,3,7,8,9 H_xCDF, 2,3,4,6,7,8 H_xCDF, 1,2,3,4,6,7,8 H_pCDF, 1,2,3,4,7,8,9 H_pCDF, OCDF PCB 189, PCB 170, PCB 180	16
PCDD	2,3,7,8 TeCDD, 1,2,3,7,8 PeCDD, 1,2,3,4,7,8 H_xCDD, 1,2,3,6,7,8 H_xCDD, 1,2,3,7,8,9 H_xCDD, 1,2,3,4,6,7,8 H_pCDD,OCDD	
PCB	PCB 77, PCB 126, PCB 169, PCB 105, PCB 114, PCB 118+123, PCB 156, PCB 157, PCB 167	

Table 3. Toxic equvivalents of PAHs (TEF)

Analytes	Value of TEF
Benzo(a)pyrene	1
Benzo(a)anthracene	0.1
Benzo(b)phluoranthene	0.1
Benzo(k)phluoranthene	0.01
Indeno(c,d)pyrene	0.1
Phluoranthene	0.01

90% percentiles of the average contents were calculated for the individual substances from POPs group as "background values". These values were compared with background values of POPs in our agricultural soils (Němeček et al. 1996). The evaluation of PAHs contents was based on the sum of toxic equivalent factors (TEF). TEF values of PAHs add the multiples of the concentrations and toxic equivalents of individual substances with increased cancer risk (Table 3). The standard principle of the international toxic equivalent factor (I-TEQ) was used for the evaluation of PCDD/F contents (Podlešáková et al. 2000). The comparison of congener analysis of PCDD/F between individual sludge samples was done.

RESULTS AND DISCUSSION

The values on POPs contents except PCDD/F are demonstrated in Table 4. The highest average and maximum values from the monocyclic aromatic hydrocarbons (MAHs) were detected in the case of toluene. The 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.

Fluoranthene reached the highest average concentrations among PAHs. This finding corresponds with the fact that fluoranthene concentrations in the environment belong to the highest between 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 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 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 the outlying values. These background values are compared with background values of POPs in agricultural soils (Němeček et al. 1996) in Table 5. 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 the 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 the proposed limit of EU directive (6 mg/kg) was observed. No limit value regarding PAHs is included in Czech directive No. 382/2001. The evaluation of PAHs on the base of TEF values shows good coincidence of TEF of PAHs and the sum of PAHs in sewage sludge (Figure 1). It could be emphasized that the increased contents of PAHs in sludge brings increased risk regarding human health on the base of TEF evaluation (SZÚ 2002). A decrease of PAHs content in sewage sludge could be the only recommended way for the harmonisation with EU legislative norms in the future. The most problematic area is the Nord-Moravian region in the Czech Republic (Figure 1). An increased load in the environment by PAHs in the Nord-Moravian region was demonstrated by the increased content of PAHs in the soils (Podlešáková et al. 1997) for example.

On the basis of comparison of background values of POPs in sewage sludge and soil (Table 5) emerged the 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 the soil. The contents of PCBs in the sludge are cca 10-fold higher in sludge, compared to soil while the contents of DDT (including

Table 4. Basic statistical characteristics of the POPs in sewage sludge samples

		PAHs (μg/kg)													MAHs (μg/kg)					ChlHs (μg/kg)					PHs (mg/kg)
		A	N	P	Ch	Ph	Fl	B(a)P	B(b)F	B(k)F	B(a)A	B(ghi)P	I(cd)P	ΣPAHs	B	T	X	Eb	ΣMAHs	PCB	HCB	DDT	DDD	DDE	
2002 (20 samples)	AM	164	47	1 442	616	1 131	2 499	709	906	409	595	508	398	9 930	37.9	3 815	39.8	12.5	3 950	110	6.96	3.72	6.11	17.2	5 845
	GM	122	26	1 219	527	940	2 131	634	810	368	517	453	355	8 488	27.6	1 431	13.5	7.30	1 680	98.0	5.54	3.13	4.94	13.8	5 303
	std	120	43	814	363	704	1 511	333	435	187	368	255	190	5 964	33.8	4 316	47.8	10.6	4 366	49.0	4.00	1.97	3.38	9.24	2 310
	max	484	140	3 330	1 490	2 880	6 860	1 440	1 930	806	1 900	1 210	762	26 434	120	16 400	170	40.0	16 820	201	15.4	7.85	11.5	36.3	8 800
	min	16	2	363	189	240	596	206	334	141	193	161	156	2 631	12.0	70.00	0.10	0.10	111	33.0	1.00	1.00	1.00	1.00	2 300
	med	160	30	1 250	552	947	2 115	635	798	370	560	413	333	8 516	20.5	2 900	26.0	8.00	2 974	103	6.70	3.51	6.18	15.5	6 450
2001 (25 samples)	AM	252	45	1 096	692	1 479	904	316	329	173	504	216	165	5 912	14.8	498.8	36.5	28.2	608	122	9.13	16.9	4.24	21.5	11 309
	GM	173	11	852	535	1 067	709	241	250	133	392	163	123	4 646	3.80	163.1	2.60	6.00	288	98.0	5.44	12.4	2.98	15.9	7 848
	std	188	55	474	333	977	427	156	166	85	223	118	73	2 571	13.8	553.0	59.0	27.3	614	75.0	7.13	12.6	3.74	12.4	6 987
	max	791	203	1 870	1 570	3 910	1 710	596	732	368	927	506	305	9 714	44.1	2 040	192	82.1	2 324	358	20.1	45.0	16.6	45.8	29 000
	min	3	1	14	11	17	18	7	6	4	10	3	1	95	0.10	0.100	0.10	0.10	0	7.00	1.00	1.00	1.00	1.00	20.00
	med	199	23	1 115	676	1 230	889	319	322	176	497	201	172	6 170	11.1	350.0	5.70	20.2	360	104	8.23	11.4	3.24	20.8	9 100
Sum (45 samples)	AM	201	50	1 159	685	1 330	1 405	540	617	294	508	352	283	6 566	22.4	2 209	38.0	16.5	2 293	110	8.17	8.00	5.13	20.3	6 827
	GM	143	17	949	547	1 010	1 088	400	438	217	425	264	205	5 497	8.30	522.4	5.30	5.40	739	95.0	5.49	5.62	3.79	15.3	6 219
	std	144	55	536	383	887	815	364	454	200	205	229	192	2 632	22.8	2 998	54.4	16.1	2 998	52.0	6.05	6.54	3.69	12.2	2 631
	max	548	207	2 550	1 750	3 910	3 630	1 440	1 930	806	927	940	762	11 218	120	10 200	192	59.8	10 355	234	20.1	25.4	16.6	51.8	13 000
	min	3	1	14	11	17	18	7	6	4	10	3	1	95	0.10	0.100	0.10	0.10	0	7.00	1.00	1.00	1.00	1.00	2 200
	med	164	30	1 170	632	1 070	1 220	467	455	240	518	311	213	6 525	17.0	617.0	13.0	9.50	675	103	7.53	6.24	4.13	19.8	7 000

AM – average, GM – geometric mean, std – standard deviation, max – maximum, min – minimum, med – median

PAHs – polycyclic aromatic hydrocarbons, MAHs – monocyclic aromatic hydrocarbons, ClHs – chlorinated hydrocarbons, PHs – petroleum hydrocarbons, A – anthracene, N – naphthalene, P – pyrene, Ch – chrysene, Ph – phenanthrene, Fl – phluoranthene, B(a)P – benzo(a)pyrene, B(b)F – benzo(b)phluoranthene, B(k)F – benzo(k)phluoranthene, B(a)A – benzo(a)anthracene, B(ghi)P – benzo(ghi)perylene, I(cd)P – indeno(c,d)pyrene, B – benzene, T – toluene, X – xylene, Eb – ethylbenzene

Table 5. The comparison of background values of POPs in soils and sludge (µg/kg)

	PAHs												MAHs				ChlHs					PHs (mg/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	B	T	X	Eb	PCB	HCB	DDT	DDE	DDD	
Soil	300	200	150	100	100	50	100	100	50	50	100	50	30	30	30	40	20	20	15	10	10	100
Sludge	2 412	1 626	2 407	1316	759	433	949	535	572	686	1 148	132	50	7 300	150	37	183	18	20	36	10	9 440
Sludge/soil (%)*	804	813	1605	1316	759	866	949	535	1144	1372	1 148	264	167	24 333	500	92	917	89	130	361	98	9 440

*background value represents 90% percentile of POP contents in the set of sewage sludge samples

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 statistical procedure. The resulting average I-TEQ PCDD/F is 22.5 ng/kg in the set of sludge samples. For the 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 basis of congener analysis of PCDD/F indicates regional differences (with the dominance of octo-chlorinated dibenzodioxins in sludge), which are dependent on the wastewater load from the different sources very probably (the rate of communal and industrial wastewater of different type). This data is 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 in the set of sludge samples seems to be complicated considering the regional differences. Congener patterns of the individual sludge samples could be used for the localisation of sources of wastewater contamination by PCDD/F (Holoubek et al. 2002).

On the basis of monitoring the POPs in the collection of 45 sludge samples it was concluded, that the load of sewage sludge corresponds with the references and fulfils the limits of Czech and European legislative norms in most cases. Only PAHs concentrations overcame proposed limit value of EU directive in many sludge samples and the decreasing of PAHs in sewage sludge is not rapid sufficiently in our conditions. While average concentrations of PAHs fluctuated from 29–125 mg/kg in German sewage sludge in the beginning of the ninetieth (Starke et al. 1991), the contents of the sum of PAHs were decreased to the limit value 6 mg/kg in current European directive. The other observed parameters (PCBs, PCDD/F) in the set of sludge samples fulfil limits of European directive. The content of petroleum hydrocarbons (PHs) in sewage sludge is not limited in the used legislative norms considering difficulties in the evaluation of their contents. The contents of PHs in our set of sludge samples do not correspond with the references of Webber and Singh (2001) for Canadian sewage sludge where the contents fluctuated only from 2 to 10 mg/kg. For all that the contents of PHs will be observed during the project.

Further activities of the project are focused on the influence of the application of sewage sludge with increased POPs contents into soil on the load of soil and plants by POPs with the dependence on soil type and soil use. This project will be finished in the last decade of 2004.

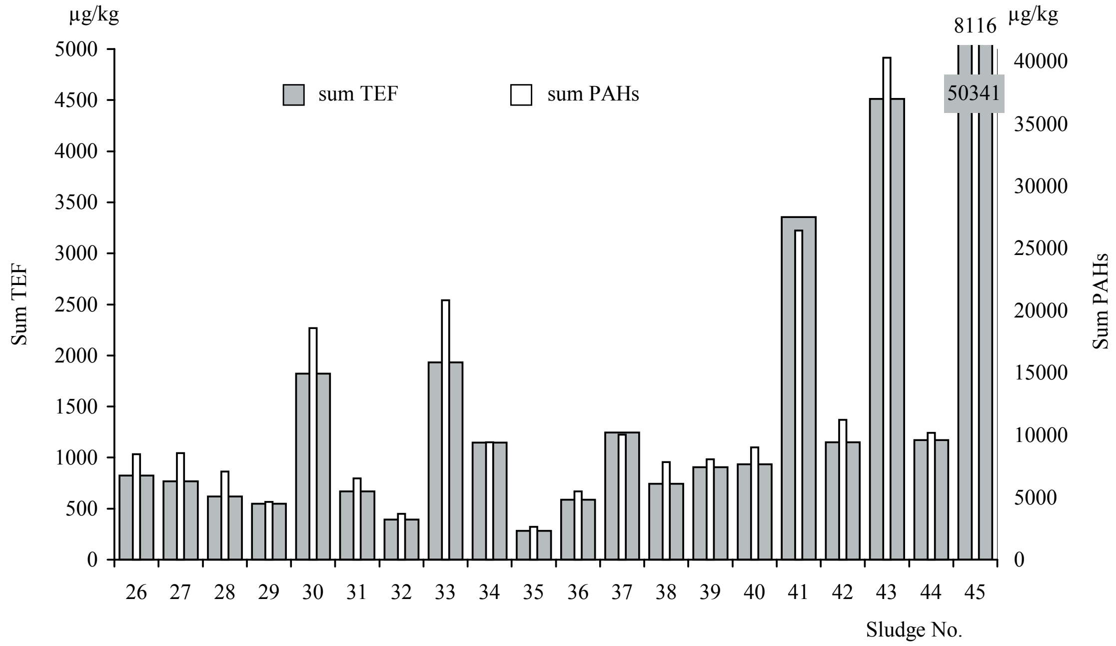

Figure 1. The comparison of sum TEF and sum PAHs in sludge samples collected in 2002

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ABSTRAKT

Aplikace kalů ČOV do zemědělských půd a problematika perzistentních organických polutantů

Byl odebrán soubor 45 vzorků kalů z čistíren odpadních vod. Jejich výběr byl realizován v závislosti na velikosti spádové oblasti a zastoupení odpadních vod z průmyslu. Ve vzorcích byly stanoveny obsahy perzistentních organických polutantů (POP). V 16 vzorcích byly dále sledovány obsahy dibenzo-p-dioxinů a dibenzofuranů (PCDD/F). Vyhodnocení přineslo informace o zátěži našich kalů POP. Výsledky byly porovnány s vyhláškou MŽP ČR 382/2001 a návrhem legislativy EU, aktualizovanou směrnicí 86/278. Většina sledovaných parametrů splňuje uvedené normy, pouze obsahy sumy polyaromatických uhlovodíků (PAU) překročily navržený limit směrnice EU.

Klíčová slova: kaly z čistíren odpadních vod; perzistentní organické polutanty; polyaromatické uhlovodíky; dibenzo-p-dioxiny a dibenzofurany

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