POSSIBILITY OF RELEASE OF PCDDS AND PCDFS FROM SEWAGE SLUDGE IN THE PRESENCE OF SLS

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Abstract
The possibility of co-leaching of dioxin and furan congeners from sewage sludge in the presence of sodium lauryl sulphate (SLS) was studied. Sewage sludge from a municipal wastewater treatment plant (with naturally occurring PCDDs and PCDFs) was used in column experiments and eluted by solutions of different SLS concentrations. Experiments showed that elution by concentrations as low as 0.1 mg/dm^3 was hardly detectable. SLS solutions at concentrations considerably higher than usually found in natural waters (1mg/dm^3 and 1 g/dm^3) did, however, result in leaching of PCDD/Fs from sludge. Such concentrations might be expected in wastewaters and/or sludge. Highly chlorinated congeners moved faster in the column experiments than lower chlorinated tetra- and penta- ones, and dioxins faster than furans. Differences between translocation of particular congeners may result from the sorption-desorption mechanism.

Introduction

The decreasing levels of PCDD/Fs in environmental matrixes observed worldwide in recent years have been put down to new technologies of waste incineration, emission control and stricter regulations. But dioxins still enter the environment as unwanted byproducts and the environmental fates of PCDD/Fs are still not clear, because the environment is a complicated system of many natural and anthropogenic compounds interacting with one other.
With the decreasing level of dioxin emission from known sources we observe two new problems. First, the recirculation of dioxins released in the past, and the growing impact of abiotic sinks, such as sewage sludge produced by municipal wastewater treatment plants and waste deposited on landfills. Second, new pollutants spilled into the environment, which undergo unexpected transformations, sometimes to dioxins (e.g. triclosan).
Levels, patterns and possible sources of PCDDs and PCDFs in sewage have been widely studied since 1987, when they were identified for the first time in sludge[1].
Dioxins in sludge from municipal wastewater treatment plants are incorporated into organic matter, mainly to the small particles of biological sludge[2]. No studies of possible leaching of PCDDs and PCDFs from sludge were found in the literature, contrary to the experiments in the soil.
According to Puri and co-workers[3], a combination of TCDD with waste oil can account for the enhanced translocation of TCDD and related compounds in soils. This may be confirmed by the fact that soils contaminated with wood preserving oil exhibit a significant translocation of PCDD/Fs into the lower horizons, but in the absence of this oil, the mobility of PCDD/Fs in the aqueous phase is low[4].
Similar results were presented by Schramm and co-workers[5] for fire-extinguishing waters. Leaching experiments from fly ash with fire-extinguishing water resulted in significant amounts of PCDD/Fs in the related leachates. The co-solvents present in the fire-extinguishing water enhance PCDD/Fs solubility and the PCDD/Fs concentrations in the leachate.
Hence, substances in which dioxins dissolve better than in water, e.g. alcohols, ethers, and surfactants, might significantly change the dioxins properties and influence their transportation.
Similar behavior might be expected for sludge. Horstmann and McLachlan[6] noticed that effluents from washing machines are important sources of PCDD/Fs in domestic sewage due to the increasing solubility of dioxins adsorbed on cloths in the presence of detergents (surfactants).
Nowadays modern wastewater treatment plants collect influents containing more and more substances of different properties. Surfactants are said to be responsible for problems during wastewater treatment and in water reservoirs, but up to now there was no evidence about their influence on the possible leaching of PCDDs and PCDFs from sludge, and increasing concentration of dioxins and furans in the effluents. Therefore in this work,

an attempt to examine such a possibility in the presence of sodium dodecyl sulphate (*sodium lauryl sulfate* - SLS) was undertaken.
Sodium dodecyl sulfate (*sodium lauryl sulfate* - SLS) is an anionic surfactant, commonly used in detergent powders, deodorants, toothpastes, and other domestic products. The major part of the SLS degrades in the biological step of the municipal wastewater treatment plant, but about 0.1 – 0.5 mg/dm^3 might be found in the effluents.

Material and methods
Digested sludge from a mechanical-biological municipal wastewater treatment plant (MWTP) was used in the experiments. The initial concentrations of 17 2,3,7,8-substituted PCDDs and PCDFs in the sludge are presented in Table 1. Sludge was mixed with quartz sand in 1:1 w/w ration and 20 g of mixture (dry weight) was placed in glass columns 15 cm high and 2 cm diameter. Columns were eluted by sodium dodecyl sulphate (SLS) solutions of concentration 0.1 mg/dm^3, 1 mg/dm^3 and 1 g/dm^3, respectively. Every column was eluted by 1 dm^3 of solution. Each experiment was performed in triplicate. After the leaching experiments, columns were frozen to -18^{0}C, the glass was broken and sludge samples were examined for 17 congeners. Analytical measurements were performed in the Laboratory of Environmental Analysis of the Institute of Environmental Protection, Lublin University of Technology. Analytical details are described elsewhere[7].
Sludge samples were spiked with mixture of ^{13}C – labeled solution of PCDD/Fs (from CIL) and extracted in a Soxhlet apparatus for 48 hours with toluene. Extracts were concentrated to incipient dryness and transferred to hexane, and then treated by concentrated H_2SO_4, followed by purification via 3-stage (multilayer silica, alumina, carbon/silica) open column chromatography procedure.
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Discussion

Results of PCDD/Fs measurements are presented in Table 1 and Figure 1. As may be seen in Table 1, surfactants may cause leaching of PCDD/Fs from sewage sludge, but elution strongly depends on the surfactant concentration. Experiments showed that elution by such low concentrations as 0.1 mg/dm^3 is practically negligible. Only for solutions of [SLS] >=1 mg/dm^3 could elution be observed.
Decrease of the PCDD/Fs concentration in sludge increased with increased concentration of SLS. For both solutions (1 mg SLS/dm^3 and 1 g SLS/dm^3), highly chlorinated congeners moved faster in the column experiments than lower chlorinated tetra- and penta- ones, and dioxins slightly faster than furans.
About 80% of the examined hexachloro dibenzo-p-dioxins were retained in the sludge after elution with 1 dm^3 of solution containing 1mg SLS/dm^3, while only 71% of hepta- and 68% of octa-congeners were retained, respectively. Elution with 1 g SLS/dm^3 resulted in the retention of 57-62% of hexachloro dibenzo-p-dioxins, and 55% of hepta-congeners and only 48% of OCDD. Furans containing 7 and 8 atoms of chlorine were retained in 63-71% after elution by 1 dm^3 of SLS solution of concentration 1 mg SLS/dm^3 and in 55-60% after elution by [SLS] = 1 g /dm^3, respectively (see Fig. 1.).
As a result, lower chlorinated, but higher toxic congeners, were more persistent in sludge. Higher SLS concentrations, such as 1 g/dm^3 caused more significant leaching of PCDD/Fs from sludge, but such high concentrations are very rare and are not observed under normal environmental conditions.

Table 1. Concentrations of PCDD/Fs congeners (ng/kg s.m.) in the examined sludge after elution by 1 dm^3 of SLS solution .

Lp.	congener	Initial concentration	PCDD/Fs (ng/kg) levels after elution by 1 dm^3 of SLS at concentration:		
			0. 1 mg/dm^3	1 mg/dm^3	1 g/dm^3
1	2,3,7,8-TCDD	1.1	1.0	1.0	< 1.0
2	1,2,3,7,8-PeCDD	4.89	4.5	4.2	3.4
3	1,2,3,4,7,8-HxCDD	6.35	6.2	5.18	3.8
4	1,2,3,6,7,8-HxCDD	234	250	188.8	145
5	1,2,3,7,8,9-HxCDD	35.8	34.4	30.1	21.9
6	1,2,3,4,6,7,8-HpCDD	2388	2321	1690	1321
7	OCDD	12 800	12 680	8 880	6100
	Σ PCDDs	*15 470*	*15 297.1*	*10 719.28*	*7595.1*
8	2,3,7,8-TCDF	5.12	5.2	5.0	< 5.0
9	1,2,3,7,8-PeCDF	5.72	ND	< 5.0	ND
10	2,3,4,7,8-PeCDF	5.24	5.24	5.24	< 5.0
11	1,2,3,4,7,8-HxCDF	6.32	6.32	5.32	ND
12	1,2,3,6,7,8-HxCDF	6.95	6.0	< 5.0	< 5.0
13	1,2,3,7,8,9-HxCDF	ND	ND	ND	ND
14	2,3,4,6,7,8-HxCDF	7.34	6.94	5.34	ND
15	1,2,3,4,6,7,8-HpCDF	96.50	91.50	72.2	59.76
16	1,2,3,4,7,8,9-HpCDF	8.25	8.25	5.86	4.99
17	OCDF	234	234	157	128.7
	ΣPCDFs	*374.44*	*363.37*	*256.59*	*193.45*
	ΣPCDD/Fs	15844.44	15 660.47	10 975.87	7788.55

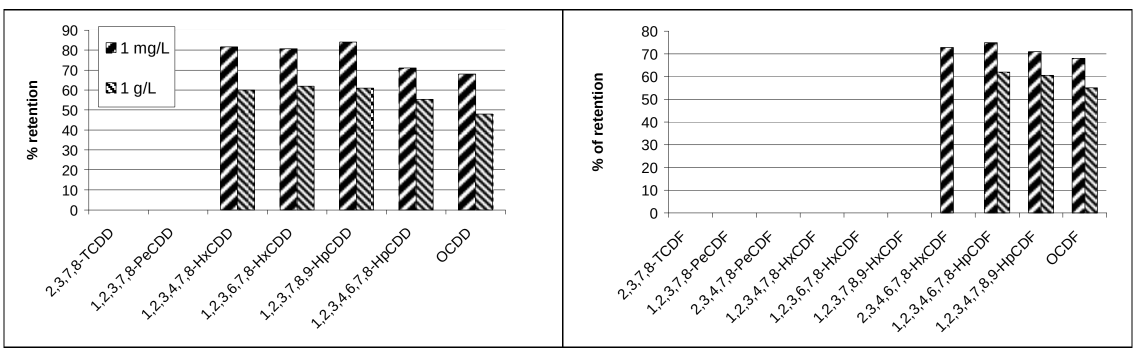

Fig. 1. Retention of PCDD/Fs in sewage sludge after elution of SLS solutions (1 mg/L and 1 g/L).

The experiments showed that even low concentration of such co-pollutants as surfactants may increase the leachability of PCDD/Fs. Leaking of PCDD/Fs from sludge in the presence of surfactants poses a potential danger of increase of PCDD/Fs levels in the effluents from the municipal wastewater treatment plant, as both types of contaminants are present in the wastewater streams.
This migration of PCDD/Fs in columns was caused by sorption-desorption processes as pathways of particular congeners vary – higher chlorinated isomers moved faster. But from the point of view of hazard assessment it should be pointed out that the compounds of lower toxicity migrate faster. In most cases the solubility enhancement of the PCDD/Fs will lead to environmental problems.

Acknowledgements
This research was carried out within the Project **No 1269/T09/2004/27,** financed by the Polish Ministry for Science and Higher Education.

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