

FIRST ATTEMPT TO ESTIMATE THE PCDD/Fs LOADS FROM SEWAGE SLUDGE TO THE SOIL ENVIRONMENT IN POLAND

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Introduction

PCDD/Fs are emitted or spilled from many processes, but as they were found in the emissions from all combustion processes, independently from the fuel, thermal processes are recognized to be a main source, especially processes of waste incineration. But „dioxins problem” is attributed to all human activities, connected either with the production or utilization of solid wastes and wastewaters. The presence of PCDD/Fs as trace impurities in paper, textile and chemical products as well as in petrol incineration products (emissions from the car engines) lead to PCDD/Fs presence in urban run off waters, sewages and sludge.

The growing amount of sludge, generated every year by wastewater treatment plants is one of the crucial environmental problems. From the one side, improved methods of wastewater treatment result in the growing amounts of sludge, from the other, the minimization of waste became a “prime directive” of modern societies. Among the possible methods of the sludge utilization, the interest in agriculture utilization is growing, although a lot of limitations have to be considered, as sewage sludge is the well known abiotic sink for persistent chemicals. Pathways of heavy metals from sludge to the water/soil environment have been studied for years, and strict regulations introduced in many countries. The environmental pathways of stable, hydrophobic chloroorganic pollutants, which may easily accumulate in the food chain, have not been fully recognized, although evidence of enzymatic reactions leading to PCDD/Fs formation during natural composting processes¹ and thermal sludge treatment has been found².

PCDD/F levels in sewages and sludge have been studied in different countries since the 80's, when dioxins were found in emissions from sludge incinerator³. Recently, the contamination of PCDDs and PCDFs in sewage sludge is well documented and analytical results have been reported for the USA⁴, Canada⁵, Switzerland⁶ and EU countries⁷. However, there are no data for a number of European countries, specially accessing EU.

First attempts to measure the PCDD/Fs levels in Polish sludge were made in March –April, 2001 for the samples of digested sludge from Municipal Wastewater Treatment Plant in South-Eastern Poland “Hajdow”⁸. In autumn 2002, the second series of measurements was undertaken at the same MWTP.

Methods and Materials

“Hajdow” is a typical Polish municipal wastewater treatment plant and consists of a primary (mechanical) treatment part and secondary (biological) treatment part. The total treatment procedure lasts about 22 hours. The primary sludge and excess sludge are water reduced separately and go together to the digester. Samples of influent sewages, primary, excess and digested sludges

are collected during dry weather period, in autumn, just before the “campaign time”, what allowed to compare results with the results from the preliminary measurement in Spring 2001. During the “campaign time” for different food processing factories (mainly sugar-beet factory) the loads might differ.

PCDD/Fs levels were measured for inlet sewages, primary, excess and digested sludge. The influent sewages and sludge samples were collected to pre-washed glass containers, with respect to the 22 hours flow. Digested sludge was sampled after 12 days, during one month (one sample per week). Sludge samples were air-dried at 40°C and grounded before extraction. 20 g of dry weight sludge samples were spiked with ¹³C – labeled solution of PCDD/Fs (from CIL) and extracted in Soxhlet apparatus for 18 hours with toluene. The extracts were concentrated to incipient dryness and transferred to hexane, and then treated by concentrated H₂SO₄, followed by purification via a 3-stage (multilayer silica, alumina, carbon/silica) open column chromatography procedure. Finally, the samples were concentrated to incipient dryness prior to the addition of recovery standard. Wastewater samples of 15 dm³ volume were spiked by the ¹³C – labeled solution of PCDD/Fs and extracted with dichloromethane. The further purification procedure was similar like for sludge extracts. Purified samples were analyzed on GCQ Finnigan system GC/MS/MS, equipped with DB5ms column. Gas chromatograph conditions were as follows: helium flow set to 1 ml/min., oven temperature 150°C, 1 min., injector temperature 270°C.

Results and Discussion

The obtained results, based on the average from the 3 samplings, are gathered in Table 1. TEQ calculations were made based on the WHO-TEFs for seventeen 2,3,7,8-substituted PCDDs and PCDFs. “Dioxin like” PCBs were not measured. Municipal Wastewater Treatment Plant collects municipal wastewater discharge by sewage systems from Lublin, a city of 400 thousand inhabitants and Swidnik, a small town of 20 thousand inhabitants, which gives 165 thousand m³ influent/day. This part of Poland is generally agricultural, with relatively small industrial enterprises (food and machine). Industrial streams from Lublin (brewery, beet-sugar factory, pharmacy plant) are discharged to the municipal sewage system after primary on-site pretreatment. Increasingly intensive car traffic from the West to the Ukrainian and Belarusian borders have been passing through Lublin in the last few years, but street run-offs are collected by a separate system and discharged directly to the surface waters.

The congeners present in the influents and primary sludge suggest the household wastewaters as the main source of dioxins in the sludge (domination of hepta- and octa-CDDs, and the increase of concentration with the increasing degree of chlorination). But also tetra-congeners, including tetra-furans have an impact for the total TEQ. This may express the influence of atmospheric deposition within the wastewater treatment plant.

Congener profiles for influent sewages and primary sludge show similarity, as most of PCDD/Fs in wastewaters are attached to suspended solids. This should lead to the highest concentration of PCDD/Fs in primary sludge, which was reported previously⁹. In our measurements, the primary sludge displays the lowest concentrations - 12.16 ng WHO-TEQ/kg d.m. and digested sludge the highest concentration 53.50 ng WHO-TEQ/kg d.m. (in respect to the TEQ values). Considering the sum of PCDD/Fs, specially PCDDs, the levels in the excess and digested sludge are very similar. High TEQ-WHO values are due to the higher concentrations of lower chlorinated congeners in the digester sludge and higher concentration of furans.

Table 1: Results for Influent (ng/m³) and Sewage Sludge (ng/ kg d.m.).

No	Conger	Influent ng /m ³	Primary sludge	Excess sludge	Digested sludge
1	2,3,7,8-TCDD	ND	0.7	0.89	1.3
2	1,2,3,7,8-PeCDD	ND	2.11	4.48	2.1
3	1,2,3,4,7,8-HxCDD	1.0	-	1.3	4.5
4	1,2,3,6,7,8-HxCDD	5.2	1.17	14.5	68
5	1,2,3,7,8,9-HxCDD	2.1	11.3	39.4	24
6	1,2,3,4,6,7,8-HpCDD	38	28	1679	1900
7	OCDD	320	236	9630	9 200
	Σ PCDDs	366	279	11370	11199
	WHO-TEQ PCDDs	<i>1.24</i>	<i>4.36</i>	<i>28.64</i>	<i>32.97</i>
8	2,3,7,8-TCDF	1.6	6.13	6.13	18
9	1,2,3,7,8-PeCDF	ND	7.44	6.3	6.95
10	2,3,4,7,8-PeCDF	ND	-	-	9.66
11	1,2,3,4,7,8-HxCDF	0.5	26.88	24.1	8.5
12	1,2,3,6,7,8-HxCDF	1.6	34.12	48.5	11
13	1,2,3,7,8,9-HxCDF	ND	-	-	ND
14	2,3,4,6,7,8-HxCDF	1.4	-	16.2	12
15	1,2,3,4,6,7,8-HpCDF	11	71.3	148.3	210
16	1,2,3,4,7,8,9-HpCDF	1.0	-	-	9.87
17	OCDF	15	102	436	780
	Σ PCDFs	32.1	248	686	1066
	WHO-TEQ PCDFs	<i>0.63</i>	<i>7.80</i>	<i>11.33</i>	<i>20.53</i>
	Σ PCDD/Fs	398	527	12055	12266
	PCDD/Fs WHO-TEQ	2.08	12.16	39.97	53.50

Congener profiles for digested and primary and secondary sludge show differences, so a generation or transformation of PCDD/Fs during digestion process may occur.

Conclusions

In our previous attempt in the year 2001, only levels in the digested sludge were measured⁸. Comparing data for 2001 and 2002 measurements, very similar loads in the digested sludge were found. Having in mind 165 thousand m³ daily flow through the examined plant, the obtained results may respond to 18 g Σ PCDD/Fs in the influent /a (0.12 g WHO-TEQ, considering only PCDD/Fs contribution) of the examined MWTP. Most of this load is retained in the sludge. The amount which may be emitted to the atmosphere during aeration processes was not measured or estimated.

In the year 2000, more than 360 thousand tons of dry matter sludge was produced by Polish municipal wastewater treatment plants¹⁰. Assuming roughly, that the obtained results may be taken as Polish average, it may mean that in the year 2000 about 18.0 to 24 g WHO-TEQ was concentrated in the sewage sludge in Poland. From the total amount of 360 thousand tons only 15% of the sludge was utilized in agriculture (directly or used in compost production)¹⁰. It does

not mean "high" annual load of PCDD/Fs to the soil from that source, which may give 2.8-3.5 g TEQ/a. The new Polish Waste Act (issued May 2001) strictly regulates sludge application. The disposal of sludge to the land used for vegetable cultivation as well as to pastures and meadows is prohibited, which minimizes the possibility for persistent chemicals to enter the food chain.

But the growing amount of sludge will force agricultural utilization. And a potential risk from utilization in land remediation as well as from deposition on landfills should be taken into consideration, so more measurements are needed to estimate real loads¹¹.

Because PCDD/Fs became to be recognized as the most hazardous for the environment and human beings, very restricted limits in the emission were introduced in most countries. But only in a few countries, PCDD/Fs levels in sewage sludge are regulated⁷, although sludge is one of the ultimate sinks for persistent chemicals.

With regard to the aspects of the minimization of contaminants and meeting legal requirements limit values in environmentally related matrices, the degradation and formation of PCDDs and PCDFs by microorganisms are of special interest. At present the agricultural application of sewage sludge, which is supposed to be the most important accumulation medium for organochlorine compounds, is under discussion because of the persistence of the PCDD/F compounds in soil. There are still very limited field data on the effect of sludge application on the levels of PCDD/Fs in the food chain¹².

Acknowledgments

This research was carried out within the Project No 3 T09C 00618, financed by Polish State Committee for Scientific Research.

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