

TIME-RELATED TRENDS IN PCDD/F LEVELS IN SEWAGE SLUDGE IN SOUTH-EASTERN POLAND

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Introduction

PCDD/F levels in sewages and sludge have been studied in different countries since 1980s, when dioxins were found in emissions from a sludge incinerator¹. A number of papers have been published^{2,3,4} to determine the main source in the sludge. Recently, the contamination sewage sludge by PCDDs and PCDFs has been well documented, and analytical results have been reported for the USA⁵, Canada⁶ and EU countries⁷. Since the late 1990s decrease in the PCDD/F levels in sludge from different regions has been noted by a number of researchers⁷.

However, data for such countries as Poland, in which no regular monitoring systems for dioxins have been introduced, are very scarce. In fact, the first attempts to measure PCDD/F levels in Polish sludge were made in 2000 (unpublished data). In 2001 results, concerned samples of digested sludge from the "Hajdow" Municipal Wastewater Treatment Plant located in an agriculture area of South-Eastern Poland were published⁸. In autumn 2002, a second series of measurements was made at the same MWTP by the same authors⁹. Total WHO-TEQ PCDD/F values for the samples analyzed in 2001-2002 ranged from 45.38 to 65.26 ng WHO-TEQ/kg dry mass. The variation in the TEQ concentrations was probably attributable to varying loads during the sample-collection period. Irrespective of the sampling, the concentrations of PCDDs were higher than those of PCDFs. A general increase in concentration with increasing degree of chlorination was observed and – in a trend also reported by other researchers^{10,11} for urban sewage sludges, OCDD was the predominant congener. The results for south-eastern Poland showed similarities in patterns and levels to those for sludges from Western Europe, particularly Germany at the beginning of the 1990s.

A paper presenting results for sludges from southern Poland (city of Zabrze) was published in 2005 by Oleszek-Kudlak, *et al.*¹² and lower concentrations were found in digested sludge (16.9 ng I-TEQ/kg d.m., based on 2 measurements). Measurements in southern Poland were made at a municipal wastewater treatment plant situated in an industrial area, albeit in a smaller city with lesser water influents, than at the MWTP examined by Dudzinska and Czerwinski^{8,9}.

In the light of the fact that decreasing concentrations of PCDD/Fs have been noted in many European countries, another series of measurements was made at "Hajdow" MWTP in 2005.

The Municipal Wastewater Treatment Plant

"Hajdow" Municipal Wastewater Treatment Plant collects municipal wastewater discharge via sewer systems of Lublin (city of 400 thousands inhabitants) and Swidnik (a small town of 20 thousands inhabitants) located in South-Eastern Poland. This part of Poland is generally agricultural, with a relatively small number of industrial enterprises (in the food and machinery sectors). The helicopter factory located in Swidnik has its own separate wastewater treatment system. Industrial streams from Lublin (a brewery, a sugar-beet factory, and a pharmaceutical plant) are discharged into the municipal sewage system after primary on-site pretreatment. Intensive car traffic from the West to the Ukrainian and Belarusian borders has been passing through Lublin in recent years, but street run-off has been collected via a separate system and discharged directly into the surface waters. The majority of the region's solid waste is deposited at a municipal landfill, from which leachates are collected, removed periodically and treated along with other wastewater at the "Hajdow" MWTP. Only medical wastes are incinerated at a Hospital Waste Incinerator of the Hoval type, located to the west of the municipal wastewater treatment plant.

The "Hajdow" MWTP is a municipal wastewater treatment plant typical for Poland, consisting of a primary (mechanical) treatment part and a secondary (biological) treatment part. The overall treatment procedure lasts for about 22 hours. The primary sludge and excess sludge are water reduced separately and go together to the digester.

The 2000-2002 samples of digested sludge were collected during a dry-weather period, in spring, prior to the so-called "campaign time" in the sugar-beet factory. Similar sampling was performed in the spring of 2005.

Methods and Materials

Samples of digested sludge, collected to pre-washed glass containers, were freeze-dried before extraction. The same procedure as in 2000-2002 was used to measure 17 congeners. Sludge samples of 20 g dry weight, were spiked with a mixture of ^{13}C – labeled solution of PCDD/Fs (from CIL) and extracted in Soxhlet apparatus for 18 hours with toluene. Extracts were concentrated to incipient dryness and transferred to hexane, before being treated with concentrated H_2SO_4 , and then purified via a 3-stage (multilayer silica, alumina, carbon/silica) open-column chromatography procedure. Finally, samples were concentrated to incipient dryness prior to the addition of recovery standard. Purified extracts were analyzed on GCQ Finnigan GC/MS/MS system, equipped with two capillary columns: CPSil-8CB (or DB-5ms) and CPSil-88 for dioxins. The exact gas chromatography conditions were as given previously^{8,9}.

Results and Discussion

The results of measurements performed in spring 2000, 2001, 2002 and 2005 are gathered in Table 1.

Table 1. PCDD/F concentrations (ng/kg dry matter) in sludge samples.

Congener	S –2000	S - 2001	S - 2002	S -2005
2,3,7,8-TCDD	0.9	1.1	1.3	1.7
1,2,3,7,8-PeCDD	4.9	4.89	2.1	4.1
1,2,3,4,7,8-HxCDD	5.2	6.35	4.5	27
1,2,3,6,7,8-HxCDD	108	234	68	54
1,2,3,7,8,9-HxCDD	53.1	35.8	24	7.2
1,2,3,4,6,7,8-HpCDD	2182	2388	1900	1540
OCDD	12100	12 800	9 200	15400
Σ PCDDs	12554.1	15 470	11199.9	17034
<i>WHO-TEQ PCDDs</i>	<i>45.46</i>	<i>58.76</i>	<i>32.97</i>	<i>31.56</i>
2,3,7,8-TCDF	5.18	5.12	18	11.4
1,2,3,7,8-PeCDF	2.8	4.72	6.95	4.1
2,3,4,7,8-PeCDF	3.9	5.24	9.66	11.2
1,2,3,4,7,8-HxCDF	7.9	6.32	8.5	9.4
1,2,3,6,7,8-HxCDF	5.75	6.95	11	14.6
1,2,3,7,8,9-HxCDF	0.6	ND	ND	2.7
2,3,4,6,7,8-HxCDF	8.3	7.34	12	9.4
1,2,3,4,6,7,8-HpCDF	66.50	96.50	210	178
1,2,3,4,7,8,9-HpCDF	5.65	8.25	9.87	16.7
OCDF	280	234	780	611
Σ PCDFs	386.58	374.44	1065.98	859.4
<i>WHO-TEQ PCDFs</i>	<i>6.50</i>	<i>6.50</i>	<i>12.41</i>	<i>13.14</i>
Σ PCDD/Fs	12940.68	15844.44	12265.88	17893.4
PCDD/Fs WHO-TEQ	51.96	65.26	45.38	44.70

ND – not detected

TEQ calculations were made on the basis of WHO-TEFs for seventeen 2,3,7,8-substituted PCDDs and PCDFs. Congeners below the detection limit were omitted from the calculation. Total WHO-TEQ PCDD/F values for the analyzed samples ranged from 44.70 to 65.26 ng/kg dry mass. The concentrations of 2,3,7,8-substituted congeners are shown in Figure 1 (logarithmic scale).

The results obtained in 2005 were similar to those measured in 2001 and 2002. Both congener pattern or total concentrations and TEQ values were at the same level. The concentrations of PCDDs were higher than those of PCDFs. A general increase in concentration with increasing degree of chlorination was observed. Sludges were dominated by hepta- and octa- CDDs, probably as a result of the loads from household wastewater. However, tetra-congeners, including tetra-furans also had impact on the total TEQ. This may express the influence of atmospheric deposition within the wastewater collection area.

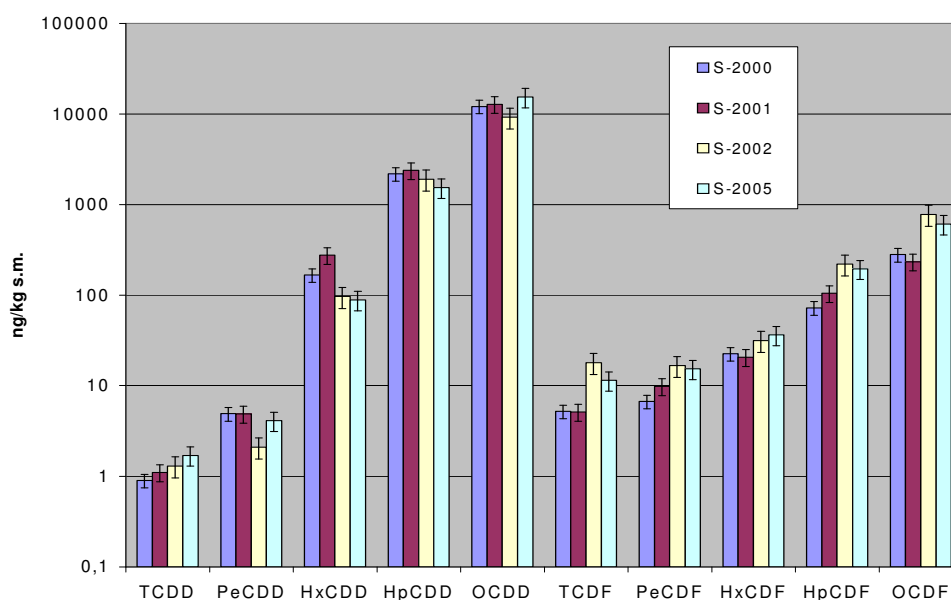


Fig.1. Concentrations of 2,3,7,8-substituted PCDDs and PCDFs in the examined sludge samples.

No particular decrease in concentrations was observable when the 2005 data were compared with those from previous measurements, despite a decrease in the concentration of hexachlorodioxins. The other observed change is the slight decrease in the TEQ values coming from dioxins and an increase in the toxicity coming due to furans. This effect was caused by an increase in the concentration of lower chlorinated furans as compare with the years 2000-2001.

The above phenomena might probably be explained by reference to declining levels of chlorinated compounds in wastewaters and solid wastes (leachates from the municipal landfill are treated together with municipal sewages at MWTP), as well as increasing levels of furans in the ambient air. The Hospital Incineration Plant in Lublin works 7 days a week, cf. 2-3 days in the years 2000-2001.

In all the samples, the total TEQ concentrations were below the values proposed as limits for agricultural utilization, though no significant decrease has been observed in the Lublin area within the last 5 years.

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