PCDD/F LEVELS IN SEWAGE SLUDGE FROM MWTP IN SOUTH-EASTERN POLAND

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Introduction

Environment is a dynamic system and toxic chemicals released into one phase of the environment invariably migrate into the others. Polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs), in contrast to other chlorinated chemicals, have never been commercially manufactured or are of any benefit or known use. They enter the environment as unintentional trace impurities and background levels of PCDD/Fs have been reported in a series of abiotic reservoirs. PCDD/Fs are emitted or spilled from many processes, but as they were found in the emissions from all combustion processes, independly from the fuel, thermal processes are recognized to be a main source, specially processes of waste incineration. But „dioxins problem" is attributed to all human activities, connected either with production or utilization of solid wastes and wastewaters. 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 industrial wastewaters.

PCDD/F levels in sewages and sludge have been studied in different countries since 80ties, when dioxins were found in emissions from sludge incinerator[1]. A number of papers have been published[2,3,4] to determine the main source in the sludge. Generally atmospheric deposition (thermal sources) and domestic sewages (laundry) have been accused of generation the main load of PCDD/Fs into the sludge.

Recently, the contamination of PCDDs and PCDFs in sewage sludge is well documented and analytical results have been reported for USA[5], Canada[6] and UE countries[7]. However, there are no data for a number of European countries, specially accessing UE, and Poland is one of them. So far, in Poland only levels in emissions from selected incineration processes and levels in food samples have been measured[8]. There is a crucial need to estimate PCDD/Fs loads from sources in Poland, including sewage sludge utilization.

Municipal Wastewater Treatment Plant

"Hajdow" Municipal Wastewater Treatment Plant collects municipal wastewater discharge by sewage systems from Lublin, city of 400 thousands inhabitants and Swidnik, small town of 20 thousands inhabitants in South–Eastern Poland. This part of Poland is generally agriculture, with relatively small industrial enterprises (food and machine). Helicopter factory located in Swidnik has separate wastewater treatment system. Industrial streams from Lublin (brewery, beet-sugar factory, pharmacy plant) are discharged to municipal sewage system after primary on-site pretreatment. Intensive car traffic from the West to Ukrainian and Belarusian borders have been passing through Lublin last years, but street run-offs are collected by separate system and discharged directly to the surface waters.

"Hajdow" MWTP is a typical Polish municipal wastewater treatment plant and consists of primary (mechanical) treatment part and secondary (biological) treatment part. Total treatment procedure lasts

about 22 hours. The primary sludge and excess sludge are water reduced separately and go together to the digester.

Methods and Materials

Samples of digested sludge, collected to pre-washed glass containers, were air-dried at 40 °C and grounded before extraction. 5 g dry weight sludge samples were spiked with mixture of ^{13}C – labeled solution of PCDD/Fs (from CIL) and extracted in 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. Finally, samples were concentrated to incipient dryness prior to the addition of recovery standard. Purified extracts were analyzed on GCQ Finnigan system GC/MS/MS, equipped with two capillary columns: CPSil-8CB and CPSil-88 for dioxins. Gas chromatograph conditions were as follows: helium flow set to 1 ml/min., column temperature from 90 - 270 °C, transfer line temperature adjusted to 260 °C.

Results and Discussion

Samples were colleted in spring 2001 (March and April) during dry weather period. In autumn, which is the "campaign time" for different food processing factories (mainly sugar-beet factory) the loads might differ. Obtained results are gathered in Table 1. TEQ calculations were made based on both - the WHO-TEFs and I-TEFs for seventeenth 2,3,7,8-substituted PCDDs and PCDFs. Congeners below detection limit were omitted in the calculation. "Dioxin like" PCBs were not measured. Total WHO-TEQ PCDD/F values for the analyzed samples range from 45.38 to 65.26 ng/kg dry mass. Calculations, based on I-TEFs were also made, to allowed comparison with the literature data. The variation in the TEQ concentration may be attributed to varying loads during the sample collection period. Despite of the sampling, the concentrations of PCDDs were higher than those of PCDFs. A general increase of concentration with the increasing degree of chlorination was observed and OCDD was the predominant congener, which is the trend reported by other researchers [9, 10, 11] for urban sewage sludges.

Sludge was dominated by hepta- and octa- CDDs, what was probably caused by the loads from household wastewater. But also tetra-congeners, including tetra-furans have impact for the total TEQ. This may express the influence of atmospheric deposition within the wastewater treatment plant. At this stage of research and lack of archival samples, it was impossible to compare recent levels with historical ones, so any comments about decreasing or increasing concentrations are not justified.

Conclusions

We had no possibility to compare the obtained results to concentrations in sludge from the others MWTP in Poland. Because of development of the new municipal sewage treatment plants and improving efficiency of the existing ones, it is very difficult to get recent data about annual production of sewage sludge. But in the year 2000, about 1243 million m^3 of sewage was treated in Poland[12], what gives 255 thousands tons dry matter sludge per year, assuming sludge unit index equal 0.217 kg d.m. /m^3 (Polish average[13]). Sewage sludge has been used for agricultural purposes in very limited amounts in Poland. 52 % of sludge is disposed on landfills, 33 % used in land leveling and remediation of post-industrial degraded area. Only 3-5 % of total sludge production is used in agriculture[13]. Assuming roughly, that obtained results may be taken as Polish average, it does not mean "high" annual load of PCDD/Fs to the soil from that source. But to estimate real loads, more measurements are needed. Specially, that growing amount of sludge will force agricultural utilization. And potential risk from utilization in land remediation as well as from deposition on landfills should be taken into consideration.

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

Congener	**S - IV/01**	**S-2-IV/01**	**S - III/01**
2,3,7,8-TCDD	1.1	ND	1.3
1,2,3,7,8-PeCDD	4.89	5.62	2.1
1,2,3,4,7,8-HxCDD	6.35	6.38	4.5
1,2,3,6,7,8-HxCDD	234	119	68
1,2,3,7,8,9-HxCDD	35.8	32.6	24
1,2,3,4,6,7,8-HpCDD	2388	2838	1900
OCDD	12800	14700	9200
WHO-TEQ PCDDs	*58.77*	*51.27*	*32.97*
I-TEQ PCDDs	67.854	61.64	40.20
2,3,7,8-TCDF	5.12	4.17	18
1,2,3,7,8-PeCDF	4.72	3.72	6.95
2,3,4,7,8-PeCDF	5.24	4.94	9.66
1,2,3,4,7,8-HxCDF	6.32	6.32	8.5
1,2,3,6,7,8-HxCDF	6.95	5.75	11
1,2,3,7,8,9-HxCDF	ND	ND	ND
2,3,4,6,7,8-HxCDF	7.34	8.34	12
1,2,3,4,6,7,8-HpCDF	96.50	56.5	210
1,2,3,4,7,8,9-HpCDF	8.25	6.25	9.87
OCDF	234	185	780
WHO-TEQ PCDFs	*6.50*	*5.76*	*12.41*
I-TEQ PCDFs	6.71	5.93	13.11
PCDD/Fs WHO-TEQ	**65.27**	**57.03**	**45.38**
PCDD/Fs I-TEQ	**74.56**	**67.57**	**53.31**

ND – not detected

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, what minimizes the possibility for persistent chemicals to enter the food chain.

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 the most countries. But only in a few countries limits are also pursuit for PCDD/F levels in sewage sludge, although sludge is one of the ultimate sinks for persistent chemicals.

Although decreasing dioxin levels in sludge has been reported in several European countries since 80-90ties[11, 14, 15], the need to monitor PCDD/Fs loads from this source remains. And we can expect the growing amounts of sludge production after introducing the Directive COM 91/271 on wastewater treatment, requires the installation of treatment systems in all towns with over two thousands inhabitants before year 2005.

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References

1. Clement R.E., Tosine H.M., Osborne J., Ozvacic V., Wong G. and Thorndyke S. (1987) Chemosphere 16, 1895.
2. Gihr R., Klopffer W., Rippen G. and Partscht I. (1991) Chemosphere, 23, 1653.
3. Horstmann M., Kaune A., McLachlan M.S., Reissinger M. and Hutzinger O. (1992) Chemosphere, 25, 1463.
4. Horstmann M. and McLachlan M.S. (1995) Chemosphere 31, 2887.
5. Telliard W.A., McCarty H.B., King J.R. and Hoffman J.B. (1990) Organohalogen Compounds 2, 307.
6. Ho A.K. and Clement R.E. (1990) Chemosphere 20, 1549.
7. European Dioxin Inventory, (1999), Report for European Commission, DG XI.
8. Grochowalski A., Chrzaszcz R. (2000) Organohalogen Compounds 47, 310.
9. Hagenmaier H. and Linding C. (1994) Chemosphere 29, 2163.
10. Rappe C. (1993) Chemosphere, 27, 211.
11. Eljarrat E., Caixach J., Riviera J. (1999) Environ. Sci. Technol., 33, 2493.
12. Statistical Yearbook of the Republic of Poland (2001).
13. Bernacka J., Pawlowska L. (1998) Sewage Sludge Management in Poland (*in Polish*), ISBN 83-908960-1-X.
14. Sewart A., Harrad S.J., McLachlan M.S., McGrath S.P. and Jones K.C. (1995) Chemosphere 30, 51.
15. Rappe C., Anderson R., Karlaganis G. and Bonjour R. (1994) Organohalogen Comp. 20, 79.