Comparison of PCDD/Fs Levels and Profiles in Leachates from \"New\" and \"Old\" Municipal Landfills

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Introduction

PCDD/Fs are emitted or spilled from many processes, but since they have been found in the emissions from waste incineration, this process has been recognized widely as its main source[1]. Recently, because of law regulation and technological progress, emissions from this source have been significantly reduced[2]. Nevertheless, the presence of PCDD/Fs as trace impurities in paper, textile and chemical products as well as in petrol incineration products (emissions from car engines) lead to the contamination of urban run off waters, sewages and wastewaters as well as the contamination of solid wastes. As a result, PCDD/Fs became a problem of all methods of further treatment of wastewaters and solid wastes. It appears that "dioxins problem" is attributed to all human activities, connected either with the production or the utilization of solid wastes and wastewaters.

The reduction of PCDD/Fs levels in the emissions from waste incineration makes other sources more significant. Eduljee et al.[3] calculated the possibility of PCDD/Fs release from all strategies of wastes management and presented data for PCDD/Fs content in municipal wastes, as well as the estimation of possible PCDD/Fs release with landfill gases and leachates.

In some dioxin inventories presented in the literature, the deposition of solid wastes is included as one of the minor sources.

Although the presence of PCDD/Fs in landfill leachates has been confirmed, not many experiments have been undertaken in this area, probably because of a very low solubility of PCDD/Fs in water. Modern, properly designed landfills should secure (seal) all deposited wastes and possible leakings within the damp. Leachates are collected and treated on the site or transported to a wastewater treatment plant, so they should not cause a release of any pollutants into the soil or groundwater. But PCDD/Fs as well as a number of chlorinated compounds, which may act as precursors of dioxins under aerobic or anaerobic conditions have been identified as trace contaminants in municipal wastes. The formation of dioxins during municipal waste deposition has not been studied, contrary to the formation of OCDD from precursors under aerobic conditions during composting of waste[4] or treatment of sewage sludge[5]. Some information about the possible dioxin formation during landfilling might be obtained from the comparison of PCDD/F levels in the leachates from "old – closed" and "new" sites.

Methods and Materials

PCDD/Fs levels were measured in the leachates from two parts of Rokitno landfill. Rokitno site was established as a municipal landfill for the 400 thousand Lublin community in 1994.

Rokitno is a fully equipped and protected modern landfill, situated in a rural area, 14 km to the north-east from Lublin. The total area of 39.19 ha was divided into four independent basins. The first basin (Basin 1) of area 6.03 ha was filled up in 2001, because for seven years municipal wastes were deposited in Rokitno without any segregation. During these years two kinds of transformations were observed. First, a transformation of the deposited wastes, thanks to aerobic and anaerobic biochemical reactions. Second, a transformation of the content of the landfilled wastes, mainly because of life conditions improvement. Now, degasification and reclamation of this area is continued. Totally over 817 thousand tons of wastes were deposited in Basin 1.

In 2001 the exploration of the second basin (Basin 2 – area 5.59 ha) started and its capacity is predicted for 7 years of deposition. In 2002 a limited program of waste segregation in some of Lublin quarters was introduced, so municipal wastes deposited in Basin 2 contain less paper, glass and plastics than in Basin 1. Although these fractions have not been totally removed, it is expected that every year the deposited wastes will contain less recyclable materials.

Photo 1: Rokitno Landfill – Basin 2.

Leachate waters from the drainage systems are periodically collected and transported to the municipal wastewater treatment plant in the Lublin city. Prior to transportation, samples for the presented measurements were collected from the drainage system. Two series of sampling were performed - Serie 1 was collected in autumn 2003, while Serie 2 in spring 2004.

Samples were collected to pre-washed glass containers and analyses were carried out immediately after the arrival at the laboratory. 5 L samples were spiked with a mixture of ^{13}C – labeled solution of PCDD/Fs (from CIL) and extracted with 3 of 200mL aliquots of toluene. The extracts were concentrated to incipient dryness and transferred to hexane, and then treated by concentrated H_2SO_4, 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 the recovery standard. Purified samples were analyzed on GCQ Finnigan system GC/MS/MS, equipped with a DB5ms column. The gas chromatograph and mass spectrometer conditions were described previously[6]. Recoveries of analytes were on the level of 67-75% depending on the congener. Examples of chromatogram of Serie 2 are presented on Figure 1 and 2 for leachates from Basin 1 and 2, respectively.

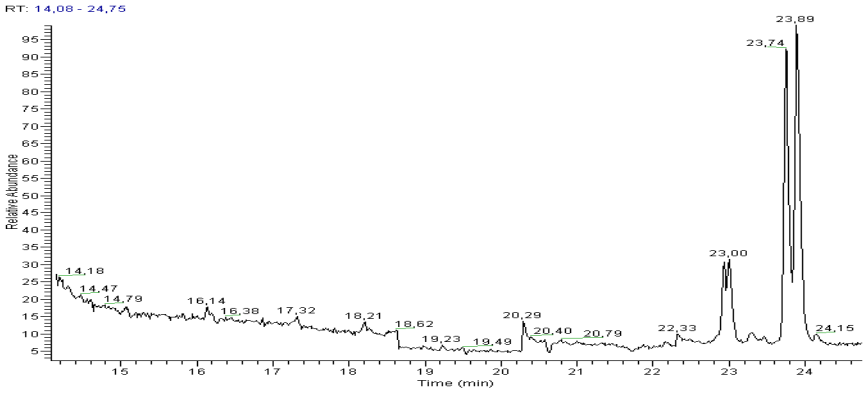

Figure 1: GC/MS (SIM) chromatogram of dioxins and furans in the leachates from Basin 1 ("old landfill").

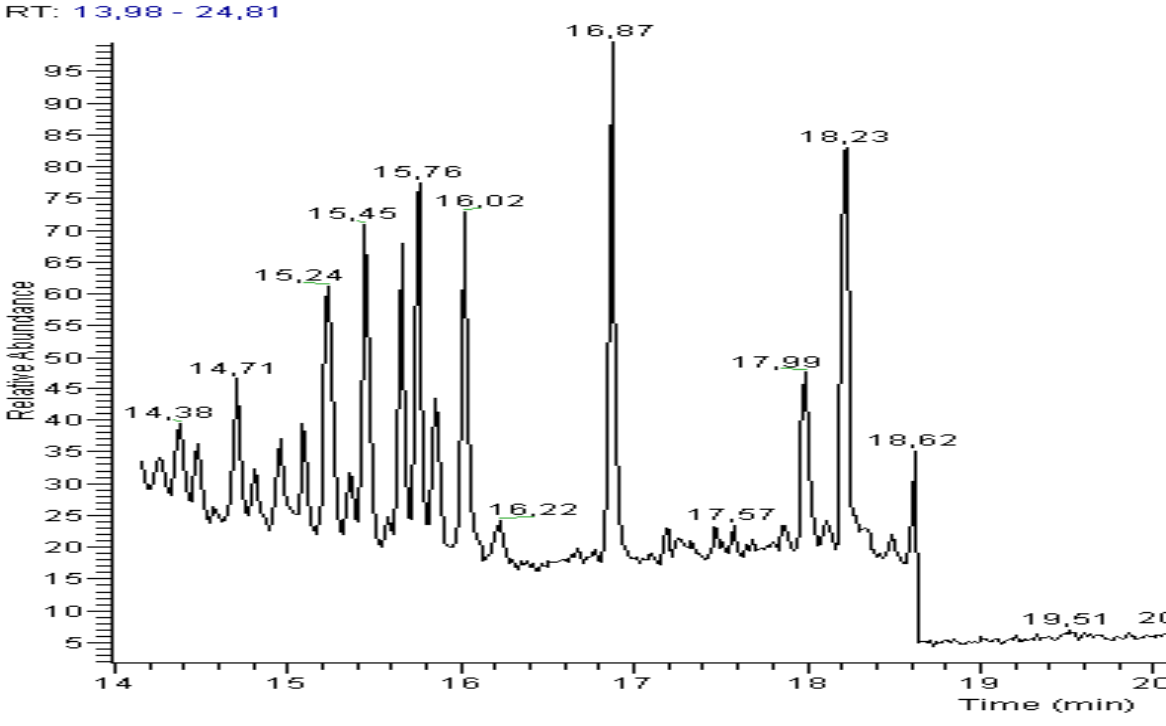

Figure 2: GC/MS (SIM) chromatogram of dioxins and furans in the leachates from Basin 2 ("new landfill").

Results and Discussion

The obtained results, based on the average from the 3 samplings, are gathered in Table 1 and presented in Figure 3. 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. Congeners below the detection limits have not been considered for calculations.

As it might be seen from Table 1 and Figures 1-3, there are differences in the dioxins and furans distribution in the leachates from Basin 1 and Basin 2. Total WHO-TEQ PCDD/F values for the analyzed samples from the "old" Basin 1 were within the similar range of 25 – 36 ng TEQ/L. For the "new" Basin 2, wider discrepancies might be observed – from 7.8 ng/L to 21.74 ng TEQ/L.

Table 1: PCDD/Fs concentrations in the leachates from Rokitno landfill (ng /L)

Congener	Basin 1 Serie 1	Basin 1 Serie 2	Basin 2 Serie 1	Basin 2 Serie 2
2,3,7,8-TCDD	18	7	5.0	-
1,2,3,7,8-PeCDD	nd	nd	nd	-
1,2,3,4,7,8-HxCDD	47	35	5.0	-
1,2,3,6,7,8-HxCDD	nd	nd	7.0	-
1,2,3,7,8,9-HxCDD	nd	nd	nd	-
1,2,3,4,6,7,8-HpCDD	53	43	2.0	-
OCDD	29	17	nd	-
ΣPCDDs	*147*	*102*	*19*	-
WHO-TEQ PCDDs	*23.23*	*10.95*	*6.22*	-
2,3,7,8-TCDF	9	nd	21	7.5
1,2,3,7,8-PeCDF	10	nd	16	23
2,3,4,7,8-PeCDF	7	14	23	11
1,2,3,4,7,8-HxCDF	32	21	11	-
1,2,3,6,7,8-HxCDF	nd	nd	-	-
1,2,3,7,8,9-HxCDF	41	45	-	3.2
2,3,4,6,7,8-HxCDF	nd	nd	-	0.8
1,2,3,4,6,7,8-HpCDF	87	112	-	-
1,2,3,4,7,8,9-HpCDF	nd	nd	2.0	-
OCDF	98	135	-	-
ΣPCDFs	*284*	*327*	*73*	*45.5*
WHO-TEQ PCDFs	*13.17*	*14.73*	*15.52*	*7.8*
ΣPCDD/Fs	**431**	**429**	**92**	**45.5**
PCDD/Fs WHO-TEQ	**36.40**	**25.68**	**21.74**	**7.8**

In the leachates from the closed Basin 1 considerably high concentrations of the higher chlorinated dioxins have been found, while in the leachates from the "new" landfill – Basin 2, dioxins levels were very low, or below detection limits. For all the samples higher loads from furans have been found than from dioxins, with the exclusion of Serie 1 for Basin 1. But for Basin 2 – the levels of lower chlorinated furans were higher. In the closed landfill disturbances between different series of sampling are not very significant. No matching was observed in the leachate samples from the "new" landfill.

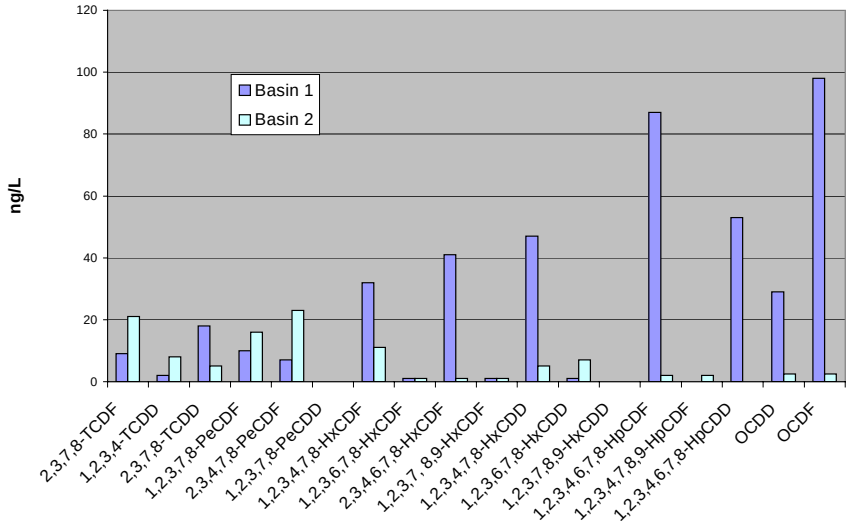

Figure 3: Dioxin and furan congeners distribution in the leachates from Basin 1 and Basin 2 (Serie 1).

Rokitno is located in a rural area, without any known source of PCDD/Fs emission in the nearby surroundings. Lublin city with a Hospital Waste Incinerator, heavy traffic and a local Power Station is situated in a 14-km distance, and thanks to prevailing west winds, no special deposition from these source might be expected directly on the site. Every 2 m high layer of the deposited wastes is covered by the soil-sand intermediate layer, which reduces the influence of "normal" background atmospheric deposition. It might be concluded, that the main source of PCDD/Fs are wastes themselves. High levels of furans, especially lower halogenated are expected to originate indirectly from the atmospheric deposition and thermal sources in the city (via adsorption on waste products). A higher

content of highly halogenated dioxins in the leachates from the closed "old" landfill might be caused rather by the transformation of possible precursors than by any source of dioxins in the chemicals found in textiles, papers and other wastes. Although confirmation of such a statement requires further research.

After years of research, the environmental fate of PCDDs and PCDFs is still not fully understood, because of the complexity of the processes involved in the environmental transformations and path-ways.

Spilling of PCDD/Fs in the landfill leachates might have a long-time effect on the environment if leachates are treated together with municipal sewage. As it was prooved before, the main stream of PCDD/Fs from the sewages goes to the sludge[6,7] and might be introduced again into the environment if sludge is utilized in agriculture.

The presence of lower chlorinated furans in the leachates may also explain considerably high levels of lower chlorinated furans in the wastewater treatment plant influents in the Lublin city, which was reported previously[8]. Lublin has a separate rain waters collecting system and street run-offs are not introduced into the municipal wastewater treatment plant, so furans could not originate directly from this source.

The presented results are preliminary but landfills cannot be omitted in dioxin balances. Old landfills can also be an additional source of PCDD/Fs from the processes under anaerobic conditions, although the interpretation of data is complicated as the composition of wastes varies.

Acknowledgements

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