

Control of PCDDs/PCDFs, PCBs & PAHs emissions in exhaust of landfill gas fed engines

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Introduction

Wallonia in Belgium, like many countries around the world, planned to reduce amounts of waste generated by human activity and stored in landfills. Since they experienced a couple of crisis situations in the past, both with former and presently used landfill sites, authorities launched a demanding landfill monitoring program which covers now 9 out of the 10 major sites.

Biogas produced in these landfills are collected and eliminated in two different ways. Either simply burned in a flare, or, when the methane grade and flow are high enough, the biogas can be burned in electricity producing engines. This later use represents an energy recovery from the waste.

In the context of difficulty for landfill sites to be accepted by the public (the well-known NIMBY phenomenon), the question has been raised whether combustion of the biogas did not entail production of dioxins and other polyaromatic compounds.

For the exhaust gases of engines operated with biogas, a check on the presence of dioxins and associated organic pollutants, composed of three different runs or days of sampling for each of 5 landfill sites was performed upon demand of responsible authorities.

Methods and materials

The temperature at the exit of the flare is around 1200°C. No sampling material can sustain such temperatures. Besides, various (representative) sampling requirements cannot possibly be met for flares. In particular, sampling conditions in isokinetic mode (assuming that the exit speed of the whole exhaust matches a laminar flow model) cannot be done. Anyway, the flame temperature and the conditions of the combustion (large excess of air) are highly unfavourable for any synthesis of PCDDs/PCDFs.

This is why the present study was limited to the exhaust of the electricity producing engines.

Sampling

The sampling was essentially similar to what is usually done on municipal waste incinerators following part 1 of Standard EN-1948 (Filter/condenser method). Since stack diameters were in the 20 to 30 cm range, only one sampling point was used. The sampling probe and the filter were heated. After the filter, the sample flow was cooled down to remove water, prior to pass through an

XAD-2 resin cartridge which is used to trap semi-volatile compounds such as PAHs, PCBs and PCDDs/PCDFs. Thus the PAHs, PCBs and PCDDs/PCDFs were trapped in a three phases sample. Each sampling duration was 6 hours, giving a typical volume of 7 ± 3 cubic meter.

Extraction

Extraction of PAHs, PCBs and PCDDs/PCDFs was done for each of the 3 phases. The glass fibre filter (folded) and the XAD-2 cartridge were set in a Soxhlet vessel. A 24 h toluene-acetone extraction was performed.

Extraction from the condensation water was performed 3 times with 60 ml of dichloromethane.

After extraction (filter, XAD-2 cartridge and water), the 3 organic fractions were merged in a single sample. Three parts were made out of this resulting extract : one for PCDDs/PCDFs and PCBs, the second one for PAHs, while a third one was kept for possible later checks.

Clean-up, concentration and analysis: PCDDs/PCDFs and PCBs

An automated Power-Prep[®] system, which combines silica, alumina and carbon materials, was used for purification.

The purified toluene fraction was concentrated (N₂ stream) and a solvent exchange was done prior to analysis.

The final extract (100 µl in n-nonane) was analysed by HRGC-HRMS using a MICROMASS Autospec ULTIMA (SIM Mode, RP>8000, 10% Valley) equipped with a HP-Agilent (GC6890 Series) Chromatograph.

The 2,3,7,8 congeners were separated by a 60m x 0,25µm Df CP-Sil 8 CB-MS Low Bleed CHROMPACK-VARIAN (5%Phe-95%Me silicon gum) column. The injected volume was 2 µl (Spitless, EPC Constant Flow Mode), using a HP-Agilent 7683 Series Autosampler. Concentration calculations were reported in compliance with EN-1948 (Isotopic dilution method).

Clean-up and analysis: PAHs

The extract was dried on Na₂SO₄ and concentrated with a Turbovap[®], before a solvent exchange (cyclohexane). The sample was then submitted to an alumina column clean-up. The final steps were concentration and solvent exchange (acetonitrile) with Turbovap[®].

The HPLC separation was achieved on a Vidac[®] 201 TP54 column (acetonitrile/water), coupled with a fluorimeter 122 Gilson detector.

Results and discussion

Results are reported for a dry gas at 273 K, 101.3 kPa and 5 % O₂.

PAHs**Table 1:** PAHs results (sum of the 6 Borneff PAHs) - $\mu\text{g}/\text{Nm}^3$

| Landfill | Sampling day | | | Mean |
|----------|--------------|-----------|-----------|-----------|
| | 1 | 2 | 3 | |
| A | 2.4 | 1.3 | 1.3 | 1.7 |
| B | 0.20 | 0.09 | 0.20 | 0.16 |
| C | 0.37-0.50 | 0.10-0.24 | 0.13-0.26 | 0.20-0.33 |
| D | 0.50 | 0.40-0.55 | 0.20-0.35 | 0.37-0.47 |
| E | 0.30-0.45 | 0.20-0.38 | 0.20-0.37 | 0.23-0.40 |

PCBs**Table 2:** PCBs results (sum of #77, #126 and #169) - WHO-TEQ ng/Nm^3

| Landfill | Sampling day | | | Mean |
|----------|--------------|------------|---------------|---------------|
| | 1 | 2 | 3 | |
| A | 2.4 | 1.3 | 1.3 | 1.7 |
| B | 0.20 | 0.09 | 0.20 | 0.16 |
| C | 0.003 | 0.001 | 0.001 | 0.002 |
| D | < 0.01 | < 0.01 | 0.00005-0.013 | 0.00002-0.011 |
| E | 0.0003-0.001 | 0.001-0.01 | 0.005 | 0.0004-0.005 |

PCDDs/PCDFs**Table 3:** PCDDs/PCDFs results (17 congeners) - I-TEQ ng/Nm³

| | | Sampling day | | | Mean |
|----------|---------------|--------------|--------------|---------------|-------------|
| Landfill | | 1 | 2 | 3 | |
| A | Tot.2378-PCDD | < 0.03 | 0.0002-0.01 | 0.00002-0.01 | < 0.02 |
| | Tot.2378-PCDF | < 0.04 | < 0.02 | 0.00004-0.02 | < 0.03 |
| | Total | < 0.07 | 0.0002-0.03 | 0.00006-0.03 | < 0.04 |
| B | Tot.2378-PCDD | < 0.03 | < 0.02 | < 0.03 | < 0.03 |
| | Tot.2378-PCDF | < 0.02 | < 0.03 | < 0.03 | < 0.03 |
| | Total | < 0.05 | < 0.05 | < 0.06 | < 0.06 |
| C | Tot.2378-PCDD | 0.006 | < 0.002 | 0.002 | 0.003 |
| | Tot.2378-PCDF | 0.017 | 0.0005-0.003 | 0.003-0.004 | 0.007-0.008 |
| | Total | 0.023 | 0.0005-0.005 | 0.005-0.006 | 0.010-0.011 |
| D | Tot.2378-PCDD | 0.01-0.02 | < 0.037 | 0.00005 | 0.003-0.02 |
| | Tot.2378-PCDF | 0.001-0.03 | < 0.035 | < 0.038 | 0.0003-0.03 |
| | Total | 0.01-0.05 | <0.07 | 0.00005-0.038 | 0.003-0.05 |
| E | Tot.2378-PCDD | < 0.03 | 0.001-0.03 | < 0.03 | 0.0003-0.03 |
| | Tot.2378-PCDF | 0.01-0.05 | 0.01-0.02 | 0.006-0.02 | 0.009-0.03 |
| | Total | 0.01-0.08 | 0.01-0.05 | 0.006-0.05 | 0.009-0.06 |

Results are given as “< xyz” when they are below the limit of quantification. This limit of quantification is not fixed but may vary, not only with the sampled volume, but also with the sensitivity of the spectrometer.

Discussion

The levels found are always low, and in particular, for dioxins, below the 0.1 I-TEQ ng/Nm³ European limit value imposed on waste incinerators.

The conditions of combustion (high ignition temperature and stoichiometry : large excess of oxygen) could explain the very low level of measured halogenated organic pollutants.

This ascertains that these biogas fed engines are not a significant source of dioxins, in comparison with the well-known dioxins sources. A further monitoring of these installations for dioxins emissions is not justified.

References and Acknowledgments

Monitoring scheme and results of the Walloon landfills monitoring are available at:

<http://mrw.wallonie.be/dgrne/data/dechets/cet/> and

<http://mrw.wallonie.be/dgrne/data/air/valorisation/>

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