

EVALUATION OF MUNICIPAL SOLID WASTE INCINERATORS IN THE WEST OF FRANCE : PCDD/F LEVELS IN THE DIFFERENT COMPONENTS OF THE FACILITIES AND IN RAW MILK SAMPLES COLLECTED NEARBY

Céline Helen^{1,3}, Philippe Marchand², Alain Laplanche¹

¹Laboratoire Chimie des procédés et Analyses pour l'Environnement, Ecole Nationale Supérieure de Chimie, 35 700 Rennes, France

²LABERCA, Ecole Nationale Vétérinaire de Nantes, 44 307 Nantes, France

³Société de Diagnostic Air Eau, 35 830 Betton, France

Introduction

In recent years, municipal solid waste incinerator (MSWI) have been the subject of much controversy because of their emissions into the atmosphere, which constitute a potential risk to the environment.

Among the most toxic compounds emitted, there are the polychlorodibenzo-p-dioxins (PCDD) and polychlorodibenzofurans (PCDF). Given their persistent nature and relative immobility, all terrestrial and aquatic organisms are liable to exposure. Recent reports showed high concentrations of these compounds in samples of cow's milk taken in the vicinity of incinerators¹.

Unfortunately, information presented to the public about health risks of incineration are often incomplete, including only data on PCDD/F levels in stack gas sample.

In order to have an overall information on incineration release and impact, in 2001 a wide program to determine the levels of PCDD/F in incineration (fly ash, slag and stack gas) and in milk samples collected in the vicinity of the facilities was initiated in the Brittany and Pays de la Loire areas. This program concern 4 incinerators of different size and gas treatment, spread out in the both areas and evaluated over 3 years.

The first incinerator under investigation is presented in this study at the same time as the first results of PCDD/F levels in cow's milk of this area.

Methods and materials

The MSWI began operating in 1974 and handles an amount of approximately 5000 tons of MSW per year and is considered as a small MSWI.

Stack gas sample was collected using a filter/condenser method in accordance with EN-1948-1. Fly ash and slag samples were collected at the same time.

The MSWI has recently been retrofitted with a modern system cleaning gas in order to comply with the limit of 0.1 ng I.TEQ/Nm³. The measurements were done just before and after this change to test the efficacy of the new equipment.

Samples of raw milk were directly collected in the farms in the vicinity of the incinerator during this period.

All samples were kept respectively at 4 °C and -20 °C before being analysed in the laboratory of Rennes for the stack gas, fly ash and slag and in the laboratory of Nantes for the milk samples.

Fly ash was treated with HCl 1N for 2 hours prior to extraction. All the pollutants were removed

FOOD AND FEED I

from fly ash, slag, XAD-2 and filter by soxhlet extraction using toluene for 8 hours. Liquid-liquid extraction with toluene was performed to remove dioxin compounds from condensed water.

For milk samples, fat was extracted according method tested in many collaborative studies².

Samples were cleaned-up on the classic liquid-solid adsorption chromatography using silica (Merck, France), florisil (Merck, France), and for the milk samples on CarboPackC/Celite (Supelco) in open glass columns at atmospheric pressure.

All incinerator samples were analysed by high resolution gas chromatography coupled to low resolution mass spectrometry (HRGC/LRMS) using MS/MS. For HRGC, a TRACE GC 2000 (ThermoFinnigan, France) equipped with a DB-5ms (J&W Scientific) fused silica capillary column (60m, 0.25mm I.D., 0.25µm film thickness) was used. For LRMS, a quadrupole ion trap GCQ (ThermoFinnigan) mass spectrometer was used in MS/MS mode. The MS/MS method have already been reported in details³.

For milk samples HRGC/HRMS-detection was performed on a JMS 700D (Jeol) at 10000 resolution using a 30m DB-5ms column.

Results and Discussion

The results of the measurements on the incinerator in july 2001 are presented in the Table 1. Levels of PCDD/F are relatively higher than the values traditionnaly observed but are in accordance with the results obtained on small MSWI³. As traditionnaly observed, the contribution of PCDF in the TEQ result is the most important and represent in all the samples at least 72 %.

Table 1. PCDD/F levels in the different components of the incinerator. Between brackets are the contribution of PCDF in the final result.

	Fly ash (ng TEQ/g)	Slag (pg TEQ/g of dry mater)	Stack gas (ng TEQ/Nm ³ at 11% O ₂) First value	Second value
ΣPCDD	2.9	7.3	0.53	0.0078
ΣPCDF	7.8 (72 %)	35.7 (83 %)	4.79 (90 %)	0.023 (74 %)
Total	10.7	43.0	5.32	0.031

Figures 1a and 1b show that in fly ash mainly highly chlorinated compounds are found (HpCDD, OCDD, 1,2,3,4,6,7,8-HpCDF and OCDF) while in slag low chlorinated PCDF are also observed (TeCDF and 2,3,4,7,8-PeCDF). On the other hand, in stack gas low chlorinated compounds are in majority⁴.

The levels of PCDD/F found in the raw milk samples collected at the vicinity of the incinerator are presented in Table 2. The results are in accordance with the legislation since they are under the limit of 1pg/g of ... which is the limit accepted. The different samples collected before and after the measure on the incinerator do not show any important variations, except for the farm B1 where the PCDD/F level is higher and still under the limitation.

The location of the farms and the incinerator are shown in Figure 2. From the windrose it can be seen that the primary direction of airflow is from the west. Therefore, the farms B1 and B2 are downwind of the incinerator and that B3 is the furthest and considered as the reference. The levels decrease as the distance of the farms from the incinerator incresaes. This incinerator has a limited

Table 2. PCDD/F levels in the different farms, results are in pg TEQ/g of

	Farm B1	Farm B2	Farm B3
June 2001	0.53	0.40	0.38
July 2001	0.78	0.37	0.30
January 2002	0.90	0.51	0.44

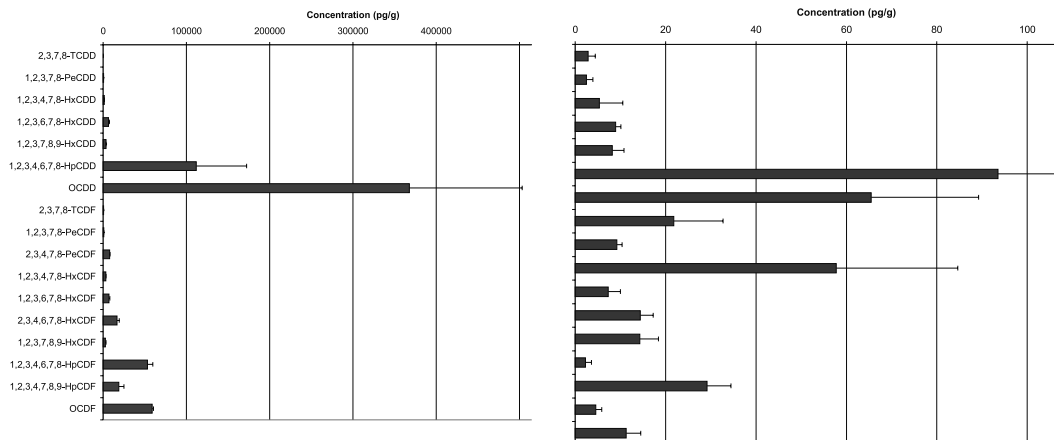


Figure 1. Profile of the 17 congeners in fly ash (a) and in slag (b)

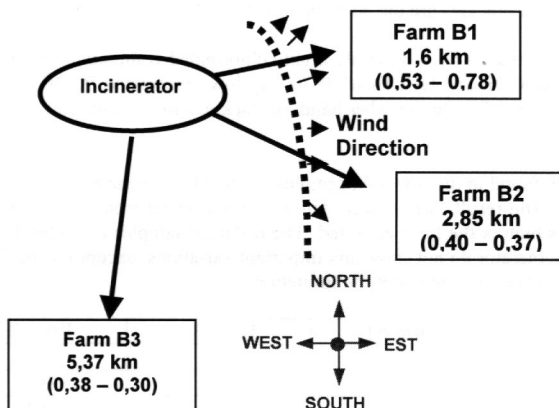


Figure 2. Localisation of the different farms around the incinerator

FOOD AND FEED I

influence on the PCDD/F levels in the milk of the most exposed cows even when the emissions were elevated.

The comparison of PCDD/F repartition in stack gas and in milk samples do not show a direct correlation (Figure 3). This can be explain since during transport, wet and dry deposition as well as chemical transformation and degradation processes may alter the PCDD/F composition⁵. All theses reactions of transformation are likely to occure on lower chlorinated PCDD/F and would then enhance the relative concentration of higher chlorinated congeners that will remain on the vegetation. Therefore, higher chlorinated compounds as 1,2,3,6,7,8-HxCDD and 2,3,4,6,7,8-HxCDF are obtained in milk samples after the cows have eaten the grass. Although the main compound is still the 2,3,7,8-TCDF as observed in the stack gas at very high level.

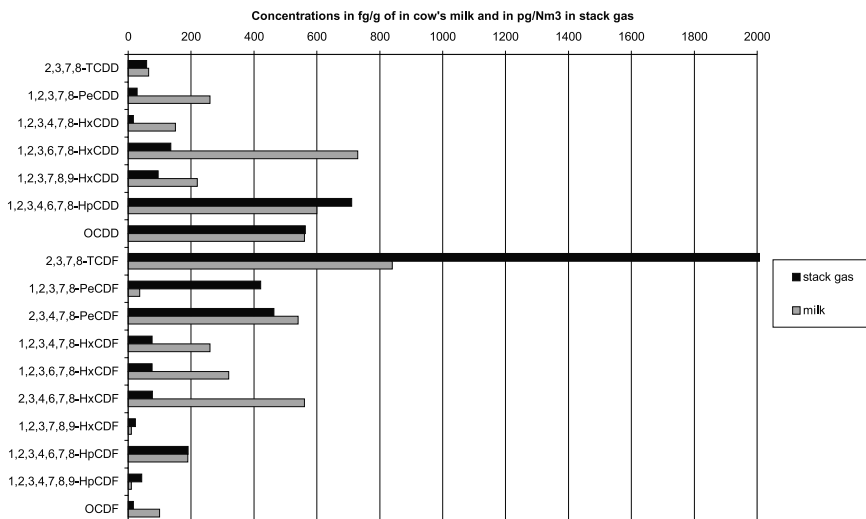


Figure 3. Profile of the 17 congeners in stack gas and raw milk sample of the farm B1

Aknowledgements

This research is financially supported by the Brittany and Pays de la Loire regions.

References

1. Eitzer B.D. (1995) *Chemosphere*, 30, 1237-1248
2. Fürst P., Krause G.H.M., Hein D., Delschen P., Wilmers K. (1993) *Chemosphere*, 27, 1349-1357
3. Helen C., Lemasle M., Laplanche A., Genin E. (2001) *Journal of Mass Spectrometry*, 36, 546-554
4. Ling Y.C., Hou P.C.C. (1998) *Journal of Hazardous Materials*, 58, 83-91
5. Domingo J.L., Schumacher M., Llobet J.M., Müller L., Rivera J. (2001) *Chemosphere*, 43, 217-226