A TWO YEARS SURVEY ON PCDDs AND PCDFs IN AN AREA AFFECTED BY A MUNICIPAL SOLID WASTE INCINERATOR. STUDY OF SOILS, GRASS, FORAGE, COW'S MILK AND CATTLE FAECES.

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Introduction

After the discovery of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in fly ash and flue gas from Municipal Solid Waste Incinerators by Olie et al.¹, incineration of wastes has been a topic of great concern during the last two decades due to their potential to release to the environment highly toxic pollutants. Even if PCDDs and PCDFs are emitted in trace amounts from Waste Incinerators², this toxic compounds are of great concern, specially when they can enter the food chain in such a way that the man could be affected.

The present study was performed over two years after an initial monitoring program focused on the contamination by PCDDs and PCDFs in soils located in the area influenced by emissions produced by a Clinical Waste Incinerator (CWI). Initially when the CWI was operating during 1993 an intensive study was performed to investigate PCDD/PCDFs contamination in soils. PCDD and PCDF levels have been reported in the literature to be in the range of 56 to 677 pg/g on a dry weight basis³. This former study was followed by a new intensive study carried out during 1995 when the CWI was closed and before a new Municipal Solid Waste Incinerator (MSWI) started operating in order to have reference values to be used in the assessment of the potential contamination by PCDDs and PCDFs produced by the new MSWI. Data from this study are to be published⁴. In a recent work it was reported⁵ the variation in PCDD an**#**CDF levels in milk from cows exposed to both previously mentioned incinerator plants and it was observed a noticeable difference between the two years studied. In fact it was observed that total PCDD/F levels found in cow's milk collected in 1998 were approximately 4 times lower than in 1995 when the old CWI was operating.

Environmental modelling efforts have suggested that feed is the main route of dioxin to the cow, and that water and air uptake can be neglected⁶. Other authors have suggested that the ingestion of soil by grazing animals could play a dominant role⁷. The present study presents results concerning a two years PCDD and PCDFs monitoring program in the area affected by the MSWI where the cows graze. PCDD and PCDF levels in soils, grass, straw, fodder, faeces and cow's milk are evaluated.

Material and Methods

The study area selected was located in the surroundings of a Clinical Waste Incinerator (CWI) and a Municipal Solid Waste Incinerator (MSWI). The cow's farm selected for the long-term study was located 2.5 Km far from the MSWI and 3 Km far from the CWI in the south direction.

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The existence of the cattle farm was known in 1995, so there is not information available corresponding to previous years. During 1995 and 1998 it was possible to collect cow's milk samples. Due to the fact that the farm was closed by the end of 1998 cow's milk samples were no longer available for this study. Cow's milk was chosen because milk is relatively easy to analyse for dioxins and cows graze relatively large areas and any dioxins present on herbage and soil eaten by the cows would concentrate in the fat content of the milk produced⁸.

Two main reasons were taken into account when selecting the two soil sampling points considered in this study. Zone A was selected because it was near the MSWI at a distance of about 1 Km and cow's were found to graze in this area. In 1998 and 1999 soil and grass samples were taken in Zone A. Zone B selected corresponds to the area where the farm is located. Soil, grass, straw, fodder, and cattle faeces were taken in Zone B during 1998 sampling campaign. During 1999 sampling campaign only soil and grass collected were collected since the farm was closed at that time.

Analytical Determination.

Extraction and Clean Up.

PCDD/F analysis was performed on approximately 20 g of soil, 15 g of herb, or 10 g of faeces dried, spiked with a mixture of 15 $[^{13}C_{12}]$, and Soxhlet extracted with toluene for at least 24 h. Clean up was performed as previously described in detail³. Basically this consisted of a multilayer column containing neutral, acid, and basic modified silica gel. Further cleanup was carried out on a second column containing Florisil®.

Quantification. Resolution and quantification of PCDDs, PCDFs and coplanar PCBs were performed by HRGC-HRMS using a VG AutoSpec Ultima (VG Analytical, Manchester, UK) coupled to a Fisons Series 8000 (8060) Gas Chromatograph. A fused silica capillary column DB-5 and a DB-DIOXIN (60 m, 0.25 mm id., 0.25µm film thickness, J&W Scientific, USA) were used. Helium at a column head pressure of 175 Kpa was used as the carrier gas. A minimum resolution of 10,000 was used when operating with the HRMS instrument. Methods blanks were routinely analyzed, and no contributions were detected. Total valuesreported were calculated assuming that all values less than the limit of detection (LOD) are equal to the half the LOD.

Results and discussion.

Data from previous studies conducted in 1993 indicated a typical combustion profile and pattern in soil samples studied within a radius of 5 Km round the CWI. It was found that reaching a distance 3000 meters far away from the incinerator plant, PCDD and PCDF levels in soils exhibited extremely low values. It was evident that the highest concentrations were found between 400 and 2000 m. At that time total levels ranged from 44.6 ppt in control sites up to 677.4 ppt in the most contaminated location. In this study it was found that the higher levels were found in the South direction, at about 1200 and 2000 m distance from the incinerator plant. The present study is concerned with this area, named here Zone A.

Total PCDD and PCDF levels found in the present study are presented in Figure 1. Some interesting findings could be remarked. Regarding total PCDD and PCDF levels found in soils samples studied, a clear difference can be observed between both zones studies. Total PCDD/F levels are higher in Zone B where the cattle farm is located. This could be explained taking into

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account that soil samples collected in Zone B had a higher organic matter content. On the other hand considering that PCDD/PCDF levels found in cattle faeces are high, it could be said that faeces are contributing to the high PCDD/F levels found in these soils. Comparing both sampling periods it can be observed that both Zones A and B studied during 1999 show and increase in total PCDD/F levels with respect to 1998. In the case of Zone A the increase is of 1.3 and in the case of zone B the corresponding value is 1.5, indicating a possible contribution from cattle faeces originated by cows grazing here.

Grass samples studied exhibited the lowest PCDD/F levels compared to the other samples studied and it can also be observed an slight decrease in total levels during 1999, although this difference could be considered negligible. This finding could be explained considering that all the grass samples studied are annual plants. If it is taken into account that air is the main route of PCDD/Fs intake to this type of plants, it cannot be expected a high contamination in these samples.

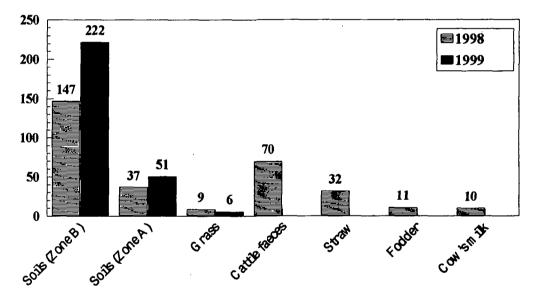


Figure 1. Total PCDD/F levels (pg/g) found in all the samples studied during 1998 and 1999 influenced by the Municipal Solid Waste Incinerator (MSWI) plant.

Considering the feed taken by the cows, it can be observed that straw (32 pg/g) had a higher contribution compared to fodder (11 pg/g), to the total PCDD/PCDF levels ingested by the cows through food. It should be considered that straw represents the main food item in the cows studied. Grass with total PCDD/F levels of about 9 pg/g is only taken by these cows during the autumn season for a couple of months so their contribution to total body burden in the cow is not as much important as straw is.

Finally an interesting remark is derived from the two main PCDD/PCDF elimination routes in the cows studied. It can be seen in Figure 1 that total PCDD/F levels in the milk were found to be 10

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pg/g but considering that cows produce milk just when they calve, this route of elimination is not as important as faeces. Regarding total PDCC/F levels found in cattle faeces it can be observed in these cows the importance of excretion as route of elimination of contaminants.

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