

## Soil contamination with PCDDs and PCDFs at some typical locations in Flanders.

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### ABSTRACT

Top soil samples were collected at six typical locations in Flanders, including potential dioxin source areas, and analyzed isomer-specifically for polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs). Concentrations in the 0-3 cm soil fraction, averaged per location, ranged between 2.1 pg/g (as TEQ) at a rural location and 8.9 pg/g (as TEQ) in an industrialized area. Generally, PCDFs made up  $70 \pm 6$  % of the TEQ content, whereas they accounted for  $34 \pm 6$  % of the sum of the concentrations of the 'dirty seventeen' congeners. At the most contaminated site a slightly enhanced contribution of PCDFs to the dioxin content was observed. The pollution levels in Flemish soils fairly agree with those detected in other West European countries.

### OBJECTIVES

The study described here is part of a screening program, aimed at elucidating occurrence and fate of PCDDs and PCDFs in Flanders in order to enable evaluation of the impact of the pollution levels on man and his environment. In view of the growing concern that soil may play a role in food and forage contamination with dioxins<sup>1</sup>, and the lack of isomer-specific data on PCDD/PCDF levels in Flemish soil, we decided to include soil among the priority matrices. Thus far the program has focused in addition on cow's milk<sup>2</sup>, ambient air<sup>3</sup>, traffic<sup>4</sup> and waste incinerator emissions.

### DESCRIPTION OF THE ANALYTICAL METHOD

Following the approach which is now being adopted world-wide, analyses comprise the isomer-specific determination of the 'dirty seventeen' PCDDs or PCDFs, i.e., tetra- to octachlorinated congeners that are chloro-substituted on at least the 2-, 3-, 7- and 8- position, allowing calculation of a TEQ-value (toxic equivalent concentration relative to 2,3,7,8-T<sub>4</sub>CDD) for each sample using the I-TEF scheme<sup>5</sup>.

Briefly, the soil sample (50 g) is spiked before extraction with a mixture of at least 10 <sup>13</sup>C-labeled congeners, i.e., one for each product class (PCDD or PCDF) and chlorination degree. The analytes and related pollutants are then extracted from the matrix in a Soxhlet apparatus, using toluene as solvent, during 24 hours. The extract is evaporated under a nitrogen stream to 1-2 ml.

Purification of the extract relies on chromatography on a silica multilayer column and on an alumina column, consecutively. For the first clean-up step, the sample is transferred onto a column containing 5 g of base-impregnated silica (33% NaOH 1N), 20 g of acid-impregnated silica (44% H<sub>2</sub>SO<sub>4</sub>) and a top layer of 5 g of sodium sulfate, using n-hexane. Elution is carried out with 200 ml of n-hexane, after which the eluate is concentrated under a nitrogen stream to 1-2 ml. For the final clean-up step, the sample is brought onto a column containing 2.5 g of alumina B Super I and a top layer of 2 g of sodium sulfate. A PCDD/PCDF fraction is collected and

prepared for GC-MS measurement as described elsewhere<sup>2</sup>.

The gas chromatographic separation is carried out on a HP 5890 Series II GC equipped with a HP 7673 auto-injector and a split/splitless injector operated in the splitless mode (270 °C, 1 µl, split time 1 min). A 60 m x 0.25 mm x 0.25 µm DB-Dioxin fused silica capillary column is mounted, connected to the mass spectrometer via a direct interface (270 °C). Helium is used as carrier gas (inlet pressure 200 kPa). The initial temperature of the oven, 160 °C, is raised after 1 min with a rate of 20 °C/min to 240 °C, which is held constant for 35 min. It is then raised with a rate of 15 °C/min to the final temperature of 270 °C, which is held constant for a further 58 min. High resolution mass spectrometric detection takes place on a VG Autospec Q instrument, according to parameters and criteria described elsewhere<sup>2</sup>.

From our experience<sup>6</sup>, particularly 1,2,3,7,8-P<sub>5</sub>CDD, being a congener that largely affects the TEQ-value, cannot completely be resolved from interfering compounds on a DB-Dioxin column. Hence the extracts are re-injected on a 50 m x 0.25 mm x 0.25 µm CP-Sil88 column. For this analysis the interface temperature is kept at 240 °C, and the carrier gas inlet pressure is set at 180 kPa. The initial temperature of the oven, 110 °C, is raised after 1 min with a rate of 30 °C/min to 170 °C, and then with a rate of 3 °C/min to 230 °C, which is held constant for 22 min. Then it is raised further with a rate of 5 °C/min to the final temperature of 240 °C, which is held constant for another 43 min.

## PCDDs AND PCDFs IN FLEMISH SOIL

Top soil samples were collected at seven, geographically spread, locations in Flanders, being:

- Mol: a rural location, further characterized by a coal-fired power station and some nuclear industry at 1-4 km E from the sampling site
- Moerkerke: a rural location, the nearest known point source being a large municipal waste incinerator (MWI, 175000 ton/yr) at about 10 km W from the sampling site
- Berendrecht: a location in the harbour area near Antwerpen, with (petro)chemical industry extending 2-15 km SE to SW from the sampling site, and the city of Antwerpen at 15 km SE
- Zelzate: a location at the canal Gent-Terneuzen, with metallurgical and chemical industry and a highway at 1-15 km SW from the sampling site and the city of Gent at 20 km SW
- Ham: a location characterized by a highway and chemical industry (production of vinyl chloride, incineration of chlorinated waste) at 2-7 km SE to W from the sampling site
- Vilvoorde: a location at about 15 km NE from the city centre of Brussel, characterized in addition by a coal-fired power station at 1 km W and industry extending 1-7 km SW-W, including a MWI at about 6 km SW from the sampling site.

The above locations were also selected for air and cow's milk sampling, the results of which have been reported elsewhere<sup>2,3</sup>. The soil samples were collected in May-June 1992 in the immediate vicinity of the air sampling points, from as undisturbed areas as possible. At each location three squares of 0.5 m x 0.5 m were demarcated. Within two of the squares the top soil was removed to a depth of 3 cm using a small trowel. In the third square the soil was collected in three successive fractions of 1 cm depth, which were analyzed separately, and the results of which have been combined when appropriate. Vegetation, if present, consisted of short grass, and was included. All soil samples were dried at ambient temperature in aluminium foil - covered dishes to constant weight. Afterwards they were ground and homogenized.

Table I summarizes the results of the PCDD/PCDF determinations, expressed both as the sum of the concentrations of the 'dirty seventeen' congeners and as the TEQ content. All data represent the average concentration ± standard deviation for three 0-3 cm soil samples collected at each location. The analyses indicate that Zelzate, and to a minor extent also Vilvoorde, may be more heavily polluted with dioxins than the other locations. In both of these industrialized areas a significantly higher TEQ content is found than at both of the rural locations, whereas the others rank in-between. The coefficients of variation of the TEQ values for the three separate 0-3 cm samples at each location range between 3 and 15%, which may be considered satisfactory.

LOCATION	SUM 17 PCDD/F (pg/g)	TEQ (pg/g, as TEQ)
Mol	71 ± 22	2.14 ± 0.24
Moerkerke	64 ± 6	2.27 ± 0.06
Berendrecht	126 ± 11	3.81 ± 0.57
Zelzate	238 ± 33	8.94 ± 1.06
Ham	138 ± 8	2.72 ± 0.20
Vilvoorde	224 ± 39	5.76 ± 0.21

Table I: Dioxin concentration in top soil samples from some typical locations in Flanders; concentrations refer to the 'dirty seventeen' PCDD/PCDF.

The typical contribution of the individual congeners to the dioxin content is illustrated in Figure 1. Averaged over all analyses, the PCDFs made up  $70 \pm 6\%$  (average  $\pm$  standard deviation) of the TEQ value, whereas they accounted for  $34 \pm 6\%$  of the sum of the concentrations of the 'dirty seventeen' congeners. Only slight deviations from the characteristic profile were observed at the various locations. Interestingly, the results from the most contaminated site (Zelzate) revealed a somewhat enhanced proportion of PCDFs, amounting to 79% of the TEQ content or 40% of the sum of concentrations. At the occasion of soil analyses at a severely contaminated metal reclamation site, which contained up to 1.9 ng/g (as TEQ) of PCDDs and PCDFs, we earlier noted a pronounced increase in the share of PCDFs (83% of the TEQ content or 61% of the sum of concentrations). Furthermore, within each product class the relative importance of the higher chlorinated compounds, particularly octa-CDD and -CDF, appeared to be influenced to some extent by the location; whereas in Ham the concentrations of OCDD and OCDF represented  $81 \pm 2\%$  and  $42 \pm 1\%$  of the sum of the levels of the seven PCDDs or the ten PCDFs, respectively, in Moerkerke these figures dropped to  $68 \pm 2\%$  and  $26 \pm 2\%$ .

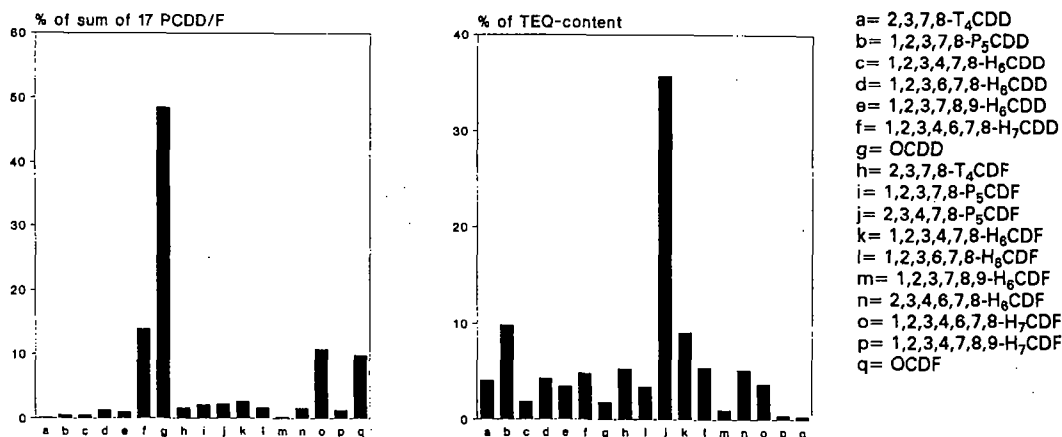


Figure 1: Typical contribution of the individual 'dirty seventeen' congeners to the sum of the concentrations (left) or to the TEQ content (right).

The collection and analysis of separate 1 cm fractions from each location did not yield decisive information with regard to possible depth-profiles, as the sampling points could not be proven unquestionably to have been untouched since several years.

In Table II data on PCDD/PCDF concentrations in soil from a number of other countries have been compiled. This literature survey, though not exhaustive, demonstrates that the dioxin contamination levels assessed in the present study agree well with those in rural and urban/industrialized areas in other West European countries. Obviously, in the immediate vicinity of dioxin point sources much higher immission values may be expected; this has been demonstrated, e.g., by our earlier top soil analyses near the municipal waste incinerator at Sint-Niklaas<sup>11</sup> as well as by the elevated soil contamination with PCDDs and PCDFs at metal reclamation sites in several countries, amounting up to 98 ng/g (as TEQ)<sup>12</sup> and thus largely exceeding proposed guidelines<sup>1</sup>. In Flanders more research is needed towards inventoring and characterizing of point sources that emit PCDDs and PCDFs, before the extent of dioxin pollution, as compared to that in similar industrialized regions, can be fully evaluated.

LOCATION	TYPE	CONCENTRATION (pg/g d.w., as TEQ)		FROM REF.
		AVERAGE	RANGE (N)	
Northrhine-Westfalia, Germany	R	4.68	0.60 - 11.15 (69)	7
	U/I	8.64	0.84 - 27.32 (28)	
Doncaster, UK	U/I	8	3 - 20 (12)	8
Salzburg, Austria	R	1.1	0.1 - 3.0 (5)	9
	U/I	4.1	1.0 - 11.5 (19)	
Lickebaert-area, The Netherlands	R	4.8	1 - 9 (6)	10
	MWI	24.2	10 - 55 (15)	
Sint-Niklaas, Belgium	MWI	27.5	6.6 - 67.4 (12)	11

Table II: Survey of the dioxin concentrations in soil reported for some other West European countries; R= rural, U/I= urban/industrialized, MWI= municipal waste incinerator.

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