LEVELS AND PATTERNS OF DIOXINS IN COW'S MILK IN THE VICINITY OF MUNICIPAL WASTE INCINERATORS AND METAL RECLAMATION PLANTS IN THE NETHERLANDS.

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ABSTRACT

In the period May 1989 - March 1990, samples of cow's milk from dairy farms located in the vicinity of municipal waste incinerators and metal reclamation plants were analysed for the seventeen toxic chlorinated dibenzodioxins and dibenzofurans. Increased levels were found of up to 13.5 pg TEQ/g of milk fat. Principal component analysis showed remarkable differences in congener patterns in milk from farms in the neighbourhood of different sources.

INTRODUCTION

In May 1989, a large-scale study was initiated to investigate the possible dioxin contamination of cow's milk from dairy farms, located in the vicinity of potential sources, particularly municipal waste incinerators (MSWs). This study revealed increased dioxin levels in milk samples from areas near Rotterdam ("Lickebaert area") and Zaandam of up to 13.5 pg 2378-TCDD-equivalents (TEQ)/g of fat. A potential health risk by consumption of milk and milk products from these areas could not be excluded. The Dutch government proclaimed an upper limit for dioxin levels in milk and milk products of 6 pg TEQ/g on a fat basis and provisionally restricted the consumption of these products from dairy farms in the Lickebaert area and Zaandam.

Increased levels of dioxins in milk from cattle grazing in the neighbourhood of waste incinerators and metal reclamation plants have been reported earlier [Rappe *et al.*, 1987; Riss *et al.*, 1988 and 1989]. Due to the occurrence of increased dioxin levels in Dutch cow's milk, several studies were initiated to understand the mechanisms which influence the dioxin level in cow's milk, i.e. all factors between emission and excretion in the milk. One of the long-term objectives is to design predictive models for the level of dioxins in milk from cow's grazing in areas at a certain distance from a potential dioxin source.

Patterns of dioxines and furans are multivariate data which can be studied by pattern recognition techniques like principal component analysis (PCA) [Massart *et al.*, 1988]. The use of such techniques for the interpretation of environmental patterns has been reviewed by Stalling *et al.* [1985].

In this paper, the analytical results are summarized. The occurrence of dioxins in milk samples from the Lickebaert area is discussed in more detail and results are presented of the application of principal component analysis on congener patterns in milk collected in the vicinity of different sources.

MATERIALS AND METHODS

Sample material. Samples of 150 g of cow's milk were collected from storage containers of dairy farms. In order to study so-called time-averaged dioxin levels (see Results and Discussion), samples of 25 ml of milk were taken at regular intervals over a three to four week period (see Table 1) and were subsequently mixed to a time-averaged

sample. All milk samples were stored at -20°C until analysis.
Sampling strategy. Sampling locations were chosen at a distance of a few km from the suspected source and north east to the source, based on a predominantly south-western wind (average Dutch situation) [Jaarsveld & Onderdelinden, 1989]. Criteria were formulated in order to guarantee (as far as possible) the representativity of cow's milk from dairy farms in each particular area. Therefore an inquiry was made about the grazing and feeding conditions in the preceding period on each participating dairy farms.

Analysis of PCDDs and PCDFs in cow's milk

Analytical procedure. The analytical method has been described earlier [Liem *et al.*, 1990]. The procedure is based on isolation of the PCDD and PCDF containing fat fraction by liquid-liquid extractions with organic solvent. Fat and interfering compounds are removed from the fat extract by using activated carbon and alumina. Analyses were performed with capillary gas chromatography/mass spectrometry (GC/MS; R=3000:1). The seventeen toxic 2378-chlorine substituted dioxin and furan congeners are identified and quantified by the use of $^{13}C_{12}$-labeled reference standards. These standards are added to the milk sample prior to extraction.
Levels of each congener are expressed in pg/g on a fat basis (pg/g, ppt). The fat content is determined by weighing the amount of fat after extraction. In addition, total PCDD and PCDF levels (TEQ-value) were determined by calculating the sum of the levels of each congener expressed in pg 2378-TCDD equivalents/g of fat, using the International Toxicity Equivalence Factors (ITEF) [Van Zorge *et al.*, 1989].
The $^{13}C_{12}$-labeled quantification standards (Cambridge Isotope Laboratories, Woburn, MA, USA) were calibrated against a standard solution of dioxins and furans. This standard was obtained in a recent WHO-coordinated interlaboratory quality control study on levels of PCBs, PCDDs and PCDFs in human milk and blood [WHO, 1989].
The limit of detection was 0.1 to 1 pg/g on a fat basis for tetra to octachlorinated PCDDs and PCDFs.

QA/QC-procedures. The accuracy and reproducibility of the analytical method has been determined in validation experiments by the addition of known amounts of native PCDD/Fs to subsamples of cow's milk [Liem *et al.*, 1990]. The accuracy ranged for individual congeners from 92 to 112% and was 101% on a TEQ basis. An overall reproducibility, expressed in the relative standard deviation of the TEQ-value, of 5.3% is calculated for concentrations higher than 2.5 pg TEQ/g. For TEQ-values below 2.5 pg TEQ/g, an absolute standard deviation of 0.13 pg TEQ/g was used.
For quality control (QC) purposes, a QC-sample was incorporated in each serie of milk samples. This QC-sample is an aliquot of a large volume of cow's milk from a dairy farm at Schalkwijk (Utrecht, NL). From these analyses, the long-term repeatability has been estimated. At present, the inter-assay coefficient of variation is 8% (n=17) at a mean TEQ-value of 1.37±0.11 pg TEQ/g of fat. This is in good agreement with the assumed standard deviation of 0.13 pg TEQ/g for levels below 2.5 pg TEQ/g.

RESULTS AND DISCUSSION

In Table 1, results are presented from analyses of samples of cow's milk from several regions in the Netherlands. These results show that in the vicinity of the investigated sources, a relatively broad range of dioxin levels was found. The highest levels were found at locations in the Lickebaert area (range: 5.1-12.2 pg TEQ/g) and near the MSW in Zaandam (range: 3.1- 13.5 pg TEQ/g of milk fat). Milk samples from reference locations showed dioxin levels between 0.7 and 2.5 pg TEQ/g of milk fat.

Figure 1 shows the dioxin levels in milk from the Lickebaert area, collected in May and June (day production) and in the period September-October 1989 (time-averaged samples). It can be seen that for the Lickebaert area, the highest dioxin levels have been systematically found at a distance of approximately 2 km north-east from the MSW (marked with "+").

Milk from particular dairy farms showed remarkable differences in the level of dioxins, when collected at different months. Milk samples from two particular farms in the Lickebaert area, collected in May and June 1989, showed a decrease in the TEQ-value of approximately 28%. These fluctuations might be due to differences in emissions, weather conditions (i.e. discrimination between long-range transport vs. short-range deposition),

feeding conditions etc. It was concluded that dioxin levels in samples from the day production only reflect a momentary situation. To eliminate these time fluctuations, it was decided to alter the sampling strategy and to collect the so-called time-averaged samples (since September 1989).

Table 1. Results from analyses of PCDDs and PCDFs (expressed in pg TEQ/g of milk fat) in samples of cow's milk in the vicinity of potential sources and from reference locations in the Netherlands.

Location/area	potential source [a]	Sampling date/period-year	Number of samples	Dioxin level (range in pg TEQ/g of fat)
Lickebaert	MSW	25 May 1989	11	5.3 - 12.2
Lickebaert	MSW	21 June 1989	2	6.5 ; 7.5
Lickebaert	MSW	19 Sep-7 Oct 1989	5	5.1 - 10.3
Zaandam	MSW	1 Aug 1989	3	4.7 - 6.3
Zaandam	MSW	27 Sep-27 Oct 1989	5	3.1 - 12.1
Zaandam	MSW	19 Feb 1990	3	9.2 - 13.5
Duiven	MSW	11 July 1989	4	4.2 - 5.4
Duiven	MSW	27 Sep-27 Oct 1989	4	3.3 - 5.8
Culemborg	metal reclamation	4 Sep 1989	3	2.4 - 6.4
Culemborg	*metal reclamation*	28 Sep-28 Oct 1989	5	3.6 - 6.5
Eight other MSWs	MSW	July 1989 - Feb 1990	35	1.6 - 8.1
Oudenhoorn	unknown	21 June 1989	5	1.8 - 3.8
Schiedam	unknown	21 June 1989	5	2.2 - 3.6
Reference locations	none	25 May & 21 Jun 1989	10	0.7 - 2.5

[a] MSW= municipal solid waste incinerator.

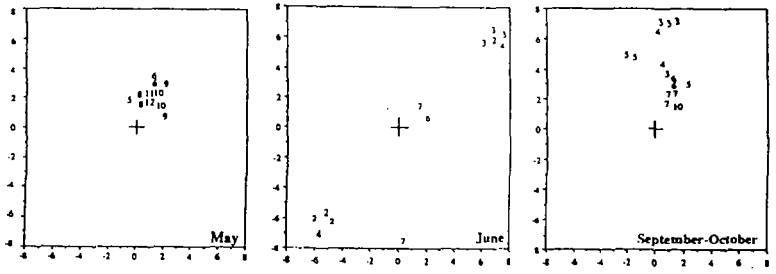

Figure 1. Maps of levels of PCDDs and PCDFs (in pg TEQ/g of fat) found in samples of cow's milk from the Lickebaert area, collected on May 25, June 21 and in the period September 19-October 7, 1989 and from areas near Schiedam and Oudenhoorn, collected on June 21, 1989. The position of the source is marked with a "+". Distances are given in kilometers.

The application of PCA revealed remarkable differences in congener patterns in milk from farms in the neighbourhood of different sources (see Fig.2) [Hoogerbrugge *et al.*, 1990]. The following could be observed: (1) cow's milk from dairy farms in the vicinity of metal reclamation plants contained relatively more furans than dioxins, when compared to milk from farms in the vicinity of waste incinerators (first PC) and (2) waste incinerators at different locations can be distinguished from each other on the basis of the relative amounts of lower (tetra and penta) and higher (hexa and hepta) chlorinated compounds (second PC). The first observation is not surprising, since in metal reclamation plants cables are processed, which may contain considerable amounts of polyvinylchloride (PVC). In the combustion of PVC, predominantly furans are formed [Christmann *et al.*, 1989]. Two of the samples which are marked in Fig.2, have pattern projections which differ significantly from the patterns found in milk samples from the same area. The marked sample from Duiven appeared to originate from an area not only in the vicinity of the MSW, but also near an illegal metal reclamation plant. The marked

sample from the Lickebaert area originated from dairy cattle which were fed with grass from the very south-east corner of the area, which is positioned more closely to other potential sources of dioxins and furans.

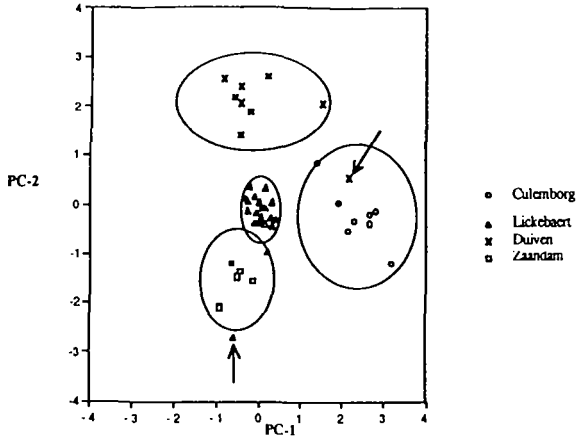

Figure 2. Projections of the patterns of congeners of dioxins and furans found in Dutch cow's milk samples on the two first principal components. The samples are from the vicinity of a metal reclamation plant at Culemborg and of three of the investigated MSWs. The ellipses shown in this picture are the estimated 95% confidence contours. The sample projection points marked with an arrow are treated individually and are not incorporated in the calculation of the confidence contours.

CONCLUSIONS

Increased levels of up to 13.5 pg TEQ/g of milk fat were found in cow's milk in the vicinity of municipal waste incinerators in the Netherlands. Levels in cow's milk can vary in time and demand a well-considered sampling strategy (time-averaged samples). Principal component analysis appeared to be useful in distinguishing sources of dioxins, based on patterns of dioxins and furans in cow's milk.

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