

## DIOXINS AND NON-ORTHO PCBS IN DUTCH CONSUMER MILK IN THE PERIOD 1997-2002

R.A. Baumann, A.C. den Boer, G.S. Groenemeijer R.S. den Hartog,  
W.C. Hijman, B.H.G. Stoffelsen, R. Hoogerbrugge

National Institute for Public Health and the Environment, P.O. Box 1  
3720 BA Bilthoven, The Netherlands

### Introduction

In 1989 high levels of PCDD/Fs were found in cow's milk from the Lickebaert area (near Rotterdam) in the vicinity of a large waste incinerator<sup>1,2</sup>. In the 90's some waste incinerators were closed and some others were equipped with flue gas cleaning installations. This resulted in a considerable reduction of PCDD/PCDF emission estimated from 488 to 77 g (i)-TEQ/year in the period 1991-1996<sup>3</sup>. Consequently also a reduction in the background level of Dutch cow's milk was expected. To study the levels of PCDD/PCDFs a monitoring programme of Dutch consumer milk was started in 1997. In this year unexpectedly high levels were found due to the so-called Brazilian citrus pulp incident<sup>4</sup>. Since cow's milk, and milk products, are heavily consumed in the Netherlands the dioxin levels in cow's milk can contribute largely to the intake of dioxins. Therefore this monitoring programme is continued until now.

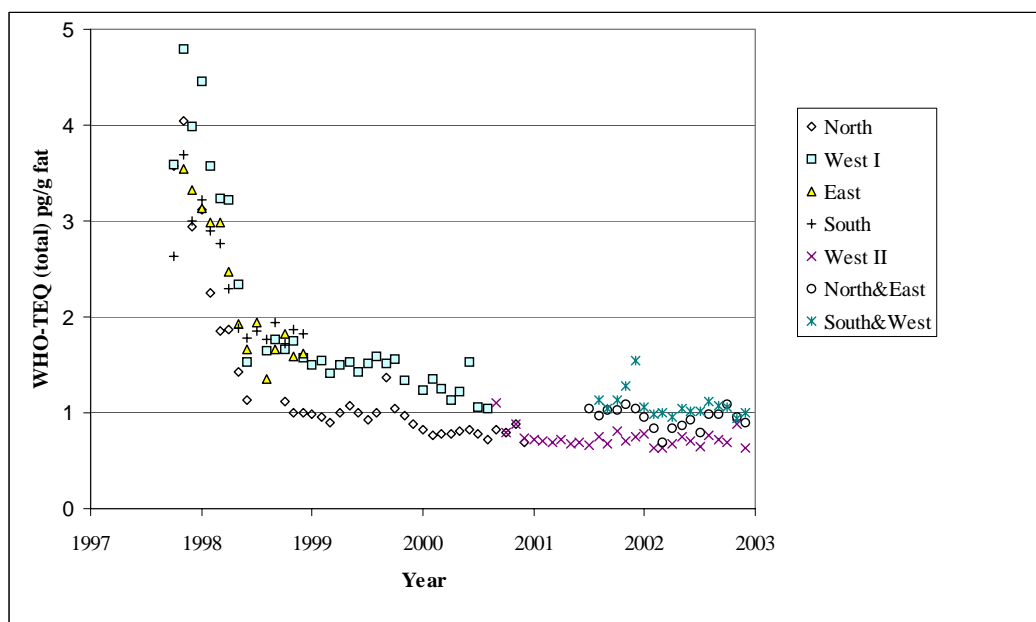
### Methods and Materials

In 1997 the production of consumer milk in the Netherlands was divided over 4 large companies with raw milk originating from the Northern, Eastern, Western and Southern part of the country. The companies from the Northern and Eastern part merged in 1999 and also the companies from the Western and Southern part. Therefore sampling was reduced from 4 to 2 companies. For each consumer milk producing company a carton of one litre of full fat milk is bought from a supermarket every week. The milk from each company is collected during one month and then a monthly-pooled sample is made for each company.

To the test portions, a solution of toluene containing <sup>13</sup>C<sup>12</sup>-labeled internal quantitation standards (Cambridge Isotope Laboratories, Woburn, MA, USA) of the 2,3,7,8-chlorine substituted PCDDs and PCDFs, and non-ortho PCBs 77, 81, 126 and 169 was added at levels between 5 and 30 pg/g of (extracted) fat. <sup>13</sup>C<sup>12</sup>-labeled OCDF was excluded to avoid interference with OCDD analysis. After refluxing, all extracts were evaporated to dryness and the amount of (extracted) fat was weighed to determine the fat content of the original sample. Extracted lipids were redissolved in dichloromethane (5 ml/g of fat) and brought onto the top of a Carbosphere column. Then an Al<sub>2</sub>O<sub>3</sub> clean up, evaporation to dryness and redissolution in 50 µl of toluene took place. GC/MS analyses were performed on a double focussing mass spectrometer coupled to a gas chromatograph. GC separations were carried out on a non-polar column (60 m DB-5MS ; J&W Scientific, Folsom, USA; 0.25 mm ID, 0.10 µm film thickness). Ionisation of samples was performed in the electron impact mode. Instruments were operated at increased resolution. The resolving power (RP) was typically between (static) 3000 and 5000. Detection was performed by selected ion recording.

In every batch of analysis a quality control sample is analysed. Over a period of 10 years the PCDD/F contribution for this sample is 3.54 pg (WHO)-TEQ/g fat with a RSD of 6.0% (n=117) and the non-ortho PCB contribution 3.24 pg (WHO)-TEQ/g fat with a RSD of 6.4% (n=67).

The limit of detection, LOD, is usually 0.1 pg/g fat for each congener. The 2,3,7,8-TCDD is often analysed with a LOD of 0.05 pg/g fat. Despite this low limit of detection still quite some congeners were sometimes not detected. In the results shown here these non-detects are replaced by half the LOD. This approach was shown to give reasonable TEQ estimates for cow's milk TEQ levels<sup>5</sup>.



**Figure 1. Levels WHO-TEQ in monthly-pooled samples consumer milk. To reduce the effects of non detects  $nd=0.5LOD$  is used.**

### Results and Discussion

The congener specific results quite comprehensive and can be found in a detailed report<sup>6</sup>. The TEF values changed in the time period, therefore older measurement results were recalculated using the 1998 WHO-TEF values<sup>7</sup>. Also PCB 81 was added in the time course which however has no notable influence on the TEQ value. Figure 1 shows the sum of WHO-TEQ of the toxic PCDD/Fs and the non-ortho-PCBs. Levels are obviously decreasing over the whole *time range*. Especially the change in levels is large in the 1997- 1998 period. The high level found in the last months of 1997 and the first half of 1998 is most likely due to animal feed prepared with contaminated Brazilian citrus pellets. The effect of this contamination presumably disappeared after 1999. In the years after 1999 a small but consistent decrease still seems to be present. However in the latter period, due to the decreasing levels, the number of results that was below the LOD increases. This decrease correlates with decreasing emissions as achieved especially in the beginning of the 1990's.

The milk producing companies obtained their raw milk from distinctive *regions* in the Netherlands. At first glance the levels in all regions follow the same trend. After a closer look the levels in the North seem to be consistently lower than the levels in the southern part of The Netherlands. A similar North-South gradient is also found in emission calculations and might be

due to the fact that emission control measures were more strongly and/or more early implemented in The Netherlands than in our southern neighbours; Belgium and France. After 2001 the regional difference seems to disappear. This is not surprising since only two major milk producing companies are left which cover such large areas that regional differences might fade out easily. In the time trend some small seasonal variation seems present. Levels in autumn and wintertime slightly exceed the levels in summer and springtime. Such variation was observed earlier and correlates with the assumption that levels in grass vary due to the difference in speed of grass growth.

Next to the total TEQ also a comparison of the relative contribution of the 4 major components is made. Figure 2 shows these contributions for samples from the region North which is later replaced by North-East. Results below the limit of detection are not shown in this plot. Obviously the contribution of the 2,3,7,8-TCDD was highest in 1997 which corresponds with the Brazilian citrus pellet contamination. On the other hand the contribution of PCB-126 gradually increases over the years. This increase is consistent with the strong reduction of particularly the emission of waste incinerators. This might effect levels in PCDD/Fs more strongly than levels in PCBs.

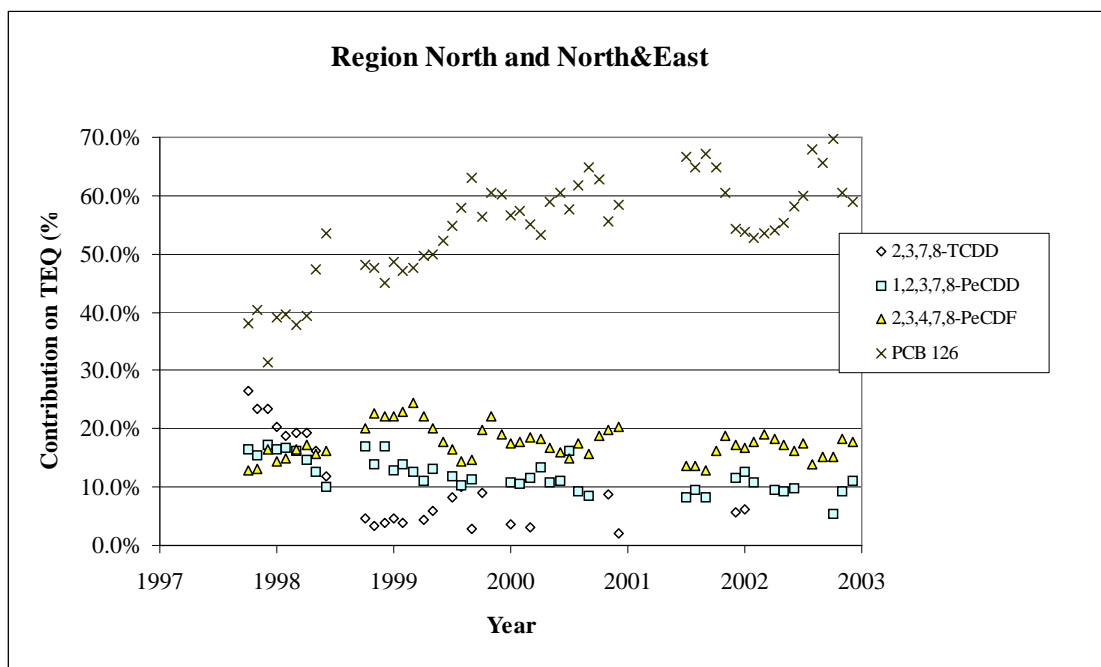
In the contribution of 2,3,4,7,8-PeCDF some seasonal variation seems present because the contribution of this component in the autumn period exceeds the contribution in the summer period. This supports the observation than in contrast to PCB-126 this component is associated with grass which, due to growing speed, is more contaminated in the autumn than in the summer period.

In 1990 the average Dutch intake of PCDD/Fs and non-ortho PCBs due to the consumption of cow's milk and dairy products was 1.3 pg WHO-TEQ kg bw/day (43 % of the total). In 2002 this estimated intake is reduced to 0.25 pg WHO-TEQ kg bw/day. These results show that the Dutch measures to reduce the emissions of dioxins apparently were successful in reducing the dioxin intake.

### **Conclusions**

Dioxin levels in Dutch consumer milk in the period October 1997- March 1998 exceeded levels found in 1992-1993. In the period 1998-2002 a gradual decreasing in the WHO-TEQ is observed. Small regional and seasonal variations were observed. Both seem to fade out towards the end of the analysis period.

The relative contribution of 2,3,7,8-PCDD was large in the 1997-1998 period and then decreased. The relative contribution of PCB-126 gradually increases over the time period.



**Figure 2. Relative contribution of 2,3,7,8-TCDD, 2,3,4,7,8-PeCDD, 2,3,4,7,8-PeCDF, and PCB-126 to the total WHO-TEQ in monthly pooled samples of consumer milk originating from the northern region.**

### References

- 1 Liem, A.K.D., Olie, K., Jong de, A.P.J.M., Theelen, R.M.C., Marsman J.A., Boer den, A.C., Groenemeijer, G.S., Hartog den, R.S., Laar van A., Werken van de, G., Hoogerbrugge, R., Knaap A.G.A.C., Klooster van 't, H.A., Heijden van der, C.A. (1989). Dioxinen en dibenzofuranen in koemelk afkomstig van melkveebedrijven in het Rijnmondgebied en enkele andere lokaties in Nederland, RIVM rapport 748762001, Bilthoven.
- 2 Liem, A.K.D., Hoogerbrugge, R., Kootstra, P.R., Velde van der, E.G., Jong de, A.P.J.M., *Chemosphere* (1991) 23, 1975-1684.
- 3 Cuijpers, C.E.J., Bremmer, H.J., Lucas Luijckx, N.B., Zorge van, J.A., Liem, A.K.D. (1998) *Organohalogen Compounds* 38, 59-64.
- 4 Malisch, R, *Chemosphere* (2000) 40, 1041-1053
- 5 Hoogerbrugge R., Liem A.K.D. *Organohalogen Compounds* (2000) 45, 13-16.
- 6 Baumann, R.A., Boer, A.C. den, Groenemeijer G.S., Hartog, R.S. den, Hijman, W.C. Liem, A.K.D., Marsman, J.A., Hoogerbrugge, R., (2002) Dioxinen en dioxineachtige PCBs in Nederlandse consumptiemelk: trendonderzoek 1997-2001, RIVM rapport 639102024/2002.
- 7 Berg van den, M., Birnbaum, L.S., Bosveld, A.T.C., Brunström, B., Cook, Ph., Feeley, M., Giesy, J.P., Hanberg, A., Hasegawa, R., Kennedy, S.W., Kubiak, T., Larsen, J.C., Leeuwen van, F.X.R., Liem, A.K.D., Nolt, C., Peterson, R.E., Poellinger, L., Safe, S., Schrenk, D., Tillitt, D., Tysklind, M., Wærn, F., Younes, M., Zacharewski, T. (1998). *Environmental Health Perspectives* 106, 775-792.