DIOXIN-LIKE PCB LEVELS IN FEED AND FOOD FROM ACROSS THE EUROPEAN UNION

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Introduction

In their "Community Strategy for Dioxins, Furans and Polychlorinated Biphenyls"[1] the European Commission evaluated the available data base for dioxin-like PCBs as insufficient. Therefore the Commission initiated a study to collect information on concentrations of dioxin-like PCBs in food, feed and in environmental samples on a Europe-wide scale[2]. Analyses of dioxin-like PCBs in food and feed samples from all over Europe was one component of this study.

Materials and methods

Samples have been taken Europe-wide between April and October 2001 on basis of a product oriented approach representing 8 European regions[3]. 231compound samples were prepared from ~2600 individual samples, representing 42 different types of products including meat and meat product (pig lard), milk and milk products, eggs, fish and fish oil, cereals, oil seeds, vegetables, vegetable oils, feedingstuff (oil cakes, compound feedingstuff, green crop), fruits, further plant products and bone- and blood meal . For food analyses only edible parts of the samples were used. Fruits were washed if total fruits were used. Potatoes and oranges were peeled, pips were removed if usually not eaten (apples, olives).

Analysis of dioxin-like PCBs includes the four non-ortho-substituted PCBs (PCB 77, PCB 81, PCB 126, PCB 169) and 8 mono-ortho-substituted PCBs (PCB 105, PCB 114, PCB 118, PCB 123, PCB 156, PCB 157, PCB 167, PCB 189) according to the WHO list[4].

Analysis was based on isomer dilution method using $^{13}C_{12}$ labelled internal standards. Analyses were executed in Oekometric´s laboratory accredited according to DIN EN ISO/IEC 17025. Wet samples were freeze dried. Three basic extraction methods were used for different matrices, cold extraction (mixing of sample with a Na_2SO_4/sea sand (1:1 w:w), extraction with hexane/acetone (2:1 v:v)), liquid/liquid extraction (tert.-butylmethylether/pentane (1:1 v:v)) and soxhlet extraction (toluene, 24 h). Fat content was determined by weight after evaporation of the solvent. For pure fat samples (animal raw fat, oils) fat was dissolved in hexane and was directly given to the cleanup. Cleanup for individual matrices were based on mixed silica column, florisil column, aluminium oxide column and gel permeation chromatography (Bio Beads S-X3) methods.

Measurement of non-ortho and mono-ortho PCBs were performed using high resolution capillary gas chromatography with a DB5-MS GC-column (HRGC) and high resolution mass spectrometry (HRMS) on a Finnigan MAT 95 at a resolution of 5000 – 10000. Usual achievable limits of quantification (LOQ) for the 12 dioxin-like PCBs were 0.03 pg PCB-TEQ/g fat and 0.005 pg WHO-PCB-TEQ/g d.m., respectively.

QA/QC requirements for dioxin-like PCBs were adopted from the dioxin analyses where accepted quality criteria are available[5]. In compliance with these requirements, tolerable recovery ratios were

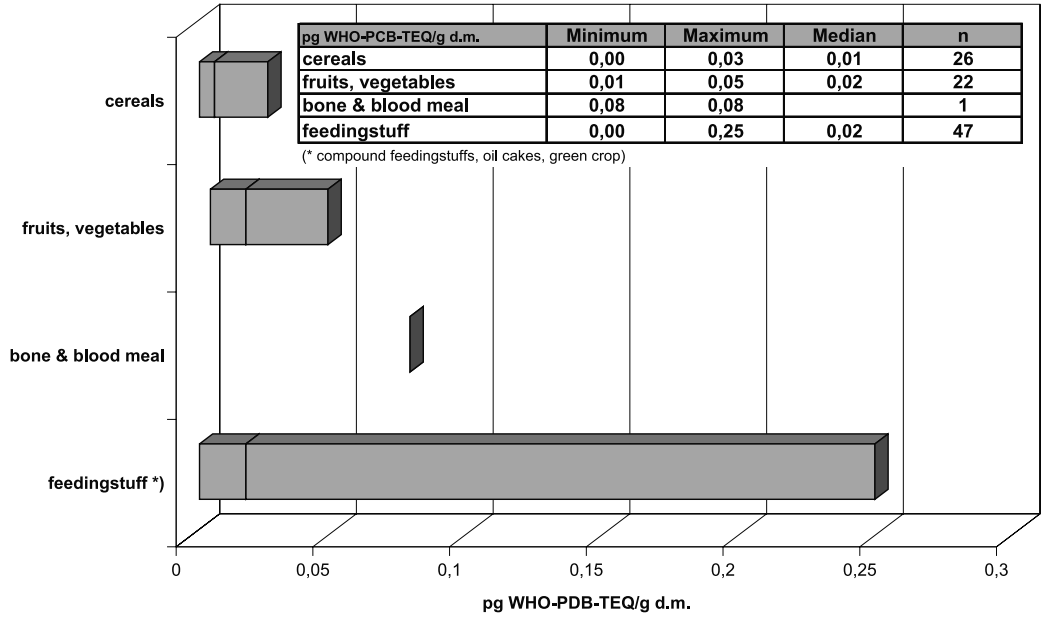

Figure 1. Dioxin-like PCBs in food and feedingstuff samples: dry matter based results (European-wide survey, minimum – median - maximum as WHO-PCB TEQ including LOQ (upper bound levels))

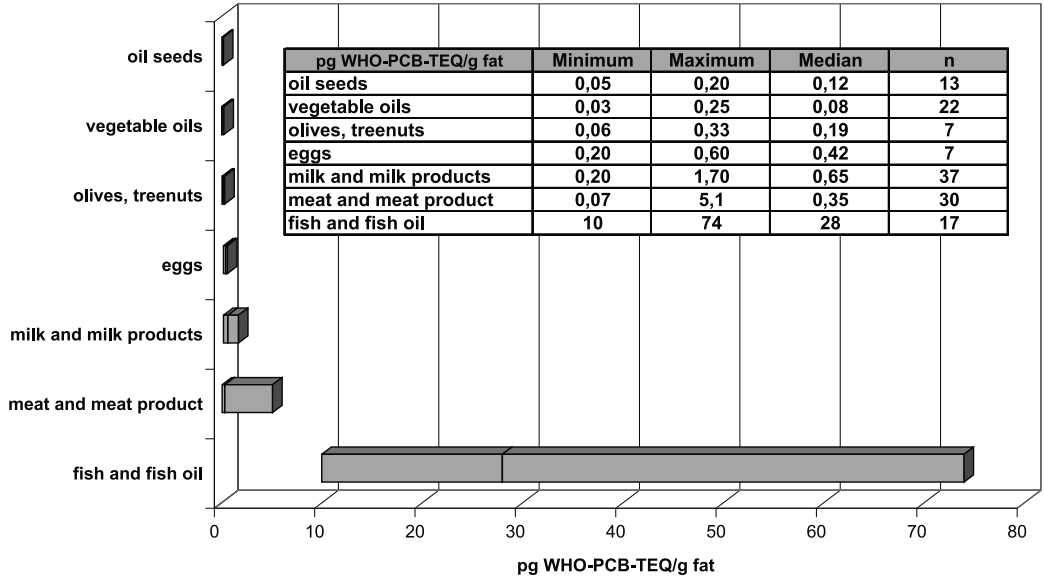

Figure 2. Dioxin-like PCBs in food and feedingstuff samples: fat based results (European-wide survey, minimum – median - maximum as WHO-PCB TEQ including LOQ (upper bound levels))

fixed between 50 and 120 %, respectively. Tolerable deviations of the retention time of the native congeners were accepted if they were within a time window of +3 seconds of the corresponding $^{13}C_{12}$ labelled internal standard. The isotope ratio between the isotopes monitored have to be within +/- 20 % of the theoretical value.

QC protocol included comprehensive blank tests and – as a minimum criteria - individual congener data have to be at least threefold above the corresponding blank to be accepted. Repeated analyses of total samples resulted in an average reproducibility of below 20 %.

Results and Discussion

Results are presented as upper bound levels on a dry weight basis for cereals, feedingstuff, bone- and blood meal, fruits and vegetables (Figure 1) and on a fat weight basis for meat and meat products, milk and milk products, eggs, fish and fish oil, oil seeds, vegetable oils and further fatty plant products (Figure 2).

With respect to the dry matter based samples, all matrices were below the 0.1 pg WHO-PCB-TEQ/ g d.m. level with the exception of some green crop samples included in the feedingstuff category.

Three categories of the tested samples can be qualitatively grouped looking on fat based results:

Vegetable oils, oil seeds, olives, tree nuts	Samples with levels around 0.1 pg WHO-PCB-TEQ/g fat and below 1 pg WHO-PCB-TEQ/g fat
Milk, milk products, meat, meat product, eggs	samples with levels around 0.5 – 1 pg WHO-PCB-TEQ/g fat and below 10 pg WHO-PCB-TEQ/g fat
Fish and fish oil	samples with levels equal or above 10 pg WHO-PCB-TEQ/g fat and below 100 pg WHO-PCB-TEQ/g fat

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References

1. European Commission (2001) Communication from the Commission to the Council, the European Parliament and the economic and social Committee, *Community Strategy for Dioxins, Furans and Polychlorinated Biphenyls*, COM(2001) 593 final, 24 October 2001
2. European POPs Expert Team (EPET) (2002) *Preparatory actions in the field of dioxin and PCBs.* On behalf of the European Commission, Brussels, April 2002
3. Joas R., Potrykus A., Schott R. Hosseinpour J., Rottler H. (2002) Organohalogen Compounds, submitted
4. Van den Berg M., Birnbaum L., Bosveld B.T.C., Brunström B., Cook P., Feeley M., Giesy J., Hanberg A., Hasegawa R., Kennedy S.W., Kubiak T., Larsen J.C., van Leeuwen F.X.R.., Liem A.K.D., Nolt C., Peterson R.E., Poellinger L., Safe S., Schrenk D., Tillitt D., Tysklind M., Younes M., Wærn F., and Zacharewski R. (1998): Environm. Health Persp. 106, 775
5. Malisch R., Baumann B., Behnisch P.A., Canady R., Fraisse D., Fuerst P., Hayward D., Hoogenboom R., Hoogerbrugge R., Liem D., Papke O., Traag W., Wiesmuller T. (2001) Organohalogen Compounds 51, 53