

Polychlorinated Biphenyl (PCB) Contents in Curly Kale Cultures in the Conurbation of Munich, Germany

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1. Introduction

Due to their low combustibility PCB compounds were used in 'closed systems' as fluid transformers and rectifiers, in hydraulic fluids, for heat exchange in cooling circuits and radiators, and in joint sealings^{1,2)}. In 1989 a regulation - "Prohibition of Polychlorinated Biphenyls, Polychlorinated Terphenyls and Limitation of Vinylchlorid"³⁾ - was declared in Germany. But PCB pollution can still originate from diffuse waste-from-the-past emissions. The air path represents the main PCB transfer pathway into plants, which are on the first step of the food chain (only a slight percentage is taken up via soil⁴⁾).

The toxicity of the lipophilic PCB depends on the number and location of the 1 to 10 possible chlorine atoms of the molecule⁴⁾. Toxicological studies have shown that coplanar PCB compounds with structural similarity to 2,3,7,8-congeners of polychlorinated dibenzodioxins and -furans (PCDD/F) exert analog pathological and biochemical effects on humans, e.g. chloracne and edema⁵⁾. Little is known about the occurrence and behaviour of toxicologically relevant coplanar PCB in plant. Therefore PCB toxicity assessment must be restricted to a small number of single congeners: non coplanar congeners PCB 28, PCB 52, PCB 101, PCB 138, PCB 153 und PCB 180 can be detected in vegetation with sufficient analytical sensitivity. For these 6 DIN congeners⁶⁾ carry-over-rates - food to animal fat tissue - were defined⁷⁾. However, scarcely any biomonitoring studie about PCB accumulation in vegetation exists up to now. According to present knowledge only a few institutions have dealt with active biomonitoring of PCB in Germany, e.g. with curly kale^{8,9,10)}.

PCB biomonitoring was performed in 1993 with curly kale cultures at various locations with different densities of development and residential areas (cities - Munich, Dachau, Freising, small housing estates, rural areas) in the conurbation of Munich, Germany. Cultures were analysed for PCB isomer sum concentrations and the 6 DIN congeners to describe the present range of airborne PCB levels in curly kale as a representative for vegetation and to compare the results with other investigations, as far as available. This contribution shows two different ways to characterize total PCB bioaccumulation by certain compounds. Attempting to differentiate local inmission situations, PCB congener patterns are examined additionally.

At the moment PCB pollution in curly kale can be evaluated only indirectly, by comparison

- of location specific bioaccumulation results,
- of pollution results documented in various biomonitoring studies and
- with maximum immission doses (MID).

2. Methods

22 locations were chosen according to different types of immission situations:

- X in the city centre of Munich, surrounded by motor vehicle traffic, tram ways and high buildings,
- C in urban residential areas (C1 - C13) and
- R in small housing estates and rural areas (R1 - R8).

Three of the latter type are also calculated main immission impact points of two waste incineration plants (R3, R5, R7).

After an exposition period of 49 days green leaves with midribs of 2 cultures *Brassica oleracea* var. *acephala*⁽¹¹⁾⁽¹²⁾ at each location were detached and transported in highly purified glass vessels at 4-6°C. After freeze drying und addition of a labelled PCB standard samples were soxhlet-eluated with toluene and purified with chromatographic columns. Curly kale samples were analysed for PCB sum compounds (mono- to decachloro-biphenyls) and the 6 DIN congeners PCB 28, PCB 52, PCB 101, PCB 138, PCB 153 und PCB 180 with a high resolving gas chromatography/high resolving mass spectrometry system⁽⁶⁾⁽¹²⁾⁽¹³⁾. With an analytical detection limit of 0.002 µg/kg dm for the 6 DIN congeners and of 0.02 to 0.1 µg/kg dm for isomer groups mono-, di-, ..., decachloro-biphenyl respectively, all 6 congeners and the di- to octachloro-biphenyls (= isomer sum concentration) could be identified.

3. Results

Total PCB content can be described in different manners: by multiplying the concentrations of 6 selected congeners (DIN congeners) by a factor of 5 (figure 1: black line) or by the sum of all isomer groups identified, here di- to octachloro-biphenyls. The DIN congeners x 5 reveal a somewhat different range of PCB bioaccumulation compared to the isomer sum concentrations (columns in fig. 1) and range about one quarter higher.

A peak content of 110 µg/kg dm di- to octachlorinated isomers and of 31 µg/kg dm x factor 5 respectively was found in curly kale from location X (figure 1) in the city centre of Munich. The other locations show a slight graduation of PCB bioaccumulation, corresponding with the affiliation to urban residential areas or to small housing estates and rural areas. In urban residential areas (C1-11) contents of the 6 DIN PCB congeners range from 7 µg/kg dm to 11 µg/kg dm, at small housing estates and rural areas (R1-8) lower DIN congener contents (5 to 6 µg/kg dm) as well as lower isomer sum concentrations (< 25 µg/kg dm, columns in fig. 1) are documented. Two type C locations with

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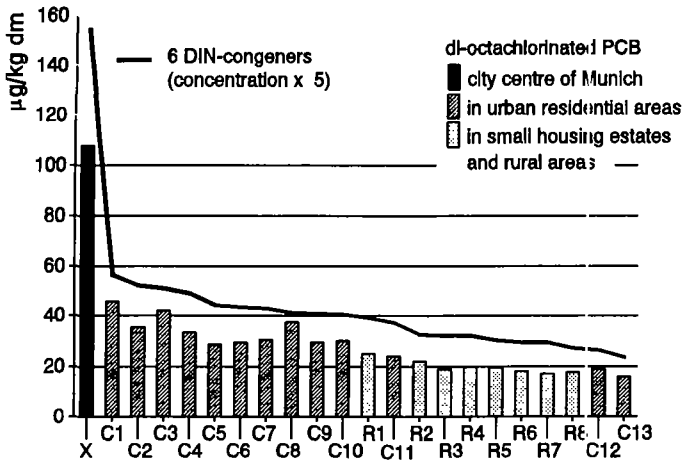


Figure 1: PCB in curly kale 1993; concentration of 6 DIN-congeners x factor 5 in descending location order and concentration of di- to octachlorinated biphenyls (isomer sum concentration) in $\mu\text{g/kg dm}$.

lowest PCB bioaccumulation are located in a fairly new estate of terraced houses (C12; north western part of Munich, outside main wind direction) and in the centre of Freising (C13; with spacious buildings). Low PCB bioaccumulation at R3, R5 and R7 indicates, that waste combustion (two plants in the surroundings of Munich) is no source of PCB.

Comparing the patterns of the 6 DIN congeners in the 22 curly kale samples generally reveals similar results:

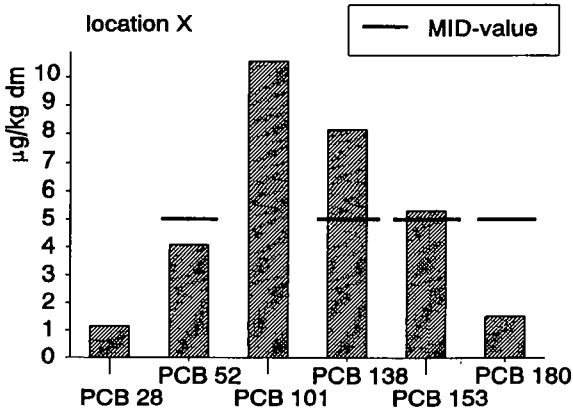


Figure 2: Example of congener pattern in curly kale (6 DIN PCB; $\mu\text{g/kg dm}$): location X

lowest concentrations of PCB 28, followed by PCB 52 and PCB 180 and highest contents of either

PCB 101 > PCB 138 > PCB 153 (figure 2: example location X) or PCB 101 < PCB 138 > PCB 153. However, first investigations do not provide significant patterns, representing typical immission situations. The maximum DIN congener content at location X ranges 4 times higher than the mean PCB bioaccumulation in the conurbation of Munich (compare fig. 1).

Concentrations of PCB 138 (2,2',3,4,4',5-hexachloro-biphenyl) and PCB 153 (2,2',4,4',5,5'-hexachloro-biphenyl) exceed maximum immission doses (MID) for milk cow feed (signed as black bars in figure 2), defined in a German guideline for protection of working animals (VDI-guideline 2310-32⁷⁾; table 1):

Table 1: Comparison of 6 DIN PCB MID values in milk cow feed⁷⁾ and in curly kale 1993 at location X (compare fig. 2)

PCB congener number	28	52	101	138	153	180
MID: milk cow ($\mu\text{g}/\text{kg}$ feed of 88% dm)	100	5	40	5	5	5
PCB congener in curly kale ($\mu\text{g}/\text{kg}$ dm)	1.2	4.1	10.6	8.2	5.3	1.5

4. Discussion

Because of their high persistence¹⁴⁾ PCB can ubiquitously be detected. Sources of PCB pollution seem to be diffuse waste-from-the-past emissions. The examination of 6 DIN congeners in curly kale in the conurbation of Munich provides a weak but plausible location graduation.

At the moment PCB pollution is assessed to be less critical than that of dioxins - although the air concentration level of PCB (there: Tri- to Octa-CB) ranges more than two scales higher than that of dioxins¹⁴⁾. This observation can be supported by the biomonitoring results: PCB in curly kale reaching >15 to $110 \mu\text{g}/\text{kg}$ dm isomer sum concentrations (compare figure 1) and PCDD/F concentrations 60 to $200 \text{ ng}/\text{kg}$ dm¹⁰⁾. HARVEY & STEINHAUER¹⁵⁾ had characterized the atmosphere above conurbations to be more heavily PCB polluted than that above rural areas. HÖPKER¹⁶⁾ described a bioaccumulation gradient in standardized grass cultures of 4 : 1 from conurbations to background. The presented 6 DIN PCB congener concentrations in curly kale range from $5 \mu\text{g}/\text{kg}$ dm - at locations with low building density and in rural areas - to above $10 \mu\text{g}/\text{kg}$ dm - mainly at highly developed locations in the city of Munich (compare fig. 1). A study with curly kale in Reutlingen/Tübingen in 1991 revealed 6 DIN PCB congener contents between 11 and a maximum of $26 \mu\text{g}/\text{kg}$ dm⁸⁾.

On the whole PCB bioaccumulations seem to be rather a local problem, because some urban areas that were object to biomonitoring investigations (e.g. with spruce needles) provided quite uniform PCB concentrations with single peak values⁹⁾. Also in Munich PCB bioaccumulation is projecting at one location: X (figure 1). Despite of the fairly uniform PCB immission situation a blanket description is not possible in general because of potential point sources.

At the moment no threshold values are defined for PCB in biomonitoring plant as representatives of vegetation and feed. Therefore PCB contents in curly kale can contribute to a risk assessment only in an indirect manner:

- by comparison of results from different locations and - as far as possible - of various studies;

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- by comparing them with VDI-guideline MID values for feed, e.g. for milk cows (see table 1).

Possible point sources, as indicated at location X (fig. 1) where two of five congener values exceeded maximum immission doses, should be identified by further investigations.

Ingestion via food represents a decisive pathway for human health risk (incorporation of PCB by inhalation to a smaller degree) and structural similarity of certain coplanar PCB congeners and PCDD/F can lead to analog effects in humans. Therefore it would be important to

- define a standardized set of PCB compounds to be analysed as a matter of routine, e.g. the 6 DIN congeners - especially because DIN congeners x 5 and isomer sum concentrations do not provide analog results,
- design further biomonitoring programs for toxicity assessment and critical value definition,
- and to intensify information exchange.

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