

WHO-PCB-TEQ OF HERBS FROM DIFFERENT ORIGINS

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Introduction

Polychlorinated biphenyls (PCBs) are a group of 209 congeners with different degrees of chlorination (up to ten chlorine atoms). They are man-made, very stable and persistent substances. Since 1929, PCBs have been industrially produced (1) for the utilisation among other purposes as transformer oil, hydraulic fluid and softening agent. PCBs have been found also as contaminants in several industrial chemicals. Since 1989 (2) the production, the import and export or the sale of PCBs is forbidden in Germany. Nowadays PCBs are still ubiquitous pollutants in the environment of most countries (3). This is the reason why it is very probable that also herbs are contaminated with PCBs. Herbs are among other spices ingredients of meat products and are able to contaminate them in detectable amounts if the PCB concentrations are high. In former studies we detected in some meat products considerable amounts of PCB even if below the maximum residue limits (MRL).

Materials and Methods

Material, reagents and samples

¹³C₁₂-labelled PCB standards and the recovery standards (deuterised or ¹³C₁₂-labelled) were purchased from Promochem (Wesel, Germany). Internal standard (50 µl of each standard solution) was added before sample extraction. The analysed herbs were harvested from private and commercial cultivation. The samples were supplemented by herbs from different regions of the world through a spice company.

Extraction

After lyophilisation of the fresh plant material, extraction cells were filled with sample material, drying substance (poly (acrylic acid) - partial sodium salt-graft-poly (ethylene oxide) from Aldrich (Missouri, USA)) and sea sand. Then the extractions were performed by accelerated solvent extraction (ASE 200 from Dionex). For extraction n-hexane was used at a pressure of 100 bar and a temperature of 100 °C. The samples were extracted in two cycles with a static time of ten minutes each.

Clean up

The evaporated extracts were separated from unwanted substances on a gel permeation chromatography (GPC) column with an ID of 25 mm that was filled with 60 g Bio-Beads S-X3 (200-400 mesh), a cross-linked divinylbenzene-styrene copolymer, from Bio-Rad Laboratories (München, Germany). The GPC (Abimed Gilson, Langenfeld, Germany) was carried out with a solvent mixture of cyclohexane-ethyl acetate (1:1; v/v) and a flow rate of 5 ml/min. The extracts which were evaporated again were eluted from Florisil columns (8 ml-SPE columns (ID: 12 mm) filled with 3g Florisil deactivated with 4% water (w/w)) with 60 ml of toluene. After evaporation of the solvent nearly to dryness the samples were dissolved in 1 ml of n-hexane. 8 ml-SPE cartridges with an ID of 12 mm were filled with NaOH-silica and H₂SO₄-silica. The sample extracts were eluted with 60 ml of n-hexane. To divide the extract (concentrated to a volume of 1 ml) into two fractions, a chromatography on activated charcoal followed. In the first fraction (20 ml n-hexane/toluene; 99:1; v/v) the di- and mono-ortho-substituted PCBs and in the second fraction (20 ml n-hexane/toluene; 75:25; v/v) the non-ortho-substituted PCBs were collected. The first fractions were concentrated to about 100 µl and the second fractions were concentrated about 15 µl. After adding recovery standard the samples were analysed by GC-MS.

Instrument and method

The GC-HRMS system used was a Hewlett-Packard 5890 series II gas chromatograph (Hewlett-Packard, Germany) with an injection in split/splitless mode and combined with a VG Autospec Micromass (Manchester, UK) high resolution mass spectrometer. A ZB-5ms column (ID = 0.25 mm, film thickness = 0.25 µm, 5% polysilarylene, 95% polydimethylsiloxane) from Phenomenex (Torrance, USA) with a length of 60 m was used. The GC program for the PCB measurement was as follows: 70 °C (2 min) to 180 °C (0 min) at 30 °C/min, to 290 °C (0 min) at 5 °C/min and subsequently at 20 °C/min to 320 °C, then maintained for 10 min at 320 °C. PCBs were measured working in the electron impact (EI) positive ion mode with an electron energy of 35 eV, the source temperature was set at 250 °C. Data was recorded in SIR mode.

Results and Discussion

The analysed herbs were harvested from five different private and commercial places in Germany and obtained from a company. Their sources of origin were Germany, France, Peru, China and Egypt. Among other varieties following species could be analysed: parsley, chive, lovage, thyme, oregano and marjoram. More than hundred samples were analysed.

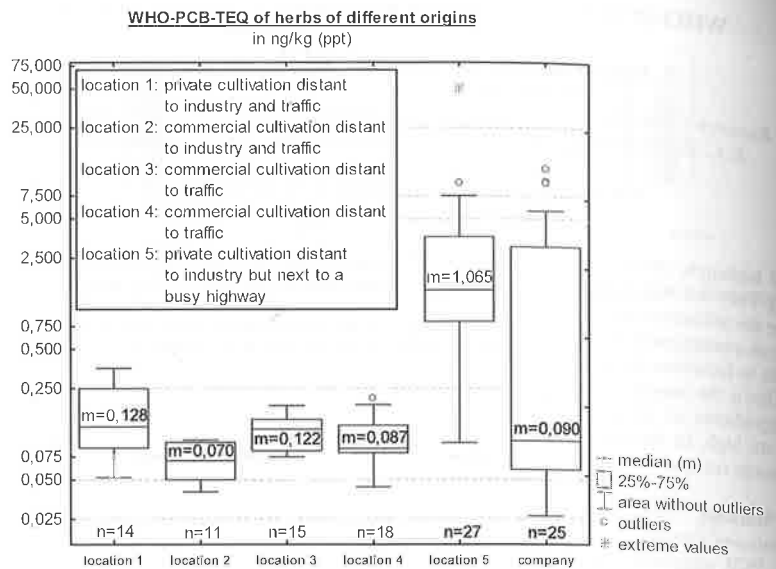


Figure 1: Comparison of WHO-PCB-TEQs in herbs from different cultivation locations in ppt (logarithmic representation) presented as box-whisker-plots.

Comparing the WHO-PCB-TEQs of the herbs in relation (Figure 1) to the different cultivation regions it is important to know the position of the cultivation field. The first four locations including one private and three commercial cultivations of herbs are areas with approximately no contact to any exhaust fumes from industry or traffic. This is the likely reason for the low medians and the small variation of the WHO-PCB-TEQs of these herbs (between 0.070 and 0.128ppt). In the case of location 5 the field for cultivating of the herb are very near to a busy highway. Despite a high distance to industrial areas the contamination of the herbs with PCBs on this location is very high. A median of 1,065ppt (WHO-PCB-TEQ) was measured. With this knowledge it is not surprising that herbs from the company with spices from many countries show a big variation in the measured WHO-PCB-TEQs but with a median of 0.090ppt. Combining all results for all analysed herbs a median of 0,123ppt arises for the WHO-PCB-TEQs.

Conclusions

18 PCBs with a toxicity equivalence factor were analysed for more than hundred herb samples. Most of the herbs have a low contamination with PCBs. Despite the long ban of PCB production (since 1989) traffic near the herb field enhances the PCB contamination by a factor of about ten.

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