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Polychlorinated biphenyls in the surrounding of an e-waste recycling facility in North-Rhine Westphalia: Levels in plants and dusts, spatial distribution, homologue pattern and source identification using the combination of plants and wind direction data

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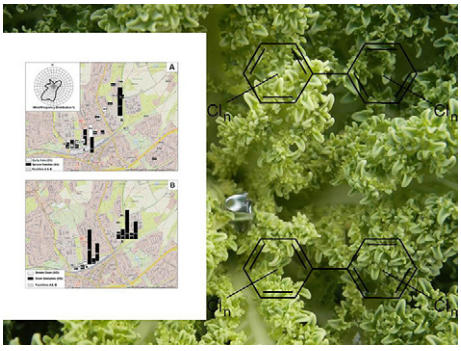
HIGHLIGHTS:

- Bioindicators (curly kale and spruce needles) have been found a valuable and naturally available passive sampler for PCBs
- A stepwise identification of a PCB emission source was successful
- Simple multiple linear regression enabled the calculation of source specific accumulation constants

GRAPHICAL ABSTRACT



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ABSTRACT

During this study the occurrence of polychlorinated biphenyls (PCBs) in the surrounding of an e-waste recycling facility in North-Rhine Westphalia was analysed. PCB levels were analysed in curly kale, spruce needles, street dusts and dusts. Conspicuously high PCB concentrations in curly kale and spruce needles were found directly northwards of the industrial premises. Furthermore a concentration gradient originating from the industrial premises to the residential areas in direction southwest to northeast was evident. Homologue patterns of highly PCB contaminated dusts and street dusts were comparable to the homologue patterns of PCB in curly kale and spruce needles. This corroborates the suspicion that the activities at the e-waste recycling facility were responsible for the elevated PCB levels in curly kale and spruce needles. The utilization of multiple linear regression of wind direction data and analysed PCB concentrations in spruce needles proved that the e-waste recycling facility caused the PCB emissions to the surrounding. Additionally, this evaluation enabled the calculation of source specific accumulation constants for certain parts of the facility. Consequently the different facility parts contribute with different impacts to the PCB levels in bioindicators.

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1. Introduction

In the last decades the environmental fate and widespread distribution of persistent organic pollutants (POPs) like polychlorinated biphenyls (PCBs) raised major concern due to their physico-chemical properties to accumulate in mammalian tissue and of their toxic character [van den Berg et al. 1998 and 2006; IARC, 2016]. PCBs describe a group of chlorinated hydrocarbons that comprises 209 individual congeners. Congeners that exhibit the same number of chlorine substituents at the biphenyl backbone are known as homologues. PCBs were purposefully produced in huge industrial scale for diverse fields of application. On the one hand PCBs were used in closed applications, e.g. in transformers, capacitors or electric motors and on the other hand in open applications as additives, e.g., in sealing materials, paints or hydraulic oils. In the late 1960s the first serious health effects became clear after the consumption of PCB contaminated rice in Yusho, Japan and consequently strict regulations and prohibitions for the handling of PCBs were introduced [Maguda and Yoshimura, 1984]. In Germany the use of PCB in open applications was prohibited in 1978 followed by a total stop of PCB production in 1989 [Verbot des Inverkehrbringens von PCB, 1978; Verordnung zum Verbot, 1989]. Furthermore PCBs were listed in the protocol of the Stockholm Convention on POPs [Stockholm Convention on Persistent Organic Pollutants, 2009] at international level. At eco-toxicological point of view PCBs are known for their persistence an ubiquitous distribution in the environment, bioaccumulation in the fatty tissue of living organisms and the ability to undergo long-range transport.

Nowadays one might assume that due to those regulations less environmental harm occurs from PCBs in developed countries. However, the identification of a secondary source of PCBs in the harbour area of Dortmund, North-Rhine Westphalia based on bioindicators (e.g. curly kale) can be mentioned as an excellent example from the recent past in Germany [Bruckmann et al., 2011]. Not only during this study bioindicators were used to show their great potential to indicate environmental pollution [Franzaring and van der Eerden, 2000; Lehndorff and Schwark, 2004; Rappolder et al., 2007; Rodriguez et al., 2010]. Semivolatile organic compounds can be accumulated by plant species on different pathway. The main route of accumulation can be seen in atmospheric deposition processes or the uptake via the gas phase and plant surface interaction, whereas the transport via the plants root system can be neglected in the first instance [Welsch-Pausch et al., 1995; Brorström-Lunden and Löfgren, 1998; Kaupp and McLachlan, 1999].

Therefore the first aim of this study was to present PCB levels, spatial distributions and homologue patterns of PCBs in bioindicators (curly kale [*Brassica oleracea* acephala 'Reflex'] and spruce needles [*Picea abies*, *Picea omorika*]) from the residential areas in the surrounding of an e-waste recycling facility as well as PCB levels and homologue patterns in street dust and dust samples taken from the surrounding of the recycling facility as well as from the premise, respectively.

The main objective of this study was to use some of those one year old spruce needles for the identification of PCB sources in the study area (Essen-Kray). Concurrently we want to demonstrate that the combination of PCB concentrations in spruce needles and wind direction data enables a suitable estimation for the wind direction sectors that mainly transport PCBs to the plants surfaces. Hereby, we considered that the PCB concentration in spruce needles is proportional to the gaseous ambient air PCB concentration as well as the PCB accumulation constants, and hypothesized that I) short-term PCB accumulation constants are dependent on the wind-direction, II) meteorological conditions (e.g. humidity, precipitation) are the same for all stations and need not be incorporated for the calculation of the source specific PCB accumulation constants and III) the spruce needle sampling points are that near to the possible emission source that the distance to the emission source does not influence the PCB accumulation rate in spruce needles.

2. Experimental

2.1. Chemicals and reagents

All chemicals were analytical grade and purchased from Merck (Darmstadt, Germany). The solvents for extraction and clean-up were picograde for residue analysis and purchased from LGC Promochem (Wesel, Germany).

Alumina and silica were purchased from MP Biomedicals GmbH (Eschwege, Germany). All $^{13}C_{12}$- and native PCB standards were purchased from Cambridge Isotopes Laboratories (Andover, USA). The contribution of isotope labelled standard mixed used for all extractions during this study can be taken from the Supporting Information.

The extraction of the curly kale and spruce needle samples was based on an initial weight of 10 g and performed by Soxhlet extraction with toluene. Prior to extraction isotope labelled standard was added.

A Dionex ASE 200 system (Sunnyvale, USA) and toluene [Klees et al., 2013] were used for pressurized liquid extractions of street dust and dust samples. 1 g of the material was extracted.

After extraction all sample extracts were subjected to a clean-up procedure to eliminate interfering co-extracted matrix components from the crude sample extract. Multi-layer solid phase chromatography with silica modified with either H_2SO_4, NaOH or $AgNO_3$ was applied as the primary clean-up step. Subsequently applied to a basic alumina column (MP Alumina B – Super I, MP Biomedicals, Eschwege, Germany) for the separation of PCBs and PCDD/PCDFs. For the separation of indicator PCBs and mono-ortho PCBs from non-ortho PCBs a second alumina column was applied. Further details of the clean-up procedure can be taken from the literature [Klees et al., 2013 and 2015b].

For the analysis of the indicator PCBs #28, #52, #101, #138, #153, #180 and the dioxin-like PCB congeners #123, #118, #114, #105, #167, #156, #157, #189 gas chromatography coupled to mass spectrometry was used (System 1: TRACE 1310 GC with a CTC Pal RSH autosampler and a TSQ 8000 Evo mass spectrometer (MS/MS) [Thermo Fisher Scientific, Dreieich, Germany]; System 2: GC 6890N with an autosampler model 7683 and a low resolution mass spectrometer (LRMS) 5973N [Agilent, Santa Clara, USA]). The mono-ortho PCB congeners #77, #81, #126, #169 were analysed using a GC model 6890 Series 2 (Agilent) with a CTC HTX PalPlus autosampler and a high- resolution mass spectrometer (HRMS) (model DFS; Thermo Fisher Scientific, Bremen, Germany). The GCs were equipped with a DB-5 column (J&W) (50 m; 0.20 mm I.D.; 0.11 μm film thickness).

2.2. Quality assurance

A five-point calibration was performed, which was checked for variation within each analytical batch run by measuring a calibration standard with a defined concentration level. During the analysis of each sample the recoveries of the single $^{13}C_{12}$-PCB-quantification standards were monitored. Recoveries were ranging between 34 ± 14% and 72 ± 11%, 53 ± 27% and 96 ± 50%, 46 ± 9.2% and 97 ± 6.2% in street dust and dust, spruce needles and curly kale.

Method blanks were systematically checked. During this study concentration data were not blank corrected. For LRMS and HRMS analysis limits of detection (LODs) for the indicator and mono-ortho PCBs analysed and for the non-ortho PCBs were established to be three times the baseline noise. For MS/MS we followed the approach for analytical criteria for the determination of PCBs in feed and food for the limits of quantification (LOQ) [Kotz et al., 2012]. Here we determined the lowest concentration point of our calibration that gives an acceptable (≤30%) and consistent deviation to the slope of the calibration curve. Specific LODs or LOQs can be taken from the Supporting Information. The laboratory routinely analyses standard reference materials for the monitoring of the laboratories' quality. A comparison with standard reference materials for PCBs is routinely performed by our institute [Klees et al., 2015a and 2015b].