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Trends of PCDD/F and PCB concentrations and depositions in ambient air in Northwestern Germany

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HIGHLIGHTS

- Time series of PCDD/F concentrations in ambient air and depositions are presented.
- PCB concentrations in ambient air decay only slightly.
- Half-lives for PCDD/F and for the sum of the six indicator PCB could be calculated.
- Removal of PCDD/F and PCB in the atmosphere is slowed down by secondary emissions.
- Input of PCDD/F via the air path will continue for another decade in conurbations.

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ABSTRACT

Time series of polychlorinated dioxins and furans (PCDD/F) and polychlorinated biphenyls (PCB) in ambient air of a large conurbation in North-Western Germany are presented and analyzed. The trend of PCDD/F concentrations, starting from as early as 1988, shows a pronounced decrease by at least one order of magnitude, demonstrating that the emission reductions were effective. The PCDD/F depositions also have decreased by a factor of 5 since 1992. However, both trends have leveled out since 2005. Time series of PCB concentrations and depositions starting in 1994 show only slight decreases for the concentrations and almost no decrease for the depositions. From the decay rates following first order kinetics, half-lives in the order of 5-15 years for the PCDD/F and 15-31 years for the sum of the six indicator PCB could be calculated, which are much longer than the half-lives estimated from their reactivity towards the OH radical. Apparently, small fresh emissions (PCDD/F), considerable secondary emissions and evaporation from contaminated soils slow down their decay in the atmosphere of big conurbations. Analyzing the decay rates of individual PCB congeners shows that the lower chlorinated and more volatile ones are removed faster than the higher chlorinated congeners, probably via gas phase reactions with the OH radical. It can be concluded from the present study that the input of PCDD/F and PCB into the food chain via the air path will continue for another one or two decades in big conurbations.

1. Introduction

The high toxicity of polychloriated dibenzodioxins (PCDD) and dibenzofurans (PCDF) (Safe, 1990) has given rise to comprehensive regulations to control their emissions. Particularly the introduction of a strict emission limit of 0.1 ng m^{-3} I-TEQ (toxic equivalents (NATO CCMS, 1988)) in 1990 for waste incineration plants (Siebzehnte Verordnung, 1990), in European waste incinerators (Directive 2000/76/EG, 2000) and for industrial installations, such as sintering plants in 2002 (Technische Anleitung zur Reinhaltung der Luft nach BImSchG, 2002) has effectively reduced their emissions by more than one order of magnitude. Taking the emission inventory in Northwestern Germany (state of Northrhine-Westphalia) as an example, the annual emissions of industrial sources decreased from 136 g I-TEQ in 1996 to 13 g I-TEQ in 2008 (LANUV NRW, 2012).

Also polychlorinated biphenyls (PCB), which were produced since 1929 for various technical applications, were strictly regulated when serious health effects became apparent in 1968 after the consumption of polluted rice oil in Japan, causing the Yusho disease, and in 1979 in Taiwan, becoming known as Yu Cheng disease (Chen and Hites, 1983; Maguda and Yoshimura, 1984). Estimated quantities produced and distributed in Germany since 1929 amount to 24 000 tons for open applications, such as paints, sealing material or small capacitors in household goods, and to 59 000 tons for closed applications such as large condensers and transformer stations. The application in open technical systems

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was prohibited in 1978 in Germany (Verbot des Inverkehrbringens von PCB, Zehnte Durchführungsverordnung, 1978), and the production of PCBs came to an end in 1988 (Verordnung zum Verbot von polychlorierten Biphenylen, polychlorierten Terphenylen und zur Beschränkung von Vinylchlorid, 1989). Internationally, PCBs were regulated in 2001 by the Stockholm convention on persistent organic pollutants (2001).

Due to the regulations, one might assume that PCBs, PCDDs and PCDFs no longer pose a danger to the environment, as "fresh" emissions would be greatly reduced (PCDD/Fs) or stopped (PCBs). However, the European thresholds, fixed for dioxins, furans and coplanar PCBs in meat, fat and eggs (European Commission, 2006 and European Commission, 2011), are still exceeded at times (EG/1259/2011 and EG/1881/2006), even if a direct contamination of fodder or high PCDD/F or PCB levels in the ground can be ruled out. This is predominantly the case for livestock and chickens kept outdoors in or near big conurbations. In particular, coplanar PCBs addition to TEQ values exceed these thresholds. It appears that the background pollution in densely habitated areas is still sufficient to give rise to exceedances of European thresholds for consumer protection in meat and fat.

Besides contaminated sediments adjacent to and along rivers or locally by effluents from landfills or other contaminated material brought into the soil, previous and present concentrations and depositions of chlorinated compounds in ambient air are an important input route into the environment. Trends extending over two decades would shed some light on the following questions:

Is the significant decrease of emissions (PCDD/F) or the halt in the production (PCBs) reflected by the trends, and have the abatement measures been successful?
Do concentrations and depositions decrease further or is there an ongoing input into the environment via the air path and what are the current lifetimes?

Trends in dioxins and furans in ambient air (Katsoyiannis et al., 2010) and other media (Lead et al., 1996; Green et al., 2001) have been studied in several countries mostly at rural sites in the framework of the EMEP programme (Lead et al., 1996; Green et al., 2001; Katsoyiannis et al., 2010). One of the longest time series in ambient air beginning in 1991 at six sites in the UK (3 urban, 3 rural/semi-rural sites) showed an exponential decay with atmospheric half-lives between 3.2 and 5.9 years, whereas at rural sites there was no discernible change since 1996 (Katsoyiannis et al., 2010). At the same sites in the UK, also temporal trends for polychlorinated biphenyls (PCB) starting in 1991 were measured (Schuster et al., 2010). They found an average half-life, averaged over the 6 indicator PCBs (Ballschmiter and Zell, 1980), of 4.7 years in ambient air. Extending the measurements to 6 remote locations in Norway and 5 rural or remote stations in the UK, an average lifetime of 8.4 years has been reported (Schuster et al., 2010).

Trends for 83 polychlorinated biphenyl congeners since 1990 were also investigated at several sites near the North American Great Lakes (Venier and Hites, 2010). The concentrations of the PCBs in air decreased with an overall half-life of 17 ± 2 years. The authors concluded that this remarkably slow decay after the banning of the compounds over 30 years ago is probably due to large amounts of PCBs in transformers, capacitors and other electrical equipment and in storage and disposal facilities that are slowly leaking into the atmosphere. More recently, half-lives of about 8 years for the PCB-18 congener and >50 years for the PCB-52 congener were determined from measurements in Chicago, whereas at the remote site Eagle Harbour, the half-lives were about 10 years (PCB-18) and 18 years (PCB-52), respectively (Venier et al., 2012). Long-term trends for PCB patterns PCB-28, 101, 153 and 180 from 1950 to 2010 have been reviewed and studied on a continental and intercontinental scale using a global atmosphere–ocean general circulation model, considering atmospheric long-range transport (Stemmler and Lammel, 2012; Lammel and Stemmler, 2012). A downwind shift of the burden maxima in terrestrial compartments (soil and vegetation) is observed with regard to the westerlies for Eurasia (but interestingly upwind for North America, due to other peculiarities) and always northwards in the northern hemisphere in the sense of a global distillation and more pronounced for the lighter PCBs with less Cl substituents (Stemmler and Lammel, 2012). Inter-continental transport from Eurasia was found to account largely for the contamination of Alaska and British Columbia.

As atmospheric lifetimes are a complex result of primary and secondary emissions and sink processes such as deposition and immobilization on the ground or decay in the atmosphere, they depend on proximity to major source areas. Trends in densely industrialized and inhabitated areas close to sources are not confounded by long range transports and show the effects of reduction measures more distinctively. On the other hand, present input into the environment by diffuse sources may slow down the apparent decay of the persistent chlorinated compounds. To get as complete an overview as possible, time trends from various locations (remote ones and near to sources) are therefore needed.

In this work, we report on long term series for dioxins, furans and PCBs in the densely habitated Rhine-Ruhr conurbation in Northwestern-Germany. Measurements (annual means) of dioxin and furan concentrations started already in 1988 at four sites, making this trend one of the longest available to our knowledge.

2. Materials and methods

2.1. Sampling of concentrations and deposition

Ambient air samples (approximately 1000 m^3) were collected monthly in accordance to VDI 3498-1 (07.2002) at the sampling sites described in Section 3.1 for the determination of PCB and PCDD/F. As sampling and analysis include the particulate as well as the gaseous phase, the concentration measurements are not influenced by gas particle partitioning. The particulate phase was sampled on a fibreglass filter (GFF) and the gaseous phase on two polyurethane foams (PUF). The sampling period consisted of 1 month each with a sampling rate of 2.2 $m^3\ h^{-1}$ and sampling intervals of 40 min per hour. After sampling, the GFFs and the PUFs were stored at laboratory conditions until analysis.

Deposition samples (bulk deposition) were collected in accordance to VDI 2090-1 (01.2001). Six suitable glass jars were positioned at each sampling site and collected monthly. After sampling, the covered glass jars were stored at laboratory conditions until analysis.

2.2. Analysis

The Soxhlet extracts were subjected to a cleanup procedure. Following DIN EN 1948-2 (06.2006), multi-layer solid phase chromatography with silica modified with H_2SO_4, NaOH and $AgNO_3$ as reaction agents were applied as primary clean-up step. The filled chromatography column was pre-washed with n-hexane before the sample was applied to this column. The elution of the analytes of interest was performed with n-hexane. The eluate was concentrated to 5 mL via rotary evaporation. Subsequently, a basic alumina column was used for the separation of PCB and PCDD/F. To that end alumina was packed into a chromatography column. Sodium sulfate was added on top of the alumina layer. A fraction of n-hexane was discarded before the PCB fraction got eluted by toluene. PCDD/F were eluted using 1:1 (v/v) n-hexane/dichloromethane. The PCB fraction was subsequently separated into two