AMBIENT AIR MONITORING OF 4,4'- AND 2,4'-DDT/DDE/DDD IN RURAL DISTRICTS OF GERMANY 2012–2013

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Introduction

DDT (**d**ichloro-**d**iphenyl-**t**richloroethane) is a legacy insecticide whose usage in agriculture and forestry was globaly banned within Stockholm Convention because of its PBT properties in 2004. Its application for vector control of leishmaniasis and malaria is further allowed until effective alternatives are developed. Also the application as precursor for the syntheses of dicofol (2,2,2-trichloro-1,1-bis-(4-chloro phenyl)ethanol), an acaricide against mites and ticks, continues[1].

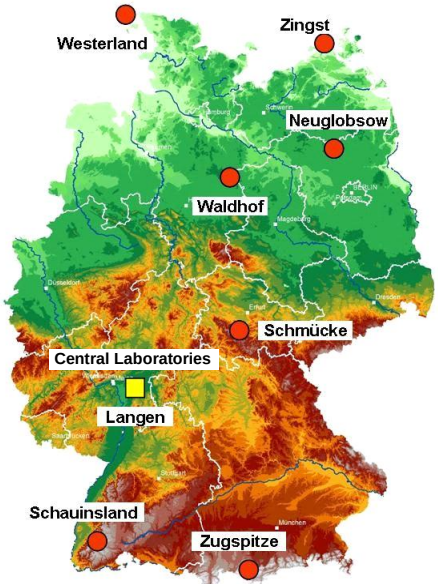

Figure 1: UBA air monitoring network[7]

In Western Germany (former Federal Republic of Germany) DDT production and application was already banned in 1972. In Eastern Germany (former German Democratic Republic) DDT delivery for agriculture and forestry was stepwise reduced from 1972 to 1989. But in 1983/1984 about 600 t DDT were aerially sprayed to control the nun moth (*Lymantria monacha*), a forest pest which especially affected the pine forests[2].

In technical DDT different isomers and byproducts were analysed: 4,4'-DDT (77.1%), 4,4'-DDE (4%), 4,4'-DDD (0.3%), 2,4'-DDT (14.9%), 2,4'-DDE (0.1%), 2,4'-DDD (0.1%) and other byproducts (3.5 %)[3].

The half-live of 4,4'-DDT in soil was estimated at 20 to 30 years in moderate climate zones[4]. The main metabolites formed by dehydrochlorination are 4,4'-DDE and by reductive dechlorination 4,4'-DDD. Therefore 4,4'-DDE is the dominating metabolite in forst soil[5] and 4,4'-DDD in suspended particulate matter of rivers[6].

Potential sources of DDT and its metabolites to the atmosphere today are emissions from historic deposits and long-range transport from countries where DDT ist still used for vector control of tropical deseases or as precursor for chemical syntheses.

Table 1: Background air monitoring stations for PAH, PCB and OCP

Station Name	Location	Station Type	Altitude [m]	Latitude	Longitude
Westerland	North Sea	Coast	12	54 55 32 N	8 18 35 E
Zingst	Baltic Sea	Coast	1	54 26 0 N	12 44 0 E
Waldhof	Lueneburg Heath	Flatland	74	52 48 8 N	10 45 34 E
Schmücke	Thuringian Forest	Mid-range Mountain	937	50 39 0 N	10 46 0 E
Schauinsland	Black Forest	Mid-range Mountain	1205	47 54 53 N	7 54 31 E

Materials and Methods

The DDT data are part of a monitoring of PAH, PCB and OCP in precipitation (monthly wet only samples since 1996) and air (since 2006) at up to five monitoring stations in rural districts of Germany (Figure 1 and Table 1)[8].

Sampling is carried out with high volume samplers (Digitel DHA-80 modified by Riemer) with a constant sampling rate of 30 m³/h, every 6 days for 24 h, resulting in a monthly sample volume of 3600 m³. The pollutants are trapped on glass fibre filter (Macherey-Nagel MN 85/90 BF Ø 15 cm) and polyurethane foam (ORBO-2000 PUF cartridge Ø 6 cm x length 7.6 cm, Supelco).

The samples were pooled on a monthly basis (5 filters+5 PUF), spiked with the extraction and clean-up standard mixture (5 ng PCB and OCP) and extracted by pressurized solvent extraction (Dionex ASE-350). The extracts were cleaned by a two column clean-up (1. Multi-layer Alumina Act. II/Silica 2. GPC EnviroSep-ABC), spiked with the recovery standard (10 ng $^{13}C_{12}$-PCB 105) and reduced to 100 µl.

1 µl was injected on-column (guard column 2 m x 0.32 mm, uncoated, deactivated) and analysed by GC/HRMS using a DB-XLB (60 m x 0.25 mm, 0.25 µm). The two most intense masses of the chlorine cluster were measured for each compound. The identification was based on retention time and correct isotope ratio for both fragments recorded. All compounds were quantified based on their corresponding ^{13}C-labeled analogues used as internal standards.

Field blanks (5 filters+5 PUF) taken in August 2013 at all monitoring stations were spiked, extracted and clean-up processed like air samples. Blank concentrations were calculated for an assumed air volume of 3600 m³. The method detection limit was determined from the mean concentration in the blank plus three times the standard deviation.

Results and Discussion

The annual mean concentrations 2012–2013 of ∑DDT (4,4'/2,4'-DDT+DDE+DDD) at five air monitoring stations in rural districts of Germany vary widely from 2 to 43 pg/m^3 (median 9 pg/m³ in 2012 and 18 pg/m³ in 2013) (Figure 2). Highest concentrations were analysed at the Baltic Sea station Zingst, lowest at the Black Forest mountain station Schauinsland. The Zingst value reflects the large-area application of DDT in forestry in the years 1983/1984, mountain Schauinsland is located most of the year above the inversion layer of the upper Rhine valley.

The ratio of 4,4'-DDE/4,4'-DDT (blue line in Fig. 2) shows a decreasing trend from west to east (Schauinsland not included) indicating metabolisation of 4,4'-DDT to 4,4'-DDE is already further advanced in Western than Eastern Germany.

4,4'-DDE is most abundant in ambient air with 44–61%, whereas the original insecticide 4,4'-DDT only counts for 16–32%. This is not surprising given the high vapor pressure of 4,4'-DDE among the DDT-related compounds. 2,4'-DDT contributes for only 11–18%, 4,4'-DDD for 1–3%, 2,4'-DDE for 2–5% and 2,4'-DDD for 1–7% (Figure 3).

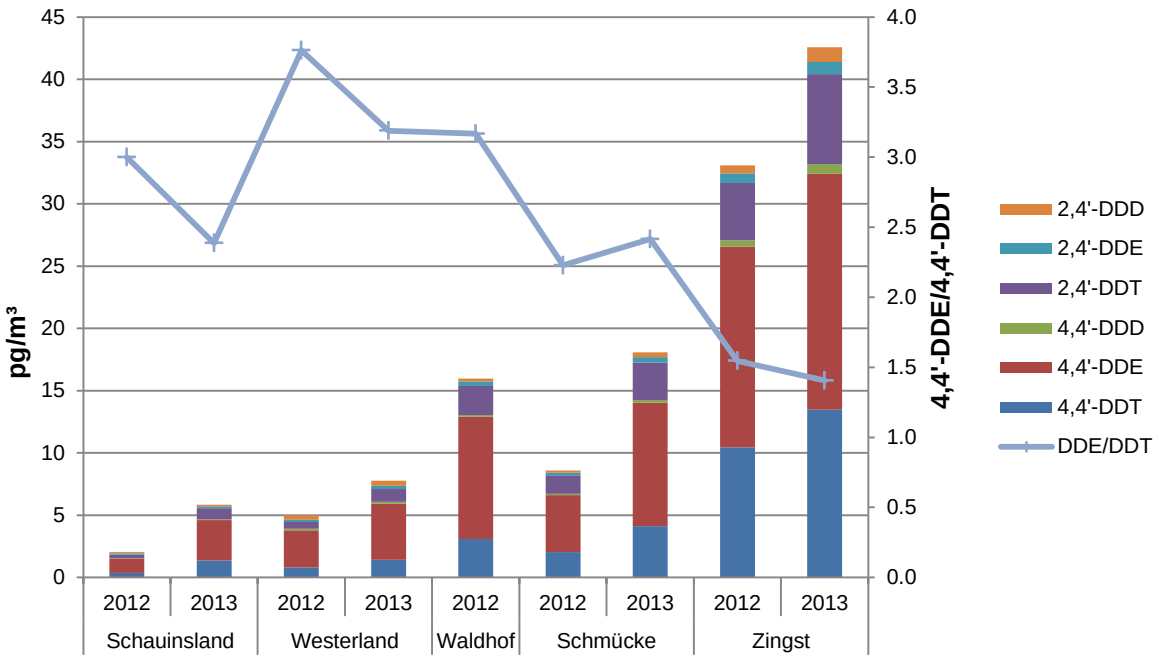

Figure 2: Annual mean concentrations 2012–2013 of ∑DDT (4,4'/2,4'-DDT+DDE+DDD) in ambient air in Germany (stacked bars) and ratio of 4,4'-DDE/4,4'-DDT (blue line). In Waldhof sampling started in February 2012 and analysis of 2013 samples is still in progress

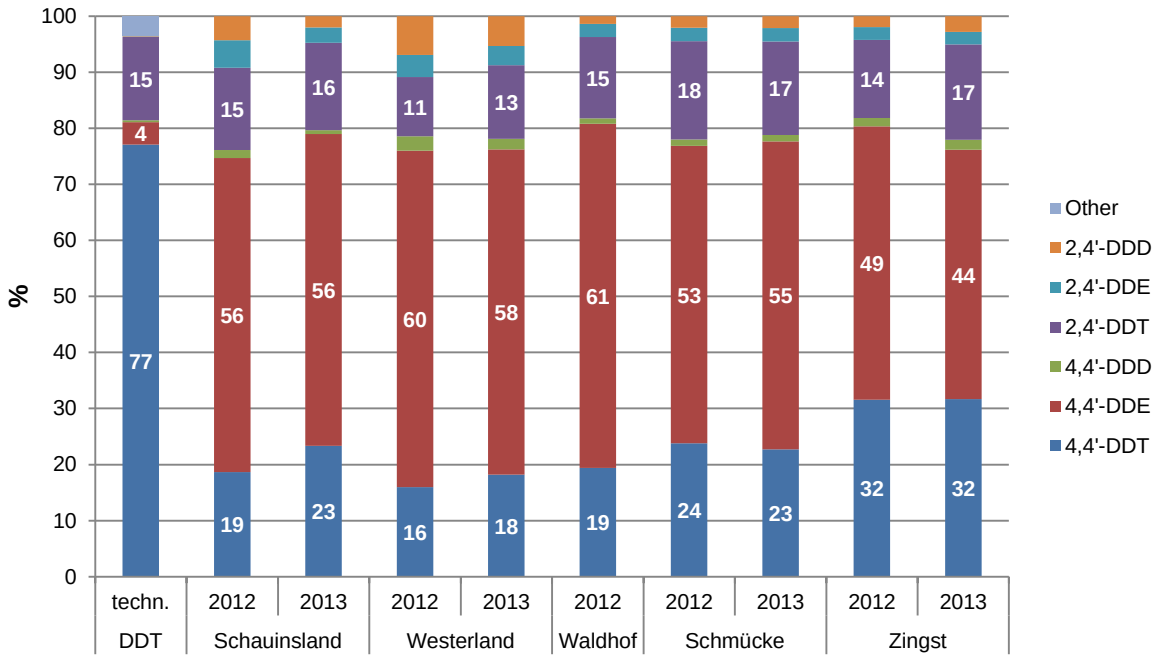

Figure 3: Percentual contribution of DDT related compounds in technical DDT and ambient air (same data as in Figure 2)

Acknowledgements

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All hyperlinks were retrieved 05 May 2014.

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