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Halogenated compounds in a dated sediment core of the Teltow canal, Berlin: Time related sediment contamination

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Abstract

To study the recent contamination history of DDT (1,1,1-trichloro-2,2-bis(chlorophenyl)ethane) and its metabolites, as well as methoxychlor (1,1,1-trichloro-2,2-bis(*p*-methoxyphenyl)ethane), chlorfenson (4-chlorophenyl-*p*-chlorobenzenesulfonate), and further halogenated aromatics, a sediment core was collected from the Teltow Canal in Berlin (Germany). The sampling site is located nearby a former industrial point source, where recently analyses on pre-samples have indicated high concentrations of halogenated organic compounds. The deposition time of the investigated sediments was determined by γ-spectrometrical dating. Pollution trends of selected contaminants were attributed to a time period between 5 and 10 years. Concentration profiles reflect not only the recent pollution history of these compounds, but also the time-depending effects of the ban, restriction and termination of DDT-production in the German Democratic Republic (GDR). DDT and other chlorinated aromatic compounds were produced onsite until the late 1980s. Maximum values of 133 mg kg^{-1} (dry weight) for *p*,*p*′-DDD (1,1-dichloro-2,2-bis(chlorophenyl)ethane) and approximately 100 mg kg^{-1} (dry weight) for *p*,*p*′-DDMS (1-chloro-2,2-bis(chlorophenyl)ethane), main metabolites of the anaerobic degradation of DDT, were determined. The occurrence of all selected contaminants, most of which have been banned more than 10 years ago, demonstrate recent contamination pathways, and the necessity of a continuous long-term monitoring of the affected environment.

1. Introduction

For a time period of 50 years organochlorine pesticides, in particular *p*,*p*′-DDT (1,1,1-trichloro-2,2-bis (chlorophenyl)ethane) and γ-HCH (γ-hexachlorocyclohexane, lindane), were extensively used as insecticides in agriculture, for pest control in forestry and vector control in hygiene against diseases like malaria and typhus (Heberer and Dünnbier, 1999; Eganhouse et al., 2000; Gong et al., 2004). Today residues of *p*,*p*′-DDT and other chlorinated pesticides are ubiquitously distributed and despite the ban in most industrialised countries in the early 1970s, significant concentrations are determined worldwide in water, sediment and soil samples of former affected environments (Eisenreich et al., 1989; Wong et al., 1995; Kim and Smith, 2001; Grimalt et al., 2004). In the German Democratic Republic (GDR) DDT was extensively used in forestry and

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Table 1
Production data of DDT and other halogenated compounds of the GDR

	Production period [year]	Production GDR [t a^{-1}]	Import GDR [t a^{-1}]	Production nearby the sampling site [t a^{-1}]
DDT	1968	7500[a]	n.d	n.d.
	1973	2500[a]	n.d	
	1980	–	65[b]	
	1984	–	440[b]	
	1987	–	100[b]	
Technical HCH/Lindane	1968	2580/185[c]	n.d.	
	1972	8411/778[b]		158/11[b]
	1977	5225/734[b]		–
	1984	–/116[c]		–
	1985	–/0.03[c]		–
Methoxychlor	1973	n.d.	n.d.	202[b]
	1977			138[b]
	1981			127[b]
	1985			201[b]
	1988			16[b]
Bromonaphthalene	Until 1987	n.d.	n.d.	42[c]

[a] Heinisch et al. (1993).
[b] Heinisch and Wenzel-Klein (1994).
[c] Ricking and Schulze (2003); n.d. = no data available.

agriculture until 1983/84 (Heinisch and Wenzel-Klein, 1994). The DDT-production in the GDR decreased from 7500 t $year^{-1}$ in 1968 to 0.05 t $year^{-1}$ in 1985 (see Table 1 for production data). Heinisch et al. (1993) reported that approximately 1 t of DDT and γ-HCH-containing products were used in the GDR in 1988.

The Teltow Canal, located in the south of Berlin (Germany), was built at the beginning of the 20th century to connect the rivers Dahme and Havel for industrial shipping activities. It was also used as rainwater and industrial wastewater drainage system. Main sources of the environmental contamination of the Teltow Canal were untreated local industrial effluents, industrial and municipal sewage treatment plants and rainwater drainage systems. The sampling site chosen for this study is located closed to a chemical production plant one of three main production sites of the GDR (Heinisch and Wenzel-Klein, 1994). Organochlorine pesticides, technical additives and other halogenated compounds were produced and processed on a large-scale from 1949 to 1989 (Heinisch and Wenzel-Klein, 1994; Ricking et al., 2003).

As previously reported numerous halogenated and non-halogenated compounds in significant levels were detected in water, soil and sediment samples (Heberer and Dünnbier, 1999; Schwarzbauer et al., 2001; Ricking et al., 2002, 2003; Schulze et al., 2003; Schwarzbauer et al., 2003a,b) taken from different locations along the Teltow Canal, as illustrated in Fig. 1. Main contaminants were DDT-related compounds with concentrations up to 300 mg kg^{-1} (dry weight) in the extractable fraction and more than 125 mg kg^{-1} (dry weight) of DDX (standing for *o,p′*- and *p,p′*-DDT and its metabolites), determined in the non-extractable fraction (Schwarzbauer et al., 2001, 2003a,b). Schulze et al. (2003) investigated the real toxic potential of DDT, its metabolites and halogenated pesticides, for a wide range of samples. Pointing out some differences of the metabolite-composition they expected a contamination decrease since 1986 and a distribution and attenuation of the contaminants within the system.

Further chlorinated compounds produced and treated until 1990 by the chemical production plant nearby the sampling site are other chlorinated pesticides (e.g. methoxychlor, chlorfenson, dicofol, chlorobenzilat, etoxinol) as well as halogenated naphthalenes. Interestingly, dicofol production was based on *p,p′*-DDT as basic raw material. Therefore, DDT-contamination not only as the result of DDT- but also dicofol-production can be assumed. However, both production lines were stopped in 1990. Methoxychlor (DMDT) and chlorfenson were produced and used there as insecticides (acaricides). The agricultural usage of methoxychlor in East and West Germany is restricted since 1989 (see Table 1). Chlorinated naphthalenes are further global environmental pollutants which reaching the river system mainly by industrial sources (Falandysz, 1998 and references therein). They are used in replacement to polychlorinated biphenyls in hydraulic oil, as pesticides and in wood preservatives; treated in Europe since 1981 (Borwitzky et al., 1997). Brominated naphthalenes, are generally used as key intermediates in industrial and laboratory preparation (Cakmak, 1999). Chlorostyrenes