# **Environmental Levels P5**

# Polychlorinated Biphenyls (PCBs) and Organochlorine Pesticides (OCs) in Water of the Vistula River at the Kiezmark site, Poland

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#### Abstract

Organochlorine pesticides (OCs) such as DDT and its metabolites (DDTs: p,p' - DDT, o,p' - DDT p,p' - DDD and p,p' - DDE), hexachlorocyclohexane isomers ( $\alpha$ ,  $\beta$  and  $\gamma$ -HCH; HCHs) hexachlorobenzene (HCBz) and chlordanes (*trans*-chlordane, *cis*-chlordane, *trans*-nonachlor and heptachlor; CHLs) and polychlorinated biphenyls (PCBs) were analysed in water of the Vistula River (Poland) to investigate seasonal variations, possible sources and their runoff to the Gulf of Gdańsk (Baltic Sea). The concentrations of HCH isomers quantified in the Vistula River water were apparently high (350 and 410 ng/l) in August and September 1991 indicating usage of HCHs, and were much lower for other chemicals examined. The total loads of DDTs, HCHs, HCBz, CHLs and PCBs transported by the Vistula River to the Gulf of Gdańsk during 12 months studied were assessed for: 10.5, 1380, 0.73, 0.38 and 5.0 kg, respectively.

Key words: DDTs, HCHs, hexachlorocyclohexane, HCBz, hexachlorobenzene, CHLs, heptachlor, chlordanes, PCBs, Vistula River, water, Gulf of Gdańsk, Baltic Sea

#### Introduction

Both a drainage area (193910 km<sup>2</sup>) and water runoff (1081 m<sup>3</sup>/s) makes that the Vistula River is a very important source of the fresh water and water-born pollutants to the southern part of the Baltic Sea, and particularly to the Gulf of Gdańsk and the Gdańsk Basin. Organochlorine pesticides such as DDT, Lindane, technical BHC (a mixture of HCH isomers), Toxaphene (Melipax) and metoxychlor were used nearly continuously and relatively in large quantities in the Baltic States and mainly in the 1950s ~ 1970s, and minor substances were such as HCBz, aldrin, dieldrin, heptachlor. For example in Poland 48152 t of DDT (1947-1980), 7510 t of Lindane (1956-1982), 19525 t of metoxychlor

(1957-1990), 381 t of Camphechlor (1958-1969), 188 t of HCBz (1958-1969), 83 t of dieldrin (1958-1971) and 16 t of Aldrin (1958-1971) were sold (1). The Vistula River water samples were collected in 1991-1992 to investigate concentrations, runoff and possible sources of DDTs, HCBz, CHLs and PCBs.

### **Materials and Methods**

12 water samples (20-100 l) were collected in clean polyethylene containers from the Vistula River at the Kiezmark site near Gdańsk in August 1991- July 1992. A pre-cleaned Amberite XAD-2 resin packed in a glass column (length 300 mm, i.d. 22 mm) was used as adsorbent of OCs and PCBs. The XAD-2 resin before use was cleaned-up with water and ethanol in a Soxhlet apparatus (2, 3). Organochlorine substances trapped on XAD-2 resin were eluted with 300 ml of ethanol and transferred to 100 ml of *n*-hexane in a separatory funnel. The *n*-hexane extract was then concentrated down to 5 ml using a Kudern-Danish concentrator and next it was cleaned-up with 5 % fuming sulphuric acid in concentrated sulphuric acid, washed with *n*-hexane-washed water, microconcen-trated under a gentle stream of purified nitrogen gas down to 100  $\mu$ l, and then further HPLC cleanedup and fractionated prior to capillary GC/ECD separation and quantification. The details of chemical analysis were the same as reported by Iwata *et al.* (2, 3).

#### **Results and Discussion**

A summary of the data for twelve samples from the Vistula River water at the Kiezmark site are presented in Table 1 and the data for the seasonal loads of organochlorine pesticides and PCBs transported to the Gulf of Gdańsk in Figure 1.

Compound	Median	Mean±S.D	Range
HCBz	24	27±14	7.6-52
α-HCH	1400	48000±110000	410-310000
β-НСН	650	7200±15000	200-39000
HCH	1800	12000±23000	930-63000
HCHs	4200	67000±150000	1600-410000
p,p' - DDT	26	32±25	3.4-91
<i>o,p'</i> - DDT	15	19±16	2.3-60
<i>p</i> , <i>p</i> ′ - DDE	100	110±40	57-170
<i>p,p'</i> - DDD	170	250±210	43-570
DDTs	320	410±230	120-840
Trans-chlordane	9.1	9.8±5.6	<4.0-19
Cis-chlordane	3.9	4.5±2.9	<4.0-9.6
Trans-nonachlor	3.6	4.9±3.6	<4.0-9.6
Heptachlor	5.5	6.1±5.1	2.1-20
CHLs	12	15±13	2.6-40
PCBs	190	200±60	120-300

Table 1. (	OCs and	PCBs in	the	Vistula	River	water	(pg/)	D
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HCHs highly dominated as OCs quantified in the Vistula River water and since their seasonal pattern in water well correlate to the pattern found in the ambient air (4) a recent use of Lindane ( $\gamma$ -HCH) somewhere in or close to Poland in summer 1991 can be an explanation for relatively high concentrations and runoff of those substances. DDTs and followed by HCBz and CHLs were found in much lower concentrations than HCHs (Table 1). DDT is an insecticide with relatively high application rates in the past in Poland, hence surface soil still can be a main source of DDTs in the Vistula River water.

The *trans*-nonachlor to *cis*-chlordane ratio (N/C) close to 1 indicates distant sources of pollution for those compounds, while for the sites exposed to continuous use it is likely to be nearly 0.15-0.45 (2). Both a low concentration of CHLs in the Vistula River water and the N/C ratio close to 1, *i.e.*  $0.98\pm0.04$  (n = 7), which is a value similar to that of  $1.2\pm0.8$  observed recently for surface layer of sandy sediments from the nearshore area of the Puck Bay or 0.91 found for subsurface plankton collected in the Gdańsk Depth in 1992, what imply on a long-range aerial transport through movement of air masses from distant regions of the Northern Hemisphere as a source of CHLs for the southern part of the Baltic Sea (5, 6).

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