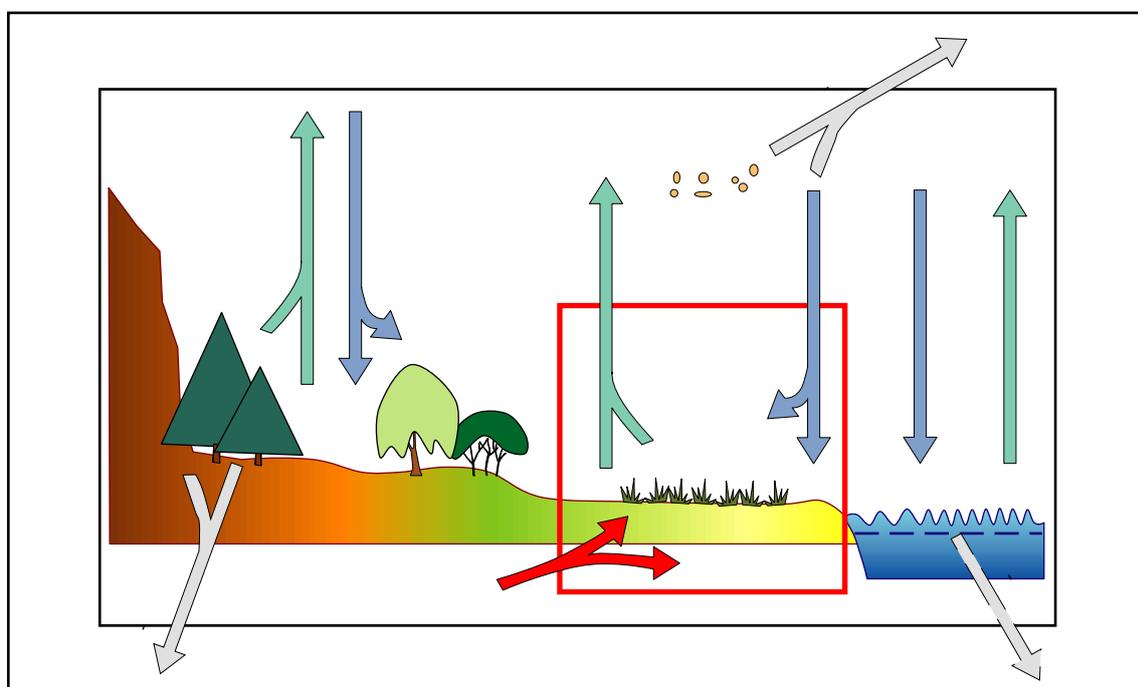


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Proceedings of the International Workshop

SLOWLY DEGRADABLE ORGANICS IN THE
ATMOSPHERIC ENVIRONMENT AND AIR-SEA EXCHANGE

Edited by

Gerhard Lammel

Hamburg, November 2001

Editor

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held 26 September 2001

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Slowly Degradable Organics in the Atmospheric Environment and Air-Sea Exchange

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Why slowly degradable organics matter

As with other environmental concerns, scientific investigation into the fate of man-made chemicals was triggered by the recognition of related and potential effects. Early warnings (Carson, 1962) over the decades matured into assessments of governmental and non-governmental organisations aiming to provide advice for the identification of the borderline between tolerable and unacceptable risks (e.g. CEQ, 1980; CEC, 1996; Greenpeace, 1999; WBGU, 2000).

Today, research receives much of its impetus from the links between exposure on one hand and effects on the other hand made in the emerging international chemicals law (OSPAR, 1994; UNEP, 1999; UN-ECE, 2001): Only exposure to harmful substances matters. However, persistent and bioaccumulative substances bear a risk, too, albeit unknown, as long as effects cannot be excluded. There is no total agreement on whether an unknown risk is a risk at all. In fact, the conclusion that no risks are related to a chemical's introduction into the environment sometimes has been based on ignorance (cf. Berg and Scheringer, 1994; Steinhäuser, 2001).

As a research object, the characterisation of chemical risks is an interdisciplinary undertaking. In order to cover adequately both the exploration of causes and the measures, the combined efforts of chemistry and geosciences, ecology and toxicology, political science analysis and participatory elements are required.

The study of the environmental fate of substances which migrate between two or more media, i.e. air, water, sediment, soils, and biota, is also a worthwhile research object per se: Understanding the partitioning between media (and within media between phases) and at the same time geographically as a consequence of efficient geophysical transports in some of these media is an ambitious goal and in the very heart of what environmental chemistry is all about. Through re-emission upon deposition, the total residence time in the atmosphere and, hence, the long-range transport potential may well exceed the values one would expect for substances readily degradable in the surface compartments. With respect to these propensities, the current state of knowledge is certainly not satisfactory. Observations in the environment show that exposure towards xenobiotics extends also to remote areas, far from the areas of application (cf. e.g. AMAP, 1998; Unsworth et al., 1999; MacDonald et al., 2000; van de Meent et al., 2000). Important hypotheses, such as the 'global distillation' and the 'grasshopper effect', put forward for the explanation of observations (e.g. Wania and Mackay, 1993) still lack state-of-the-art investigation and approval or rejection. They are based on the assumption of thermodynamic equilibria to be established and on transports represented in a generic way.

Because of political activities and the recent progress achieved in science (i.e. in chemical and geophysical disciplines), research on slowly degradable semivolatile organic substances (SOCs) in the environment is expected to become a rapidly growing field. It was suggested that research in this field should soon be organised as a broad programme (Lammel and Graßl, 2000), then constituting an essential piece of sustainability science (Kates et al., 2001).

Short summary and some highlights of the workshop

The intention of the workshop documented here was the

- Exchange of research strategies, methodological approaches and results between scientists active in the field
- Discussion about the significance of other slowly degradable organics apart from the so-called persistent organic pollutants (POPs)

The workshop was held at the Max Planck Institute for Meteorology, Hamburg, on 26 September 2001. Scientists representing 15 research groups in 4 countries participated and contributed studies on the cycling of slowly degradable organics with a clear focus on the atmospheric and oceanic environments. They grouped into studies on the storage in environmental compartments and the mass exchange between them (Section 1), observations in areas where xenobiotics entered into the environment (Section 2), and observations and modeling of persistent substances which undergo long-range transport (Section 3). The substances investigated were persistent and toxic substances (PTS, most of them pesticides or industrial chemicals) and other pesticides of various persistence. Even for the most prominent of these substances important properties are not known. Information about degradation and usage/application is in general sparse.

In the context of small-scale studies into the environmental fate of pesticides, it became obvious that investigations – at least in Germany and in China – are hampered by the ignorance of pesticide application patterns. Pesticides observed in samples of atmospheric origin in agricultural areas during the season of application include herbicides (e.g. atrazine and other triazines), fungicides (e.g. chlorothalonil), insecticides (e.g. methyl parathion) and some of their metabolites. Obviously, at least a detectable fraction of these substances undergoes atmospheric transport within the wider area.

Recent and earlier observations of PTS in the ocean, marginal seas and in rivers resemble a deficient mosaic of trends. At least at some sites in China coastal areas, HCH and DDT decreased largely in the late of the 1980s and in the 1990s. So far, hardly any notice of these and other related findings was taken internationally. After approximately 50 years of entry into the environment, the HCHs seemingly have now reached equilibrium with respect to air-sea mass exchange in the northern hemisphere, whereas the ocean in the southern hemisphere is still accumulating γ -HCH. The global (and historical) budgets even of the HCHs – considered to be the best understood species within the group of PTS – are by far not complete, indicating severe lack of understanding of sources and/or sinks. Also, the distribution of PCB in the North Sea is difficult to understand, being obviously the result of several significant processes. The understanding of the air-sea exchange of PCBs in the Baltic Sea is limited by the knowledge of substance properties (in this case, Henry's law constant). Through the action of waves, surface films and precipitation, air-sea exchange might well be controlled by more processes than we are aware of to date.

Multi-year time series of atmospheric levels of PTS are available from the EMEP monitoring programme (EMEP, 2000). The data on HCHs, PCBs, HCB, DDT/DDE and chlordane measured at a rural, central European monitoring station (Košetice, Czech Republic) reveal a complex superimposition of various significant factors, interannual variabilities and emission trends, apart from other findings. 3D transport and chemistry modeling of semivolatile substances has started only recently and is expected to improve our understanding of the cycling of substances undergoing long-range transport. From these as well as from more generic models, indicators that characterize persistence and long-range transport potential can be derived - information which is very useful in chemicals regulatory and international policy frameworks.

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Programme of the Workshop

09:00-14:10 short contributions (20-25 min each incl. discussion):

Lammel

(MPI & U Hamburg/Meteorology) Welcome

Bernhardt/Palm

(U Lüneburg/EnvChem) Pesticide fluxes in a beech forest

de Rossi/Bierl

(U Trier/Hydrology) Observations of pesticides in the region of Trier

Deuerlein/Hurle

(U Hohenheim/Phytomedicine) Observations of pesticides in the Beijing area (air, rain and surface water)

Zhang/Gao

(Ocean U Qingdao/MarineEnv) Observations of POPs and pesticides in China (ocean, rivers)

10:40-11:00 Break, Coffee

Karbe

(U Hamburg/Hydrobiology) Observations of POPs in and effects on biota of the river Elbe (Labe) and the North Sea

Holoubek

(Masaryk U Brno/EnvChem) Background monitoring of POPs in Czechia (air) and comparison with model results

Leip/Lammel

(MPI & U Hamburg/Meteorology) Long-range transport of modern pesticides: Model results

Lakaschus/Schrems

(AWI Bremerhaven/AtmChem) Measurements of PCBs, HCHs and HCB in air and water on a transect across the Atlantic in 1999-2000

12:40-13:20 Break, Snack

Marks

(U Szczecin/MarineSci) The Hg vapour air-water exchange as an indicator of POPs fate

Bruhn/McLachlan

(IOW Rostock/MarineChem) Quantifying air/sea gas exchange of POPs

14:10-15:00 Discussion:

- Do pesticides create environmental problems (which substances, which media, where) ?
- Strategies for future research in the field of slowly degrading SOCs

15:00 Departure

1. Storage in and Mass Exchange Between Environmental Compartments

1.1 Studies on Persistent Organic Pollutants in Coastal Areas of China

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Abstract

In 1980 in the Bohai Sea, the mean DDT levels were much higher (319 ng/g) in suspended matter than in surface sediment (0.69 ng/g) and in the aqueous phase (1.28-6.17 ng/l). In the Changjiang Estuary the general concentrations of POPs are lower than in the Bohai Sea. In 1996 the polyaromatic hydrocarbons (PAHs) in a sediment core taken from the intertidal flat ranged from 0.08 to 11.7 µg/g. The concentration levels of total and individual PAHs changed dramatically with depth. The historical record of PAHs in the core shows one or more subsurface maxima, i.e. a lower level close to the surface. The PAH sediment record in the core profile is in agreement with historic sewage discharge events during the 1980s to 1990s. From the variations of hexachlorocyclohexanes (HCH) and DDT contents in surface sediments in Changjiang Estuary-Hangzhou Bay the temporal distributions of the two substances decreased largely in the late of 1980s and in 1990s. Inverse relationships between levels of HCH and DDT with salinity in water indicate the dispersion of POPs from near shore to the open sea.

The Pearl River sediments deposited after 1980 have higher concentrations of total PAHs than those deposited earlier. Furthermore, higher fluxes of PAHs discharged to the Pearl river were found after 1990. HCHs and DDT decreased (1995 vs. 1981). DDT as well as hexachlorocyclohexane (HCB) decreased also in Macao estuary (after 1993 vs. 1993). In Victoria Harbour, Hong Kong, DDT (1.38-97 ng/g) and PAHs (1.2-454 µg/g) are spatially highly variable in the sediment, while the distribution of PCBs is relatively homogeneous (6.2-81 ng/g). Levels of PAHs (0.4-61 µg/g in 1993 and 1999) and HCHs (0.14-1.1 ng/g with γ -HCH being the highest concentrated isomer; 1999) are lower in western Xiamen harbour, but the contamination by DDTs is larger.

1. Introduction

Environmental pollution by persistent organic pollutants (POPs) such as organochlorines has received considerable attention as a result of public awareness of environmental problems and expectations for a good quality of life.

In coastal areas of China the occurrence and behaviour of POPs such as PCBs, HCHs, HCB and DDTs as well as of polycyclic aromatic hydrocarbons (PAHs) in water, surface sediments, sedimentary core and in suspended particulate matter have been studied mainly since the 1980s (Fig.1).

Fig. 1: The coastal areas and marginal seas of China.

2. Distributions of POPs in the Bohai Sea and in Changjiang Estuary

2.1 Levels of POPs in the Bohai Sea

Table 1: Distributions of POPs in the Bohai sea

Location	Study period	Compartment	PAH		PCBs		HCH		DDT		Reference
			Mean value	Range	Mean value	Range	Mean value	Range	Mean value	Range	
Bohai Bay	Aug. 1980	Water ^a		17.0 -3184.0							Dai et al., 1983
Bohai Bay	Aug. 1980	Surface Sediment ^b		36.8 -330.0							Dai et al., 1984
Bohai Bay	Aug. 1980	Surface Sediment ^b			5.03	2.17 -8.87	21.94	5.58 -36.24	0.69	0.27 -3.15	Gu et al., 1988
Bohai Bay	Aug. 1980	Water ^a			5.02	3.48 -6.67	152.2	55.3 -328.3	2.19	1.28 -6.17	Gu et al., 1988
Bohai Bay	Aug. 1980	Suspendid matter ^b					94.9	65.8 -109.8	318.9	229.2 -486	Gu et al., 1988
Dalian Bay	July, 1996	Surface Sediment ^b			19.1	1.0 -153.1	21.2	7.5 -92.3	21.7	2.1 -72.3	Li et al., 1998
Jinzhou Bay	Apr., 1996	Surface Sediment ^b			5.8	0.6 -32.6	58.6	5.8 -323.1	23.9	1.0 -154.9	Li et al., 1998
Tianjin Harbour	Mar.-May 1997	Water ^a					272	225 -330			Zhang et al., 1998
Bohai Strait	Sept. 1998	Core Sediment ^b		60.3 -2076.5							Wu et al., 2001

^a Concentrations of POPs in ng/l in water

^b Concentrations of POPs in ng/g in sediment

Vertical Profiles of PAHs in core sediments from the Bohai Strait were determined by Wu et al., 2001.

2.2 Levels of POPs in Changjiang Estuary

Table 2: Distributions of POPs in Changjiang Estuary

Location	Study period	Compartment	PAH		PCBs		HCH		DDT		Reference
			Mean value	Range	Mean value	Range	Mean value	Range	Mean value	Range	
Chanjiang Estuary	Jan. 1986	Water ^a			3.85	1.08 -8.22	2.11	1.07 -4.10	0.66	0.18 -1.58	Ye et al., 1991
Chanjiang Estuary	July 1986	Water ^a			1.46	0.75 -2.65	29.01	4.71 -66.98		0.11 -6.80	Ye et al., 1991
Chanjiang Estuary	July, 1981	Surface Sediment ^b					3.28	0.95 -5.90	10.9	6.9 -16.0	Lin et al., 1983
Chanjiang Estuary	Jan. 1991	Water ^a			1.59	0.43 -5.68	8.89	2.30 -56.90	3.13	0.7 -4.8	Ye et al., 1995
Chanjiang Estuary	Jan. 1991	Surface Sediment ^b			12.63	2.2 -25.3			0.94	0.56 -1.85	Ye et al., 1995
Chanjiang Estuary	Oct. 1997	Core Sediment ^b					0.47	0.158 -0.449	0.31	0.176 -0.940	Chen et al., 1999
Chanjiang Estuary	Dec. 1987	Suspendid matter ^b					11.13	0.19 -51.25	11.88	3.57 -47.86	Chen et al., 1999

^a Concentrations of POPs in ng/l in water

^b Concentrations of POPs in ng/g in sediment

2.3 Temporal Variation of POPs in Changjiang Estuary

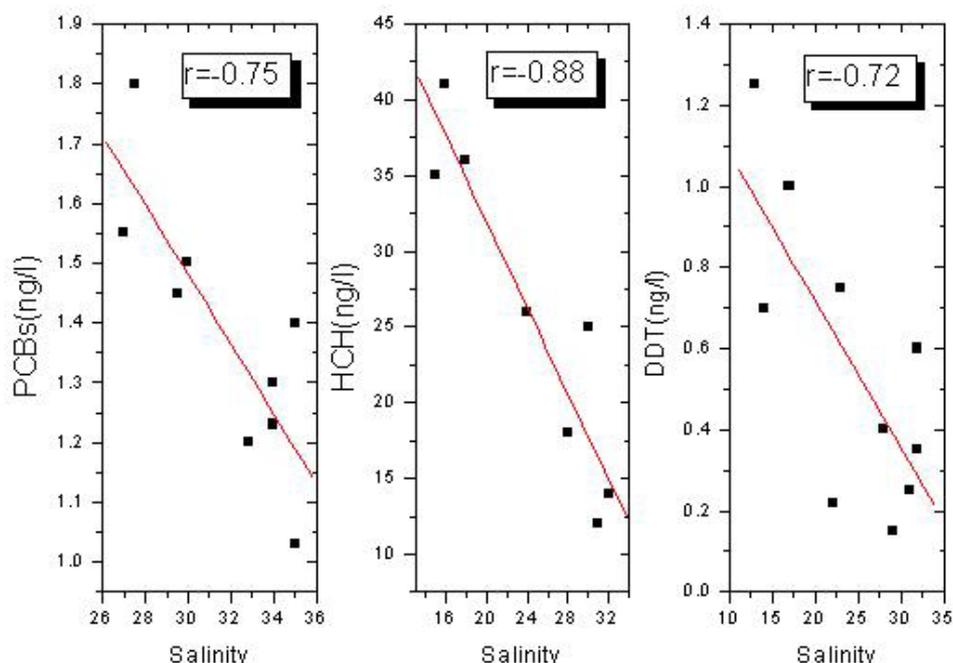
Table 3: Variations of HCH and DDT contents in surface sediments in Changjiang Estuary, Hangzhou Bay

Study period	HCH	DDT	Reference
Aug. 1981	3.28	10.9	Lin et al., 1983
Oct. 1988	0.78	2.19	DeMaster et al., 1995
Jan. 1992		0.94	Chen et al., 1999
Oct. 1997	0.47	0.31	Chen et al., 1999

Vertical distributions of HCH and DDT contents in Cores from Changjiang estuary and in the Hangzhou Bay, different stations, have been determined (Chen et al. 1999).

2.4 Relationship between POPs Contents and Salinity

Fig. 2: The relationship between POPs contents in water and salinity in Changjiang estuary in Summer (from Ye et al., 1991)



2.5 Main Findings Including Temporal Trends

In the Bohai Sea, the mean DDT levels are much higher (319 ng/g) in suspended matter in 1980 than in surface sediment (0.69 ng/g). In water it was in the range 1.28-6.17 ng/l. The HCHs ranged from 7.5 to 92.3 ng/g in the surface sediment in 1996 in Dalian Bay, while it was in the range 5.8-323 ng/g in Jinzhou Bay.

In the Changjiang Estuary the general concentrations of POPs are lower than in the Bohai Sea. In surface sediments DDT concentrations ranged from 6.9 to 16.0 ng/g in 1981 and from 0.56 to 1.85 ng/g in 1991. HCHs levels ranged from 0.19 to 51.2 ng/g in suspended matter in 1987. In the core sediment, PAH levels were in the range 0.06-2.1 $\mu\text{g/g}$ in 1998. In 1996 the PAHs in a sediment core taken from the intertidal flat ranged from 0.08 to 11.7 $\mu\text{g/g}$. The concentration levels of total and individual PAHs changed dramatically with depth. The historical record of PAHs in the core shows one or more subsurface maxima, i.e. a lower level close to the surface. The PAH sediment record in the core profile is in an agreement with historic sewage discharge events during the 1980s to 1990s (Liu et al., 2000).

From the variations of HCH and DDT contents in surface sediments in Changjiang Estuary-Hangzhou Bay the temporal distributions of the two substances decreased largely in the late of 1980s and in 1990s. HCH levels varied from 3.28 ng/g in 1981 to 0.47 ng/g in 1997, while DDT levels decreased from 10.9 ng/g in 1981 to 2.19 ng/g in 1988 and 0.31 ng/g in 1997.

Inverse relationships between levels of POPs, HCH and DDT with salinity in water indicate the dispersion of POPs from near shore to the open sea.

3. South China Estuaries and Harbours

3.1 Distributions of POPs in Pearl River Estuary and Hong Kong Coastal Areas

3.1.1 Levels of POPs in Pearl River Estuary and Coastal Areas

Table 4: Distributions of POPs in Pearl River Estuary and Hong Kong coastal areas

Location	Study period	Compartment	PAH		PCBs		HCH		DDT		Reference
			Mean value	Range	Mean value	Range	Mean value	Range	Mean value	Range	
Pearl River Estuary	1981	Water ^a						200 -1800		200 -2000	Liao, 1983
Pearl River Estuary	1981	Surface Sediment ^b						7.8 -65.0		3.0 -20.0	Liao, 1983
Pearl River Estuary	1981	Organism ^b						150 -560		150 -15	Liao, 1983
East part of Guangdong Coast	1983-1984	Water ^a					1800		500		Liao, 1983
East part of Guangdong Coast	1983-1984	Surface Sediment ^b					34.9	9.5 -62.4	63.6	16.9 -94.3	Liao, 1983
Pearl River Estuary	Nov. 1994	Surface Water ^a					87	57 -156	80	ND -236	Cai et al., 1997
Pearl River Estuary	Nov. 1994	Bottom water ^a					117	36 -306	506	ND -1220	Cai et al., 1997
Pearl River Estuary	Nov. 1994	Surface sediment ^b					11.15	4.98 -20.27	33.46	17.79 -51.71	Cai et al., 1997
Pearl River Estuary	July 1995	Surface Water ^a					45	21 -84	41	ND -86	Cai et al., 1998
Pearl River Estuary	July 1995	Bottom water ^a					48	28 -85	35	10 -72	Cai et al., 1998
Pearl River Estuary	July 1995	Surface sediment ^b					11.07	2.13 -24.65	17.88	4.13 -83.84	Cai et al., 1998
Pearl River Estuary	July 1995	Aerosol ^c					0.136	0.038 -0.262	0.078	0.051 -0.130	Cai et al., 1998
Guangzhou Channel	March 1997	Surface Sediment ^b			50.17		13.0		66.34		Kang et al., 2000
Inside Macao Harbour	March 1997	Surface Sediment ^b			338.53		2.85		1628.81		Kang et al., 2000
Lingding Ocean	March 1997	Surface Sediment ^b			11.54		1.64		26.8		Kang et al., 2000
Macao Estuary	March 1997	Core Sediment ^b					3.88	0.48 -26.28	10.53	1.92 -39.13	Kang et al., 2001

^a Concentrations of POPs in ng/l in water

^b Concentrations of POPs in ng/g in sediment

^c Concentrations of POPs in ng/m³ in aerosol

ND = not detected

3.1.2 Levels of POPs in Surface Sediments of Victoria Harbour

Table 5: Concentrations of HCH, DDTs, PCBs [ng/g dry weight] and PAHs [$\mu\text{g/g}$ dry weight] in surface sediments of Victoria Harbour, Hong Kong, August 1992 (Hong, et al. 1995)

Station	VM2	VS1	VS2	VS3	VS4	VS5	VS6	VM8	VS9	VS10	VS14	VS16
α -HCH	<0.1	<0.1	<0.1	<0.1	0.29	0.94	<0.1	<0.1	<0.1	1.8	7.7	1.8
β -HCH	<0.1	<0.1	<0.1	<0.1	0.37	<0.1	<0.1	<0.1	<0.1	<0.1	1.2	<0.1
γ -HCH	<0.1	<0.1	<0.1	<0.1	0.16	<0.1	<0.1	<0.1	<0.1	<0.1	0.52	3.6
δ -HCH	<0.1	<0.1	0.56	<0.1	<0.1	<0.1	<0.1	2.3	<0.1	<0.1	<0.1	<0.1
Σ -HCH	ND	ND	0.56	ND	0.82	0.94	ND	2.3	ND	1.8	9.4	5.4
P,p-DDT	1.4	2.7	4.8	5.8	3.9	2.2	2.0	1.9	0.32	7.6	7.9	47
P,p-DDD	3.6	6.9	15.3	4.1	3.7	1.8	2.5	1.3	0.53	15.5	22	33
P,p-DDE	2.7	3.5	5.3	4.8	4.0	1.1	2.0	0.78	0.53	7.2	26	17
Σ p,p-DDTs	7.7	13.1	25.4	14.7	11.6	5.1	6.5	4.0	1.38	30.3	56	97
PCBs	6.2	10	16	6.8	14	5.6	11	4.3	3.2	27	81	38
Parent-PAH	3.1	1.4	2.3	2.5	3.7	1.6	3.1	0.72	0.72	18	52	19
Alkylated-PAH	4.0	4.2	10.4	10.1	10.3	8.0	1.8	3.2	0.48	50	402	120
Total PAH	7.1	5.6	12.7	12.6	14.0	9.6	3.1	3.9	1.20	68	454	139

ND = not detected

- The HCH in Victoria Harbour is low, 0.56-9.4 ng/g.
- DDT levels in the sediment ranged from 1.38 to 30.3 ng/g, which fell at the low end of the world-wide concentration range (near-shore surface sediments world-wide ranged from < 0.1 to 44 ng./g, Fowler, 1990).
- PAHs concentrations in surface sediments varied from 1.2 to 454 $\mu\text{g/g}$ with high heterogeneous distribution spatially.
- The distribution of PCBs was relatively homogeneous with levels of 6.2-81 ng/g.

3.2. Distributions of POPs in Fujian Coastal Areas

3.2.1 Levels of POPs in Fujian Coastal Areas

Table 6: Levels of POPs in Fujian coastal areas

Location	Study period	Compartment	PAH		PCBs		HCH		DDT		Reference
			Mean value	Range	Mean value	Range	Mean value	Range	Mean value	Range	
Jiulong River Estuary	Aug.1980 -July 1981	Water ^a					200	100-300			Wu et al., 1983
Xiamen Harbour	Sept. 1982	Surface Sediment ^b					11.0	1.5-27.0	24.0	4.7-150.0	Chen et al., 1986
Xiamen Harbour	June-Dec. 1982	Water ^a					150.0	90.0-270.0			Xu et al., 1986
Xiamen Harbour	June-Dec. 1982	Surface Sediment ^b					10.22	0.0-27.0	33.84	0.0-150.0	Xu et al., 1986
Western Xiamen Harbour	Nov. 1993	Surface Sediment ^b	20333	2900-61000	1.74	0.05-7.24	0.45	0.14-1.12	42.8	4.45-311	Zhang et al., 1995
Xiamen Harbour	Oct. 1994	Core Sediments ^b				0.09-0.46		0.12-0.32		4.64-10.5	Chen et al. 1996
Xiamen Harbour	July 1998	water ^a			0.74	0.12-1.69	8.57	3.51-27.8	1.45	0.95-2.25	Zhang et al., 2000
Xiamen Harbour	July 1998	Surface Sediment ^b				ND-0.32		ND-0.14		ND-0.06	Zhang et al., 2000
Jiulong River Estuary	June 1999	Water ^a					71.8	0.58-353	12.8	0.16-63.2	Zhang et al., 2001
Jiulong River Estuary	June 1999	Porewater ^a					2123	31.5-17415	31.1	1.0-193	Zhang et al., 2001
Western Xiamen Harbour	June 1999	Surface Sediment ^b	1058.6	425.3-1522.4	25.09	9.24-33.72			46.12	8.61-73.70	Yuan et al., 2001
Minjiang Estuary	Oct. 1996	Surface Sediment ^b	723	316.8-1260.7	16.43	8.71-30.55			21.63	6.17-63.88	Yuan et al., 2001

^a Concentrations of POPs in ng/l in water

^b Concentrations of POPs in ng/g in sediment; ND = not detected

3.2.2 Time variations of POPs in Xiaman harbour

Table 7: The concentration of HCHs and DDTs in Sediments of Xiaman harbour in different years [ng/g]

	Range			Mean level			Reference
	1986	1993	1998	1986	1993	1998	
							Chen et al. (1986)
HCHs	1.5-27	0.14-1.12	ND-0.45	11	0.45	0.056	Zhang et al. (1996)
DDTs	4.7-94	4.45-17.4	ND-0.06	23	9.27	0.025	Zhang et al. (2000)

3.2.3 Concentrations of POPs in surface sediments of Xiamen harbour

Table 8: Concentration of HCHs, DDTs, PCBs [ng/g] and PAHs [$\mu\text{g/g}$] in surface sediments of Xiamen harbour, November 1993 (Hong et al., 1995)

Station	XM1	XM2	XM3	XM4	XM5	XM6	XM7	XM8	XM9
α -HCH	0.12	0.17	ND	0.08	0.07	0.14	0.10	0.09	0.14
β -HCH	ND	ND	0.78	0.41	ND	ND	ND	ND	ND
γ -HCH	0.23	ND	ND	0.63	0.19	ND	0.29	0.24	0.35
δ -HCH	ND								
Σ -HCH	0.35	0.17	0.78	1.12	0.26	0.14	0.39	0.33	0.49
P,p-DDT	2.20	263	7.75	8.08	2.35	1.75	4.91	6.20	2.20
P,p-DDD	1.52	35.0	7.13	4.43	3.02	2.69	3.73	3.36	2.15
P,p-DDE	0.73	12.6	2.25	1.65	1.32	1.04	1.30	1.24	0.75
Σ p,p-DDTs	4.45	311	17.4	14.2	6.69	5.48	9.94	10.8	5.20
PCBs	0.70	7.24	3.88	0.05	0.96	0.48	0.95	0.56	0.80
Parent-PAH	2.7	4.0	3.6	54	0.80	2.5	1.3	3.5	1.6
Alkylated-PAH	0.86	9.3	6.5	7.1	2.1	12	5.8	45	19
Total PAH	3.6	13.3	10.1	61	2.9	15	7.1	49	21

ND = not detected

- The levels of HCHs are about 0.14-1.12 ng/g in Xiamen harbour, and the concentrations of γ -HCH are bigger than the other isomers
- The levels of DDTs are about 4.45-311 ng/g in Xiamen harbour
- The levels of PCBs are about 0.05-7.24 ng/g in Xiamen harbour
- The levels of PAHs are about 3.6-61 $\mu\text{g/g}$ in Xiamen harbour

3.3 Concentrations of POPs in Air and Rivers of China

Table 9: Concentrations of POPs in air and rivers of China

Location	Study period	Compartment	PAH		PCBs		HCH		DDT		Reference
			Mean value	Range	Mean value	Range	Mean value	Range	Mean value	Range	
Pearl River Estuary	July 1995	Aerosol ^c					0.136	0.038 -0.262	0.078	0.051 -0.130	Cai et al. (1998)
Hangzhou	Sept. 1999	Air ^a		8.24 -14.23							Zhu et al. (2001)
Second Songhua River		River Sediment ^b				0.6 -337		2.3 -48.2		2.0 -21.3	Liu et al. (1998)
Xizang		Soil ^b				0.625 -3.501					Sun et al. (1986)
Eastern China	1990's	River Sediment ^s ^b				10.5 -25.5					Chen et al. (1999)

^a Concentrations of POPs in $\mu\text{g/m}^3$ in air

^b Concentrations of POPs in ng/g in sediment and soil

^c Concentrations of POPs in ng/m³ in aerosol

3.4 Main findings including temporal trends

In organisms sampled in the Pearl River and its estuary the HCH levels are higher than in surface sediment ranging 0.15-0.56 $\mu\text{g/g}$ (only detected in 1981). In aerosol these ranged 0.038-0.26 ng/m^3 (1995).

The mean levels of PCBs inside Macao Harbour are 339 ng/g in surface sediment in 1997. Also in 1997 in the Guangzhou channel of the Pearl River, total PAHs concentrations in sediment core varied 2.8-16 $\mu\text{g/g}$. The sediments deposited after 1980 have higher concentrations of total PAHs than those deposited earlier. Furthermore, higher fluxes of PAHs discharged to the Pearl river were found after 1990. PAH contamination is concentrated near the western shore of the Pearl River estuary, in Lingding Bay, because of the hydrodynamic and sedimentation conditions. In Victoria Harbour the HCHs levels ranged 0.56-9.4 ng/g (1992). In the sediment DDT levels ranged 1.38-97 ng/g , PAHs 1.2-454 $\mu\text{g/g}$, both showing a large spatial variability, while the distribution of PCBs was relatively homogeneous with levels of 6.2-81 ng/g . HCH mean levels in water in Jiulong River estuary was 200 ng/L in 1980 and 100-300 ng/L and 71.8 ng/L in 1999. In the porewater HCH levels ranged 0.03-17.4 $\mu\text{g/L}$ (1999). In western Xiamen harbour in surface sediment PAH levels ranged from 2.9-61 $\mu\text{g/g}$ in 1993 and 0.42-1.5 $\mu\text{g/g}$ in 1999. The levels of HCHs in surface sediment were about 0.14-1.1 ng/g and the concentrations of γ -HCH were bigger than the other isomers (1999). The levels of DDTs were about 5-310 ng/g higher than in Victoria Harbour.

Samples of sub-surface water, suspended particulate matter and surface sediments were also collected from Daya Bay in 1999 (Zhou et al., 2001). Total PCB levels varied from 0.09 to 1.35 $\mu\text{g/L}$ in water and from 0.85 to 27.4 ng/(g dry weight) in sediments. The levels of total organochlorine insecticides were in the range 0.14-5.1 $\mu\text{g/L}$ in water and 2.43-86 ng/(g dry weight) in sediment. None of the target compound was detected in suspended particulate matter. The levels of total HCHs in water varied from 35.5 to 1230 ng/L , while in sediments they ranged from 0.32 to 4.16 ng/g dry weight . The levels of the sum of DDTs were in the range 26.8-976 ng/L in water and 0.14-20.3 ng/(g dry weight) in sediments. In comparison, the levels of total PCBs in Daya Bay waters are two to four orders of magnitude higher than those detected in Xiamen Harbour (0.1-1.7 ng/L ; in 2000).

From the time trend of HCB and DDTs in a sedimentary core in Macao estuary, South China, the concentrations of HCB in the core sediment dated from 1962 ranged from trace level to 82.4 ng/g , and those of DDTs ranged from trace level to 79.0 ng/g . The highest concentrations of both DDTs and HCB were found in sediment dated 1993, while significant decreases in concentrations of HCB and DDTs were observed in the sediments which were later deposited. The levels of POPs in water and sediment of coastal areas show that the concentrations of HCHs and DDT in surface sediments decrease since the 1990s. The levels of PCBs in sediments are bigger than those in water (Zhang et al., 1999).

4. Summary

Table 10: Levels of POPs in water of China coastal areas

Location	PAH		PCBs		HCH		DDT	
	Mean value	Range	Mean value	Range	Mean value	Range	Mean value	Range
Bohai Sea		17.0-3184.0	5.02	3.48-6.67	212.1	55.3-330	2.19	1.28-6.17
Changjiang Estuary			2.21	0.43-8.22	13.3	1.07-66.98	1.89	0.18-6.8
Fujian Coastal area					107.6	0.58-363	7.13	0.16-63.2
Pearl River Estuary					74.3	21-306	165.5	ND-1220

Table 11: Levels of POPs in sediment of China Coastal areas

Location	PAH		PCBs		HCH		DDT	
	Mean value	Range	Mean value	Range	Mean value	Range	Mean value	Range
Bohai Sea		36.8-2076.5	9.97	0.6-153.1	33.91	5.58-323.1	15.43	0.27-154.9
Changjiang Estuary			12.63	2.2-25.3	1.87	0.16-5.9	4.05	0.18-16.0
Fujian Coastal area	7371.3	316.8-61000	14.4	0.05-33.72	7.22	0.0-27.0	33.7	ND-150
Pearl River Estuary					12.2	0.48-62.4	36.43	1.92-94.3

ND = not detected

- The concentrations of HCH and DDT in surface sediments decrease since the 1980s.
- The levels of PCBs and PAHs in sediments are bigger than those in water.
- Higher inverse relations between levels of PCBs, HCH and DDT with salinity in water, which indicates the dispersion of POPs from near shore to the open seas.
- The concentrations of POPs in water and sediments are smaller in Changjiang Estuary than in other coastal areas in China.

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1.2 Observations of POPs in and effects on biota of the river Elbe (Labe) and the North Sea

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Introduction

A number of studies related to Biological Effects of Contaminants and Toxic Potentials of Water and Sediment of the Elbe River and the North Sea have been conducted by our working group (BIOTOX Elbe / BIOTOX North Sea). The main objectives of these studies was/is to come to a better understanding of the fate and on biological effects of contaminants in the aquatic environment. Examples of results are presented in two BIOTOX Status Seminars (Karbe et al., 1992 and 1994). For more detailed information on research objectives and ongoing projects please contact the home page of the Marine and Freshwater Ecotoxicology working group.

The major focus of our studies is: Hazard identification and evaluation of risks, risk for ecosystem health, human health and the sustainable development of our natural resources using a differential diagnostic approaches to analyze cause effect relationships under complex and highly variable multiple exposure scenarios. Eco-epidemiological field surveys resulted in findings that should be discussed in the context with short and long range atmospheric transport, and atmospheric deposition of contaminants.

Results

Results of a large scale interdisciplinary research program covering the North Sea as a total as well as parts of the NE Atlantic are summarized by different authors in Sündermann, 1994.

An unexpected result of this study was that different inorganic or organic contaminants including POPs and PTCs are characterized by a regional distribution pattern with high concentrations (1) in the continental waters of the southern North Sea influenced by the river discharges (e.g. in the German Bight) and (2) in stretched areas of the northern North Sea influenced by water masses entering the North Sea from the NE Atlantic via Scottish Waters and the Fair Isle Channel. The latter finding was interpreted as a result of long range atmospheric transport and atmospheric deposition of contaminants over the N Atlantic, followed by a further transport with the water circulation system. Regional differences in the water temperatures and the biological food webs are discussed as parameters of major concern.

Local studies in the German Bight, investigating biomarkers of neurotoxic effects in fish and blue mussels resulted in regional and seasonal differences of the biomarker responses (Galgani et al., 1992; Danischewski et al., 1994). The results can be explained by seasonal differences in the application of organophosphorus pesticides that are spread to the atmosphere, resulting in an atmospheric transport over limited distances, deposition to the marine environment and uptake by the biota.

Recent studies are related to toxic potentials of water and sediments and effects of contaminants along the Elbe river interfering with the endocrine system and the reproductive performance of fish (Hecker et al., 2001a and 2001b). Bioanalytical results were related to data of contaminants that are analyzed at a weekly or monthly basis by governmental

monitoring programs coordinated by the International Commission for the Protection of the Elbe and the ARGE Elbe (IKSE, 2000; ARGE Elbe, 2000). The exposure scenarios analyzed show complex and highly variable regional and seasonal differences in terms of quantitative and qualitative contaminant patterns. For a number of contaminants determined (like pyrogenic PAHs or polycyclic musks) seasonal differences in the formation of aerosols, atmospheric transport and deposition is considered to be of major importance (in addition to differences in discharges and runoff). More detailed evaluations are under progress.

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1.3 Mercury Vapour Air-Water Exchange as an Indicator of the Fate of Persistent Organic Pollutants in Aquatic Systems

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1. Measurements in Hel, Poland

Total gaseous mercury in air was measured over the coastal station in Hel (southern Baltic Sea coast) during the summer and winter experiments using a GARDIS-1A (atomic absorption mercury vapour analyzer; Marks and Beldowska, 2001).

Conclusions:

- during the winter time a tendency of mercury to sink to Baltic Sea water has been documented,
- during the summertime, shallow waters of the Gulf of Gdansk and southern Baltic Sea could become a source of gaseous mercury,
- evidences of enhanced water-to-air transport of Hg vapour were noted - in particular over the shallow waters of the Gulf of Gdansk
- temperature gradient at the air/sea interface (warmer air passage over the cold sea and moderate wind conditions) may enhance sea to air transfer of Hg.

2. Atmospheric transect over the Baltic Sea

This measurement was performed using a Tekran, Model 2537A, atomic gas phase mercury analyser (Marks, 2001).

Conclusions:

- the recorded elevated TGM concentrations in the air over the Baltic Sea indicate significant build-up of gaseous Hg originated over highly industrialised western Europe,
- the collected data reflects a domination of atmospheric pollution transport patterns in the Baltic region that are incorporated with southwesterly winds.

3. Transect measurements of Hg concentration in air along the southern Baltic Sea coast

Preliminary conclusions:

- The concentration of Hg within each city area was enhanced.
- The industry areas within the cities are sources of Hg.

4. Direct measurements of the gaseous mercury saturation in the sea surface water

Preliminary results of this new development (Marks et al., 2001, Marks, 2001) can be summarised as follows:

- The high variability of measured TGM saturation ranged from 0.9 to 7, indicating that TGM in the Baltic Sea water depends on local air-sea interaction conditions and regional past and present inputs.
- The highest TGM saturation in the surface water was found within the main Baltic Sea east-west shipping route south of Bornholm. It indicates that pollutants dispersed by ships, intense ship-made vertical mixing in the water as well as bubble-mediated upward transport of suspended matter contribute to the extraordinary build-up of dissolved Hg in surface water.

- Elevated Hg supersaturated surface waters were found south-east from Hoburgs Bank in the ammunition disposal region, indicating that this particular region could be a source of mercury in the water and in the adjacent air.

- In general, shallow and deeply inland-located Baltic Sea seem to be overloaded by the mercury species, that has been accumulated during last decades. The accumulated Hg is now emitted into the air and contribute to the mercury budget in the Baltic Sea and to related atmospheric transport in the Northern Hemisphere.

5. General conclusions

1. The air to water transfer of persistent pollution by rainout, washout and processes that enrich selective transfers at the ground might be an important mechanism involved in accumulation of both gaseous and particulate forms.

2. The hydrophobic behaviour of some persistent pollution indicates that they can be accumulated at the air-water interface. They can be collected by bubbles in the water column and enrich sea-derived droplets.

3. The shallow and inland located seas like Baltic Sea might be an important sink of POP-s but under specific conditions, can possibly act as significant source that contribute into long range transport of atmospheric pollution

4. A new method used to equilibrate water-to air flux of gaseous mercury may possibly offer a tool to trace the dissolved as well as sediments-water-to-air transfer of persistent organic pollution.

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1.4 Air/Sea Exchange of Persistent Organic Pollutants (POPs)

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1. Aim of the research

Air/sea gas exchange is an important process influencing the levels and fate of semivolatile organic chemicals (SOCs) in aquatic ecosystems. The deep ocean is a major sink for SOCs, and air/sea gas exchange is the dominant pathway of many SOCs into the ocean. For other substances, the surface ocean can be a major buffer, accumulating chemical during periods of high emissions and releasing chemical back into the atmosphere when the emissions decrease. Determining air/sea gas exchange is one approach to quantifying the magnitude of the oceanic sink or source term. The most commonly used method to quantify the air/sea gas exchange of SOCs is to measure the gaseous concentration in the atmospheric boundary layer and the dissolved concentration in the surface water and to calculate the flux based on the fugacity gradient. Once this is known it can be multiplied by the mass transfer coefficient to obtain the POP flux.

This work focussed on the gaseous exchange of POPs between the atmosphere and the Baltic Sea. The Baltic Sea is both a sink and – due to its high level of contamination - a source of POPs in the atmosphere. It is an important reservoir influencing the long range transport of POPs across Europe towards the Arctic as well as a permanent sink for POPs buried in sediment. While there are concerted efforts being made to monitor wet deposition of POPs, there is virtually no knowledge of gaseous exchange of POPs in the Baltic. This investigation undertook to measure the fugacity gradient by simultaneously measuring the gaseous concentrations and dissolved water concentrations.

2. Methods

For the analysis of PCB and HCH concentrations water and air samples were collected in the Arkona Sea, a region of the southern Baltic Sea, during three cruises with in March, May and June 1999. Water samples were taken from the mixed surface layer at a depth of 5-10 m with an in-situ-pump sampling device (Petrick et al., 1996). The air samples were collected on the highest reachable point of the research vessel using a high volume sampler. Detailed information on the samples and the analytical procedure are given elsewhere (Bruhn et al., in preparation).

3. Results

The dissolved aqueous concentrations and the gaseous concentrations of PCBs 28, 31, 101, 118, 138, 149, 153, and 180 and of α - and γ -HCH are given in Table 1. The mean concentrations of the individual PCB congeners in the dissolved phase were in the range of 0.2 - 3 pg/L³. The dissolved concentrations of α - and γ -HCH varied between 710 – 980 and 1200 – 1600 pg/L³, respectively. The gaseous concentrations of the individual PCB congeners varied between 0.6 and 8 pg/m³. The concentrations of α -HCH increased from 24 to 70 pg/m³ between the March and June expeditions. For γ -HCH an increase from 110 to 180 pg/m³ was observed.

Table 1: PCB and HCH concentrations in A) water samples (dissolved, [pg/L]) and B) air samples (gaseous, [pg/m³]) collected in March, May and June 1999. The arithmetic means and the coefficient of variance (CV) are given.

	Water						Air					
	March		May		June		March		May		June	
	Mean n = 3	CV	Mean n = 5	CV	Mean n = 7	CV	Mean n = 3	CV	Mean n = 5	CV	Mean n = 5	CV
PCB 28	3.0	0.05	2.8	0.3	2.5	0.3	2.2	3.3	2.3	5.7	2.7	2.6
PCB 31	2.4	0.04	2.2	0.3	2.0	0.2	0.8	6.2	1.8	4.1	1.3	3.2
PCB 101	3.0	0.2	2.3	0.3	1.4	0.6	2.0	1.7	1.5	6.6	1.7	2.8
PCB 118	1.5	0.10	0.9	0.3	0.47	0.4	0.8	1.3	0.7	4.3	0.7	2.7
PCB 138	1.9	0.09	1.3	0.3	0.55	0.1	1.7	2.2	1.1	5.5	0.9	3.9
PCB 149	1.8	0.1	1.4	0.4	0.65	0.2	2.3	1.7	1.3	6.3	1.4	3.3
PCB 153	1.6	0.04	1.6	0.3	0.50	0.3	1.6	1.9	1.0	6.1	0.9	3.9
PCB 180	0.56	0.10	0.36	0.3	0.15	0.3	0.39	1.1	0.28	4.4	0.2	3.6
α -HCH	980	0.1	710	0.2	780	0.1	24	0.1	40	0.1	70	0.2
γ -HCH	1200	0.09	1600	0.2	1300	0.1	110	1.1	150	1.0	180	0.2

On the basis of this data set and with the help of the two film model the flux over the diffusion gradient was calculated. The overall mass transfer coefficient (k_{ol}) was parameterised according to Schwarzenbach (1993). The Henry's law constants (HLCs) for the PCBs were taken from Dunnivant et al. (1992). They were extrapolated from 25°C to the measured water temperature with a modified van't Hoff relationship employing the enthalpies of phase change (Burkhard et al., 1985). The HLCs of α - and γ -HCH were calculated using relationships from Kucklick et al. (1991). The results for one set of samples from May 1999 are illustrated in Fig. 1.

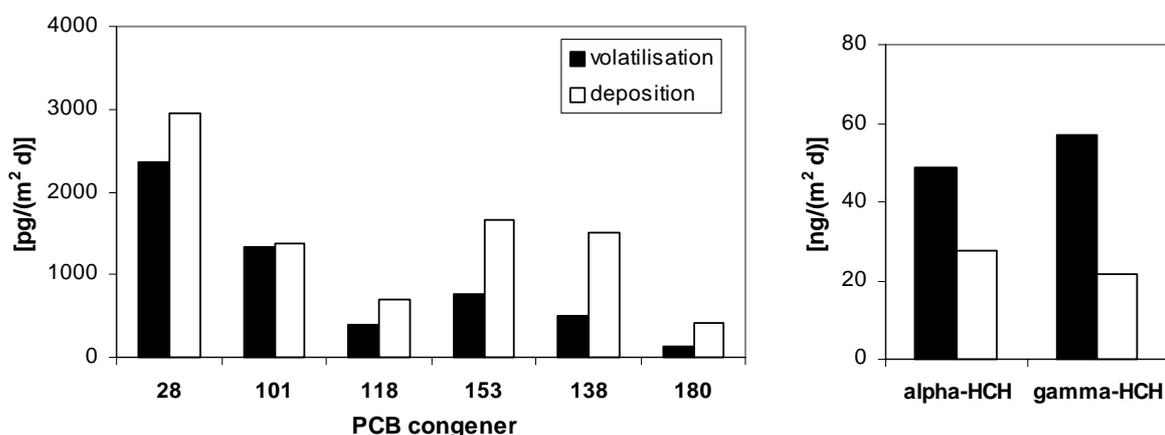


Fig. 1: Volatilisation and deposition fluxes of selected PCB congeners and α - and γ -HCH calculated for one sampling pair from May 1999. The Henry's law constants and enthalpies of phase change were taken from Dunnivant et al. (1992) and Burkhard et al. (1985), respectively, for the PCBs and from Kucklick et al. (1991) for the HCHs.

Both the gross volatilisation flux (the flux calculated assuming $C_A=0$) and the gross deposition flux (the flux assuming $C_W=0$) are shown; the net air/sea gas exchange is given by the difference between the two bars. The gross fluxes lie in the range of 0.13 to 3.0 ng/(m²d) and 22 to 57 ng/(m²d) for the PCBs and HCHs, respectively. More importantly, the magnitudes of the two processes are comparable. For instance, the calculated gross volatilisation of PCB 28 was 2340 pg/(m²d), while the calculated gross deposition was 2.97

ng/(m²d). This indicates that the system was close to a partitioning equilibrium. Clearly, the net air/sea exchange is very sensitive to changes in the magnitude of either of the bars. Consequently, small changes in either of the concentrations or in the HLC could influence the magnitude and the direction of the air/sea gas exchange dramatically.

To evaluate the sensitivity of our results to these variables, the net fluxes of the PCBs were recalculated using three different sets of HLCs and enthalpies. The mean fluxes of the PCBs using the three different sets of HLCs are presented in Fig. 2.

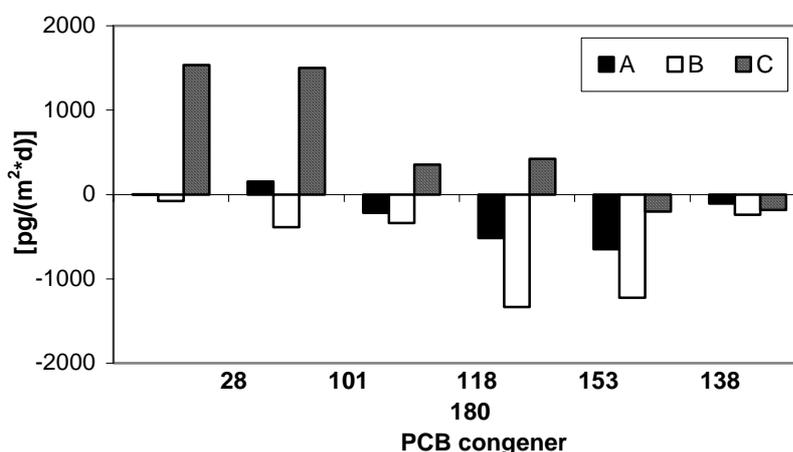


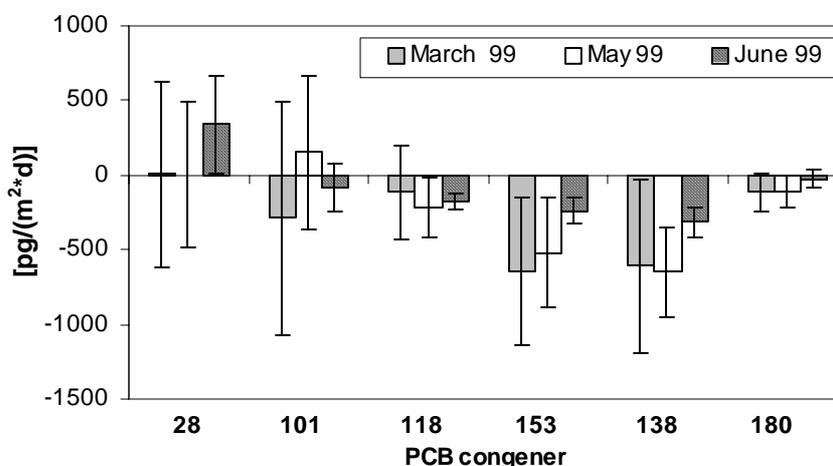
Fig. 2: Net flux of selected PCB congeners for May 1999 calculated with three different sets of HLCs and enthalpies: A) Dunnivant et al. (1992) and Burkhard et al. (1985), B) Brunner et al. (1990) and ten Hulscher et al. (1992), C) Bamford et al. (2000). The arithmetic means are shown.

There are large differences in the net air/sea gas exchange flux, depending on which set of HLCs is used. For instance, the original calculation for PCB 153 in May yielded a gaseous deposition of 0.52 ng/(m²d), while the second set of HLCs gave a net flux that is 2.5 times greater (1.3 ng/(m²d)), and the third set resulted in a net volatilisation of 0.42 ng/(m²d). This example demonstrates clearly the enormous uncertainties in this calculation arising from the choice of the HLC. Although the three HLC datasets are apparently of high quality, not even the direction let alone the magnitude of the air/sea gas exchange could be determined.

In addition to the HLC, the variability of the air and water concentrations and the meteorological conditions affect the calculated air/sea gas exchange. Figure 3 presents the means and the standard deviations of the PCB net fluxes for the March, May and June expeditions calculated again for each pair of water and air samples using the first set of HLCs. The standard deviations are very high. In half the cases the error bars intersect the zero flux line so that not even the direction of the net flux can be ascertained. For more than half of the remaining cases the error bars encompass a flux range of at least a factor of 5. The variability in the concentrations, whether due to natural variability or uncertainties in the measurements, lead to a very large uncertainty in the flux determination. The changing meteorological conditions further increase the variability of the results.

In conclusion, the PCB and HCH concentrations in the Baltic Sea are close to a partitioning equilibrium. Consequently, small changes in either of the concentrations or in the HLC could influence the magnitude and the direction of the air/sea gas exchange dramatically. Under near equilibrium conditions it is not possible to determine the gaseous flux using the method employed here.

Fig. 3: Net flux of selected PCB congeners for March, May and June calculated with Henry's law constants and enthalpies from Dunnivant et al. (1992) and Burkhard et al. (1985). The arithmetic means and standard deviations are shown.



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2. Small Scale Transports: Observations in the Areas of Entry of Xenobiotics into the Environment

2.1 Determination of Pesticide Fluxes in Beech Forests

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1. Introduction

Despite of more than two decades of intensive forest-decline research the reasons for the very high damage-levels especially of broad-leafed trees are not completely understood. In former investigations only very few groups studied a possible correlation between the usage of high-tonnage pesticides in modern agriculture and the observed damages of trees. Evans et al. have observed in greenhouse experiments a correlation between chlorophyll production of beech leafes and pesticide contamination (Evans et al., 1994). The symbiosis of a number of fungis with the roots of the tree (mycorrhiza) is observed for most of all higher plants. Concerning some useful plants like legumes this symbiosis is well known to be sensitive to pesticides (Abd-Alla et al., 2000). However, this sensitive area of the ecosystem beech-forest has never been investigated before regarding pesticide input.

Very first results of experiments to determine pesticide-fluxes in beech-forest are presented including the question whether forests may act as a sink for pesticides and dicussing the fate of pesticides in beech-forests.

2. Experimental

The beeches chosen for this investigation were located in an intensively agricultural used area in the south-west of Lüneburg in the northern low-lands of Germany. The trees were furnished with a rin made of tin-foil to collect stem-flow water. In vincinity to the trees rain-fall collectors were positioned.

The substances studied in this investigation were chosen due to their high usage in Germany and are summarized in Table 1.

Table 1: Investigated substances

Desisopropyl-Atrazine	Metazachlor
Metamitron	Isoproturon
Desethyl-Atrazine	Phenmedipham
Bentazone	Ethofumesat
2,4-D	Terbuthylazine
Bromoxynil	Prosulfocarb
Chlortoluron	Pendimethalin
Atrazine	

Clean-up and enrichment of the water-samples were carried out via solid-phase extraction using C₁₈ disposable cartridges (CHROMABOND[®] C₁₈ from Machery-Nagel). The cartridges were deluted after enrichment with 1 ml of Methanol.

Analysis of the samples were carried out with a HPLC on an endcapped octadecyl-cartridge using a methanol/water gradient, detection were conducted with a electro-spray-mass-

spectrometer (Applied Biosystems API165).

3. Results

First experiments were performed to study recoveries of pesticides from aqueous standard-solutions and spiked stem-flow samples. Therefore, stemflow-water from three different trees were collected, spiked with 100 ng of each pesticide and enriched in the described way. Obviously, the three samples collected from the trees had visual differences. While the samples from beech two and three had a slight green colour (supposedly caused by algae) the sample from beech one had a slight brown colour.

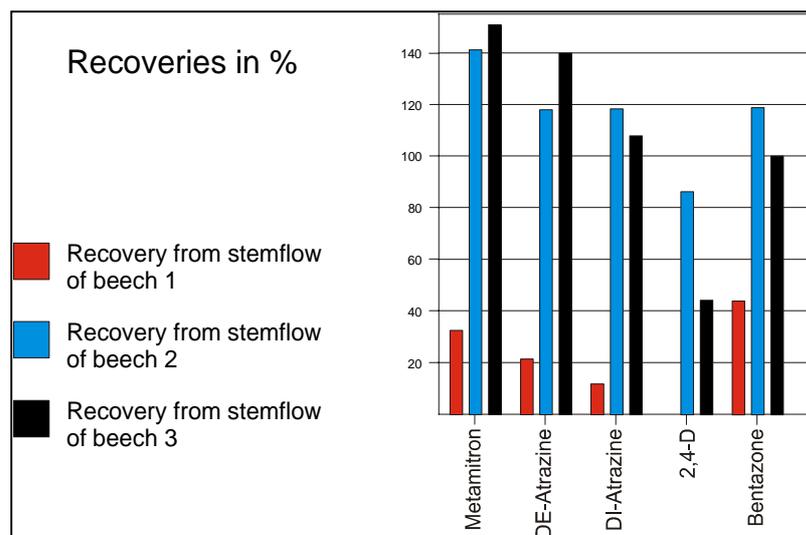


Fig. 1: Variation of recoveries of some selected pesticides from three different stemflow-samples

As could be seen in Fig. 1 recoveries for five of the pesticides investigated (not shown are results for bromoxynil and chlortoluron) from three spiked stemflow-samples varied in wide range. Errors in recoveries for all other compounds in spiked aqueous standard solutions as well as in spiked stem-flow samples were found to be in a range of about 20 % and are given in Fig. 2.

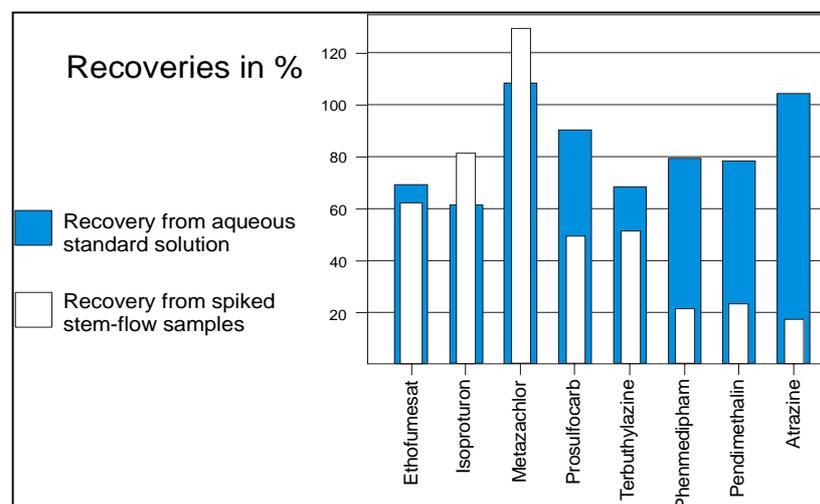
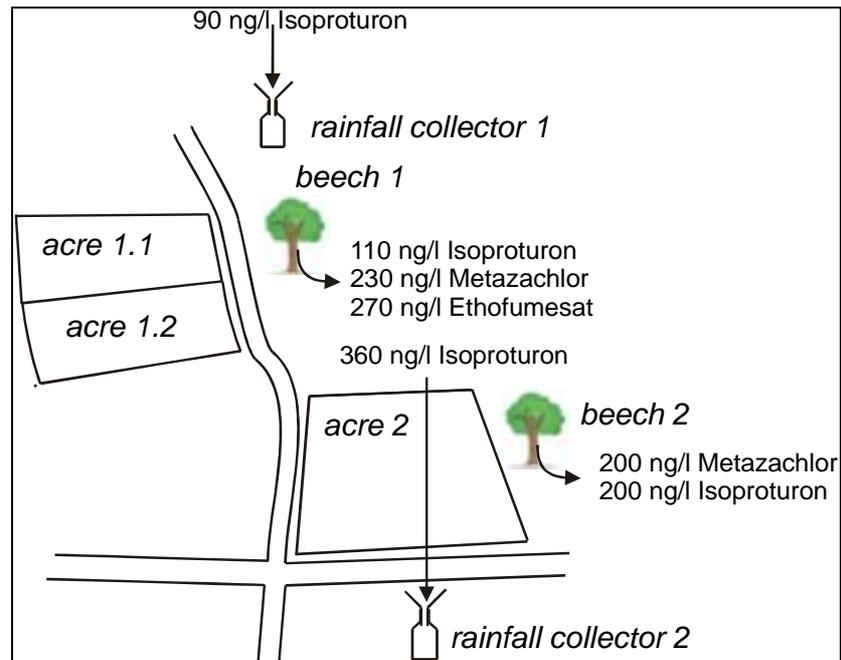


Fig. 2: comparison of recoveries for several substances from aqueous standard solution and stemflow-samples

Recoveries for ethofumesat, isoproturon and metazachlor from spiked samples were comparable to corresponding aqueous standard solutions.

However several substances like atrazine showed recoveries below 20%. Obviously matrix-effects in stemflow samples vary significantly between different trees. Hence, one has to be very careful in interpreting data acquired from stemflow-samples. The results found in rainfall and stemflow water are shown in Fig. 3.



A single rainfall event from September 25, 2000, will be discussed. Sampling was performed approximately 2 weeks after sowing of winter-crops and application of pesticides. Isoproturon was detectable in both rainfall collectors in concentrations near or above 100 ng/l. A likely interpretation of high concentrations found is a short time period between application and sampling as well as a short distance to the application site. These results are in agreement with other investigations with high pesticide concentrations found in and shortly after application time close to treated areas (Jager et al., 1998). In stemflow from the trees investigated a quite similar situation was found. In both samples isoproturon as well as metazachlor were detected in a range from 100 to 200 ng/l. Metazachlor was applied at the beginning of September 2000 on acre 2 (personal information of the farmer). Hence, the detection of metazachlor in both samples was not astonishing.

More surprisingly was the detection of ethofumesat in stem-flow of beech 1. Taking information delivered from the Federal Biological Research Centre for Agriculture and Forestry (BBA) ethofumesat is a substance applied on sugar and food beet only. Taking into consideration, that beet is sowed in spring only an interpretation of this result is still missing.

4. Conclusion

It has been shown, that pesticides are detectable in beech forests. Hence, forests may act as a sink not only for non-polar pesticides like DDT (Simonich and Hites, 1995; Weiss et al., 2000) in the atmosphere but also for polar compounds, probably underestimated in former investigations dealing with transport phenomena of pesticides. Regarding the mycorrhiza populations any affect from pesticides on fungus in the root area of the beeches can't be excluded.

Concerning the results found from recovery experiments we have to assume, that procedures used in this study are still insufficient and the interpretation is for some of the substances studied uncertain.

Acknowledgement

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2.2 Pesticides in Precipitation in the Region of Trier

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1. Introduction

During and after the application of pesticides in agriculture, a fraction of the applied dosage may enter the atmosphere. Once in the atmosphere these compounds can be transported over varying distances downwind of the target, can be transformed and finally deposited. Both the processes of gas and particle scavenging are important paths of atmospheric deposition of these compounds (Ligocki et al., 1985a and 1985b). Deposition by precipitation has turned out as an important path of atmospheric input of anthropogenic chemicals to water bodies (Dickhut and Gustafson, 1995; Golomb et al., 1997; Rawn et al., 1999).

In the framework of the SFB522 “Umwelt und Region” (collaborative research centre 522 “Environment and region”) developed in the University of Trier, a specific project (B3) is focused on organic pollutants dispersed in the atmosphere. One goal of this project is to investigate the spatial and temporal variabilities of a wide spectrum of pesticides and polycyclic aromatic hydrocarbons (PAHs) in precipitation in the region of Trier. First results will be published soon (de Rossi et al., 2001).

The town of Trier, with nearly 100000 inhabitants, is located at the river Moselle, in southwest Germany, and is one of the main centres of the vinicultural area of the Moselle-Saar-Ruwer, where pesticides are widely used, among them many fungicides.

2. Methodology

Table 1: Sampling sites

Sampling site	Altitude (m)	Description
A – Avelsbach	228	Site located in a vineyard
G – Grünflächenamt Trier town	130	Site located in town
H – Hospital Geozentrum	261	Site located on a hill, close to one of the university buildings
K – Kenn	137	Site situated in the industrial area of Trier and close to a heavy trafficked highway
M – Morscheid	174	Site located in a vineyard
MB – Mertesdorf Berg	330	Site located on a hill in a not cultivated area
MK – Mertesdorf Ruwer valley	141	Site located inside a sewage treatment plant area, nearby two biological treatment pools
T – Thomm	458	Site located in an agricultural area
U – Universität	270	Site located on a hill, on the roof of one of the university buildings

The data presented here are the first results obtained for pesticides detected in rain samples which were weekly collected between August 1999 and May 2001 in 9 sampling sites (Table 1). Urban sites were chosen as well as industrial and rural sites. In the year 1999, only 4 of the 9 sites were used for sampling collection.

Bulk precipitation (wet plus dry fall) was collected with a 60*60 cm stainless steel catch basin connected by means of a teflon tube to a 4L brown glass bottle.

Solid phase extraction (SPE) by C18 cartridges was carried out. After a 24 h freeze-drying step, cartridges were eluted with hexane, ethylacetate and acetone in sequence. Pesticides were quantified using gas-chromatography - mass spectrometry (HP 5890 Series II, 5970B MSD) in SIM mode (Rübel, 1999). The limit of determination was between 5 and 20 ng/l.

Altogether 235 samples were collected. Substances which were found in more than 30 % of the samples are the herbicides atrazine (36%) and simazine (30%), the fungicides penconazole (34 %) and procymidone (37 %), and the insecticide methyl parathion (48 %).

3. Results

Figures 1-3 show concentrations of selected herbicides and some of their metabolites are shown. All substances were detected as soon as sampling began in July 1999. A well defined temporal variation, which suggests an application time in May and June, could be observed in all sites in year 2000. However, no significant variations among the sampling stations were observed (agricultural site similar to urban and industrial sites). Moreover, given the fact that the use of atrazine is forbidden in Germany since 1991, it may be thought that the presence of this substance and its metabolites (desethylatrazine and desisopropylatrazine) in the rain is due to atmospheric transport from other areas rather than to local use. These substances are, in effect, still in use in neighbouring countries like France, Luxembourg and Belgium.

Figures 4-6 show concentrations of selected fungicides. These substances were detected as soon as May and their presence in the rain could be observed all over the summer till the end of September. Fungicides are applied every two or three weeks (depending upon weather conditions as dry conditions are required) from the first application; in all, four or five applications are carried out during the summer. Concentrations of tebuconazole, a triazole fungicide, detected in the site located in the Ruwer valley (see Fig. 6) indicate the temporal variation of its release in the environment.

The insecticide methyl parathion (see Fig. 7) showed high differences between concentrations detected in 1999 and 2000. From July 1999 till September 1999 very high levels were detected in all 4 sampling sites. During this period losses of the pure substance were found on an agricultural road in the southwest of the sampling area. In the year 2000, lower concentrations were detected from May until August in all 9 sampling sites.

In conclusion, seasonal trends could be observed for all substances detected, in all sampling sites. On the other hand, concentration levels showed no spatial variation, though the sites were located in different valleys, at different height, some were very close to vineyards, some others in the middle of the town.

Fig. 1: Herbicide concentrations in a rural site (vineyard).

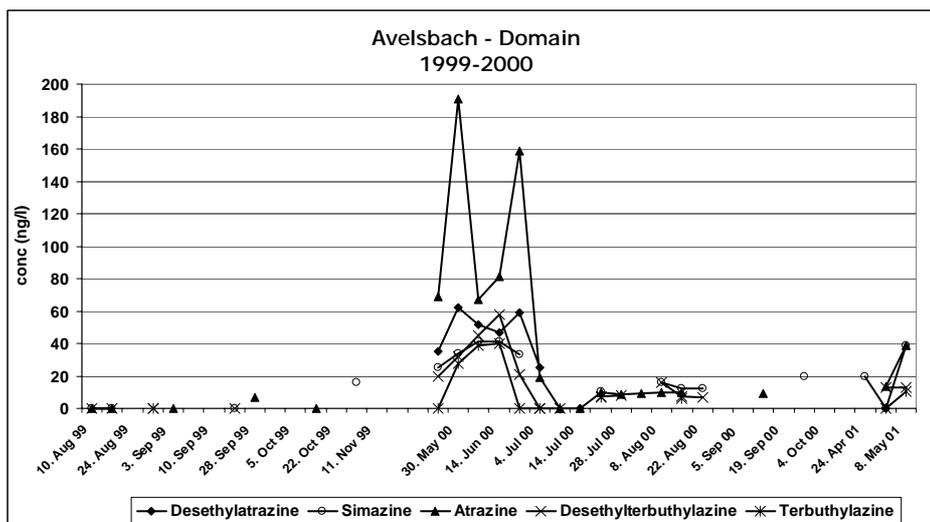


Fig. 2: Herbicide concentrations in an urban site.

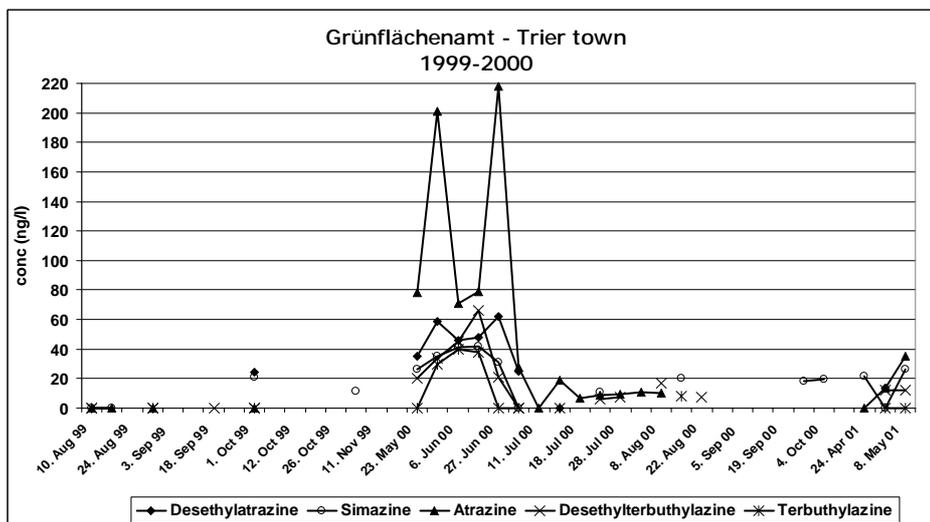


Fig. 3: Herbicide concentrations in an industrial site.

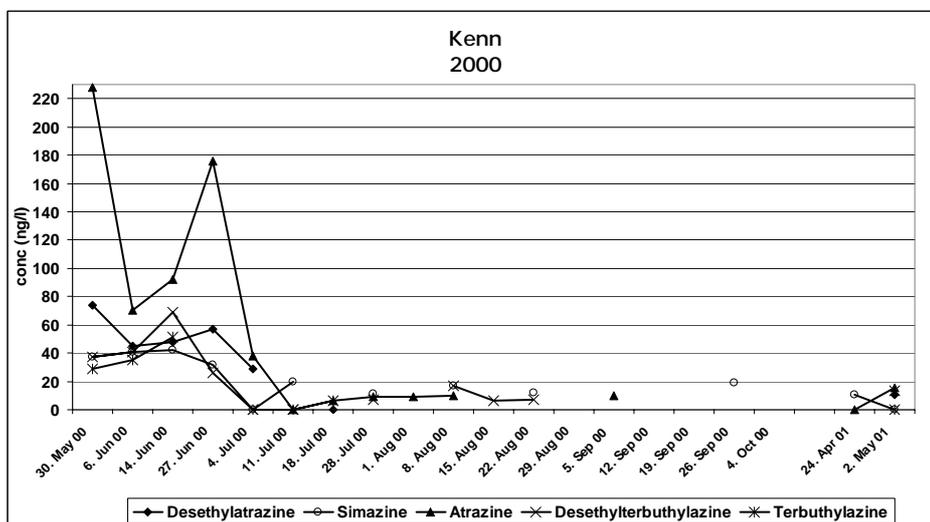


Fig. 4: Fungicide concentrations in a rural site (vineyard).

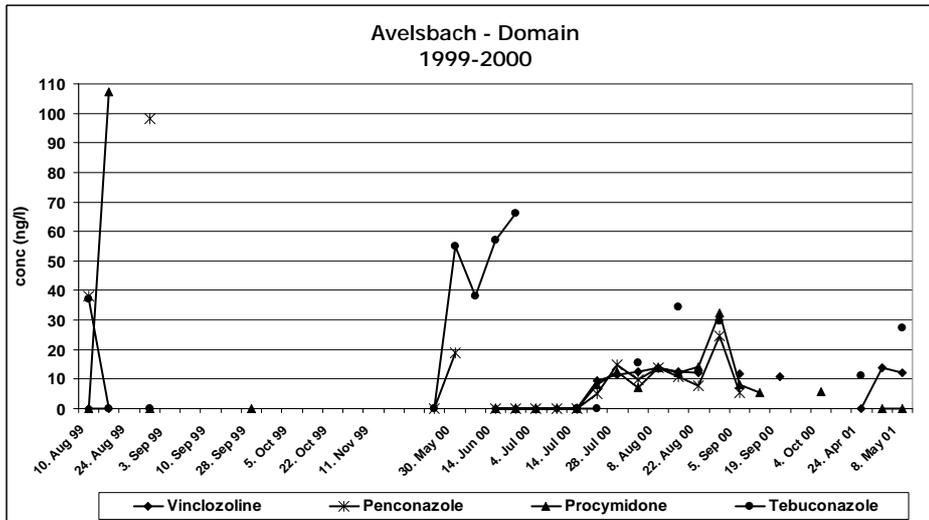


Fig. 5: Fungicide concentrations in an urban site.

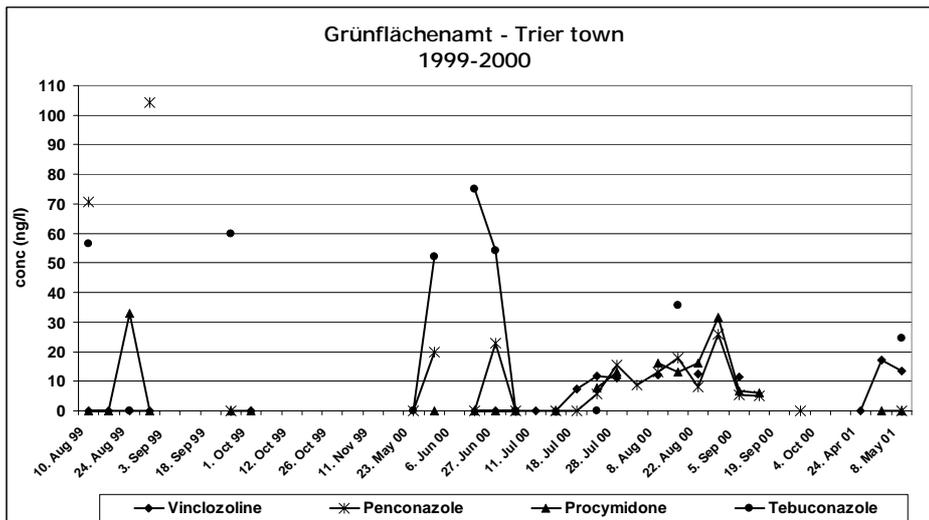


Fig. 6: Fungicide concentrations in a countryside site.

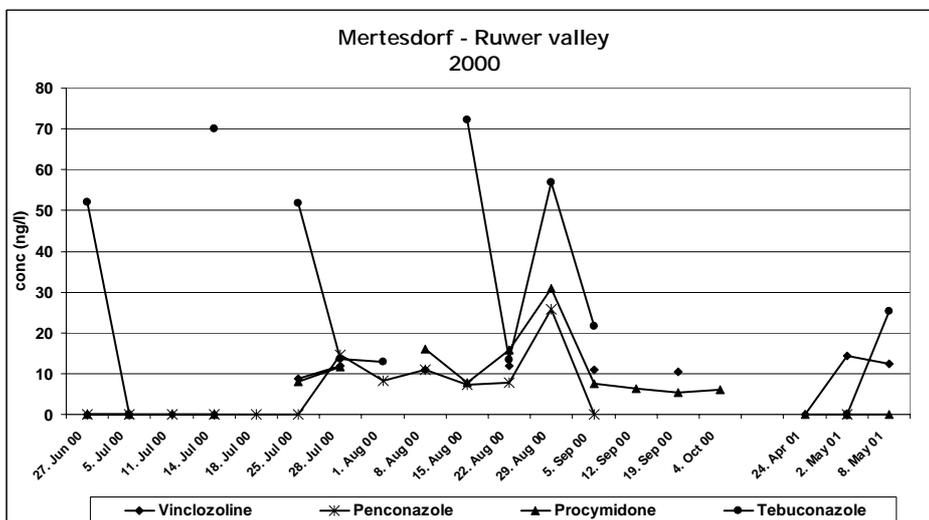
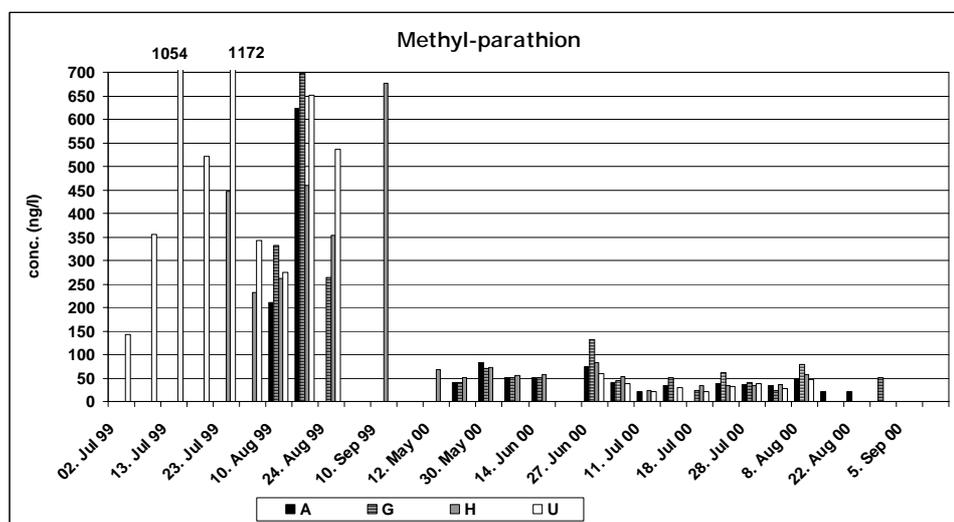


Fig. 7: Methyl parathion concentrations detected in four sampling sites (A = Avelsbach, G = Grünflächenamt Trier town, H = Hospital Geozentrum, U = Universität; cf. Table 1).



Pesticide concentrations measured in the year 1999 turned out to be much higher than the levels detected in the year 2000. The year 2000 was characterised by a very unusual rainy summer. In July 2000, 229 mm of precipitation were measured, while only 35 mm were measured in July 1999. This fact may be responsible of a higher dilution of the samples. Higher concentrations in rainwater can be observed during a very brief rain event, while a more significant storm may deliver more pesticide mass to a region despite lower overall rainwater concentrations. Therefore a further determination of mass deposition of single compounds will be carried out. Moreover, rain samples collected in 2001 will be analysed and more data will be available for a better understanding of the temporal trend and eventual spatial variations of these substances in precipitation in the region.

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2.3 Observations of Pesticides in the Beijing Area (Air, Rain and Surface Water)

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1. Aims

China is one of the world's largest pesticide producers and users. Pesticide use in China is increasing, but safety and environmental aspects are not considered adequately so far.

The aims of the investigations presented here were to establish a monitoring program for surface, ground, rainwater and air, to contribute data about pesticide occurrence in the environment.

For air monitoring a newly developed passive sampler was tested.

2. Methodology

2.1 Monitoring program – sampling sites

All water sampling was done in the Beijing area, in the year 2001.

2.1.1 Surface water

Jingmi Irrigation Canal: This canal provides the city of Beijing with drinking water, and is one of the city's main drinking water sources. To a lesser extent the water is also used for irrigation. The water comes from the Miyun Reservoir, about 100 km northeast of Beijing. The catchment area of the reservoir is a mountain area with little agricultural activity and pesticide use. Along the canal there is high agricultural intensity, and the crops grown are mainly rice and wheat (The People's Government of Haidian District, 1996). Samples were taken at 5 sites: at the Miyun Reservoir, and 30 km, 50 km and 70 km downstream and where the canal enters the city area of Beijing.

Branch I: the branch is fed by the Jingmi Irrigation Canal, and provides water for the wheat, maize and rice fields. Samples have been taken at the Dongbeiwang experimental field, about 5 km from the main canal.

Branch II: the branch is also fed by the Jingmi Irrigation Canal, and provides water mainly for the rice fields. Samples have been taken at the Tun dian Village, about 5 km from the main canal.

Wanquan River and Nansha River: Both rivers are in the Haidian District. In this area rice is dominating (about 44 km²) but also wheat, corn and vegetables are cultivated. The Wanquan River is relatively small and only 8.5 km long. At this river there was one sampling site halfway. The Nansha River, which is 21 km long, flows through the main rice growing area, and ends in the Shahe Reservoir. The three sampling sites were every 5 km downstream, and started at Daoxiang Lake, which is the origin of the river.

At all sites sampling was done at least once a month. The samples were taken with a bucket from a bridge and transferred to brown glass bottles.

2.1.2 Rainwater

There were seven sampling sites: one in a village (Dongbeiwang), two in the city of Beijing (Campus of China Agricultural University and Xiaojiahe), two in agricultural fields

(Dongbeiwang, and Shangzhuang), two in a mountain area (Baiwang mountain and Miyun mountain). Rain was sampled with 50 cm (diam.) permanently open collectors (material: steel) into brown 2 L glass bottles. With this type of collector wet and dry deposition is sampled. Samples were taken after every rain.

2.1.3 Ground water

Ground water was pumped from two wells, both 100 m deep: One at the Dongbeiwang experimental field where the water is used for irrigation. The other well was in the Shangzhuang village, where the water is used as drinking water. Samples were taken once a month.

If any possible all the surface, rain and ground water samples were analyzed right after sampling or stored in glass bottles in a dark and cool room, not longer than one week.

2.2 Air monitoring

2.2.1 Active sampling

Investigations were done in a greenhouse in Beijing near the China Agricultural university. Chlorothalonil was applied to tomato plants (500 g a.i./ha). 90 minutes after application air sampling was started with high volume samplers (flow-rate 1.67 L/h) and passive samplers. Sampling was done daily (24 h samples) until 4 days after application. One background sample was taken the day before application.

2.2.2 Passive sampling

Besides active sampling, passive sampling was tested for its suitability for air monitoring. The tube-type sampler was made from aluminium with an inner diameter of 11 cm, a diffusion length of 2 mm and a teflon membrane as draught shield. XAD4 was used as adsorbent. The sampler is shown in Fig. 1.

Fig. 1: Diffusive sampler – dismantled and assembled



Samples with the passive sampler were taken on day 1 (24 h), days 2+3 (48 h), days 3+4 (48 h), days 1-4 (96 h) and the day before application (24 h).

2.4 Pesticide analysis

2.4.1 Water samples

31 pesticides of major use in agriculture in the Beijing area were included in analysis. Water samples were extracted via liquid-liquid extraction and solid phase extraction (SPE). Extracts were concentrated and analyzed by GC-NPD and GC-MS.

2.4.2 Air samples

Polyurethane foams from active sampling and XAD4 resins were solvent extracted, concentrated and analyzed by GC-MS.

3. Results

3.1 Monitoring program - water

3.1.1 Surface water

Out of the 113 surface water samples 11% were contaminated with pesticide residues. The compounds detected were three herbicides: butachlor, metolachlor and molinate, and three insecticides: chlorpyrifos, diazinon and dichlorvos. The concentrations were similar for herbicides and insecticides and were in the range of $< 0.1 \mu\text{g/L}$ to $5.1 \mu\text{g/L}$.

No pesticides were detected in the main Jingmi Irrigation Canal although it flows through an intensively used agricultural area. One of the two branches (I) was contaminated with dichlorvos but only at the end of August, while the other (II) showed significant contamination with butachlor and molinate at the end of May, and some minor residues of metolachlor, chlorpyrifos and butachlor in April, July and August. The situation is similar with the Nansha River and the Wanquan River.

From the insecticides it was dichlorvos which had the highest concentrations, while the others were of minor importance. It occurred at that time in branch I of the Jingmi Irrigation Canal and the Wanquan River.

In none of the water samples fungicides were detected.

3.1.2 Rainwater

During the period from March to October 75 rainwater samples were collected. From the 75 samples collected, only 4 showed pesticide residues. Out of the herbicides there were atrazine, metolachlor and molinate, and of the insecticides dichlorvos and parathion. Dichlorvos was the dominating compound especially from mid July until the end of August with concentrations up to $24 \mu\text{g/L}$. Dichlorvos was present in the rain at all sampling sites except the Miuyun mountain. The highest dichlorvos concentrations were found in the rainwater collected in the village and Shangzhuang village. In comparison to dichlorvos the concentrations of the herbicides were much lower. Except for a very small residue of molinate ($< 0.1 \mu\text{g/L}$) in September, herbicides were only present in the rain from May to July.

All compounds, which had been detected in surface water, were also present in rainwater, except for butachlor, which was the dominating compound in the rice growing areas. As with surface water, no fungicides were detected.

3.1.3 Ground water

From the 15 ground water samples none showed pesticide contamination.

3.2 Air monitoring in greenhouses

3.2.1 Active sampling

Chlorothalonil concentrations (gaseous) measured by active sampling showed a peak concentration of $2.3 \mu\text{g}/\text{m}^3$ on the first day after application. The concentrations on the following days decreased to $0.22 \mu\text{g}/\text{m}^3$ on day 4 after application. Chlorothalonil was also detected the day before application at a concentration of $0.14 \mu\text{g}/\text{m}^3$.

3.2.2 Passive sampling

With passive samplers, chlorothalonil was detected on day 1 after application (24 h exposure) and days 1-4 (96 h exposure). In all other samples chlorothalonil was below the detection limit.

Chlorothalonil concentrations measured by passive sampling correlate well with the corresponding concentrations measured by active sampling. Chlorothalonil concentrations measured with two passive samplers on day 1 after application were 1.7 and $3.0 \mu\text{g}/\text{m}^3$. The average concentration of $2.2 \mu\text{g}/\text{m}^3$ correlates well with the concentration of $2.3 \mu\text{g}/\text{m}^3$ determined by active sampling. This also applies to the 96 h average concentration from days 1 to 4 after application ($0.70 \mu\text{g}/\text{m}^3$: active sampling, $0.84 \mu\text{g}/\text{m}^3$: passive sampling). All concentration data are shown in Table 1.

4 Conclusions

4.1 Monitoring program – water

Since branch II of the Jingmi Irrigation Canal, Wanquan and Nansha River flow through rice growing areas, and butachlor as well as molinate are the predominating herbicides in rice, it is obvious that the source of their contamination is chemical weed control in rice.

It is assumed, that the occurrence of dichlorvos in branch I of the Jingmi Irrigation Canal and the Wanquan River is related with pest control measures in the fruit plantations in this area. Whether spray drift or other processes led to the contamination of these surface waters is unknown.

The reason for the rather high concentrations of dichlorvos in the rainwater of villages is not clear. It is assumed that the excessive use of dichlorvos for pest control on houses contributes to a great extent to air contamination and hence to the contamination of rainwater.

Out of all compounds dichlorvos has the highest vapour pressure, and hence it may be expected in the atmosphere and consequently in rain. Whether dichlorvos in the rain collected in the field and on mountain I originates from its use in houses nearby or from agriculture, is not known. However, it seems, that non-agricultural use contributes to a great extent to the occurrence of this chemical in rainwater.

No pesticides were detected in groundwater. This is most likely due to the geological situation in the area.

The results demonstrate clearly, that pesticides used in the investigated area do contaminate surface water and rainwater. These first results should help to focus on the general problem of agricultural use of pesticides and the undesirable contamination of the environment. Although the data presented are limited, they should be a signal for agriculture to minimize this pollution, and develop adequate strategies in order to have a satisfactory but also environmentally safe crop protection.

4.2 Air sampling in greenhouses

Higher concentrations of chlorothalonil could be detected with passive samplers.

The reason for the big difference in measured air concentrations between the two samples taken on the first day after application is not clear.

Due to its much lower sampling rate (8.3 L/h compared to 6000 L/h of active sampling), passive sampling needs much longer exposure times than active sampling. To determine short-time concentrations in air, the passive samplers are not adequate. However, this experiment indicates that the developed passive sampler can be used for environmental pesticide air monitoring, provided that exposure times are long enough.

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3. Long-range Transports: Observations and Modeling of Persistent Substances

3.1 Regional Background Monitoring of Persistent, Bioaccumulative and Toxic Compounds in Central Europe and Comparison with Model Results

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1. POPs in EMEP strategies

The choice of the compounds listed below follows EMEP, 1998:

1) Determination of compounds most frequently found in air and deposition samples and which are easy to detect:

- Hexachlorobenzene (HCB)
- Hexachlorocyclohexanes (HCHs): α -, γ -HCH
- Polychlorinated biphenyls (PCBs): IUPAC Nos. 28, 52, 101, 118, 153, 138, 180
- Polyaromatic hydrocarbons (PAHs), where the choice will depend on method of analysis
- Chlordanes: α -, γ -chlordanes

2) POPs which are present in low atmospheric concentrations and consequently require more specialised analytical methods, but are of great environmental importance (groups of compounds):

- Current used pesticides (endosulfan, atrazine etc.)
- DDTs
- Chlordanes (other than mentioned above)
- Toxaphene
- Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/Fs)
- PCBs: coplanar congeners
- Brominated flame retardants
- Chlorophenols
- Polychlorinated naphthalenes (PCNs)
- Polychlorinated diphenyl ethers (PCDEs)

The overall aim of integrated monitoring was originally to determine and predict the state and change of terrestrial and freshwater ecosystems in a long-term perspective with respect to the impact of air pollutants including persistent organics (CLRTAP, 1998).

Integrated monitoring of ecosystems means physical, chemical and biological measurements over time of different ecosystem compartments simultaneously at the same location. A small catchment (or other hydrologically well defined area), such as in integrated monitoring site, is large enough to encompass all the interacting components: atmosphere and vegetation, plants and soils, bedrock and groundwater, brook or lake, and surrounding land. A small catchment

comprises a terrestrial ecosystem usually with a linked aquatic ecosystem of an adjacent brook. Some basins contain one or more ponds or lakes. A terrestrial ecosystem is conventionally viewed as an assemblage of living organisms interacting in a complex way with one another and with their environment, air, soil and water.

The regional and global nature of the processes make international efforts to generate comparable measurements the only basis on which further knowledge on the pools and fluxes can rest. Only a few POPs had been measured at a few sites.

For persistent organic pollutants the reversibility of deposition processes and the consequent re-emission make soils and vegetation relevant sinks and resources as well as receptors at risk and therefore the assessment of existing concentrations in different media is an important step to develop effective control measures based on an improved understanding the current status of the relevant pathways and potential effects of the different substances under consideration in different environments.

The contribution of Integrated monitoring programme in the future could be very significant if comparable and simultaneous measurements of atmospheric concentrations, wet, bulk and dry deposition, concentration in soils, sediments, water and vegetation (lichens, mosses, needles, leaves, bark) could be obtained for a range of different ecosystems in different regions such as the ICP IM network.

Such information would be of very great value to a) enhance the precision of vegetation samples as indicators, b) improve the estimates of local pools and fluxes and of uncertain, substance and site specific parameters on which exposure estimates can be developed and c) by reporting the information's to the modelling community improve the accuracy of extensive regional modelling of long range atmospheric transport of POPs.

The workshop EMEP (1996) recommended for an initial phase of measurements the following compounds (CLRTAP, 1998):

- polycyclic aromatic hydrocarbons (PAHs): benzo(a)pyrene (B[a]P)
- polychlorinated biphenyls (PCBs) congener IUPAC number 28, 52, 101, 118, 153, 138, 180
- hexachlorobenzene (HCB)
- α -, γ -chlordanes
- α -, γ -hexachlorocyclohexanes (HCHs)
- DDT/DDE

2. Project TOCOEN – regional background monitoring of PBTs

The regional background monitoring of PBTs (POPs) as a part of the research project TOCOEN (Toxic Organic Compounds in the Environment) is realised at the area of Košetice observatory since 1988. This monitoring is a part of long-term co-operation between the Czech Hydrometeorological Institute (CHMI) and Research Centre for Environmental Chemistry and Ecotoxicology (RECETOX; Holoubek, 1993; Holoubek et al., 1990 and 1996). TOCOEN involves many Czech and Slovak universities, research institutions and various companies and, at the present time, also some universities and institutions from other countries.

This part of project TOCOEN is focused on the determination of PAHs, chlorinated pesticides and PCBs in the air samples (A - once in a week), rain water samples (RW - every event), surface waters (W), sediments (SED), soils (S), terrestrial biota (earthworms (E), mosses (N)

and needles (N) – all once in a year. The sampling period started in fall of 1988. The sampling sites are described in Table 1.

Table 1: The overview of sampling sites, types of samples and frequency of sampling

Name	Start	Site	TOCOEN Site No. (Fig. 1)	Frequency
Ambient air	1988	03	01	Weekly
Wet deposition	1988	03	01	Evently
Surface waters	1988	71, 72, 74, 75, 76, 77	04, 02, 10, 12a, 12b, 14	Yearly
Sediments	1988	71, 72, 74, 75, 76, 77	04, 02, 10, 12a, 12b, 14	Yearly
Soils	1988	03, 85, 86, 87, 88, 89, 90, 91	01, 03, 05, 07, 08, 09, 11, 13, 15	Yearly
Litter	1997	89	09	Yearly
Spruce and pine needles	1988	86, 87, 88, 89, 91	05, 07, 08, 09, 13, (15), (16)	Yearly
Mosses	1988	86, 87, 88, 89, 91	05, 07, 08, 09, 13, (15), (16)	Yearly

Analysis: polycyclic aromatic hydrocarbons (PAHs) - 16 US EPA; organochlorinated pesticides - Σ DDTs (DDT + DDE + DDD), Σ HCHs (hexachlorocyclohexanes = $\alpha + \beta + \gamma + \delta$), hexachlorobenzene (HCB), polychlorinated biphenyls (PCBs) - congeners IUPAC nos. 28, 52, 101, 118, 138, 153, 180), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/Fs) - 2,3,7,8-substituted congeners and homologues groups

QA/QC set of procedures as absolutely necessary to achieve any kind of meaningful results are performed according to conclusions of an EMEP workshop (EMEP, 1998).

3. Regional levels of PBTs

The first information concerning to ambient air levels of PBTs compounds in former Czechoslovakia was published as results of TOCOEN (Holoubek, 1993; Holoubek et al., 1990 and 1996).

The Ministry of the Environment (MoE) and RECETOX established the System of Monitoring of Organic Compounds in the Ambient Air (SYMOS), a preliminary monitoring system of PBT compounds in ambient air in the Czech Republic. During the SYMOS pilot study in 1994-1995, PAHs, PCBs, chlorinated pesticides and PCDDs/Fs were monitored in the area of Košetice observatory (located in south Bohemia, run by CHMI). It was established as a regional background station of international (EMEP, GAW, GEMS) and national monitoring programmes (MoE, Project TOCOEN, GEOMON).

From 1996, the regular monitoring of semi-volatile PBTs was continued at the Košetice observatory, under a co-operation scheme between CHMI, Prague, and RECETOX-TOCOEN & Associates, Brno. The Košetice Observatory is included among regional background stations under both international (GAW, EMEP) and national (TOCOEN) programmes (CHMI, 1997, 1998 and 1999). In present time, the TOCOEN monitoring programme of PBTs at Košetice observatory has been carried out on a regular basis for already 13 years – a unique achievement globally. The sampling procedure (one samples per week for determination of PAHs, PCBs and OCPs) and analytical determination is based on conclusions of the EMEP workshop (EMEP, 1998). Pollutants mentioned above are monitored in the gaseous state as well as in atmospheric particulates. The Tables 2 and 3 summarize these results of measurements of PAHs (Table 2) and OCPs and PCBs (Table 3) from 1996 to 1999.

Table 2: Observed concentrations of total PAHs (gas and particulate phases) at Košetice 1996-1999 [ng m^{-3}]

PAHs	Minimum	Maximum	Arithmetic mean	Geometric mean	Median
Naphthalene	0.0025	56.6900	2.5409	0.5111	0.3820
Acenaphthylene	0.0025	38.1700	0.8339	0.1114	0.1230
Acenaphthene	0.0025	6.9300	0.3323	0.1164	0.1215
Fluorene	0.0025	56.0600	4.0805	1.7470	1.9610
Phenanthrene	0.0025	117.5000	8.2358	4.4350	4.8635
Anthracene	0.0025	8.9200	0.3202	0.1329	0.1385
Fluoranthene	0.0025	77.3300	2.8638	1.3362	1.6785
Pyrene	0.0025	54.7300	1.8350	0.7902	1.0750
Benz(a)anthracene	0.0050	23.7800	0.5172	0.1056	0.1200
Chrysene	0.0050	32.3700	0.8841	0.2599	0.2730
Benzo(b)fluoranthene	0.0050	34.4500	0.7704	0.1889	0.1920
Benzo(k)fluoranthene	0.0050	9.7100	0.4295	0.1160	0.1325
Benzo(a)pyrene	0.0050	13.7700	0.3864	0.0773	0.0750
Indeno(123-cd)pyrene	0.0050	20.4200	0.5682	0.1221	0.1500
Dibenz(ah)anthracene	0.0050	2.8400	0.0668	0.0000	0.0095
Benzo(ghi)perylene	0.0050	14.0000	0.4145	0.1012	0.1235
Sum of PAHs	0.06	567.67	25.08	11.65	13.17

Table 3: Observed concentrations of total PCBs and other organochlorinated pesticides (gas and particulate phases) at Košetice 1996-1999 [ng m^{-3}]

OCPs	Minimum	Maximum	Arithmetic mean	Geometric mean	Median
PCB 28	0.0007	0.1640	0.0201	0.0000	0.0150
PCB 52	0.0010	0.1070	0.0190	0.0000	0.0170
PCB 101	0.0007	0.0790	0.0156	0.0000	0.0130
PCB 118	0.0006	0.0130	0.0027	0.0000	0.0030
PCB 153	0.0006	0.1620	0.0268	0.0000	0.0180
PCB 138	0.0005	0.1120	0.0183	0.0000	0.0130
PCB 180	0.0004	0.1170	0.0132	0.0000	0.0090
Σ PCBs	0.0045	0.4670	0.1155	0.0600	0.0965
α -HCH	0.0006	0.2130	0.0315	0.0000	0.0270
β -HCH	0.0005	0.0740	0.0059	0.0000	0.0005
γ -HCH	0.0008	0.6990	0.0561	0.0000	0.0170
δ -HCH	0.0005	0.0100	0.0006	0.0000	0.0005
Σ HCHs	0.0020	0.8410	0.0935	0.0000	0.0510
p,p'-DDE	0.0005	0.2130	0.0306	0.0000	0.0250
p,p'-DDD	0.0012	0.0220	0.0025	0.0000	0.0012
p,p'-DDT	0.0030	0.0780	0.0056	0.0000	0.0033
Σ DDTs	0.0010	0.2130	0.0363	0.0000	0.0280
HCB	0.0004	0.8350	0.1036	0.0000	0.0870

The PAHs concentrations identified follow characteristic course prompted by the higher occurrence of these compounds in winter when they are produced by various combustion processes. PCBs and OCPs concentrations display a totally different profile in which no such "seasonality" has been identified. These compounds are present in the atmosphere today due to their volatilisation from soil and sediments, i.e. as secondary inputs from old deposits, and also due to a long-range atmospheric transport from regions in which they are still used. These results reflect the global trends. PCBs occurrence remains at the level of the European background. From the PCBs pictures we can see the decreasing tendency during this period. The DDT compounds are dominated by the degradation metabolites, DDE and DDD. The

same trend exists in all environmental samples from this observatory (Holoubek et al., 1998a, 1998b, 2000a, 2000b and 2001). This predominance reflects old loads – input from old usage and environmental accumulation of DDT rather than long-range transport from regions where the compound is still in use.

The identification of PBT sources is a focus of the long-term ambient air monitoring programme. Relationships between levels of PBTs in air and day average wind direction show that the main sector of air masses, which are transported to the location of Košetice observatory, is between 220° and 320°. In this sector, wind collects the PBTs from industrial and urban sources such as Prague, Plzeň or České Budějovice (in the case of the nearest sources in the Czech Republic). Of course, this is only the end of wind trajectories of air masses and we can determine the other sources, which are located in these ways of air masses. From this reason, the more detailed study of major contributors to the air masses contamination will be based on the comparison of the results with trajectory analyses (NOAA).

4. Comparison between results from measurements and modelling

This part describes the results of co-operation between the modellers from EMEP MSC-East, Moscow, Russia, and RECETOX–TOCOEN & Associates in the field and experimental validation of POP transport models (Shatalov et al., 2000a and 2000b). For this comparison the data of POP transport and accumulation in Europe for 1997, were used. For adequate description of contamination the calculations of POP transport and accumulation should be performed for decades. Consequently, to assess the contamination in 1997, the calculations were carried out for the period from 1970 to 1997.

The 3-D Eulerian multi-compartmental model (MSCE-POP) operates with the EMEP grid with spatial resolution 150 km * 150 km. Along with the pollution transport in the atmosphere and ocean, the model includes the description of exchange processes between different environmental compartments.

The model considers the following compartments: air, soil, sea, vegetation and litter fall. It is assumed that initially emitted POP enters the atmospheric air. Then in the course of dry and wet depositions of the gas and particulate phases a pollutant enters soil, sea and vegetation. Dry deposition process of the pollutant gas-phase is considered to be reversible allowing us directly in the modelling course to consider the re-emission process important for some pollutants. From vegetation with fallen leaves a pollutant enters the litter fall where from in some time finds its way to the soil. The accumulation in compartments decreases due to POP degradation in the course of chemical, biochemical and photochemical reactions.

Due to advection and diffusion in the atmosphere and sea pollutants are transported at long distances from the emission source and partially are exported outside the calculation domain. The pollutant fraction transported outside the EMEP grid can be used as an estimate of the considered pollutant capability for the long-range transport.

The input information on POP modelling is emission fields, meteorological data, land use, properties of soil, vegetation and marine environment including sea currents and physical chemical properties of a pollutant in question.

According to the POP Protocol, B[a]P, PCB, and γ -HCH were judged priority for modelling.

These substances can be characterized as persistent, toxic, subject to long-range transport. From the viewpoint of model development these substances are interesting since they are differently distributed between the atmospheric gaseous and particulate phases. Namely, the largest fraction of B[a]P is settled on particles, while γ -HCH exists in the atmosphere mainly in the gaseous phase, and PCB is an intermediate substance.

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3.2 Long-range Transport and Environmental Fate of Modern Pesticides – Model Development and Application

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1. Approach and model components

3D global chemistry-transport-models have not been used for the study of the transport and the environmental fate of semi-volatile substances (SOCs) by now, although they are in principle suitable tools for determining the exposition of the environment to these substances. We are developing a multicompartment chemistry-transport model which is based on a state-of-the-art climate model (Roeckner et al., 1996). This has been modified in the past (Feichter et al., 1996, besides others) for the study of atmospheric gas-phase and cloudwater chemistry and deposition of short-lived substances, and, more recently (Lammel, 2001; Lammel et al., 2001), for the study of SOCs. In order to cover SOCs, additional media were represented as 2D arrays of boxes and linked to the atmosphere and a number of intra- and intermedia processes were parameterised.

1.1 Media represented and intermedia mass transfer

In the current state of development, the model comprises atmosphere, vegetation, soils and ocean. No sediments and other biota exist in the model world. A cryosphere is part of the climate system but does not specifically interact with SOCs. Vegetation and soil are distributed geo-referenced as single layer boxes. The ocean is represented as a well-mixed surface layer with locally and seasonally varying depth. This information is taken from a 3D global circulation model run of the ocean (based on the criterium of water density not exceeding the surface water density + 0.2 kg m⁻³; Drijfhout et al., 1996). The global annual mean depth is 80.2 m.

The atmosphere is a three phase system (gas, particles, cloudwater), with the mass exchange between them being controlled by instantaneous equilibria (Junge model for gas-particle partitioning, Henry equilibrium for air-cloudwater partitioning). Degradation is controlled by the hydroxyl and nitrate radical concentration (3D fields varying with time of day and month). In the first simulations we assumed the same kinetics to obey independently of whether the substance is in the gaseous or in the adsorbed/absorbed state. There are no chemical sinks in the cloudwater. Wet and dry deposition processes are considered for various types, each.

Exchange processes of SOCs with vegetation are hardly understood. In the model, the vegetation is represented as providing a surface for application, deposition and volatilization, but not as a volume for mass exchange. The soil contains water filled pore space (according to local soil hydrology) and a organic matter content. Volatilization from soil is described as flux from the soil air upon establishment of phase equilibrium between organic matter, soil water and soil air. The dynamics of this flux is based on many greenhouse and field studies of pesticide emission upon application (Smit et al., 1997). The ocean is a single phase (water, thus neglecting the hydrosol), two layer system. Only the upper layer is interacting with the atmosphere. It is assumed to be well mixed and the depth is varying locally and with time. No river runoff, which in reality transfers mass from the vegetation and soil compartments to the ocean compartment, is considered.

Degradation on vegetation and in soil is assumed to obey the same kinetics. In these compartments as well as in the ocean, a first-order rate constant and a default temperature dependence of the degradation rate, namely a factor of 2 every 10° temperature increase is assumed.

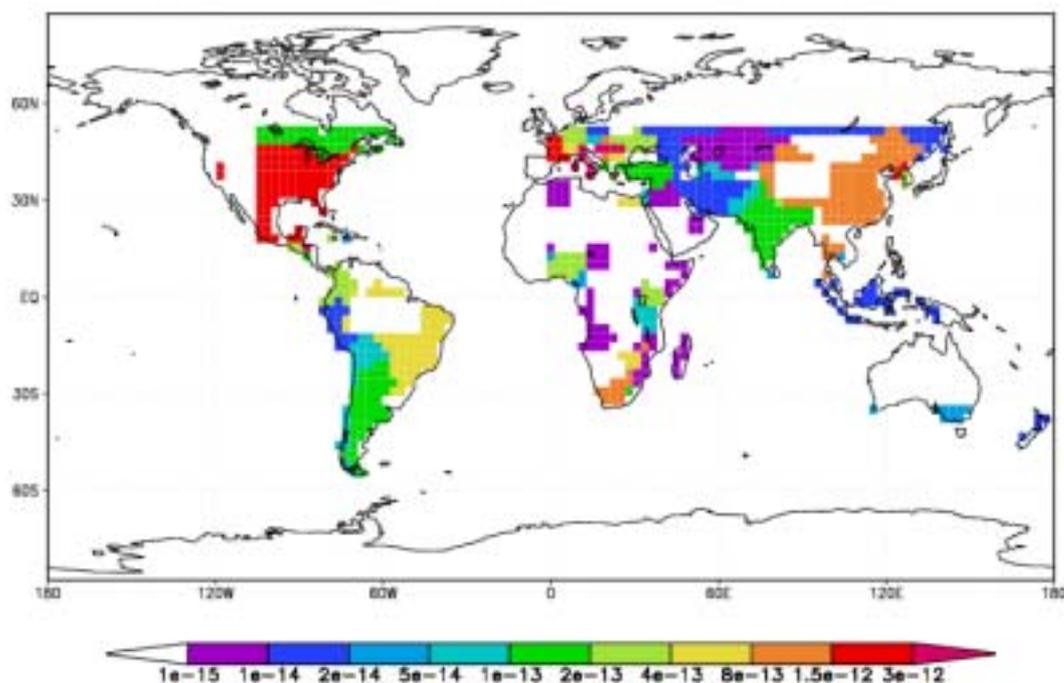
1.2 Intramedia mass transfer

Transport is considered within the atmosphere (19 levels, 1000-10 hPa) only. For the simulation of substances long-lived in the ocean, a 3D ocean model is planned to be coupled. The hydrosphere is only represented by the ocean (no rivers, lakes).

1.3 Entry into the environment

The emissions of pesticides are based on application inventories which, in turn, are based on the use patterns and crop distributions (data sources are FAO, U.S. National Agricultural Statistics Service, besides others). A validation exercise showed that applied amounts of pesticides can be predicted with an uncertainty of ca. factor of 2 on a per-country basis (Lammel et al., 2001). The deviations might be higher for tropical countries. Within the individual countries we distribute the applied amounts according to the crop area density. Once the pesticides are applied, the model climate turns these into emissions as influenced by the local conditions of temperature and soil hydrological statues. The same processes govern re-emission upon atmospheric deposition.

Fig. 1: Application inventory of atrazine based on global maize crops only (resolution 2.8° * 2.8°; kg m⁻² s⁻¹ during the month of application, i.e. May), upper estimate (see text).



Global application inventories of atrazine (Fig. 1), one of the most important herbicides, and methyl parathion, one of the most important insecticides, were set up based on the assumption that these agrochemicals are exclusively used in maize (0.090-0.148 Tg a⁻¹ of atrazine on 1.33 * 10⁸ ha) and cotton (0.051 Tg of methyl parathion on 5.52 * 10⁷ ha) cropping. The 50%ile of the cumulative zonal distributions of the applications are at 38°N and 35°N, respectively. We assume, that application takes only place during dry daylight hours in May (atrazine) or in July-August (methyl parathion) without geographical differentiation else as far as controlled by precipitation. The amounts not distributed during rainy periods are then accumulated and applied in the first half hour after the precipitation stops. In tropical regions with rare half hours without precipitation, this scenario produces mostly intermittent application.

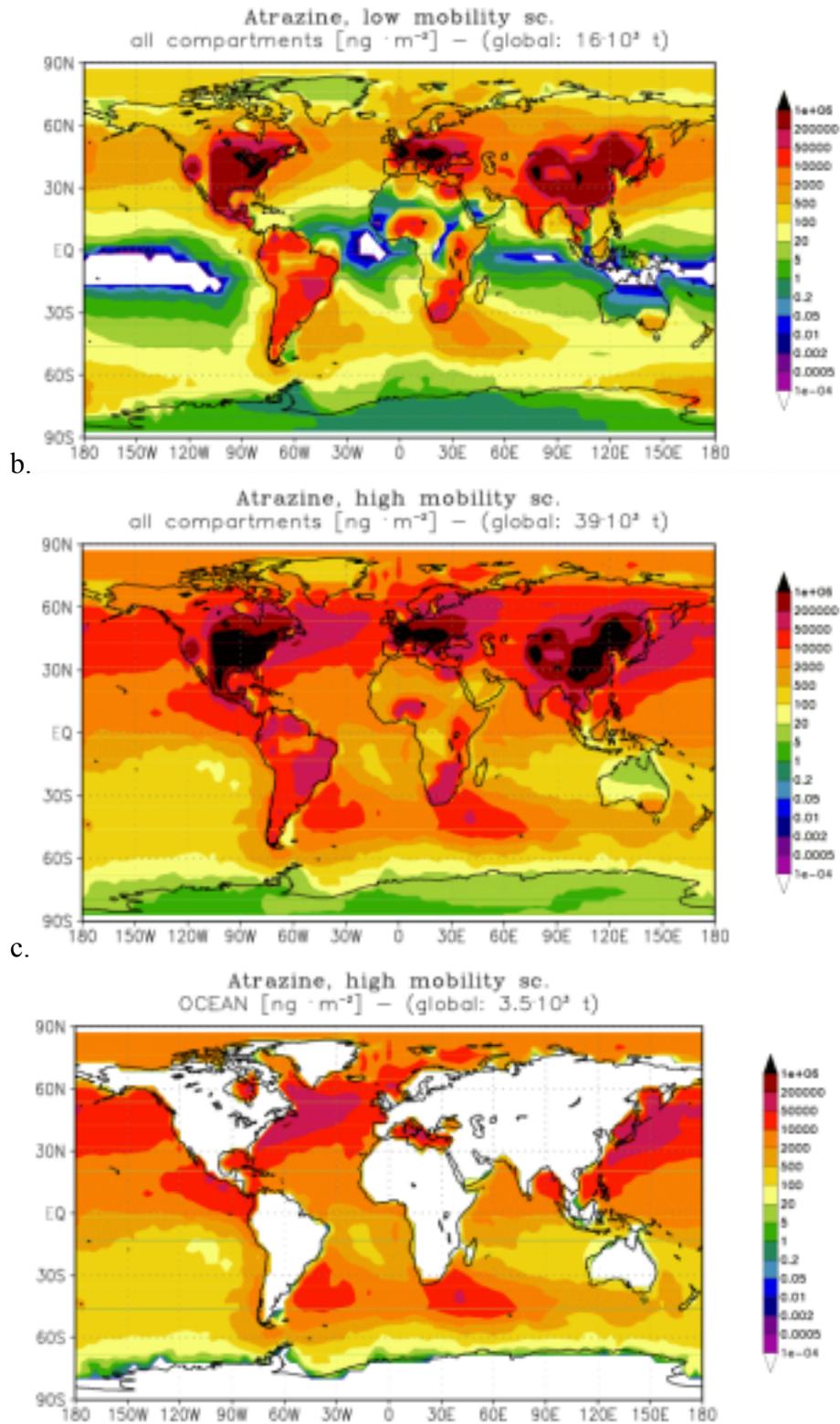
2. Simulation of the environmental fate of modern pesticides

Many widely used pesticides are subject to considerable volatilization losses upon application and undergo long-range transport as a result of limited environmental degradability. The data information used to predict environmental fate is uncertain. In the case of pesticides of intermediate overall persistence ($\tau_{1/2 \text{ total}} \leq 1 \text{ a}$) and for analysis of model results with reduced geographical ($< 1^\circ \times 1^\circ$) and time resolutions ($\ll 1 \text{ d}$), major uncertainties are introduced through degradation rates in all compartments, abundances of atmospheric aerosols, deposition velocities of the substance in the gaseous state, applied amounts to the cropland, its time pattern and its geographical distribution. A deterministic prediction based on a combination of best-guess values of all the initial parameters cannot provide a means to assess the uncertainties. Monte-Carlo type simulations are not within the reach of complex, high-resolved 3D chemistry and transport modeling. To account for the uncertainties we, therefore, perform 2 simulations based on different sets of initial parameters which are aimed to represent a lower and an upper estimate for the substance mobility in the overall environment (Lammel et al., 2001). Ambiguities of parameter choice are decided such as to favour little (low mobility scenario) or large (high mobility scenario) tendency to partition into or sustain within the mobile compartment, i.e. the atmosphere.

The results show that methyl parathion and atrazine despite their certainly significant affinity to the hydrosphere (not mobile in our model world) are nevertheless subject to significant long-range transport – at least under the high mobility scenarios (Fig. 2). This in turn, implies, that the data uncertainties which are related to (published) data availability are large enough to support a perception of long-range transport even for a substance like methyl parathion.

Fig. 2: Annual mean spatial distributions of atrazine (a.) in the total environment (low mobility scenario), (a.) in the total environment (high mobility scenario) and (c.) in the ocean (high mobility scenario). Scenarios: see text.

a.



3. Development of indicators for the characterization and communication of environmental fate

Persistence and long-range transport potential should be characterized by suitable indicators. Overall persistence (i.e. persistence in the total environment) is derived from global total environmental decay times during periods without entry into the environment. For methyl parathion we find for the environmental half-time, $\tau_{1/2 \text{ total}}$, by average 201 d (range of 142-264 d in individual months) and for atrazin we find $\tau_{1/2 \text{ total}} = 128$ (40-218) d and 203 (54-387) d under the low and high mobility scenarios, respectively. Hence, it is concluded, that the seasonal variability of the overall persistence of these two pesticides, even as a global mean, is very significant (maximum during NH winter months).

Long-range transport, being a multidimensional phenomenon should be characterized by more than one indicator. We use the cumulative zonal and meridional distributions of the geographical 2D projection of the compartments for the identification of characteristic locations: The center of gravity, COG, of a 2D distribution is located at the 50%iles of both cumulative distributions ($\text{lat}_{50}/\text{lon}_{50}$). The movement of this location in time reflects the migration of a plume. We characterize the edges of the distribution using the 5%iles and the 95%iles and derive measures for spatial scale (at time t) and for spatial spreading (relative to time t_0 ; see below). When disregarding the absolute amount of substance present, these indicators characterize for $t > t_0$ the potential spatial mobility a substance undergoes within $\Delta t = t - t_0$, which is an intensive substance property, I_{pot} . During Δt a significant fraction of the emitted amount might have been degraded. In order to characterize the substance environmental fate as referring to a particular scenario of entry (effective spatial mobility), the spatial characteristics of this fraction, which did not reach far, can be accounted for by weighing with the ratio of the amount of substance present at t and the amount of substance which was present at t_0 : $I_{\text{eff}} = (m/m_0) * I_{\text{pot}}$. For application of indicators in regulatory contexts I_{pot} should be related to hazard, I_{eff} to risk assessment.

The displacement of the plume relative to the location of emission, based on a 2D (plume displacement, PD), or a 1D, i.e. zonal analysis (zonal displacement, ZD), and the tendency for spreading of the plume, based on a 2D (spatial spreading, SS), or a 1D analysis (zonal spreading, ZS) are given by:

$$\text{ZD}_{\text{pot}}(t) = \text{distance between } \text{lat}_{50_t} \text{ and } \text{lat}_{50_{t_0}}$$

$$\text{PD}_{\text{pot}}(t) = \text{distance between the location } \text{lat}_{50_t}/\text{lon}_{50_t} \text{ and the location } \text{lat}_{50_{t_0}}/\text{lon}_{50_{t_0}}$$

$$\text{ZS}_{\text{pot}}(t) = \text{ZW}(t) - \text{ZW}(t_0)$$

$$\text{SS}_{\text{pot}}(t) = 0.5 * (\text{ZW}(t) * \text{MW}(t))^{0.5} - 0.5 * (\text{ZW}(t_0) * \text{MW}(t_0))^{0.5}$$

With: zonal width at time t : $\text{ZW}(t) = (\text{lat}_{95_t} - \text{lat}_{05_t})$
 meridional width at time t : $\text{MW}(t) = (\text{lon}_{95_t} - \text{lon}_{05_t})$
 spatial scale at time t : $0.5 * (\text{ZW}(t) * \text{MW}(t))^{0.5}$

ZS and SS are relative measures with respect to the distribution at time of entry, t_0 . All these measures are a function of time elapsed since entry, time profile of emission and of location, time and mode of entry. They are applicable to distributions in individual media or the total environment and, furthermore, all scenarios of entry, be it point (e.g. accidental release from thought-to-be closed cycles) or wide spread area sources (e.g. diffuse sources). For the same time elapsed since entry different results are expected as depending on the time profile of emission (emission scenario), e.g. singular or repeated emission pulses or continuous emission.

For atrazine and methyl parathion we report on values of annual mean potential zonal shift and potential and effective spatial scale (Table 1). As these substances persist < 1 year in the total environment (see above) and in the individual compartments, these results are constant in time. Potential and effective spatial scales address the absolute or weighted (by m/m_0) extension of the plume, respectively. According to the scenario used the spatial scales for t_0 are 6080 km (methyl parathion) and 6750 km (atrazine). These values indicate that methyl parathion is much more mobile and substance entry through the vegetation compartment is in particular prone to long-range transport.

Table 1: Characterization of the long-range transport potentials of methyl parathion (MeP) and atrazine (Atr) in the total environment and in individual compartments by annual mean (a.) potential zonal shift [$^{\circ}$ N], (b.) potential and (c.) effective spatial scales [km]. For (a.), the values in brackets refer to the range in individual months. n.d. = not defined because of $m_0 = 0$.

	Mobility Scenario	Total Environment ⁽¹⁾	Atmosphere	Soil	Vegetation	Ocean
a.						
MeP	high	+11.8 (+6 - +17)	-5.5 (-17 - +10)	+13.3 (+9 - +17)	+15.4 (+4 - +21)	+7.3(+0- 11)
Atr	low	+4.9 (+2 - +6)	+5.0 (+2 - +8)	+4.6 (+2 - +6)	+8.8 (+7 - +10)	-10.4(-38 - +3)
Atr	high	+5.7 (+2 - +7)	+3.3 (± 0 - +6)	+5.2 (+2 - +7)	+9.4 (+5- +11)	-3.3 (-17 - +2)
b.						
MeP	high	7370	9100	5770	7300	10600
Atr	low	4300	4950	4320	3730	5160
Atr	high	4880	5900	4120	5920	9670
c.						
MeP	high	3760	n.d.	15800	20000	n.d.
Atr	low	760	n.d.	770	n.d.	n.d.
Atr	high	1290	n.d.	230	2960	n.d.

⁽¹⁾ Average based on compartmental distribution

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3.3 Measurements of POPs in Air and Water on a Transect Across the Atlantic Ocean

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Abstract

In 1999/2000 air and seawater samples had been collected simultaneously during two *RV-Polarstern* cruises between Bremerhaven and Neumayer Station (Ekström Ice Shelf, 70°S/8.2°W) and between Bremerhaven and Ny-Ålesund, Svalbard (79°N/12°E). The samples had been analyzed for selected persistent organic pollutants (POPs) including PCBs, HCB and HCHs using ion-trap mass spectrometry –gas chromatography.

We presented the results of the HCH measurements at the Hamburg meeting. They were recently submitted for publication (Lakaschus et al., 2001).

The main goal of the present study was to determine the state of equilibrium that has been reached by the HCHs within the last decade, after the ban of technical HCH in India. Earlier estimates around 1990 may have lost their currency due to the change of the global usage pattern. Secondly, we hoped to establish the time trend of the HCHs in the South Atlantic using archived samples and third we wanted to compare the latitudinal profiles and time trend with model results.

The concentrations of α -HCH and γ -HCH in air and surface waters of the Arctic exceeded those in Antarctica by one to two orders of magnitude (Figures 1 and 2). The gaseous concentrations of γ -HCH were highest above the North Sea and between 20°N and 30°S. Fugacity fractions were used to estimate the direction of the air-sea gas exchange. These showed for α -HCH that the measured concentrations in both phases were close to equilibrium in the North Atlantic (78°N-40°N), slightly under-saturated between 30°N and 10°S and again close to equilibrium between 20°S and 50°S. γ -HCH has reached phase equilibrium in the North Atlantic as α -HCH, but the surface waters of the tropical and southern Atlantic were strongly under-saturated with γ -HCH, especially between 30°N and 20°S.

These findings are significantly different from two earlier estimates (Iwata et al., 1993; Schreitmüller and Ballschmiter, 1995) around 1990 as a result of global emission changes (Li et al., 1996) within the last decade (Fig. 3). The earlier studies reported equilibrium of both HCHs in the South Atlantic and depositional net fluxes in the North Atlantic. Therefore, we investigated the time trend of the HCHs in the surface waters of the Atlantic between 50°N and 60°S on the basis of archived samples taken in 1987-97 and those from 1999. A decrease of α -HCH by a factor of approximately 4 is observed at all sampling locations. No decrease of γ -HCH occurred between 30°N and 30°S, but there was a decrease in the North Atlantic, North Sea and in the South Atlantic south of 40°S. The constant level of γ -HCH in the tropical Atlantic confirms the conclusion that the tropical Atlantic acts as a sink for γ -HCH at present time.

The measured α -HCH seawater concentrations from the six cruises between Bremerhaven and Antarctica were compared with results from a global multimedia fate and transport model

(Wania and Mackay, 1999; Wania et al., 1999; cf. Fig. 4). While the time trend over 13 years and the latitudinal gradient were well reproduced by the model, the absolute levels were too high by a factor of 4-5. This may be explained by the zonal averaging employed in the model as well as uncertain emissions and degradation rates. With respect to the Arctic the model concentrations were closer to the measured which may indicate that averaging might be more appropriate in the Arctic.

Fig. 1: HCHs in air 1999/2000

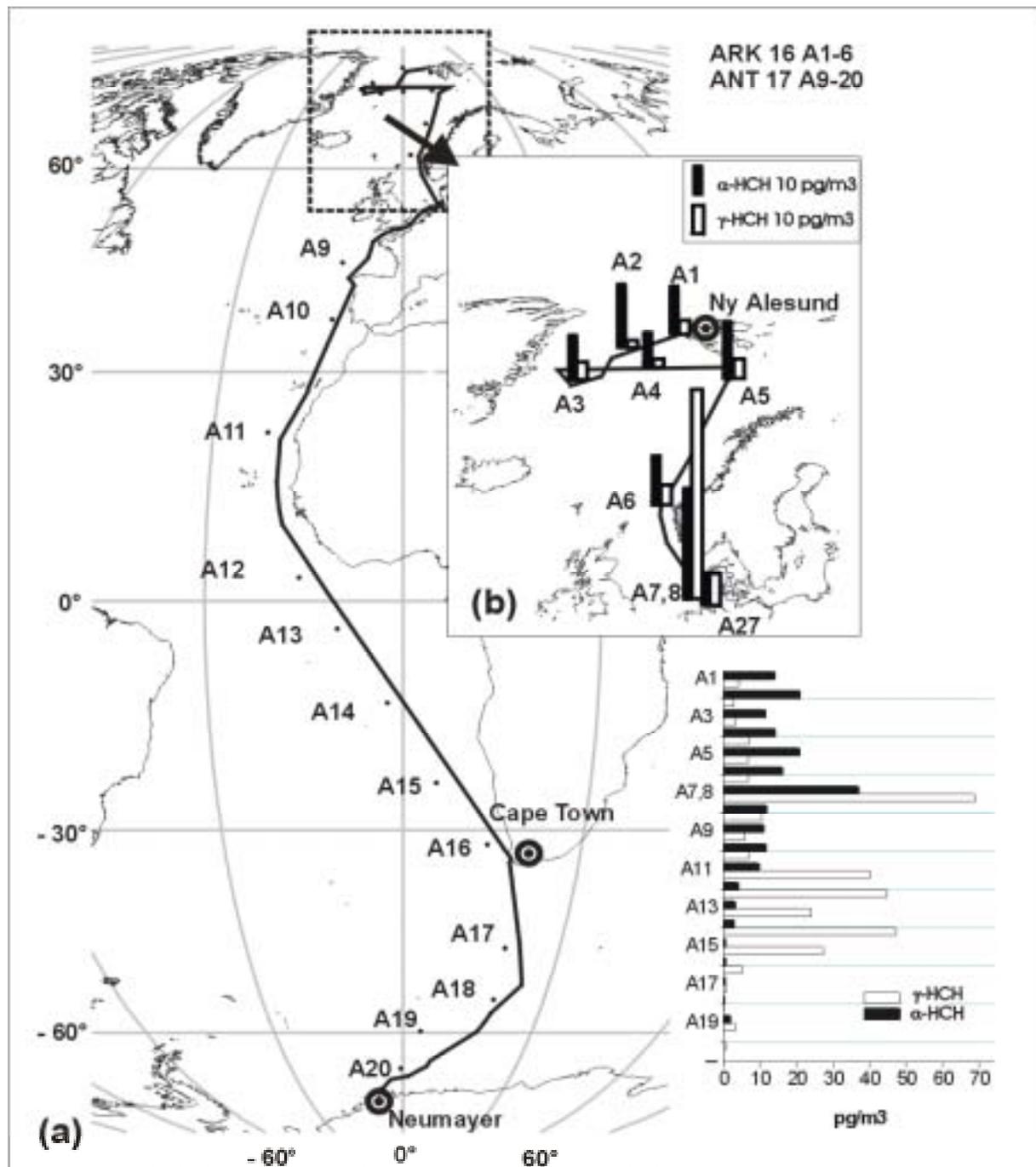


Fig. 2: HCHs in water 1999/2000

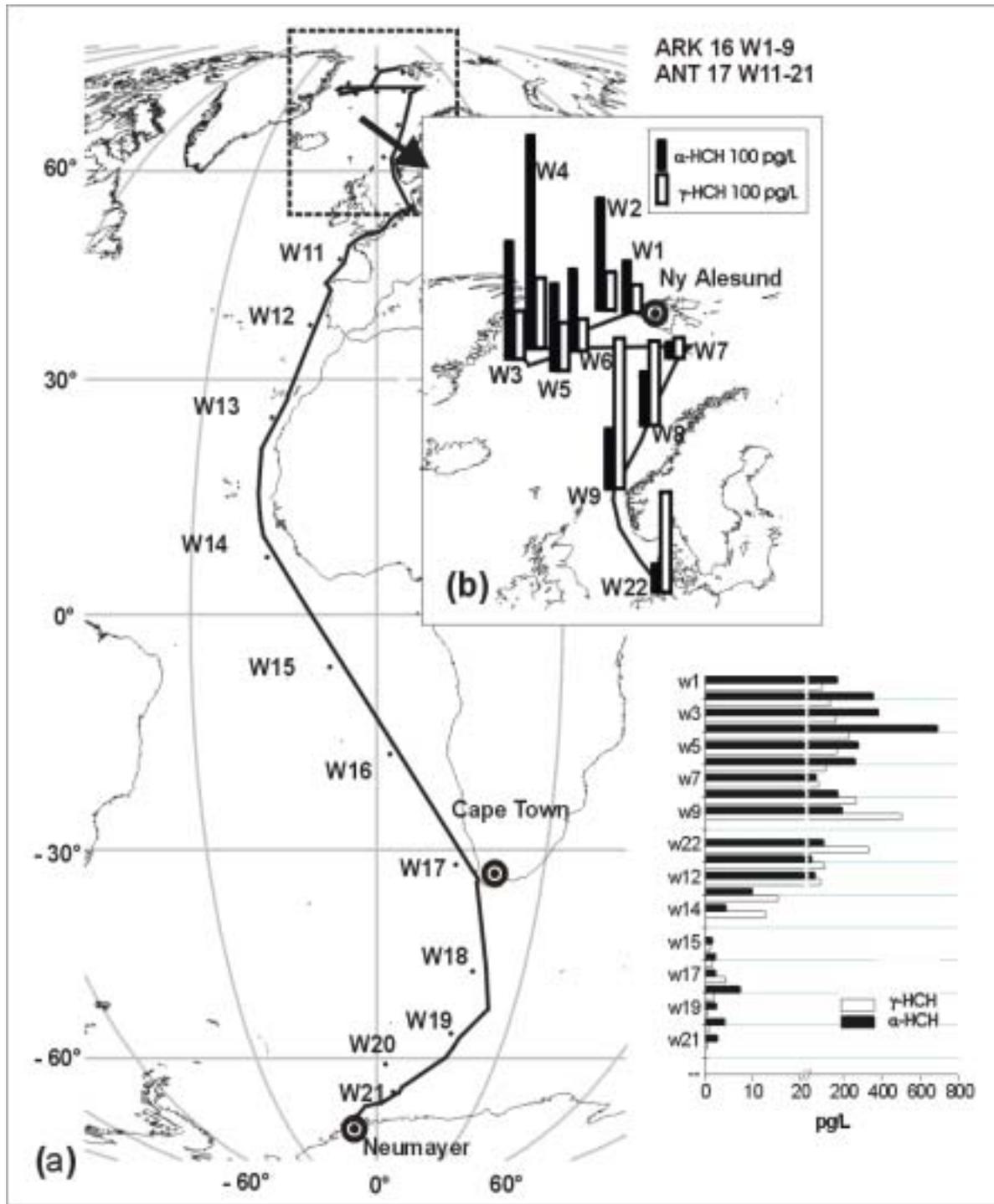
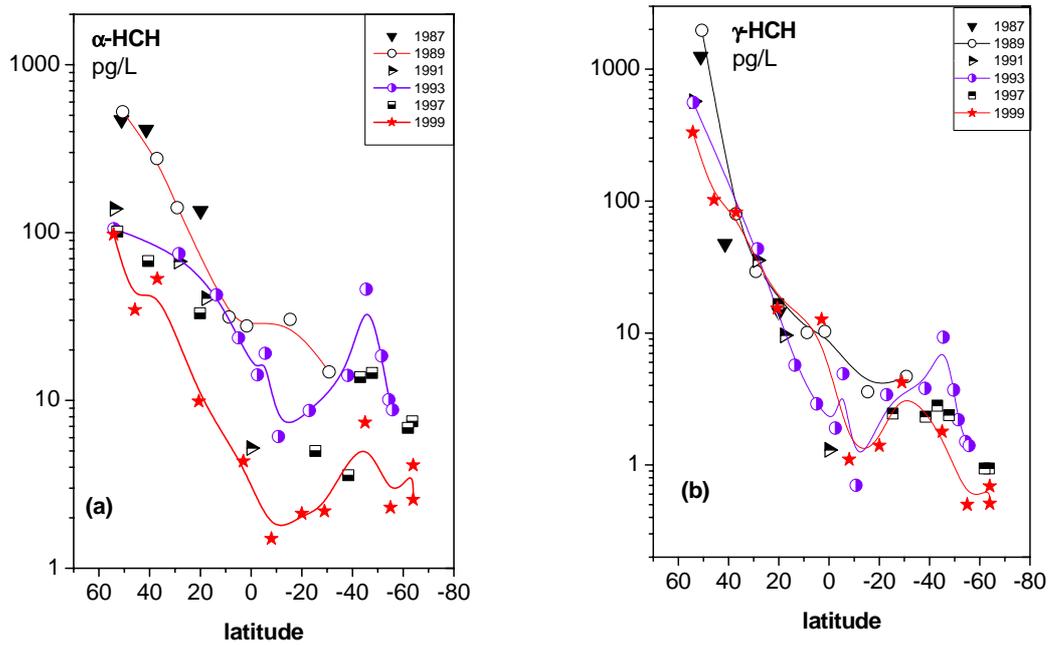
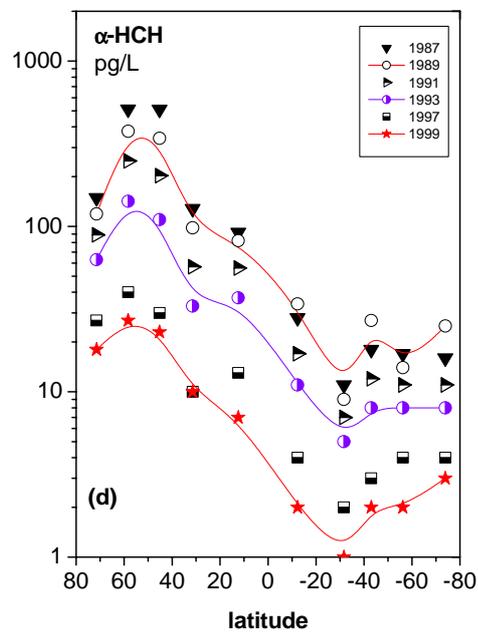


Fig. 3: Measured time trend of α -HCH and γ -HCH in the Atlantic Ocean 1987-1999**Fig. 4:** Model calculation of α -HCH seawater concentration (Li et al., 1996; Wania et al., 1999)

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