3. ENVIRONMENTAL LEVELS, TOXICOLOGICAL AND ECOTOXICOLOGICAL CHARACTERISATION

Persistent organic pollutants (POPs) or persistent toxic substances (PTS) may be divided into a set of traditional chemicals or classes of chemicals, some of the former being well studied while still several of the traditional PTS are not. In-depth studies have been performed to describe the fate and effects of DDT/DDE, PCBs and PCDDs/Fs ("dioxins") and it is basically the only pollutants it is possible to make temporal and geographical comparisons for. Enough data is available to study bioaccumulation and magnification properties. The highest environmental concentrations (ppm conc.) have been reported for DDE and Σ PCBs, levels 5-6 orders of magnitude higher than those reported as TEQs for PCDDs/Fs, detected in ppt concentrations. In-between ppt and ppm concentrations we may see several other POPs such as HCB, Chlordane, Mirex, Toxaphene and others. However it is difficult to point out the effects of these latter chemicals since their effects, as indicated in toxicological experiments or through accidents, are hidden behind the effects observed for the POPs present at the highest concentrations and/or the effects of the most toxic pollutants.

It is clear relation between decreased egg-shell thickness, as determined in bird of pray, and DDE concentrations. Exposure levels of PCBs, determined as internal doses and a range of effects on reproduction among seals, otters and mink including fetotoxicity, teratogenicity and endocrine mediated effects are accepted as effects in these wildlife species living in certain more polluted areas. However, there are some other less well established effects that may be discussed of PCBs such as immunotoxicological effects and neurobehavioral effects. The latter being the most evident since experimental data clearly indicate that several PCB congeners and other POPs (e.g. polybrominated diphenyl ether congeners) induce learning disabilities in mice and rats. Also, the neurobehavioral effects reported in young children support a link between PCB levels and the effect. The PCB effects observed in wildlife is due to their exposure to weathered PCBs, which means that the composition of the PCB congeners is highly different from the composition in the PCB products, once manufactured.

Both DDTs and PCBs are transformed to what we may regard as traditional lipophilic and persistent compounds. Hence methylsulfonyl-DDE is one of those compounds, an extremely potent toxicant for the adrenal in which it is inducing cell necrosis in the cortex *zona fasciculate*. It is reasonable to believe that the hypertrophic growth of the adrenals observed in grey seals from the Baltic Sea is due to this DDE metabolite. Depending on their structure, some of the rapidly metabolised PCB congeners are transformed to more persistent metabolites, PCB methyl sulfones ($MeSO_2$-PCBs). These are compounds with only slightly lower lipophlicity than the parent compound but for the majority of all $MeSO_2$-PCBs their reactivity is lowered by the introduction of the methylsulfonyl group in the molecule. Consequently we have a new group of persistent compounds potentially causing toxic effects in species with high enough levels of the metabolites. So far endocrine related effects have been observed as well as some strong potencies to induce Cytochrome P450 enzymes. Further, among the approximately 15 PCB congeners that are transformed to 30 $MeSO_2$-PCBs we have a number of chiral PCB congeners. Five pairs of 3- and 4-$MeSO_2$-PCBs make a total of 10 chiral $MeSO_2$-PCBs congeners, that are known to be present in mammals, leading to the occurrence of 20 atropisomers, in total. It is still unknown which atropisomers that may accumulate or to be excreted as well as which effect each one of those may have. *In short, even with the PCBs and DDTs we still do not fully understand what is exactly going on from a toxicological point of view.*

The latter statement is supported by the observation that a large number of hydroxylated PCB metabolites (OH-PCBs) are retained in the transport organ, the blood. Hitherto approximately 40 OH-PCB congeners have been identified in the blood, 3-5 making up the major proportion of these metabolites in the blood. Also other halogenated phenolic compounds (HPCs) are retained in the blood, pentachlorophenol and 2,4,6-tribromophenol making up the major two substances. The occurrence of these chemicals in the blood is not particularly due to their lipophlicity but their protein binding capacity. *Hence, persistency may not only be a matter low reactivity and high lipophilicity but*

also due to particular interactions with biomacromoleculs such in this case with a transport protein. A similar situation is evident from the (protein) receptor interaction with the toxic "dioxins". Several phenolic compounds occurring in the environment are however NOT retained but both easily and rapidly excreted through the metabolic pathways acting in the organisms. This is true for compounds such as bisphenol A, tetrabromobisphenol A, alkylpehenols and a vast majority of the metabolites of halogenated aromatic compounds.

Going from the traditional to the less traditional environmental contaminants much more data are required. Unfortunately, only limited datasets are available for several of the 12 POPs that are included in the Stockholm convention on POPs. Some of these POPs are still manufactured and in use. Simultaneously it should be emphasised that there are other environmental contaminants with similar characteristics and known as environmental pollutants. Some of these are present in humans and in wildlife at concentrations lower than the most persistent PCB congeners and DDE but at higher levels than the toxic PCDD/F congeners. *It is worth to stress; it is only a few PCB congeners that make up the high concentrations observed in organisms at the highest trophic levels; also, PCB levels are much lower at lower trophic levels even though there is a larger number of PCB congeners present in these organisms/in those environments. Also, the toxicity of a class of chemicals may be due to only a few congeners of that particular class (c.f. the dioxins).*

This discussion is highly relevant looking at the class of polybrominated diphenyl ethers (PBDEs) with a total of 209 theoretically possible congeners to be formed but of which only 10-20 are relevant from an environmental perspective. The large volume PBDE congener decabromodiphenyl ether is NOT particularly persistent even though it has a high lipophlicity. This compound can easily be photochemically transformed but also metabolically making this one of more toxicological concern from this standpoint than from the fact that this is a highly persistent and lipophilic contaminant. On the other hand 2,2',4,4'-tetrabromodiphenyl ether is the most persistent PBDE congener observed so far (c.f. its similarity to 2,2',4,4',5,5'-hexachlorobiphenyyl (CB-153)) requiring our attention to this as a marker for the persistent PBDEs. There are a few more PBDEs that are persistent and determined in all environmental compartments worldwide today. PBDEs may be biologically transformed to hydroxylated PBDEs. An interesting fact is that OH-PBDEs are also present in the environment as natural products, also as their methyl ethers. These compounds do accumulate as well in biota, the MeO-PBDEs due to their lipophilic characteristics and OH-PBDEs due to their protein binding capabilities. *It is notable that we here are coming into an issue of natural production of persistent compounds with potential effects in wildlife and humans.* Halogenated phenoxyphenols have been and are used as bactericides (e.g. triclosan, hexachlorophen) and one may speculate if this is the reason for their natural production by certain species.

There are more chemicals to include for further research and possibly legislative measures depending on their persistency and bioaccumulative properties without focusing to much on their toxicity. Among these chemicals I may mention *hexabromocyclododecane* (HBCDD), a compound which evidently is persistent and lipophilic since it is present in the environment at even higher levels than the PBDEs and is showing increasing time trends in e.g. guillemot from the Baltic Sea. HBCDD is also potentially reactive since it may eliminate hydrogen bromide or undergo nucleophilic substitution reactions.

Bis(4-chlorophenyl)sulphone (BCPS) is another persistent, lipophilic and in fact a toxic compound since it has been applied as a DDT substitute (an insecticide) but the major use of this compound is as a monomer for the production of polysulfones and other thermostable plastics. BCPS is used in the dye industry. It is also present in wildlife and levels similar to the most persistent PCB congeners have been reported. It is present in ppm levels in guillemot but at similar concentrations in fish and e.g. seals. The compound is as potent as DDT to kill flies.

Recently a group of fluorinated compounds, *perfluorinated alkylsulphonic acids* (PFOS) have been reported in certain tissues from wildlife. They also seem to have some potent toxicological properties but more need to be done to assess their importance.

Moving to more toxic compounds it is still not clear what importance polybrominated dibenzo-p-dioxins (PBDDs) and furans (PBDFs) may play but the chemicals are being mentioned in the context of brominated flame retardants.

In conclusion, PBT criteria are useful for identification of "new" chemicals of concern but there is in fact a large number of environmental pollutants for which data on their PBT characteristics are partly known and, to my understanding, still not used for prioritisation of research and legal actions.

3.1 LEVELS AND TRENDS

3.1.1 Introduction

The first part of this chapter deal with the environmental levels and trends. The relative spatial and temporal variations in environmental concentrations of PTSs are briefly described. The following sections describe ecotoxicology, toxicology and human exposure to PTS in Region III. The compartments are defined descriptively - air, marine and fresh waters, terrestrial ecosystems including the main regional hot spots.

The presence of PTS (PCDDs/Fs, PAHS) in the environment was recognized by a lot of measurements of historical and archived samples, which confirmed their environmental occurrence prior to the widespread development of the chloroaromatics (CA) industry in the 1930s (Alcock et al., 1998).

There is an increasing body of evidence for the existence of pre-1900 levels of PCDDs/Fs in the environment provided by deep sediment core data from the Europe and the US, although some studies have been ambiguous about these findings. Analytical constraints may relate to some of these uncertainties in the form of detection limits improvements that have been made over the last 10-15 years or because of greater appreciation of the need for ultraclean sample handling and preparation procedures required. This highlights the need for strict sampling and analytical protocols using high-resolution instruments that maintain low limits of detection and enable trace concentrations of individual congeners to be reported with confidence. The studies that support the existence of PCDDs/Fs prior to 1900 have generally used a more sensitive HRGC-HRMS analytical procedure.

The balance of evidence from both the Rothamsted archived soil and the recent literature supports the existence of PCDDs/Fs in the environment before the widespread development of chloroaromatics and chorine industry during the last century.

The systematic study of PTS environmental occurrence has a long-term tradition in the Region III. Region III has a lot of monitoring systems based on the international conventions such as UNECE CLRTAP and its programme EMEP, HELCOM or OSPAR activities. Also a lot of very important system for data storing and data evaluation was developed. For example from 1991, the agreement between German government and States in Germany concerning to compile, document, and evaluate data from monitoring and surveillance programs exists. Substances to be included, are PCDDs/Fs, PCBs and other organochlorine substances. This DIOXIN Database serves primarily the following objectives as:

- an overview of the level of environmental pollution,
- an indispensable basis for environmental goals and priority setting,
- a technical basis in to derive practicable and scientifically-based benchmarks and limit values,
- a means of monitoring the success of political activities.

Presently, the DIOXIN Database contains 117 measurement programs with a total of about 10 000 datasets. The results confirm that new inputs of dioxins into the environment have been drastically reduced. The median levels that were determined for the individual compartments could be used as comparative values in order to make statements on possible environmental impacts in the case of hazardous incidents.

3.1.2 Air

3.1.2.1 Regional programmes

Air is an important transport medium for PTS in general. Reporting ambient air concentrations reflects the concentration during the sampling period but, due to rapid transport and fast mixing of pollutants in air, PTS concentrations will change quite rapidly. It has been shown in many cases that ambient air concentrations exhibit a strong seasonal trend (Buckley-Golder et al., 1999).

Heavy metals and persistent organic pollutants (POPs) were included in EMEP's monitoring programme in 1999. However, 1995 by, co-operation concerning heavy metals and POPs between EMEP and other international programs was extended. This co-operation included the establishment of a database and collection of already available data on POPs among the participants. A number of countries have been reporting POPs within the EMEP area in connection with different national and international programmes such as HELCOM, AMAP, OSPARCOM, MEDPOP.

The strategic long-term plans on POPs (EB.AIR/GE.1/1997/8) recommend to take a stepwise approach, and the following compounds or groups of compounds should be included in the first step: PAHs, PCBs, HCB, chlordane, lindane, α-HCH, DDT/DDE.

Few of the sites have reported data for POPs. An overview and their programmes of the sites are given in Table 3-01 – 3-02. The stations are generally located distant from local emission sources in order to be representative for a larger region (Figure 3-01).

Table 3-01: List of monitoring stations included in the POP data base.

Country	Station codes	Station name	Location		Height above sea
			Lat.	Long.	(m)
Belgium	BE0004R	Knokke	51°21'N	3°20'E	0
Czech Republic	CZ0003R	Kosetice	49°35'N	15°05'E	534
Iceland	IS0091R	Stórhöfdi	63°24'N	20°17'W	118
Ireland	IE0002R	Turlough Hill	53°02'N	6°24'W	420
Netherlands	NL0009R	Kollumerwaard	53°20'N	6°17'E	0
Norway	NO0042G	Spitsbergen, Zeppelinfjell	78°54'N	11°53'E	474
	NO0099R	Lista	58°06'N	6°34'E	13

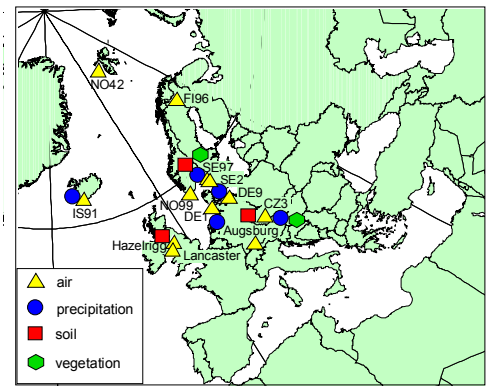

Figure 3-01: Location of monitoring stations, which have reported data to the EMEP heavy metal and POP database

Table 3-02: General information about sampling and analysis of POPs in air in 1999

Country	Sites	POPs	Sampling period	Sampler	Analytical methods
Czech. Rep	CZ0003R	PAHs, PCBs, DDTs, HCHs, HCB	24 hrs every week	High volume	GC-MS
Iceland	IS0091R	PCBs, pesticides	15d	High volume	
Norway	NO0042G	PAH, pesticides, HCHs, HCB, PCBs	48h	High volume	GC-MS
	NO0099R	α-HCH, γ-HCH, HCB	48h	High volume	GC-MS
GC-MS: Gas chromatography with mass spectrometry					

Figures 3-02 and 3-03 show temporal trends for α-HCH and γ-HCH in air at 6 stations. The concentration level of α-HCH at the Norwegian stations is relatively high compared to the other stations, but decreasing. This is probably due to higher input of technical HCH at high latitudes. Almost 80% of the remaining use of α-HCH in Europe in 1996 was assigned to the new states of the former Soviet Union (422 t of technical HCH) (Breivik et al., 1999). The other 20% were attributed to usage in some former eastern European countries (Breivik et al., 1999). Iceland is influenced by westerly air masses, which explain the lower concentrations seen at IS0091R.

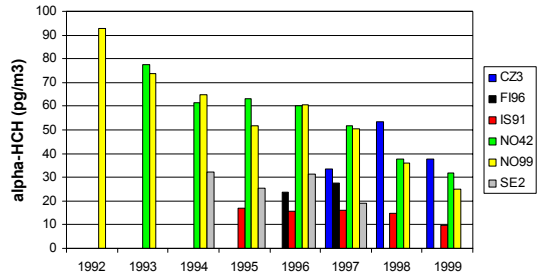

Figure 3-02: Annual weighted means for α-HCH during 1992-1999

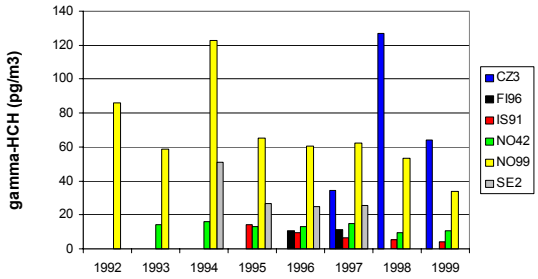

Figure 3-03: Annual weighted means for γ-HCH during 1992-1999

Lista (NO0099R) at the southern coast of Norway, shows high concentrations of γ-HCH in air, which may be due to long range transport from southern parts of Europe. According to Centre International d'Etudes du Lindane (CIEL, 1998), the average annual lindane consumption in Europe was 2 130 t during the period from 1992 to 1997. France was the major user of lindane in Europe during this period, with an annual average consumption of 1 600 t (CIEL, 1998).

Benzo(a)pyrene (also other PAHs) is rapidly destroyed by UV. In the absence of local sources, therefore, a pronounced seasonal trend is to be expected, which is seen especially for CZ03 (Figure3-04).

Data for PTS have been reported only from countries around the North and Baltic Seas, in the Arctic and from the Czech Republic.

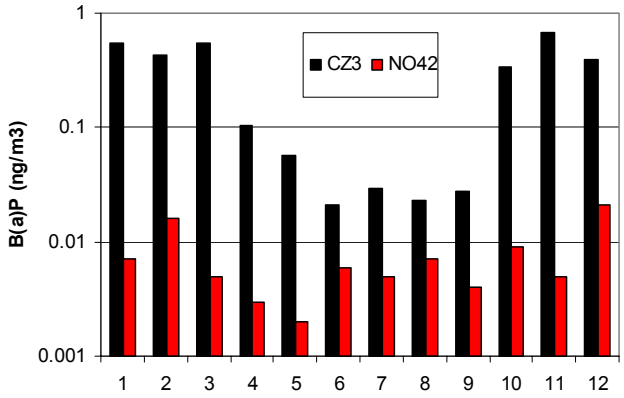

Figure 3-04: Concentrations of benzo(a)pyrene in air+aerosol at two EMEP-stations, 1999.

3.1.2.2 Subregional programmes

3.1.2.2.1 EU

Results for air samples were available for only eight Member States (Table 3-03). There are three basic approaches to determine the dioxin concentrations in air: high volume samplers which will collect particle-bound and gas-phase dioxins, Bergerhoff or similar samplers which will collect dry and wet deposition, and biomonitors such as kale, spruce needles or grass, which preferentially absorb the gas-phase dioxins. As far as was possible to determine, very similar methods have been applied to generate these results.

Table 3-03 shows that the concentrations in ambient air range from below 1 fg I-TEQ.m^{-3} to several hundred fg I-TEQ.m^{-3} and in deposition a similar range was found for the concentrations in pg I-TEQ.m^{-2}.d^{-1}. The extremely high concentration of 14 800 fg I–TEQ.m^{-3} was measured at the Pontyfelin House site, in the Panteg area of Pontypool in South Wales, which is very close (~150 m) to an industrial waste incinerator.

Table 3-03: Summary of ambient air concentrations (fg TEQ.m^{-3}) and deposition [pg TEQ.m^{-2}.d^{-1}] from EU Member States

	Ambient Air				Deposition	
	Unspecified	**Urban**	**Rural**	**Contaminated**	**Urban**	**Rural**
Austria	1.3-587					
Belgium		86-129	70-125		<1-12	<1-3.1
Germany	2-812				<1-464	
Luxembourg		54-77	30-64			
Netherlands		4-99	9-63	6-140		
Sweden	5.4-53.7	<1-29				
UK		0-810	1-24	14,800	<1-312	0-517

In several countries strong seasonal trends have been determined for ambient air concentrations. A typical seasonal trend is displayed in Figure 3-05 for the cities of Augsburg and Burgkirchen in southern Germany. Whereas Augsburg represents an urban industrial location, Burgkirchen is located in a more remote part of Bavaria with some industrial activities in the neighbourhood (modern municipal waste incinerator, chemical industry). In general, dioxin concentrations in winter are much higher than in summer and, on a TEQ basis, concentrations measured in the winter in Germany were

up to 10 times higher than concentrations in summer. A graphical representation of the median concentrations measured in two networks during 2 ½ years is displayed in Figure 3-05.

The cause for these variations is not fully understood: whereas in some regions additional combustion activities, such as heating of private homes, might be responsible for higher emissions, other authors find that meteorological conditions, with more frequent inversion layers and lower mixing heights in the air column, might explain the differences.

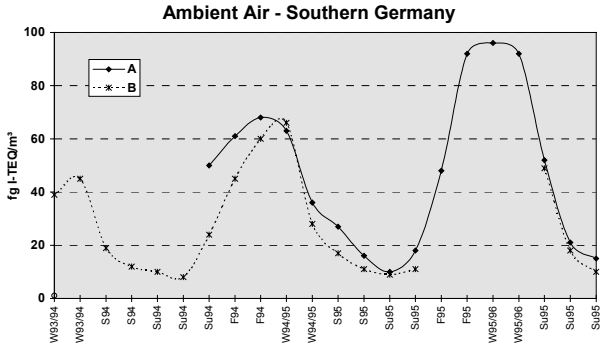

Figure 3-05: Seasonal trend of ambient air concentrations of dioxin in southern Germany. Median concentrations obtained from the networks around the MSWIs at Augsburg and Burgkirchen (n=223)

3.1.2.2.2 Baltic region

Concentrations of HCHs in air from the Baltic Sea drainage basin, specifically Southern Norway, were measured as early as 1981 (Oehme and Manø, 1984). A few years later, Bidleman et al. (1987) reported concentrations of HCHs in air in southern Sweden. Around 1990, monitoring stations measuring HCH air concentrations became operational in the southern parts of Norway and Sweden. A total of 337 measured concentration values for the western atmospheric compartment were aggregated and are shown in Agrell et al. (2001) together with the calculated concentration time trends. Non-aggregated data for 1994 and 1995 are plotted in (Table 3-08), showing the seasonal pattern of measured air concentrations at the coastal stations in Lista, Norway (Haugen et al. 1998) and Rörvik, Sweden (Brorström-Lundén, 1995; 1996).

In October 1990, a field study was initiated in order to determine PCBs (total PCB calculated from 51 identified peaks), DDTs and HCHs in air and precipitation at 16 sampling stations, within or close to the Baltic Sea. Sampling was carried out continuously during one year for most of the stations, and up to two years for some stations. The study was completed in February 1993. PCBs, DDTs, and HCHs in air and precipitation and their calculated deposition will be evaluated with respect to temperature, latitude and sampling-site. During the study a total of 299 air samples, 192 samples of precipitation and 75 river water samples were collected around the Baltic Sea (Agrell et al., 2001) (See Tables 3-02, 3-04 and 3-08).

3.1.2.3 National programmes and measurements

Extensive monitoring of PTS in the Region was/is done as part of each countries commitment to the United Nations Economic Commission for Europe's (UNECE) POPs Protocol to the 1979 Geneva Convention on Long Range Transboundary Air Pollution (Peters et al., 1999). These measurements are based on the national programme to monitor persistent organic pollutants (POPs). Example of this can be UK, where a lot of POPs monitoring programmes were initiated (see Tables 3-02 – 3-09).

The study of evidence of PTS (PCBs, OCPs, PAHs) concentrations in rural UK air has done and confirmed the declining of their levels since the early 1960s - 1970s and that the decline was most marked through the 1970s. The rate of decline over recent years has been much slower, with one site (Chilton) showing a higher 5-year average in the last period (1988 - 1992) than the one before (1983 -

1987). Atmospheric concentrations of ΣDDT have shown substantial declines over the sampling period (1972 - 1992), while ΣPAH concentrations have remained essentially constant (Figure 3-06).

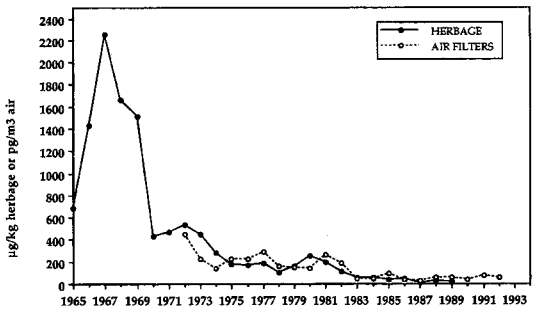

FIGURE 1. PCB concentrations detected in the archived air filters (averaged for both rural sites) and on herbage collected annually and stored at Rothamsted Experimental Station (data from ref 10).

Figure 3-06: PCB concentrations detected in the archived air filters (two rural sites) and on herbage collected annually and stored at Rothamsted Experimental Station

Within the PHARE Project EU/93/AIR/22 "Local Studies of Air Quality in the Cities of Bratislava and Kosice. National Needs Assessment of Air Pollution" PCBs, HCB, DDTs, PCDDs/Fs concentrations were measured in 24-hr ambient air samples collected around Slovakia in 1996/97 (8-times at 20 sampling sites involving urban, industrial, agricultural, and background areas).

Concentrations of α- and γ-hexachlorocyclohexane (HCH) were measured in ambient air samples on a weekly basis between 1991 and 1995 at Lista, a coastal station in southern Norway (Haugen et al., 1998). A 50 % decline of α-HCH concentrations in air could be observed during the 5 years period, while no such trend was found for γ-HCH. The analysis of trajectories has indicated the confirmation of suggestion that in 1990 (East) Germany and the Ukraine were the only European countries using technical HCH to any significant extent.

Concentrations of tetrachlorobenzenes, pentachlorobenzene, hexachlorobenzene and α–, β–, γ– and δ–HCH in air and deposition were measured at three different contaminated sites in Greppin, Roitzsch (both near Bitterfeld) and Leipzig (Germany) during five time intervals of 14 days in the summer months of 1998 (Popp et al., 2000). The mean values of the chlorobenzenes and HCHs concentrations (gas phase and particle bound portions) over the whole sampling time are shown in Tables 3-6 and 3-9. This increase of the concentration values from Leipzig over Ritzsch to Greppin indicates the influences of industrial waste sites in the Bitterfeld region on the atmospheric environment.

DDTs, HCHs, CHLs, HCB and PCBs concentrations were determined on monthly intervals in ambient air samples collected in city of Gdańsk (Poland) in 1991-92 (Falandysz et al., 1998) (Tables 3-4 – 3-6, 3-8). Ambient air levels of OCCs were studied in the Gulf of Riga (Estonia) (Roots, 1996). These compounds are carried to the Gulf of Riga by two ways: either they are carried there from the Central Europe by the means of long-range transport or with air-transport from the Kola Peninsula (Oehme et al., 1994), or from the local waste-centre near the gulf (Larsson and Okla, 1989).

Atmospheric concentrations of PCBs (indicator congeners) were measured every week from 1992 to 1995 in Lista, a coastal station in Southern Norway (Haugen et al., 1999). No obvious concentration decrease could be observed during the 4 years. PCB concentrations showed a clear seasonal fluctuation with higher levels during the summer. As far as trends, the different situation was observed in middle regional observatory, at Košetice CR.

PCBs in the lower atmosphere were studied on the regional and rural levels round the Baltic region (Backe et al., 2000; Agrell et al. (1999); Bremle and Larsson (1998); Brorström-Lundén et al. (1994)

(see Tables 3-02 – 3-09). Comparison PCB data from various studies is complicated because of the various quantification techniques and reporting conventions used by different laboratories. To assess to some extent how the concentrations at Lista compare with other locations, congener-specific concentration data (arithmetic means) reported for various European locations in the early 1990s are compiled in Table 3-6. Comparison of the data suggests that PCB levels in Southern Norway are rather high, namely, in the range of concentrations reported in recent years for urban areas in the UK and Germany. Whereas it is not surprising that the concentrations are more than one order of magnitude higher than what has been measured in Northern Norway and European Arctic, they are also considerably higher than levels reported for other European non-urban locations. They are, for example, higher than PCB concentrations measured during the same time period at several coastal stations at Sweden´s west coast.

Air samples were collected along a transect from the city of Stockholm urban area (Sweden) to the open coastal area of the Baltic Sea for determination of PAHs and PCDDs/Fs (Broman et al., 1991) (See Tables 3-07 and 3-09). The investigation area is, of course, also affected by long-range transport of PAHs and PCDDs/Fs primarily from European countries.

Some measurements of PCDDs/Fs in ambient air were also done in Poland, in city of Krakow (Grochowalski et al., 1995, 1997). Krakow, the second largest city in Poland (round 950 000 inhabitants) is one of high population density. Based on the results of one year monitoring programme for ambient air concentrations of PCDDs/Fs at industrial and population centres of Linz, Graz and Vienna, Austria (1992) in 1997 a long lasting monitoring programme started with the objective to observe long term trends of PCDDs/Fs and additionally PCBs in the air (Moche and Thanner, 2002). The current monitoring programme comprises eight sampling sites of different topographical types, samples are collected three times during winter and three times during summer.

The datasets of 1992/3 compared with the set from 1997/9 show a decrease of PCDDs/Fs in the air during winter, whereas the summer levels are almost equal (see Table 3-07). The typical seasonal trends typical for the most of industrial European countries with highest concentrations in winter clearly indicate domestic heating as the major source for increasing dioxin levels in air during winter. Austrian dataset for PCBs confirm the trends, which is permanently observed at the observatory Kosetice in Czech Republic, which in contradiction to PCDDs/Fs show the highest concentrations during summer due to the evaporation from terrestrial surfaces.

These measurements were done also as far as a study of urban air contamination by various PTS (UK, Germany) (see Tables 3-02 – 3-09). The first project was performed in early 90´s and from this time a lot of others were performed. These ambient atmosphere measurements were focused on PAHs mainly (London, Manchester and Cardiff, Stevenage - Halsall et al., 1993, 1994, 1999; Smith, 1999; west London - Beak et al., 1992). Also the effects of traffic on the PAHs emissions were frequently measured (for example Brown et al, 1996) (see Table 3-09). These findings for the UK agree well with other published European data. Extensive studies have been undertaken throughout most of the European continent including a variety of differing ambient environments in Germany, Austria, Netherlands, Belgium and Scandinavia. In 1997 eight German states measured PAHs at location varying from urban streets to rural areas (Beck, 1999).

PAHs in the regional atmosphere are associated predominantly with emissions from road traffic, although other sources such as fuel oil, coal combustion mainly in the local heating systems and incineration also contribute. The latest PAH, nitro-PAH and oxy-PAH study (particle-phase) in ambient air was sampled in the Helsinki area (Finland) by ZTV in the early 1990s (1993 - 1994) (Sandell et al., 1999; Tuominen, 1990), urban, an industrial, rural and residential areas in Flanders (Wauters and Lenelle, 1999). Analyses showed a decrease in the concentrations of the PAH compounds in the particle-phase in the ambient air during the second part of 80´s. This is a result of that the cars equipped with catalyst engines became a mandatory 1991. Also improvement of the fuel and the increased use of district heating, contribute to this trend. As far as the last 10 years, and the

annual average concentrations of PAHs seem to stagnate due to a permanent increase of motorized traffic on the one hand and a better combustion technology and an increase in the use of natural gas for domestic heating on the other hand.

Relatively worse situation can be observed in the towns in the former communistic countries, where the number of cars dramatically increased after the political changes. The same problems have all larger cities in CEE countries after the political changes – extremely high increase of town traffic and decreasing contribution from former industrial sources as the results of falling-off of production.

In the comparison with OCPs and PCBs, the PAH concentrations in the atmosphere show a seasonal fluctuation with higher values in winter and lower in summer, which trend was the same as was observed in Middle European regional background observatory in Kosetice, South part of Czech Republic (See Figure 3-04) (Vana et al., 1997, 2001, Holoubek et al., 2002).

Also ambient air measurements of newer types of POPs were done. The 43 samples for the study of background ambient air concentrations of PCNs in two UK sites (Hazelrigg and Chilton) were collected between January and September 2001 (Lee at al., 2002a). Two air sampling campaign were under taken to assess atmospheric concentrations of PBDEs reaching and within the UK and to investigate factors that control concentrations (Lee et al., 2002b). The first was based at UK remote observatory at Mace Head on the west coast of Ireland and the second campaign was under taken at two sites in England – Hazelrigg and Chilton. The results from these measurements are summarized in Table 3-10.

Table 3-10: The median values and range of determined levels of PCNs and PBDEs in UK pg.m^{-3}

Site	PCNs		Site	PBDEs	
	Mean	Range		Mean	Range
Hazelrigg	111	30.5-309	Hazelrigg	12	2.8-37
Chilton	85.0	31.2-184	Chilton	11	3.4-33
			Mace Head	3.1	0.2-11

The very special case of air contamination is the case of PTS levels in indoor air. For example PCBs were used in different kinds of building material in many countries during the fifties to the early seventies. In Sweden this occurred during the period 1956 - 1972. The most important of these building materials were presumably sealants used between concrete blocks and around windows and doors on the outside of the building. The total amount of PCB that has been used for this purpose in Sweden has been estimated to 70-190 tons. The PCB concentration in such sealants has today been found to be from a few percent up to around thirty percent but considerably lower concentrations have also been found, probably as a result of contamination. The original PCB content in the current sealants is however unknown. It was anticipated that the PCB would stay in the sealant and in the buildings as long as the sealant was not removed. However, later investigations have shown that PCB could escape from the buildings into the environment and that it also could be found in indoor air.

A residential area, built in the early seventies, was identified in Solna, north of Stockholm, Sweden. The area was chosen as contained buildings with as well as without PCB containing sealants, thereby suitable for comparative studies. The primary use of PCB containing sealant in the current area was for tightening between balconies and outer wall. As a number of these balconies later had been furnished with windows, the balcony doors had been kept open during part of the year, which led to that these sealants materially often became a part of the indoor environment. The indoor air concentration of PCB in buildings containing PCB sealants can be up to two orders of magnitude higher compared to similar buildings without such sealants. The toxicological significance of this finding is uncertain. Tentative calculations indicate that such exposure via indoor air could contribute significantly to the general exposure via food.

3.1.2.4 References

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Table 3-04: Contamination levels of DDTs in the ambient air

Country	Sampling sites /location	Duration	Frequency of measurements	Typical range [pg.m^{-3}]			Comments	References
				Urban /industrial	Rural	Background		
	Baltic				1.6		Sum of p,p'-DDT and p,p'-DDE,	?
Czech Republic	Kosetice	1997 – 1998			1 – 213			Holoubek et al., 2000; Vana et al., 1997, 2001
Latvia	Salaspils				12			?
Poland	Gdansk	1991 – 1992		31 – 1300				?
Slovakia	20 sites	1996 - 1997	8 two weeks campaings		23 – 1 100			Kocan et al., 2001
Sweden	5 coastal stations					11		?
	11 sites in Southern Sweden				11			Backe et al.

	16 sites	1991 - 1993			Median for all stations – 1.6 (DDT+DDE)		within or close to the Baltic Sea	Agrell et al., 2001
UK					4 – 97			Peters et al., 1999
					< 1.5 – 26 mean: 8.3		28 samples	Lee at al., 2000

Table 3-05: Contamination levels of HCB in the ambient air

Country	Sampling sites /location	Duration	Frequency of measurements	Typical range [pg.m^{-3}]				References
				Near the sources	Urban /industrial	Rural	Background	
Czech R.	Kosetice	1994 – 1998				0.4 – 835		Vana et al. 1997, 2002 Holoubek et al., 2002
Germany	Bitterfeld	1998	2 weeks	170 - 370				Popp et al., 2000
	Leipzig				220			
Poland	Gdansk	1991 – 1992			63 – 370			Falandysz et al, 1998
Slovakia	20 sites	1996 - 1997	8 two weeks campaigns	213	90 - 213	21 - 100	65	Kocan et al., 2001
UK	28 samples					< 28 – 76 mean: 39		Lee et al., 2000

Table 3-06: Contamination levels of PCBs in the ambient air

Country	Sampling sites /location	Duration	Frequency of measurements	Typical range [pg.m^{-3}]				Comments	References
				Near the sources	Urban /industrial	Rural	Background		
	Baltic					32 – 80			
Austria	8 sampling sites	1997 -	Three times per summer and three times per winter	PCBs (TEQ WHO 1997) – winter – 1.5 – 12.8 - summer – 4.9 – 15.6 PCBs (Σ Ballschmitter) – winter – 56.5 – 312.9 - summer – 122.2 – 500.6					Moche and Thanner, 2002
	Kosetice	1997 – 1998				4.5 – 467			Holoubek et al., 2001, Vana et al. 1997
	Prague	1994-5			79.5 – 3 018.5				AXYS, unpublished
Latvia	Salaspils					454			?
Norway	Lista	1992 – 1995				22 – 747		6 congeners	Haugen et al.
Poland	Gdansk	1991 – 1992			120 – 1100				?
Slovakia	20 sites	1996 - 1997	8 two weeks campaigns	170	59 - 391	52 - 76	47	Geometric means	
Sweden	5 coastal stations						62		?
	11 sites in Southern Sweden					87 (median) 7 – 983			Backe et al., 2000
	two-year period					130 (median)			Bremle and Larsson (1998)
	15 sites	1991 - 1993				Median for all stations – 57		within or close to the Baltic Sea	Agrell et al., 2001
	West Coast					60 - 670			Brorstrom-Lunden (1994)

					200 – 2 000				Coleman et al., 1997
					370 – 270 (mean: 520)				Lohman et al., 2000
					76 – 1 000 (295)				Currado and Harrad, 2000
						156 – 1 155 (mean: 471)		28 samples	Lee et al., 1998
						20 – 98 (51)		12 samples	Gevao et al., 1998
						54 – 375 (164)		161 samples	Lee and Jones, 1999
						51 – 84 (67)		8 samples	Lohman et al., 2000

Table 3-07: Contamination levels of PCDD/Fs in the ambient air

Country	Sampling sites /location	Duration	Typical range [fg TEQ.m^{-3}]					References
			Unspecified	Near the sources	Urban /industrial	Rural	Background	
Austria			1.3 – 587					Buckley-Golder et al., (1999)
	Brixlregg	1988			800 – 1600			Lohmann and Jones, 1998
	South Graz	1994			370			
	Vienna, Gratz	1992			9 – 590			Moche&Thanner
	8 sampling sites	1997 -	winter – 4.4 – 353 summer – 2.7 – 132.4 Three times per summer and three times per winter					Moche and Thanner, 2002
Belgium					86 – 129	70 – 125		Buckley-Golder et al., (1999)
	Flanders	1992			20 – 380			Lohmann and Jones, 1998
Czech R.	Kosetice	1994 – 1995					2 – 156	Vana et al., 1997
	Prague	1994 – 1995			16 – 161			
	Zlin	1994 – 1995			<0.2 – 299			
	Prague	1994-5			13.3 –637.0		one extreme 10 746.5	AXYS, unpublished
Germany			2 – 182					Buckley-Golder et al., (1999)
	near Hamburg				1 400			Broman et al.
	near Hamburg				3 000			Rappe&Kjeller
	Koln, Duisburg	1987			240			Lohmann and Jones, 1998
	Essen, Dortmund	1993			90			
	8 towns in NRW	1985			50 – 160			
	Hessen	1990			80 – 150	50		

	1 438 samples from Germany		Winter Urban centres - median – 54 fg I-TEQ.m^{-3} dm, 90 percentile – 127 fg I-TEQ.m^{-3} Urban fringe - median – 51 fg I-TEQ.m^{-3} dm, 90 percentile – 127 fg I-TEQ.m^{-3} Rural - median – 17 fg I-TEQ.m^{-3} dm, 90 percentile – 51 fg I-TEQ.m^{-3} Summer Urban centres - median – 8 fg I-TEQ.m^{-3} dm, 90 percentile – 17 fg I-TEQ.m^{-3} Urban fringe - median – 13 fg I-TEQ.m^{-3} dm, 90 percentile – 56 fg I-TEQ.m^{-3} Rural - median – 7 fg I-TEQ.m^{-3} dm, 90 percentile – 21 fg I-TEQ.m^{-3}					Fiedler et al., 2002
Ireland	Mace Head						3 – 4	Lohmann and Jones, 1998
Luxemburg					54 – 77	30 – 64		Buckley-Golder et al., (1999)
Netherlands				6 – 140	4 – 99	9 – 63		Buckley-Golder et al., (1999)
Norway								Lohmann and Jones, 1998
Poland	Krakow	01 – 03/1996			2 580 – 5 740			Grochowalski et al., 1997
	Krakow	06/1996			60 – 120			
	Krakow	1995			950 – 12 000			Grochowalski et al., 1995
Sweden			5.4 – 53.7		<1 – 29			Buckley-Golder et al., (1999)
	Rorvik	1989 – 1990				4 – 60		Lohmann and Jones, 1998
	Gothenburg	1988			16 – 30			
	Coast	1987					4	
	Stockholm	1987			19			
UK				14800	0 – 810	1 - 24		Buckley-Golder et al., (1999)
	Manchester	1991 – 1993			ND – 1800			Lohmann and Jones, 1998
	Cardiff	1992 – 1993			190			
	Bolsover			330				
	Hazelrigg	1997				8 – 18		
	East coast	1997					2 – 6	

Table 3-08: Contamination levels of HCHs in the ambient air

Country	Sampling sites /location	Duration	Typical range [pg.m^{-3}]				Comments	References
			Unspecified	Urban /industrial	Rural	Rural		
	Baltic					25	Sum of α- and γ-HCH,	?
Czech R.	Kosetice	1994 – 1995				100 – 720	γ-HCH	Vana et al., 1997
	Kosetice	1994 – 1995				100 – 245	β-HCH	
	Kosetice	1994 – 1995				100 – 670	α-HCH	
	Kosetice	1997 – 1998				2 – 841		Holoubek et al., Vana et al.
	Beroun	2001					3 seven days campaigns	
	Zlín	2001						
Germany	Bitterfeld	1998		310 - 690			2 weeks	Popp et al. (2000)
	Leipzig				220			

Norway	Lista	1991 – 1995				48	γ-HCH	Haugen et al.
	Lista	1991 – 1995				66	α-HCH	Haugen et al.
Poland	Swibno					103		Falandysz et al., 1998
	Dziwnow					72		
	Gdansk	1991 – 1992			29 – 250		α-HCH	
	Gdansk	1991 – 1992			42 – 2200		γ-HCH	
Sweden	Skagerack					200		Brorstrom-Lunden
	16 sites	1991 - 1993				Median for all stations – 25 (α– + γ–)	within or close to the Baltic Sea	Agrell et al., 2001
UK	Stoke Ferry	1997 – ?				28 – 100	α-HCH	Peters et al., 1999
	Stoke Ferry	1997 – ?				520 – 1360	γ-HCH	
	Hazelrigg	1997 – ?				17 – 43	α-HCH	
	Hazelrigg	1997 – ?				90 – 350	γ-HCH	
	Southern England	1987 – 1990	104 – 408				γ-HCH	Turnbull
						139 – 1 070 (500)	28 samples	Lee et al., 2000

Table 3-09: Contamination levels of PAHs in the ambient air

Country	Sampling sites /location	Duration	Frequency of measurements	Typical range [ng.m^{-3}]		Comments	References
				Urban /industrial	Rural		
Czech R.	Kosetice	1990			0.54 – 101		Vana et al., 1997
	Ostrava	1990			33.2 – 479		
	Prague	1990			85.5 – 400		
	Vresova	1990			55 – 1 158		
	Valasske Mezirici	1990			144,9 – 99 335		
		1990		100 – 5 000	0.1 – 1.0		Holoubek et al., 1993
	Kosetice	1996 – 1999			0.06 – 567.7		Holoubek et al., 1997
	Prague	1994-6		17.9 – 399.9			AXYS, unpublished
Finland	2 sites			20 – 160		18 PAHs	Tuominen et al.
	Helsinki	1985 – 1986		350 – 1 530		18 PAHs	Tuominen et al.
Germany	7 states			0.7 - 3.5		30 PAHs	Beck, 1999
	Munich, Nuremberg			2.11 – 3.47		B[a]P	Steinmetyer et al.
Hungary	Lake Balaton	1996-2001	Seasonally	0.004-0.88 – spring 0.004-0.3 – summer 0.011-1.05 – autumn 0.036-5.00 – winter		15 PAHs	Kiss et al., 1997, 2001
Sweden	Stockholm			0.1 – 2.2		B[a]P	Colmsjo et al.
UK	London	1987		14 – 93.2		18 PAHs	Beak et al.
	London	1991		35 – 735		15 PAHs	Halsall et al
	Manchester	1991		70 – 288			
	Cardiff	1991		11 – 555			
	Stevenage	1991		27 – 377			
				20 - 150			Coleman et al., 1997
				30 – 120 (62)	16 – 110 (52)	8 samples	Lohman et al., 2000
					5.3 – 254 (40)	10 samples	Gardner et al., 1995
					4.9 - 25.5 (12.3)	28 samples	Lee et al., 1998

					4 – 26 (13.9)	12 samples	Gevao et al., 1998
					1.4 – 40 (9.3)	161 samples	Lee and Jones 1999
					5.7 - 44.6	26 samples	Smith et al., 2001

3.1.3 Deposition

3.1.3.1 Regional programmes

Today, the PTS sampling stations for deposition measurements operated in Europe are few and mostly found around the North Sea as well as in the Czech Republic. Data from these stations are routinely reported to EMEP, OSPARCOM and HELCOM. The location of the sampling stations is given in figure 3-01.

Table 3-11: General information about sampling of POPs in precipitation in 1999 reporting to EMEP-database

Country	Sites	POPs	Sampling period	Sampler equipment*
Belgium	BE0004R	Pesticides, HCHs	Monthly	Wet only sampler
Czech. Rep	CZ0003R	PAHs, PCBs, DDTs, HCHs, HCB	Every event	Wet only sampler
Iceland	IS0091R	PCBs, pesticides, HCHs, HCB	15d	Bulk sampler
Ireland	IE0002R	Pesticides, HCHs, PCBs	Monthly	Bulk sampler
Netherland	NL0091R	γ-HCH	Monthly	Bulk sampler
Norway	NO0099R	α-HCH, γ-HCH, HCB	Monthly	Bulk sampler
Sweden	Se 2	PAHs, PCBs, DDTs, HCHs, HCB	Monthly	Bulk sampler

* The two collection principals, bulk or wet-only sampling, are used for deposition measurements

PCBs, DDTs, HCHs and PAHs in precipitation and their calculated deposition are evaluated with respect to temperature, latitude and sampling-site etc. The variation of the yearly deposition estimated from monthly measurements at the Swedish coast, Rörvik (Se 2) is summarised in Table 3-12. No significant decreasing trends in the deposition fluxes of the measured POPs was found at the Swedish West Coast between 1996 - 2000.

Table 3-12: Estimate of the yearly deposition of PTS

	Swedish west coast [$\mu g.m^{-2}$], 1996-2000
PAHs*	80 - 140
PCBs*	200 - 800
α-HCH	100 - 300
γ-HCH	400 – 3 500
DDTs	100 - 300
* PAHs sum of 12 and PCB sum of 7	

3.1.3.2 Baltic region

Sampling of PCBs, DDTs and HCHs was carried out continuously during 1991/92 at 16 sampling stations around the Baltic Sea (Agrell et al., 2001). The deposition fluxes of the POPs were calculated from the concentrations in rain. Overall, the variation in the PCB deposition was small between the stations. The median values varied between 1.2 to 5.6 $ng.m^{-2}.d^{-1}$. The variability between stations was larger for the pesticides, about 10 times for DDTs and 25 times for HCHs, with median values of 0.15 $ng.m^{-2}.d^{-1}$ and 1.30 $ng.m^{-2}.d^{-1}$, respectively.

Similar to the concentration in air, a negative relationship between deposition fluxes and latitude was found for DDTs and HCHs implying that the sources mainly are located in the south (see 3.1.2). No such negative relationship was found for PCBs. This indicates that the input of PCBs to the Baltic Sea will be in same order of magnitude in the south as in the north. The daily average deposition and was used to estimate the yearly input of the PTS to the Baltic Sea. The yearly deposition to the Baltic Sea was estimate to 387.1 kg for PCBs, 19.7 kg for DDTs and 226.8 kg for HCHs, reflecting the combined input through wet deposition and dry particle deposition.

Brorström-Lundén (1995) found higher deposition fluxes of HCHs and PCBs over the Skagerak during 1990-1994, compared to the Baltic Sea. (PCBs 10-15 $ng.m^{-2}.d^{-1}$ and of HCHs 5-15 $ng.m^{-2}.d^{-1}$ (α, β and γ-HCH, Tab. 3-14). Higher deposition of HCHs was also found by Hilbert and Poulsen (1992) in a study in Denmark in 1990. However, during this time lindane was used in Denmark (8.4 tons were sold in 1990). The deposition fluxes at the Swedish west coast decreased after 1995 when lindane was banned in Denmark.

A study of spatial and temporal variations of the PCBs concentrations in precipitation was also carried out in a region of southern Sweden (Backe et al., 2002). The PCBs concentration ranged between 1.18 and 81.4 $ng.l^{-1}$. However two of the sampling sites showed concentrations that were approximately 30 times higher than at the rest of the sites, which may be due to location as well as differences in weather conditions and particle content in the air. No seasonal trends in PCB concentration in precipitation were found.

3.1.3.3 National programs and measurements

In Lithunia the deposition of benzo(a)pyrene (BaP) to soil and vegetation, with special emphasis on the forest ecosystem have been investigated (Milukaite, 1998). The monthly flux of BaP at a background station (Preila) ranged from 0.3 to 3.8 $\mu g.m^{-2}.moth^{-1}$ and at a suburban site in the eastern part of Lithuania from 0.6 to 4.8 $\mu g.m^{-2}.moth^{-1}$. The average annual flux generally increased from year to year, except for 1993. The estimated the total annual flux of BaP to Lithuania, ranged from 624 kg in 1993 to 2574 kg in 1995.

Bulk deposition of PAHs and PCDDs/Fs have been measured in UK (Toxic Organic Micropollutants Survey (TOMPS)), (Halsall et al., 1995). The annual average of ΣPAH deposition in Manchester and Cardiff during 1991/92 was 5.2 and 4.1 $\mu g.m^{-2}.d^{-1}$ respectively. The deposition samples was dominated by following PAHs: phenanthrene, fluoranthene/1-methyl phenanthrene, pyrene and chrysene, which is similar to the atmospheric profile reported by Halsall et al. (1994). As a comparison, Gardner et al. (1993) reported ΣPAHs fluxes between 1.1 - 3.9 $\mu g.m^{-2}.d^{-1}$ at a suburban site located close to the city of Manchester during 1990/91. Urban fluxes are generally higher compared to rural locations (EMEP data) reflecting a) importance of the urban centre as a source of PAH and b) the large decline in many atmospheric PAH species moving away from urban areas.

In a small productive semi-rural lake in North-west of England, deposition fluxes of PCBs and PAHs were determined (Gevao et al., 1998). The mean deposition fluxes were 33.5 $\mu g.m^{-2}.moth^{-1}$ for ΣPAHs, with individual compounds varying from 0.19 to 7.76 $\mu g.m^{-2}.month^{-1}$.The monthly mean PCB deposition fluxes ranged from 0.03 (octa-PCBs) to 0.38 (tri-PCBs) $\mu g.m^{-2}.moth^{-1}$, with a ΣPCB flux averaging 0.87 $\mu g.m^{-2}.moth^{-1}$.

ΣPCDD/F (2,3,7,8-isomers) annual median flux for Manchester and Cardiff was 1.42 and 1.01 $\mu g.m^{-2}.d^{-1}$, respectively (Halsall et al., 1995. Hiester et al. (1993) collected monthly bulk deposition samples from Nov 1991 to Oct 1992 and reported a mean annual ΣPCDD/F flux of 1.52, 0.38 and 0.78 $\mu g.m^{-2}.d^{-1}$ for the German cities Düsseldorf, Cologne and Dortmund respectively. Similar to the UK study, the PCDD profile was dominated by the hepta- and octadioxins.

Previous precipitation measurements reported mostly the concentration of the POPs in water. Rain samples were analysed in Germany in the early 1980s (Georgii and Schmitt, 1983). The total concentration of PAHs were 1.8 $\mu g.l^{-1}$ in Frankfurt am Main in February, 1981. Lower values were measured by Levsen et al. (1981) in Hannover (600 $ng.l^{-1}$), Leuenberger et al., (1988), in a rural site in Switzerland (490 $ng.l^{-1}$) and Quaghebeur et al. (1983) in Belgium (140 $ng.l^{-1}$). Recently, a study of the seasonal variation of the concentrations of PAHs in precipitation has been carried out at a rural site by Lake Balaton, Hungary, (Kiss et al., 1997, 2001).

Despite the extensive investigations on the PAH content of atmospheric precipitation and aerosol samples all over the world the availability of data from Eastern Europe is limited for background monitoring programme in South Bohemia (Vana, Holoubek et al., 2001) or some studies (Kiss et al., 1997; Simkova et al., 1996).

1.3.3.4 References

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Table 3-12 Deposition DDTs [$ng.m^{-2}.day^{-1}$]

Country	Sampling sites	Duration	Frequency of measurements	Typical range			Comments	References
				Urban/ind	Rural	Background		
Estonia	Viasandi	1991-1992	monthly, n=9		0.23		sum DDTs	Agrell et al 1999

	Lahemaa	1991-1992	monthly, n=12		0.1		sum DDTs	
Finland	Vasa	1991-1992	monthly, n=12		0.05		sum DDTs	
	Pallas	1998-2000	monthly			0.05-0.5	sum DDTs	Brorström-Lundén 2002
Latvia	Salspils	1991-1992	monthly, n=2	0.64				Agrell et al 1999
Lithuania	Ventes	1991-1992	monthly, n=15		0.38			
Poland	Dziwnow	1991-1992	monthlyn=4					
	Swibo	1991-1992	monthlyn=4					
Sweden	Öland	1991-1992	monthlyn=15		0.38			
	Breanäs	1991-1992	monthlyn=12		0.19			
	Gotland	1991-1992	monthlyn=15		0.19			
	Stockholm	1991-1992	monthlyn=10		0.12			
	Docksta	1991-1992	monthlyn=15		0.08			
	Norrbyn	1991-1992	monthlyn=14		0.09			
	Holmögad	1991-1992	monthlyn=12		0.16			
	Bjuöklub	1991-1992	monthlyn=13		0.05			
	Kalix	1991-1992	monthlyn=14		0.05			
	Rörvik	1998-2000	monthly		0.04-2		Sum DDTs	Brorström-Lundén 2002

Table 3-12: Deposition PCBs [ng.m^{-2}.day^{-1}]

Country	Sampling sites	Duration	Frequency of measurements	Typical range			Comments	References
				Urban/ind	Rural	Background		
Estonia	Viasandi	1991-1992	monthly, n=9		2.2		Total PCBs	Agrell et al 1999
	Lahemaa	1991-1992	monthly,n=12		1.8			
Finland	Vasa	1991-1992	monthly,n=12		1.2			
	Pallas	1996-2000	Monthly			0.1-1	sum 7 PCBs	Brorström-Lundén 2002
Germany	Bayreuth	1994-1996	mothly	2-19			sum 7 PCBs	McLachlan M. et al., 1998
Latvia	Salspils	1991-1992	monthly, n=2	18			Total PCBs	Agrell et al 1999
Lithuania	Ventes	1991-1992	monthly,n=15		3.7			
Poland	Dziwnow	1991-1992	monthlyn=4		2.3.			
	Swibo	1991-1992	monthlyn=4		5.0			
Sweden	Öland	1991-1992	monthlyn=15		3.5			
	Breanäs	1991-1992	monthlyn=12		2.8			
	Gotland	1991-1992	monthlyn=15		2.4			
	Stockholmss	1991-1992	monthlyn=10		1.8			
	Docksta	1991-1992	monthlyn=15		2.6			
	Norrbyn	1991-1992	monthlyn=14		3.2			
	Holmögadd	1991-1992	monthlyn=12		5.7			
	Bjuöklubb	1991-1992	monthlyn=13		2.2			
	Kalix	1991-1992	monthlyn=14		1.5			
	Rörvik	1995-2000	monthly		0.3-5		Sum 7 PCBS	Brorström-Lundén 2002
UK	Esthwait water				1.1		sum PCBs	Gevao et al 1998

Table 3-13: Deposition PCDDs/Fs [ng.m^{-2}.day^{-1}]

Country	Sampling sites	Duration	Frequency of measurements	Typical range				Comments	References
				Near the sources	Urban/ind	Rural	Background		
Germany	Dusseldorf	1991-1992	Monthly		1.5			sum PCDD/F	Hiester et al 1993
	Cologne	1991-1992	Monthly		0.38			sum PCDD/F	Hiester et al 1993
	Dortmund	1991-1992	Monthly		0.78			sum PCDD/F	Hiester et al 1993
	Bayreuth	1994-1996	mothly		1-12				McLachlan M. et al., 1998

	854 samples			Winter: Urban centres - median – 6 pg I-TEQ.m^{-2} dm, 90 percentile – 21 pg I-TEQ.m^{-2} Urban fringe - median – 9 pg I-TEQ.m^{-2} dm, 90 percentile – 43 pg I-TEQ.m^{-2} Rural - median – 4 pg I-TEQ.m^{-2} dm, 90 percentile – 15 pg I-TEQ.m^{-2} Summer: Urban centres - median – 3 pg I-TEQ.m^{-2} dm, 90 percentile – 7 pg I-TEQ.m^{-2} Urban fringe - median – 4 pg I-TEQ.m^{-2} dm, 90 percentile – 24 pg I-TEQ.m^{-2} Rural - median – 3 pg I-TEQ.m^{-2} dm, 90 percentile – 7 pg I-TEQ.m^{-2}					Fiedler et al., 2002
UK	Cardiff				1.0				Hasall et al 1994
	Manchester				1.4				Hasall et al 1994

Table 3-14: Deposition HCHs [ng.m^{-2}.day^{-1}]

Country	Sampling sites	Duration	Frequency of measurements	Typical range			References
				Urban/ind	Rural	Background	
Estonia	Viasandi	1991-1992	monthly, n=9		3.7		Agrell et al 1999
	Lahemaa	1991-1992	monthly,n=12		0.53		
Finland	Vasa	1991-1992	monthly,n=12		1.3		
	Pallas	1996-2000	monthly			0.01-2	Brorström-Lundén 2002
Latvia	Salspils	1991-1992	monthly, n=2	2.5			Agrell et al 1999
Lithuania	Ventes	1991-1992	monthly,n=15		3.2		
Poland	Dziwnow	1991-1992	monthlyn=4		1.4		
	Swibo	1991-1992	monthlyn=4		5.7		
Sweden	Öland	1991-1992	monthlyn=15		0.98		
	Breanäs	1991-1992	monthlyn=12		1.9		
	Gotland	1991-1992	monthlyn=15		2.2		
	Stockholmss	1991-1992	monthlyn=10		1.3		
	Docksta	1991-1992	monthlyn=15		1.7		
	Norrbyn	1991-1992	monthlyn=14		0.61		
	Holmögadd	1991-1992	monthlyn=12		0.82		
	Bjuöklubb	1991-1992	monthlyn=13		0.22		
	Kalix	1991-1992	monthlyn=14		0.16		
	Rörvik	1998-2000	monthly		0.05-20		Brorström-Lundén 2002

Table 3-15: Deposition PAHs [ng.m^{-2}.day^{-1}]

Country	Sampling sites	Duration	Frequency of measurements	Typical range			Comments	References
				Urban/ind	Rural	Background		
Finland	Pallas	1996-2000	Monthly			0.01-0.1	sum 12 PAHs	Brorström-Lundén 2002
Germany	Bayreuth	1994-1996	Monthly	0.2-5				McLachlan M. et al. (1998)
	Zingst	1995-1996	Monthly		0.05-0.3		sum PAHs	EMEP data
Hungary	Lake Balaton	1996-1997	Seasonaly		0.46		13 PAHs	Kiss et al., 2001
Lithuania	Preila	1992-1998	Monthly	0.02-0.2	0.01-0.1		Benzo(a)pyrene	Milukate et al 1998
Sweden	Rörvik	1995-2000	monthly		0.01-2		sum PAH 12	Brorström-Lundén 2002
UK	Cardiff			4.1			sum PAH	Hasall et al 1994
	Manchester			5.2			sum PAH	
	Esthwait water				1.1		sum PAH	Gevao et al 1998

Table 3-16: Deposition chlordanes [ng.m^{-2}.day^{-1}]

Country	Sampling	Duration	Frequency of	Typical range	Comments	References

	sites		measurements	Rural	Background		
Finland	Pallas	1996-2000	monthly		not det - 0.1	sum Chlordanes	Brorström-Lundén 2002
Sweden	Rörvik	1996-2000	monthly	not det - 0.5		sum Chlordanes	

3.1.4 Snow and ice

Snow and ice influence the deposition and fate of PTS in cold regions. Due to their high porosity, falling snowflakes have been proposed to be more effective at scavenging atmospheric particles than rain. In addition, large specific surface area of ice crystals enhances the adsorption of gaseous hydrophobic contaminants from the atmosphere. Hence, the concentrations of airborne contaminants in the snowpack represent an integration of the atmospheric deposition over certain period, and can be used for estimating pollutant levels in the region. After deposition, the trapped semivolatile compounds undergo a number of processes, such as repartitioning and translocation within the snowpack, volatilisation and drainage at the time of snowmelt. Release of the accumulated substances into adjacent aquatic systems can represent a significant load of contaminants over a short period.

One from the first study of organic pollutants in snow, especially polychlorinated hydrocarbons, phenols, quaiacols and catechols have been performed by analysis of snow samples from North Pole, May 1984 (Paasivirta et al., 1984). All of these pollutants were below the limit of determination, which was estimated to be as fallout 0.1 - 0.05 $\mu g.m^{-2}$ for individual compounds. For comparison, snow samples from Central Finland and South Finland 1983 - 1985 also showed non-detectable levels of chlorinated hydrocarbons but well measurable levels of chlorophenol compounds, which were significantly higher at urban heavy traffic) than rural and higher of South than Central Finland places, respectively. One sample from Lapland, North Finland 1985, however, had no measurable amounts of chlorophenos like the North Pole sample. The chlorophenol fallout appeared to be significantly lower in Central than South Finland. No traces of chlorophenols were found in snow at rural Lapland or at North Pole.

Snow samples were collected 1) close to a heavy traffic highway passing through Umeå, Sweden; 2) beside a road downtown Umeå and 3) on the top of the water tower in Umeå (Marklund et al., 1991). The level of 2,3,7,8-TCDF in the samples 5 m from the roads is approximately 3 - 4 times higher than for the level in the samples collected at a distance of 100 m from the road to with the level of 2,3,7,8-TCDF is comparable with other background samples. This indicates that a slight direct contribution of the PCDDs and PCDFs emission to the environment can be derived from cars. The results indicate that the deposition of the PCDDs and PCDFs with originate from car emissions are very local and are found close to the road.

Snow cores were collected in the catchment area of five remote mountain lakes in Europe (Carrera et al., 2001) They were analysed for PAHs, PCBs, and OCPs (DDTs, HCB and HCHs). PAHs are found in higher amounts in the Tatra and Caledonian mountains, PCBs are higher in the Alps and HCHs are higher in the Alps and Pyrenees. The quantitative PAHs distributions are dominated by low molecular weight compounds, phenanthrene being the most abundant PAHs in all but in one site. These compounds also occur predominantly in the in the gas phase in the atmosphere. Their high abundance in the snowpack witness the occurrence of effective transfer mechanism from gas to snow flakes. Transformation of the concentration values of these compounds into annual deposition rates and correction for catchment/lake area indicates that in Scandinavia and the Alps a large proportion of PAHs incorporation is mediated by snowfallout whereas in the Tatra Mountains snow deposition only account for a small fraction of the compounds stored in the lake sediments. Among organochlorine compounds, only PCBs and HCHs have been found above method detection limit in most of the samples. The PCB congener distribution changes significantly between sites, although a predominance of the less chlorinated congeners has generally been observed.

PAHs, PCBs and HCHs are found in all snow samples collected in remote high mountain European sites. Despite the predominance of atmospheric mechanisms for the transport of these compounds to

these high-altitude sites, their concentrations in snow do not exhibit parallel geographic distributions. Thus, PAHs are found in higher amounts in the Tatra and Caledonian mountains, PCBs in the Alps and HCHs in the Alps and Pyrenees.

For example, snow cores were collected in the catchment area of five remote mountain lakes in Europe (Carrera et al., 2001) PAHs were found in higher amounts in the tatra and Caledonian mountains, PCBs are higher in the Alps and HCHs are higher in the Alps and Pyrenees.

3.1.4.1 References

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3.1.5 Aquatic ecosystems

3.1.5.1 Introduction

Inputs of POPs to the hydrological cycle are principially via discharges of sewage and industrial effluents, urban runoff, leachates from solid waste landfill sites, atmsopheric deposition and of increasing concern, agricultural runoff (Scrimshaw and Lester, 1996).

3.1.5.2 Seas

3.1.5.2.1 Introduction

Many organic substances are released to the marine environment. Many of them are degraded rather effectively, while more persistent compounds may be distributed over large areas and accumulate in organisms. Most of the PTS are made up of several hundreds or even thousands of individual compounds. This complicates the presentation of analytical results since these can represent the whole mixture or one or several individual compounds. Furthermore these results can be related to different matrices, for example wet weight, dry weight or lipid weight. Additionally variations in the composition of the matrix can influence the result, for example the number of particles in the air or water, the organic carbon content of the sediment and the lipid content of the tissue. The absence of information on these factors limits the extent to which data from different sources can be compared.

Human impacts on species and habitats are greatest in the coastal zones of regional seas. Sensitive habitats with great ecological significance are often disturbed of may even vanish due to a range of human activities. The intensive, and sometimes conflicting, use of the regional seas causes a number of problems in relation to providing a healthy ecosystem and securing its sustainable use.

Salt marshes are important and dynamic region of the coastal environment (Scrimshaw and Lester, 1996). In some region, over the last 30 years large areas of salt marsh have undergone a substantial decline (for example along the Essex Coast) (Scrimshaw and Lester, 1996). The potential reasons for the loss of salt marsh habitat are numerous; eustatic sea level rise due to the melting of the polar ice caps, isostatic tilting of the Essex coast as a result of readjusting from glacial retreat after the last ice age, land reclamation for agriculture and industry, and vegetation dieback to disease. Pollution may play the important role in stimulating the loss in salt marsh vegetation, especially the effects of residual heavy metals and POPs.

3.1.5.2.2 North Sea, Norwegian Sea – OSPAR region

The North Sea has a long history of multiple using by people from many nations. There is awareness of the need to safeguard the marine ecosystem and to achieve sustainability in respect of human use. Knowledge to the main human pressures and understanding their impact on the structure and functioning of the ecosystem and its resources is essential for the development and implementation of effective measures to achieve sustainable use.

In the Quality Status Report 2000 on the Greater North Sea, OSPAR identified a list of human pressures and ranked these into four priority classes (A-D) according to their relative impact on the ecosystem, including sustainable use:

A. *Highest impact*: fisheries, trace organic contaminants, nutrients;
B. *Upper intermediate impact*: oil and polyaromatic hydrocarbons (PAHs), other hazardous substances, heavy metals, biological impacts;
C. *Lower intermediate impact*: litter and disturbance I, dredging and dumping, engineering operations, mariculture, radionuclides; and
D. *Lowest impact*: litter and disturbance II.

OSPAR has developed and adopted 'Background/Reference Concentrations' (BRCs) and 'Ecotoxicological Assessment Criteria' (EAC) values as assessment criteria. In general man-made substances would be expected to have a background concentration of zero. However, due to their persistence and long-range transport many substances are now detected all over the world. Therefore typical concentrations in remote and selected parts of the OSPAR area are used as background/reference concentrations. For naturally occurring substances the BRC is the range of concentrations that would be anticipated to be present in the environment in the absence of any human activity (See Table 3-21). EACs are defined as concentration levels of a substance above which concern is indicated. Criteria for the specific contaminants were derived using all the available ecotoxicological data that passed predefined selection and quality criteria. In a number of cases EACs are provisional due to insufficient information and in these cases higher safety factors are included. These assessment criteria can be used to identify possible areas of concern and to indicate which substances might be a QSR 2000 (Table 3-21).

Table 3-21: Overview of ecotoxicological assessment criteria for trace metals, PCBs, PAHs, TBT and some organochlorine pesticides

PTS	Water [µg.l^{-1}]	Sediment [µg.g^{-1} dw]	Fish [µg.g^{-1} fw]	Mussel [µg.g^{-1}dw]
DDE	nr	0.0005 – 0.005†	0.005 – 0.05*	0.005 – 0.05*
Dieldrin	nr	0.0005 – 0.005†	0.005 – 0.05*	0.005 – 0.05*
Lindane	0.0005 – 0.005	nr	0.0005 – 0.005*	nr
Naphthalene	5 – 50*	0.05 – 0.5*	nr	0.5 – 5†
Phenanthrene	0.5 – 5†	0.1 – 1*	nr	5 – 50†
Anthracene	0.001 – 0.01†	0.05 – 0.5*	nr	0.005 – 0.05†
Fluoranthene	0.01 – 0.1†	0.5 – 5†	nr	1 – 10†
Pyrene	0.05 – 0.5†	0.05 – 0.5†	nr	1 – 10†
Benz[*a*]anthracene	nd	0.1 – 1†	nr	nd
Chrysene	nd	0.1 – 1†	nr	nd
Benzo[*a*]pyrene	0.01 – 0.1†	0.1 – 1†	nr	5 – 50†
$\sum PCB_7$	nr	0.001 – 0.01†	0.001 – 0.01*	0.005 – 0.058
TBT	0.00001 – 0.0001*	0.000005 – 0.00005†	nr	0.001 – 0.01*

Sediment data are for a reference content of 1% organic carbon. * firm; † provisional; ‡ this range is within the range of background values for natural waters. This value should be compared with the bioavailable fraction of copper in sea water; fc for future consideration; nr not relevant to the current monitoring programme; nd no data available or insufficient data available; ∑PCB7 represents the sum of CB28, CB52, CB101, CB118, CB138, CB153 and CB180

In sediments DDD is the major component of the DDT derivatives; but data are usually reported as total DDT. Comparison with EACs is difficult because only an EAC for DDE is available. The

available data, however, have not revealed any locations with significantly elevated concentrations. Hexachlorobenzene was previously used as a fungicide, but today the major sources are associated with incomplete combustion, limited use as a pesticide and disposal at dumpsites. As HCB is hydrophobic concentrations in the relatively few sea water samples analysed are in the ng.l^{-1} range or below the detection limit. High HCB concentrations are reported in sediments from the Forth Estuary (two orders of magnitude higher than elsewhere in Scotland) reflecting known historic inputs. There is evidence that HCB concentrations in biota have generally decreased.

Toxaphene has not been used in the OSPAR region. However, the pesticide has been used extensively in cotton-producing countries, and is another example of a pollutant that is subject to long-range transport. This pesticide, because of its high toxicity to fish, was also used as a piscicide in some non-OSPAR countries.

Dieldrin has no known use today but previous usage may still affect the environment. Data from Regions I and II indicate low and decreasing concentrations in the marine environment. Triazines, such as atrazine and simazine, are still being used in some applications and are still detected in sea water, the highest levels are observed along the coast.

Concentrations of PCBs in ocean water are generally very low and this makes reliable quantification difficult. Concentrations of PCBs in filtered ocean water are usually reported to be in the low pg.l^{-1} range. OSPAR countries have banned the major PCB uses for some years. OSPAR and EU regulations aim at a complete phase out of PCBs in the period between 1995 and 2010. However, not all PCBs in smaller applications, in particular in electrical equipment, may be removed within that period. PCBs emitted and deposited during the years of intensive production and use are still a diffuse source to the global environment. Evaporation of PCBs from polluted soils and waters has been shown to be a significant source to the atmosphere. Once in the atmosphere, PCBs enter the global circulation and can be transported to remote places. The atmospheric input through precipitation in the OSPAR Convention area is estimated to be 3 – 7 t.yr^{-1} for the period 1992 to 1994. Riverine and direct inputs of PCBs are low in absolute terms. Although it is not possible to derive reliable estimates of inputs because most concentrations are below the limit of detection, estimates derived for the Greater North Sea were in the range 0.13 – 2.4 t.yr^{-1} for the period 1990 to 1995. The declining use and progressive elimination of PCBs have been reflected in the decreasing concentrations observed in ten of the long-term monitoring programmes evaluated.

Information on dioxin levels in the Convention area is scarce, but a few point source emissions have been well studied, such as in Frierfjorden in Region II. Comparison of measurements for surface sediments shows that dioxin concentrations seem ten to twenty times lower in samples from the Barents Sea than in samples from the northern North Sea.

Lindane is also more watersoluble than most of the other chlorinated hydrocarbons discussed in this report, and a major input is via rivers from the application areas. There are indications of a slight decrease in the riverine input of lindane to the Irish Sea. In water, lindane concentrations are higher in the southern North Sea and the German Bight than in the north-western North Sea. The highest concentrations exceed the EAC (0.5 – 5 ng.l^{-1}).

Concentrations of lindane in biotic samples generally decreased during the period 1990 to 1995, especially in relatively polluted regions of estuaries, fjords and near coastal zones. In contrast, a significant upward trend was observed in dab muscle from Lista (southern Norway) for the same period. Concentrations of lindane in mussels around the Irish Sea, Bristol Channel, Celtic Sea and Atlantic coasts are in the ng.g^{-1} ww range and, in the livers of flatfish from the Irish Sea, are approximately ten times higher.

Concentrations of α-HCH ranged from 0.1 to 0.7 ng.l^{-1} (mean value 0.28 ng.l^{-1}), and γ-HCH from 0.1 to 4.0 ng.l^{-1} (mean value 1.1 ng.l^{-1}). It was concluded, that such concentrations represented background

values derived from diffuse sources. A concentration of 100 $ng.l^{-1}$ would indicate that a release of lindane from the lost container had occurred, and was of sufficient scale to necessitate further action. This would include efforts to establish to location of the container, and to assess the possible impact on the food quality of commercially exploited fish and shellfish in the vicinity. A major release would elevate concentrations over a wide area.

Over the last 30 years large areas of salt marsh along the Essex Coast have undergone a substantial decline (Scrimshaw and Lester, 1996). Along the Essex Coast, water quality is affected by wide variety of agricultural, industrial and domestic purposes and is also dependent upon shipping and off-shore activities in the North Sea. Historically the majority of sewage from coastal area in the UK has been discharged to sea with minimal treatment. Untreated sewage may be discharged to the sea by one of the three main routes – short and long sea outfalls and stormwater overflows .

Maximum of observed levels of PCBs and OCPs in UK salt marsh sediments are presented in the Tables 3-27 and 3-29. The explanation of the salt marsh sediment problem needs a more complete inventory of contaminants which would enable a more complete assessment of possible effects to be made and the impact of other, possible more contemporary contaminants monitored.

In general the two main contributors to PAHs in the environment are fossil fuels, mainly crude oil, and the incomplete combustion of organic materials such as wood, coal and oil. Both the atmospheric and aquatic pathways to the maritime area are important. Information on riverine inputs is very limited. Emissions of PAHs from North Sea riparian states have been estimated at 7 000 t in 1990. In addition to the many domestic and industrial combustion processes, coal tar containing coating systems are important sources of PAHs. Offshore activities, oil spills, offshore installations and shipping exhausts are important sources. Under anaerobic conditions some naturally synthesised compounds can be reduced to PAHs. Atlantic sea water range from 0.3 $ng.l^{-1}$ for individual, more water-soluble, lower molecular weight PAHs (two and three ring compounds) to less than 0.001 $ng.l^{-1}$ for the high molecular weight PAHs (five or more ring compounds). Higher concentrations were generally found in coastal and estuarine samples with total PAH concentrations ranging from not detectable to 8 500 $ng.l^{-1}$. On a worldwide basis, background values for PAHs in sediments appear to be within the range 0.01 to approximately 1 $\mu g.g^{-1}$ dw.

Use of several of the classic persistent organic compounds has been banned or severely restricted. There are, however, still other chemicals in use that are sufficiently persistent to show up as global environmental contaminants. These are not yet included in the ongoing monitoring programmes and knowledge of their occurrence is consequently more sporadic. For many of these substances, there are no agreed assessment criteria.

Brominated flame retardants are a diverse group of various brominated substances, some of which are used as additives to polymers and textiles. Polybrominated diphenyl ethers (PBDEs), especially those with four to six bromine atoms, are found in biota and sediments in the marine environment far from known sources.

Only few data are available on chlorinated paraffin concentrations in the Convention area. Sediment from river mouths was found to contain up to 10 $ng.g^{-1}$ dw, fish samples from the North Sea have been shown to contain up to 100 $ng.g^{-1}$ ww. A recent EU risk assessment for short-chained chlorinated paraffins with a high degree of chlorination identified a need to limit the exposure of aquatic organisms to local emissions associated with metalworking applications. PARCOM Decision 95/1 provides for the phase-out of the use in a range of applications of short-chained chlorinated paraffins.

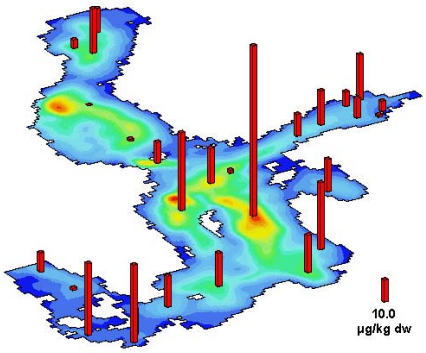
3.1.5.2.3 Baltic Sea

The Baltic Sea as a virtually enclosed and fairly shallow sea is particularly vulnerable to the toxic organic pollutants (Roots, 1996, 1999). It takes tens of years for all the water in the closed system to

be renewed. It is also a cold sea with a short reproductive season. Lower water temperature and lower concentration of bacteria in marine waters, and low exchange rates of the water body, means that the Baltic Sea ecosystem trends to trap and accumulate PBT compounds. There are then either absorbed into the sediments or accumulated, especially in marine mammals and sea birds. Above-mentioned facts are some of the reasons why the sea is sensitive to disturbance by these types of toxic organic chemicals (Roots, 1996).

The loads of many substances have been reduced by at least 50% since the late 1980`s – mainly due to the effective implementation of environmental legislation, the substitution of hazardous substances with harmless hazardous substances, and technological improvements. Consequently at the beginning of 1990s, the rivers and the atmosphere contribute about equally in PCB loads (332 kg and 387,1 kg, respectively), while for the pesticides atmospheric deposition is about five to seven times more important. The yearly deposition of pesticides to the Baltic Sea was 19,7 kg for DDTs and 226,8 kg for HCHs, reflecting the combined input through wet deposition and dry particle deposition. The river transport results in a yearly amount of 2.8 kg DDTs and 47,5 kg HCHs to the Baltic Sea (Agrell, et al., 2001). Although trends in levels of persistent pollutants in some Baltic biota are well documented, little is known about the origin of these pollutants and the flow between different compartments in the ecosystem.

In general the concentrations of PTS in the sediments and biota were found to increase from north to south. The highest level of contamination by PCBs was observed from the Eastern Gotland Basin, Western Gotland Basin and from the Lübeck Bay (Figure 3-08). Recent investigations of PCBs in sediments along the Swedish coast of the Baltic Proper show concentration range from about 2 to 33 $ng.g^{-1}$ dw. Near Stockholm elevated concentrations (up to 100 $ng.g^{-1}$ dw) were, however, measured (Meili et al. 2000). From the Landsort Deep low surfacial sediment concentrations (3-10 $ng.g^{-1}$ dw) were found (De Wit et al., 1990). Kowalewska and Konat (1999) report for 6 CP congeners (105 not included) from the Gulf of Gdansk rather low value 27 $ng.g^{-1}$ dw at the Deep of Gdansk, 14 $ng.g^{-1}$ dw near the Gdynia harbour and 7 $ng.g^{-1}$ dw near the mouth of the Vistula River. In the Gulf of Bothnia rather low values, from about 2 to 14 $ng.g^{-1}$ dw, have been measured (ICES, 2000, Bavel et al., (1995).



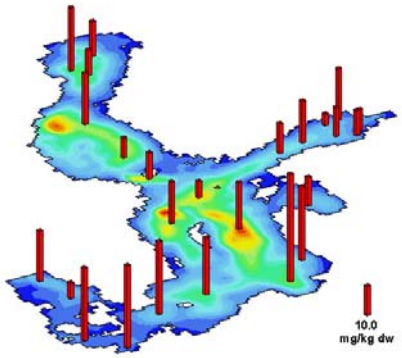


Figure 3-09: Vertical distribution of PAHs (dry weight basis) in the surface sediments (data from ICES 2000).

ICES 2000).

Recent information on spatial distribution of DDTs in surface sediments seems to be even much more limited than for PCBs. For the Gulf of Gdansk concentrations of 1,55 $ng.g^{-1}$ dw for p,p'-DDE and 2 to 5 $ng.g^{-1}$ dw for sum of DDT has been reported (Sapota 1999). Earlier Perttilä and Haahti (1986) reported total DDT concentrations from 10 to 40 $ng.g^{-1}$ dw in the surface sediments in the Gulf of Finland.

A recent study shows that DDT is degraded in the sediment and that most probably diffusion mechanisms transport DDT through the sediment core (Olsson *et al.* 2000). This makes the trends different in the cores and the biota and might explain why considerable amounts of DDT were found in sediment lamina representing the 1940s long before the extensive use of DDT.

The general concentration trend in the Baltic Proper suggests an increase of PCB concentrations from the early 1970s and onwards (ICES, 2000). This is an apposing trend to the decreasing concentration trends for PCBs in biota from the Baltic Proper (HELCOM, 1996). In the Gulf of Finland concentrations of PCBs were found to be slightly lower in the early 1990s than in the 1970s. In some areas (e.g. Gotland Basin, Gdansk Bay, Bornholm Bay) concentrations remain more or less constant or even increase after the 1970s (ICES, 2000; Nylund et al., 1992). Decrease in PCB concentrations in the Gulf of Gdansk in early 1990s has been reported (Sapota, 1999). Earlier studies of anoxic sediments from the Baltic have often failed to indicate decreasing concentrations during the most recent period but in the north western part of the Baltic several investigations have shown decreasing trends in the most recent laminas (for a review see Olsson et al. 2000).

Gulf of Finland, a sub-basin of the Baltic Sea was found to be severely polluted, with Σ PCDDs/Fs concentrations as high as 101 000 $pg.g^{-1}$ dw and 479 pg $TEQ.g^{-1}$ dw. One of the industrial processes where PCDDs/Fs are formed as by-products, is the synthesis of chlorophenols (Isosaari et al., 2002a,b; Korhonen et al., 2002). In Finland, chlorophenols were manufactured in 1939-1984, and used as a wood preservative Ky 5 (mainly 2,3,4,6-tetrachlorophenol). The chemical plant was situated next to the Kymijoki River, which discharges into the Gulf. Recent analyses have shown that the sediments of the Kymijoki River still contain high levels of PCDDs/Fs, up to 350 000 pg $TEQ.g^{-1}$ dw. It seems that the river has transported pollutants into the Gulf of Finland for many years.

The highest PAHs concentrations, up to 35.2 $ng.g^{-1}$ dw, have been found in the southern most Baltic Sea (Gulf of Gdansk, Lübeck Bay, Mecklenburg Bay, Arkona Basin) (Figure 3-09). Somewhat elevated concentrations were observed from the eastern Gulf of Finland as well as from the northern Gulf of Bothnia (up to 17.0 $ng.g^{-1}$ dw and 20.9 $ng.g^{-1}$ dw, respectively). Taking into account that PAHs reach the marine environment via effluent discharges, urban run-off, atmospheric transport, and the spillage or disposal of oil and petroleum products these elevated concentrations may be explained by the proximity of the coastal areas. For the Gulf of Gdansk, also slightly lower values (sum of 15 individual compounds) have been measured ranging from 0.010-7 $ng.g^{-1}$ dw, average being 1.830 $ng.g^{-1}$ dw (Kowalewska and Konat 1997). From the Belt and Arkona Seas PAH values from 0.8 $ng.g^{-1}$ dw up to 1.9 $ng.g^{-1}$ dw have been reported (Witt, 1995, and Witt and Trost, 1999) and for the inner coastal region, the Bodden area, from 2.18 $ng.g^{-1}$ to 0.845 $ng.g^{-1}$ dw (Witt, 1995, and Witt and Trost, 1999).

The low molecular weight PAHs can be acutely toxic, however, the major concern is for some of the higher-molecular weight compounds that, when ingested by marine animals, can form metabolites that are active carcinogens. At least four of the PAHs found in high concentrations in the southern Baltic Sea sediments (benz[a]anthracene, benzo[k]fluoranthene, chrysene, and benzo[a]pyrene) are known to be carcinogenic in mammals and are almost certainly so in fish (Woodhead et al. 1999).

The down-core PAH concentrations in general show peak concentrations in the 1970s and early 1980s, thereafter decreasing somewhat. In the sediment cores from Mecklenburg Bight, Southern Baltic Sea, increasing PAH concentrations were detected between 6 and 10 cm (between 1945 and 1965) reflecting a higher anthropogenic influence during that time (Witt and Trost, 1999; Dannenberger, 1996; Dannenberger and Lerz, 1996; 1998) (see Tables 3-25, 3-27, 3-29).

Organotin compounds, mainly tributyltin (TBT), are still regularly used as antifoulants on large-sea going vessels. Emissions from ship hull are the main source for marine TBT contamination. Organotin compounds are found in sediments as tri- (TBT), di- (DBT) and monobutyltin (MBT), of which DBT

and MBT are brake down products of TBT. TBT has estrogenic effects, which cause imposex or intersex on many snail species.

The highest concentration of organotin is typically found in sediments from harbours, port channels, near shipyards and along ship lains. In several locations he majority of butyltin compounds were present as TBT, which suggest recent exposure of the localised aquatic environment to TBT. The maximum concentrations found in the Gulf of Gdansk shipyards was 40 $pg.g^{-1}$ dw for TBT, 42 $pg.g^{-1}$ dw for DBT and 46 $pg.g^{-1}$ dw for MBT.

For polybrominated diphenylethers (PBDE), dioxins and furans information in Baltic Sea sediments is very limited. A few Swedish results reveal that dioxins and furans are present in Baltic sediments in the concentrations level of few $pg.g^{-1}$ (Kjeller and Rappe 1995, de Wit et al., 1990).

The long term monitoring of DDTs, PCBs, HCB and HCHs in biota samples that has been carried out in the Baltic since the 1970s has been used to verify the models. Interestingly, these unique temporal trends do not support the model. Concentrations decrease at a similar rate both in the warmer south as in the colder north. (Bignert *et al.* 1998). Many authors consider the Baltic herring (*Clupea harengus membras L.*) to be a good indicator of the Baltic Sea ecosystem pollution by PBTs (Roots, 1996; Falandysz, 1984; Falandysz et al., 1997d, f). Its role as a bioindicator is currently increasing.

The concentrations of ∑ DDTs and PCBs in herring muscle are highest in southern Baltic Proper and decrease to the north and west and are similar in the Kattegat and the Bothnian Bay. Concentrations vary between 61-710 $ng.g^{-1}$ lw for ∑ DDTs and between 120-2 800 $ng.g^{-1}$ lw for PCBs (Figure 3-10).

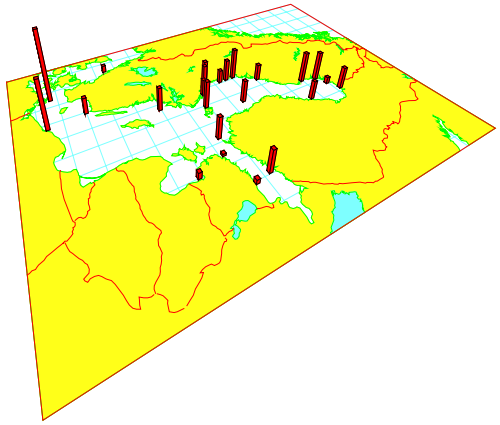


Figure 3-10: Spatial distribution in concentrations of PCBs in herring muscle. Lowest concentration is found outside the Estonian coast [120 $ng.g^{-1}$ l.w.] and highest near the Polish coast [2 800 $ng.g^{-1}$ l.w.]

The temporal trend for ∑ DDTs in herring is decreasing over the entire period. The longest time series, going back to the late 1960s-early 1970s show decreasing concentrations by about 7% per year in herring from southern Bothnian Sea and by 11-12% per year in both herring and guillemot egg from the Baltic Proper (Figure 3-11). Time series starting in the early 1980s or later all show a similar decrease varying from 9-14% in the Kattegat and the Gulf of Bothnia and 5-11% in the Baltic Proper irrespective of the studied species - herring, cod, perch or blue mussel (Figure 3-12). The decrease in concentration is statistically significant during the last 10 years for most studied matrices irrespective they represent the coastal zone like perch, the pelagic environment like herring and guillemot or the demersal habitat like cod.

The concentrations found on lipid weight basis are remarkably similar regardless of species and position in the food web. The concentrations found in the planktivorous herring (61-710 $ng.g^{-1}$ l.w.) are quite similar to what are found in the piscivorous perch (71-1 000 $ng.g^{-1}$ l.w.). The concentrations are also often quite similar in the studied invertebrates such as blue mussel, *Macoma sp*. and *Saduria*

sp. (36-390 ng.g^{-1} l.w). Slightly higher concentration of is found in salmon (1 300-2 100 ng.g^{-1} l.w.) (Aune et al., 2000).

The dioxin concentrations, expressed as the TEQ value, in 7 pools of herring muscle along the Finnish coast vary between 165 and 329 pg.g^{-1} l.w. (Vartiainen *et al.,* 1997). The highest concentrations were found in the inner part of the Gulf of Finland. Corresponding value on a wet weight basis was 2.9-24 pg.g^{-1}. The highest wet weight concentrations were found in samples comprising fat specimens of high age from the Bothnian Sea and the Gulf of Finland. The studied samples comprised pools of herring in age classes 2-18 years of age. The TEQ values for coplanar PCBs were of the same magnitude as those for the dioxins and as for dioxins the concentration (w.w.) was highest in samples from the Bothnian Sea and the Gulf of Finland. Swedish data on dioxin concentrations (TEQ) in individual young herring from the Bothnian Bay varies between 8.5 and 57 pg.g^{-1} l.w. and corresponding values for coplanar PCB is 6.8 and 35 pg.g^{-1} l.w. (mean 20 pg.g^{-1} l.w.). In the southern Baltic Proper corresponding values are 1.9-56 pg.g^{-1} l.w. (mean 22 pg.g^{-1} l.w.) and 14-105 pg.g^{-1} l.w. (mean 43 pg.g^{-1} l.w.) resp. In the Kattegat corresponding values are 4-16 (mean 8 pg.g^{-1} l.w.) and 8.5-40 pg.g^{-1} l.w. (mean 18 pg.g^{-1} l.w.) respectively (deWit *et al.* 2000). The higher concentrations found in the Finnish material is probably mainly explained by the higher age classes analysed.

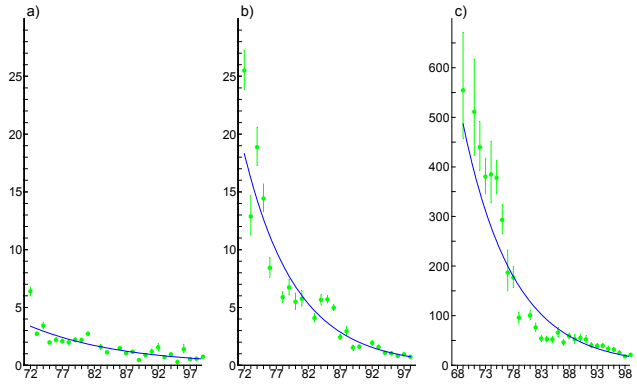


Figure 3-11: Concentrations of ∑DDTs (ng.g^{-1} l.w.) in muscle tissue of herring (1972-1998); a) southern Bothnian Sea, b) the southern Baltic Proper and c) in guillemot egg (1968-1998) from the central Baltic Proper. The 95% confidence interval for the annual geometric mean is given. The significant log linear regression line for the trend is indicated.

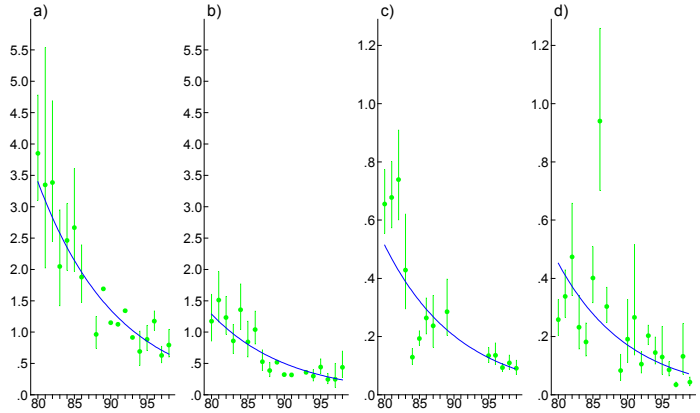


Figure 3-12: Concentrations of ∑DDTs (ng.g^{-1} l.w.) in fish samples (1980-98); cod liver in a) the Baltic Proper, b) the Kattegat; perch muscle in c) Gulf of Bothnia and d) the Baltic Proper. The 95% confidence interval for the annual geometric mean is given. The significant log linear regression line for the trend is indicated.

The European otter (*Lutra lutra*) is a widespreade species on the Euroasian continent. Since the 1950s some European otter populations have declined dramatically. There are however significant differences in the otter population density between different areas (Sjőasen et al., 1997). Many different explanations for the decline had been presented: e.g habitat destruction and direct or indirect influences of eutrophication, acidification and toxic chemicals. In the beginning of 1980s, PCBs were suggested to be an important reason for the otter population decline. Based on the results of various

studies, PCBs seemed to be an important agent for the explanation of the otter decline and the present distribution in Europe (see Table 3-30).

Table 3-30: PCBs and DDTs concentrations in otter (*Lutra lutra*) muscle tissues [$\mu g.g^{-1}$] (Sjőasen et al., 1997)

Area	N	Sampling year	PCBs Mean (range)	DDTs Mean (range)
Norway	23	1970s	17 1.6 - 30	1.7 0.18 - 5.9
Sweden	53	1970s	120 4.7 - 970	4.1 ND - 27
UK	14		53 ND - 300	18.5 ND - 85
Denmark	16		16 7.5 - 60	0.9 0.39 - 1.88
Czech Republic	8		130 19 - 260	
Spain	21		100 4.4 - 1 000	
Latvia	8	1991-2	2.3 0.4 - 10	0.22 0.028 - 0.76
Austria/Czech Republic	11	1990-4	38[1] (12.7)[2] (4.2 - 130.0)[1] (1.3 - 130.0)[2]	

[1] (Gutleb and Kranz, 1998), measured value, geometric mean and range
[2] (Gutleb and Kranz, 1998), level calculated by described model, geometric mean and range

3.1.5.2.4 The Black Sea

Almost one third of continental Europe drains into it and, during the last 30 years, the Black Sea environment has surfed a catastrophic degradation from the waterborne waste from 17 countries. Due to natural causes, subhalocline waters of the Black Sea are anoxic. In spite of this natural deficiency, the Black Sea has served mankind well in the past through its provision of food resources, as a natural setting for recreation and transportation, and even as a disposal site for waste, including nuclear wastes. In return, it has been exploited and degraded in many ways. Unregulated and unplanned freshwater withdrawal for irrigation purposes, hydro-and thermal-power generation, the use of coastal areas for construction, and the many untreated industrial and agricultural wastes discharged into the rivers that drain into the sea have all had detrimental effects on its health.

The large natural river supply of phosphorus and nitrogen, essential nutrients for marine plants and algae, has always made the Black Sea very fertile. The serious degradation it faces now can be explained by a variety of factors ranging from high pollution loads from the rivers that discharge into the sea to improper policies and inadequate management practices. Among the most serious problems is the high level of eutrophication by nutrients from land-based sources. Other factors in the degradation of the marine environment include the introduction of opportunistic species such as the comb jellyfish, *Mnemiopsis leydi*; changes in the hydrological balance caused and microbiological pollution, synthetic organic contaminants, heavy metals, radionuclides, dumping and oil pollution.

These have caused the environment of the Black Sea to deteriorate dramatically in terms of biodiversity, habitats, fisheries resources, aesthetic and recreational value and water quality. Land-based sources are identified as the primary factor causing the present crisis situation and this is where research efforts have been targeted.

Concentrations of DDTs, HCHs and PCBs in Black Sea fish and mammals are high by comparison with those reported for other regional seas (Tanabe et al., 1997a,b). In most countries of the Black Sea, the used of these pesticides has been restricted or banned. For example, in Turkey and Romania, the

use of organochlorine pesticides was controlled in the late 1970s, but effective restrictions were not imposed in Turkey until the 1980s (Tanabe et al., 1997a). Between 1976 and 1983, the annual use of organochlorine insecticides in Turkey was 1 000-2 000 tonnes (Karakay and Oylap, 1987). Despite the restriction, recent studies have shown that DDT is present in Turkish rivers, streams, and domestic and industrial discharges, which indicates their illegal use (Tuncer et al., 1998). The use of these chemicals in other Black Sea countries is currently unclear, but the DDE/DDT ratio was, however, low indicating fresh inputs and hence current usage of DDT within the Black Sea region.

The extent of contamination of the Black Sea by selected organochlorines compounds has been assessed through the analysis of surficial sediments taken from throughout the region (Filman et al., 2002). Concentrations of HCHs at sites influenced by the Danube delta are among the highest recorded on a global basis (up to 40 $ng.g^{-1}$ dw). The ratio between the α– and γ–isomers was relatively low indicating contamination through the use of lindane. Concentrations of DDTs and PCBs were not especially high in comparison to levels reported from throughout the world (See Table 3-25 and 3-27).

The highest concentrations of hydrocarbons were detected in the Danube, Dnieper, and Dniester River Estuaries and other point sources of pollution located offshore Romania and Bulgaria where oil production and refining is carried out (i.e., Constantza, Varna). The concentrations of PAHs in the SPM of the Danube, Dnieper and Dniester Estuaries (ca. 1 600 $pg.l^{-1}$) are higher than in other estuaries of the western Mediterranean (ca. 560 $pg.l^{-1}$). Concentrations of hydrocarbons decreased with increasing distance from the coast, but relatively high concentrations were found at the open stations where the particulate organic carbon (POC) is higher. The western Black Sea can be considered as a medium PAH contaminated area (compare Table 3-34). The spatial distribution of fossil PAHs in the SPM is controlled by salinity, POC and PON (particulate organic nitrogen). The highest PAHs concentrations in dissolved phase (DP) were found at the continental slope, followed by offshore Constantza (Table 10.3-3). The UCM concentrations of aliphatic hydrocarbons in the SPM maximised at the stations collected in river estuaries (Table 3-35) and point sources of oil pollution. In the DP, the concentration of the UCM in the slope was higher than in the river estuaries.

PAHs distribution characteristic of fossil fuel or uncombusted fossil fuel residues is predominant in the coastal stations. In the western Black Sea SPM, the higher contribution of the alkylated species denotes higher fossil inputs, but far from riverine inputs, pyrolytic PAHs predominate. The unresolved complex mixture (UCM) of aliphatic hydrocarbons is predominantly of a fossil common origin according to the hopane and stearane distribution.

The vertical profiles of PAHs and UCMs show maximum in surficial waters and two submaxima at the biomass and redox cline where the composition of PAHs is modified attributable to bacterial processes, there is an enrichment referred to POC. The large portion of anoxic conditions in the water column leads to a better preservation of hydrocarbons through the water column than in well-oxygenated seas allowing a large portion of PAHs to reach the sediments.

3.1.5.2.5 Caspian Sea

Two main sources of pollution of the Caspian Sea are the Volga River and drilling works of the oil companies (Lebedev et al., 2000). Caspian Sea has been considered to be seriously polluted. The Volga River brings into the Sea more than 23 km^3 of wastewater annually. However there were no reliable studies of its contamination with organic compounds so far. According to the data published in the 80th in local press petroleum hydrocarbons, phenols, surfactants and organochlorine pesticides were the priority pollutants for the Caspian Sea. High level of pollution at that time brought to histological problems, e.g. stratification of the tissues of muscles of sturgeons and weakening of the outer shell of caviar. The treat of disappearance of sturgeons became real. Since almost all resources of sturgeon species of the world are concentrated in the Caspian Sea and taking into account that besides their extreme biological value sturgeons are the source of the famous all over the world dainties the problem actively discussed in the media and various plans were proposed for the

improvement of the situation. However political changes at the beginning of the 90th, led to the diminished attention to the problem of the Sea. There were no new data on the pollution of the Sea in the period between 1992-1997. The data published in 1998 and 1999 although covering few parameters demonstrated the decreased level of the Sea contamination.

CEP, with assistance of its theme (ERACL), which is situated in Tehran, I.R. Iran conducted a series of sea cruises in the Caspian Sea (At Sea Training Programme "ASTP") with participation of all littoral states experts. Fullfillment of the gaps in contaminant levels with emphasize on the POPs in Caspian Sea for Trans-boundary Diagnostic Analysis was one of the major objectives of this programme. The ASTP investigation mainly focused on sediment of coastal area to maximum depth of 100 meters and covered the coastal area of the region. About 100 sediment samples were obtained during this investigation since October 2001 and a wide range of contaminant analysis including PAHs, PCBs, Chlorinated pesticides were made. Except for the Russian sector, the analyses of all samples have been performed in IAEA/MESL and the analysis the samples from the shallowest Northeastern part of the Caspian Sea are underway.

The levels and spatial distribution of PCDDs/Fs in 17 surface sediments sampled from 13 stations simultaneously in Volga Basin namely, north Caspian Sea region – Volga estuary, were determined (Semenov et al., 2002). This region extends approximately to the sea for 50 km beyond shoreline. Sea and river waters mixing occur at the shoal-water of the north Caspian Sea region.

Performed research disclosed contamination of all 17 samples by 2,3,7,8-TCDD (see Table 3-28), concentrations of the rest of the toxic isomers are insignificant. Replicated analysis in different laboratory confirmed these results. The reason for such abnormal results was related perhaps to the peculiarities of the sampling sites. The region under investigation presents vast aqueous area where water-salline compositions of Caspian Sea is formed, and represents one of the major factors of the water, sediments and shoreline pollution. Among natural processes which take place in Volga estuary and north of Caspian Sea the most important position occupy the processes connected with the dynamics of water flow, which form bottom topography, determine alluvium phenomenon and migration and transformation of the contaminants. In Volga estuary and north of Caspian Sea integration of the natural and anthropogenic changes in the water outlet and water quality of the whole Volga basin take place. In the region which was investigated, the mixing of the salt and fresh waters proceeds. This zone of shallow water is characterized by good warm-up and ventilation of the water layer, as well as by accelerated metabolic processing of organic matter.

PCBs, OCPs and organotin compounds were determined in blubber and liver of Caspian seals (*Phoca caspica*) found stranded on the coast of the Caspian Sea an outbreak of canine distemper virus (CDV) in 2000 (Kajiwara et al., 2002). Caspian seals, a top predator in the ecosystem, are endemic species in the Caspian Sea and are considered as one of the vulnerable species by IUCN. During the spring of 2000, a mass mortality of Caspian seals took place (Kennedy et al., 2000; Stone, 2000). High mortality was reported throughout the Caspian, with many thousands of dead seals reported throughout the spring and summer. The primary cause of the mortality in 2000 was infection by CDV as was demonstrated by Kennedy et al. (2000). Organochlorine contaminants can induce higher susceptibility to viral diseases, as was demonstrated in mammals (e.g. De Swart et al., 1996).

Among organochlorines analyzed, DDTs were the most dominant contaminants (see Table 3-41). Caspian seals collected in 2000 during the epizootic had higher concentrations of organochlorines than healthy individuals sampled in 1998. However, the blubber layer was generally thinner in the seals collected in 2000 than those in the previous surveys. Although compositions of organochlorine pesticides in seals suggested that the contamination status in the Caspian Sea is improving, the levels found in Caspian seals in 2000 were comparable to those in other marine mammals that have suffered from epizootics. This implies that the present status of contamination found in Caspian seals poses a risk of immunosuppression.

3.1.5.2.6 References

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Table 3-25: Sea levels of DDTs

Area	Sampling sites	Duration	Frequency of measurements	Typical range [ng.l^{-1}; ng.g^{-1}]	Comments	References
North Sea						
UK, Essex Coast	8			Maximum 2.3-21.1 (Median < 0.1-10.4)	Salt marsh	Scrimshaw and Lester (1996)
Baltic Sea						
Western Baltic Sea	19	1993		< 0.01 (sandy) – 9 000 (muddy)	0-3 cm	Dannenberger (1996)
Black Sea						
Danube				< 0.04-41		Equipe Cousteau (1993)
Ukraine	10	1995	Cruise of the research vessel „V. Parshin“	35-65 0.06-0.6 9.2-43	Odessa Coastline Danube costline	Fillmann et al. (2002)
Russia	5			3.3-12	Sochi	
Turkey	10			0.2-7.2	Bosphorus	
Romania	15			0.6-72	Coastline	
Caspian Sea						
Russian and Iranian part	19 - 32	2000 - 2001	2 campaigns	DDT: 13 – 7 400 DDD: 6 – 3 400 DDE: 9 – 1 700	Sediments Also o,p´- substituted isomers and DDMU were measured	Caspian Report
Russian part		2000 1998	episodicaly	6.3-470 µg.g^{-1} lw 0.78-43 µg.g^{-1} lw	Seals – infected by canine distemper virus (CDV) in 2000 Seals – healthy - 1998	Kajiwara et al. (2000)

Table 3-26: Sea levels of HCB [ng.g^{-1}]

Area	Sampling sites	Duration	Frequency of measurements	Typical range [ng.l^{-1}; ng.g^{-1}]	Comments	References
Caspian Sea						
Russian and Iranian part	19 - 32	2000 - 2001	2 campaigns	3-600	Sediments	Caspian Report
Russian part		2000 1998	episodicaly	0.0038-0.16 µg.g^{-1} lw 0.0019-0.018 µg.g^{-1} lw	Seals – infected by canine distemper virus (CDV) in 2000 Seals – healthy individuals - 1998	Kajiwara et al. (2000)

Table 3.27: Sea levels of PCBs [ng.g^{-1}]

Area	Sampling sites	Duration	Frequency of measurements	Typical range [ng.l^{-1}; ng.g^{-1}]	Comments	References
North Sea						
UK, Essex Coast	8			2-116 (Median 2-19)	Salt marsh	Scrimshaw and Lester (1996)
Baltic Sea						

Western Baltic Sea	19	1993		< 0.01-2 600	0-3 cm	Dannenberger (1996)
Southern Baltic Sea – Odra	19	1998		2.4-986 pg.l^{-1} 2-18 ng.g^{-1}	9 sediment cores 10 suspended matter 28 congeners	Blanz et al. (1999)
Black Sea						
Danube				0.02-85		Equipe Cousteau (1993)
Ukraine	10	1995	Cruise of the research vessel „V. Parshin“	5.7-6.8 ND-0.4 1.4-2.7	Odessa Coastline Danube costline	Fillmann et al. (2002)
Russia	5			0.3-4.7	Sochi	
Turkey	10			0.4-4.7	Bosphorus	
Romania	15			0.1-24	Coastline	
Caspian Sea						
Russian and Iranian part	19 - 32	2000 - 2001	2 campaigns	20 - 1 365 3 - 404	Sediments (7 indicators) (77 + 126 + 169)	Caspian Report
Russian part		2000 1998	episodicaly	2.4-320 μg.g^{-1} lw 0.95-28 μg.g^{-1} lw	Seals – infected by canine distemper virus (CDV) in 2000 Seals – healthy individuals - 1998	Kajiwara et al. (2000)

Table 3-28: Sea levels of PCDDs/Fs

Area	Sampling sites	Duration	Frequency of measurements	Typical range [pg.g^{-1}]	Comments	References
North Sea						
UK Estuaries	8	1993?	One campaign	PCDDs: 10 - 750 PCDFs: 23 - 390 TEQ: 0.58 - 15	Coastal surface sediments	Tyler et al. (1994)
				PCDDs: 287 – 4 670 PCDFs: 100 – 1 540 TEQ: 8 - 60	Mouths of rivers	
Caspian Sea						
Russian and Iranian part	19	2000 - 2001	2 campaigns	TEQ: 2 - 45	Sediments – only in Russian part	Caspian Report
Russia	13			0.42-27.37 (TCDD)	17 surface sediments sampled from 13 stations simultaneously in Volga Basin namely, north Caspian Sea region – Volga estuary	Semenov et al. (2002)

Table 3-29: Sea levels of HCHs

Area	Sampling sites	Duration	Frequency of measurements	Typical range [pg.l^{-1}; pg.g^{-1}]	Comments	References
North Sea						
English Channel	33 (1989) - 13 (1993)	1989 - 1993	annually	α – 100 – 700 γ – 100 – 4 000	water	Law and Allchin (1994)
Baltic Sea						
Western Baltic Sea Mecklenburg-West Pomerania		1993 - 1994		10 – 2 900	0-2 cm surface sediments 0-45 cm sediment cores	Dannenberger and Lerz (1996)
Black Sea						
Danube				0.03-6.4		Equipe Cousteau (1993)
Ukraine	10	1995	Cruise of the research vessel „V. Parshin“	1.3-2.3 0.02-0.3 1.3-2	Odessa Coastline Danube costline	Fillmann et al. (2002)
Russia	5			0.3-0.8	Sochi	
Turkey	10			0.08-1.1	Bosphorus	
Romania	15			0.2-40	Coastline	

Caspian Sea						
Russian and Iranian part	19 - 32	2000 - 2001	2 campaigns	α – < 1.5 – 1 100 β – 24 – 1 600 γ – 0.1 – 4.0 δ – < 2 - 520	Sediments	Caspian Report
Russian part		2000 1998	episodicaly	0.11-2.5 μg.g^{-1} lw 0.69-9.9 μg.g^{-1} lw	Seals – infected by canine distemper virus (CDV) in 2000 Seals – healthy individuals - 1998	Kajiwara et al. (2000)

Table 3-29: Sea levels of PAHs

Area	Sampling sites	Duration	Frequency of measurements	Typical range [pg.l^{-1}; ng.g^{-1}]	Comments	References
North Sea						
Northern Irish Sea-loughs	2	2000		83-2 300 95-184	30 sediments 8 mussels	Guinan et al. (2001)
Baltic Sea						
Belt Sea Arkona Basin	104 37 15	1992-4		3.849-14 095 721-1 871 (mean 1 179.5) – muddy sediments 9.5-973.1 (223.3) – sandy sediments	Surface water (2-15 m) Bottom water (above the halocline) Surface microlayer (0-0.2 cm) 15 PAHs (USEPA without ACN	Witt (1995)
Black Sea						
N-W part	28 (SPM) 11 (DP)	1998 (?)	One campaign	132 – 880 (394) – SPM 952 - DP	Shelf and slope – suspended particular matter (SPM) and dissolved phase (DP)	Maldonado
				477 – 5 612 (1 596) – SPM 104 – 5 521 (1 609) - DP	Danube Estuary Dnieper and Dniester Estuaries	
				106 – 1 036 (571) – SPM 108 - DP	Open sea	
Caspian Sea						
Russian and Iranian part	19 - 32	2000 - 2001	2 campaigns	84 – 3 000	Sediments (16 US EPA + dibenzothiophene + C_1 – C_3 naphthalenes + C_1 –C_4 dibenzothiophenes + C_1 – C_4 phenanthrenes + retene + C_1 pyrenes + C_1 –C_2 chrysenes + perylene + benzo(a)pyrene)	Caspian Report

Table 3-40: Caspian Sea – the rest

Pollutant [pg.g^{-1}]	Phase 1	Phase 2	Russian sector
Cis-chlordan	< 5	< 1.5 – 17	< 1 – 204
Trans-chlordan	20 – 130	< 2	< 1
Trans-nonachlor	< 2 – 120	< 0.6 – 12	< 1 – 351
Heptachlor	< 2 – 10	< 0.6 – 16	< 1 – 88
Aldrin	< 2 – 77	< 0.6 – 65	< 1 – 11
Dieldrin	5 – 51	< 0.6 – 32	< 1 – 349
Endrin	< 6 – 85	< 4 – 85	< 1
Heptachlorepoxide	< 1 – 45	9 – 37	< 1 – 128
Methoxychlor	< 3 – 330	1.5 – 150	< 1 – 1 476
α-Endosulfan	< 1 – 16	< 0.4 – 14	< 1 – 189
γ-Endosulfan	< 1 – 22	< 0.5 – 13	< 1 – 55
Endosulfan sulphate	< 2 - 27	1.5 – 170	NA

Table 3-41: The levels of OCPs and PCBs in Caspian seals [μg.g^{-1} lw]

Campaign	Number of specimens	PCBs	DDTs	HCHs	CHLs	HCB	Butyltin [ng.g]
1998	23	0.95-28	0.78-43	0.11-2.5	0,10-1.3	0.0019-0.018	
2000	13	2.4-320	6.3-470	0.69-9.9	0,21-14	0.0038-0.16	0.49-17

3.1.5.3 Freshwaters – rivers and lakes

3.1.5.3.1 Introduction

On of the most important environmental goals today is to decrease eutrophication (Söderström et al., 2000). However, it has been suggested that reduced eutrophication causes an increased availability and exposure of pollutants to biota in aquatic environments and there is a need for more knowledge about the processes involved. The biomass dilution hypothesis proposes that an increased biomass will contribute to a dilution of pollutants and thus decreased exposure. There are several studies demonstrating that increased biological productivity in water lowers the concentrations of persistent organic pollutants in aquatic biota. In a study comparing settling particles in a eutrophic and oligotrophic, lower concentrations, but higher settling fluxes of particle bound PCBs were found in the eutrophic lake. The higher concentration of PCBs on particles in the oligotrophic lake was related to high biomass of diatoms with high lipid content. Eutrophication results in lower volatilization compared to the oligotrophic lake. The air-water exchange increased with increasing phytoplankton biomass and thus with phytoplankton growth rate. The gas phase supports the concentrations of POPs such as PCBs, in aquatic environments.

Lot of regional rivers, have been extended meadows which are flooded at high water (Elbe, Rhine, Oder, Danube). River sediment is brought into the wetlands by the flooding, causing pollution of these areas with compounds that are transported by the river. POPs and heavy metals are typical types of pollutants that are strongly represented in the wetlands. Due to very high density the location of industrial and agricultural sources of pollution near to the main regional rivers, the most of regional river sediments is still highly contaminated or contaminated with various pollutants. Since at high flood sediment is remobilised from the river bed and transport downstream, mechanisms of self-cleaning will remove most of the contaminated material from the river bed in the future. In contrast to this, material that once deposited in the meadow will not be removed at high flood, because in summer vegetation stabilises the young sediments. The soil profiles from these rivers floodplains therefore show the history of past sediment pollution. Additionally, atmospheric inputs might contribute to their contamination.

High mountain lakes are some of the remote areas under potential stress by PTS (Vilanova et al., 2002). These lakes can be defined as those situated above the timberline receiving their waters through atmospheric fallout. Their ecological and environmental value is high because they have often support unique species of plant and animal communities. They are often the headwater catchments of water supplies and excellent sensors of environmental change for entire mountain environments.

Remote mountain lakes are excellent indicators of pollutant deposition and its effects as they are not influenced by direct forms of disturbance such as land-use change and wastewater point. Furthermore, geological and climatic factors combined with shallow soils and high relief results in their being more sensitive and vulnerable to such pollutants. The sediments records of mountain lakes are known to provide reliable archives of atmospherically deposited pollutants (Rose et al., 1999) while the ability to produce sediment core chronologies using radionuclides (e.g., ^{210}Pb,^{137}Cs, ^{241}Am) allows the date of depositional events and the rate of any recorded change to be calculated.

3.1.5.3.2 River Elbe

Monitoring the actual concentrations of chemicals in Germany was a part of activities of German Environmental Speciman Bank (ESB). This approach is very useful for the retrospective monitoring of chemicals in the future. The bases of ESB are representative bioindicators of systematically collected biological systems and environmental samples. Major ecosystems and habitat types of the Federal Republic of Germany were integrated into the routine sampling programme. This sampling is performed routinely in River Elbe and River Rhine as limnic ecosystems.

Investigations of sediments and fish (bream) along the river Elbe have shown that the eastern sampling sites (Prossen, Dresden) have been heavily contaminated by HCB, DDT metabolites, PCBs and octachlorostyrene (OCS). This observation is probably a result of the considerable pollution of the River Elbe by industrialized areas (e.g. Pardubice, Neratovice, Usti) in the CR. Furthermore, sediments at the station Dresden are highly contaminated because they were strongly subjected to effluents of a pulp mill and chemical industries until 1991. A 30 % decrease of the POPs concentrations in bream muscle tissue was found between station Dresden and Vockerode, further downstream, the total POPs burden remained nearly constant. Elevated levels of HCH isomers in bream muscles and livers were observed downstream between Aken and Heinrichsberg due to the influxes of the river Mulde and Saale as well as discharges from pesticide plants located in Magdeburg.

The comparison of the determined compounds pattern in bream livers exhibits significant distinctions between the different ecosystems. DDT metabolites and PCBs contributed to one third, respectively, to the total burden of bream livers from the limnic ecosystem Elbe. PCBs were the major organochlorine contaminants (70 %) in breams of a typical industrialized area (Saarland) in contrast to agricultural areas of East-Germany, where DDT metabolites were the dominant pollutants (80 %). This is caused by the continued application of DDT in former GDR after DDT has been banned in Western Europe.

Twenty years of practical experience in environmental speciman banking in Germany can demonstrate that the concept of long-term storage of biological specimens and environmental samples for retrospective analysis has contributed to the traditional environmental pollution monitoring as an important complement. The ESB can serve as a valuable resource for the assessment of long-term trends of pollutants affecting human and environmental health, in particular for those pollutants that have been unnoticed.

The results fullfill the proposed goals of the ESB in far as political decisions about the emission or other reglementations on pollutants can confirmed by their decrease in the environment (e.g. introduction of unleaded fuel, ban on sea burning of hazardous waste). On the other hand illegal applications of chemicals could have been identified e.g. DDT applications in former GDR.

The biomonitoring was also used in Germany for determination of others pesticides from PTS list such as for example dieldrin which was determined in eels from North Bavarian rivers (LAU Erlangen) or from Hamburg waters in 1995/96 (Götz et al., 1998); HCB residue in terrestrial and mainly aquatic ecosystems and matrices as well as for lipid-containing foods.

On the other hand, similarly as in other countries of Region III, there are only a few data for toxaphene residues in Germany for monitoring purposes. Toxaphene congeners were determined in eels from river Main in Lower Frankonia 1995 (LUA Erlangen) and in eels from the river Elbe as well as in eels from Schwarze Elster, Mulde und Saale (1998/99) (ARGE ELBE).

The same set of data as it was in the case of DDT or HCB are in Germany available also for PCBs (measurements of PCB congeners in unfiltrated surface water of the rivers Elbe, Schwarze Elster and Mulde, in sedimented suspended matter from the rivers Elbe, Schwarze Elster, Mulde and Saale, Rhine and Berlin river system; in breams, eels from these sites etc. (Heinisch and Kettrup, 2001; ARGE ELBE and LAU Halle/Saale).

As far as HCHs, especially in the region of production devices as well as landfills the ballast isomers are to be found mostly in greater amounts, whereas in the regions of application the percentage of γ-HCH predominates. These relations are demonstrated by the distribution in Berlin waters. The water of the Berlin river system is especially suitable for such a demonstration, because e.g. the Teltowkanal (TK) is strongly influenced by an enterprise, which produced lindane upto 1989. Other surface waters, e.g. the Tegeler See and the Niederneuendorfer See are completely free of such influences and show exclusively HCH loads due to applications (allotment gardens, agriculture).

A lot of very useful results from German ESB were published during last years (Marth et al., 1999). Results of ten years of experience in the determination of chlorinated hydrocarbons in herring gull eggs collected in the North and Baltic Seas, were published by Marth et al. (2000). POPs concentrations in bream livers from the River Elbe between 1993 – 1997 were also presented (Marth et al., 2001).

Differences in contamination levels of various PTS may be explained by the considerable pollution of the River Elbe by industrialized areas and leaching dumps of the formed CSFR as well as industrial activities in the area of Dresden, Coswig and Meissen. Concentrations of DDT-metabolites are still the dominant pollutants in former GDR. In samples collected in FGR the declining tendency is less obvious showing only small decreases of similar levels when compared to corresponding data from at the beginning of the study.

One from the first papers, which summarized the determination of PCBs and organochlorine pesticides in water and sediments in former Czechoslovakia, was published by Nondek and Frolikova (1991). During 1987-90, water and sediment samples taken from more than 200 localities (streams and reservoirs) were analysed. The purpose of this activity was not only to localize point sources, but also estimate the "athropogenic" background. Three different localities have been examined in detail: Labe (Elbe) River, Jizera River and three lakes in remote part of Sumava Mountains. From the results was evident that the Labe River flows through several heavily polluted regions receiving industrial and municipal wastewaters, which were mostly untreated in this time. Several chemical factories at Pardubice, Kolin, Neratovice, Steti, Lovosice and Ústi discharged their waste waters containing besides chlorinated solvents, benzene and alkylbenzene, chlorobenzenes and many other organic compounds, into the river. The contamination of bottom sediments with PCBs was therefore not surprising. From this time, the determination of water and sediment quality is determined as a part of an international programme "Project Elbe". The Jizera River is one of the main tributaries of the Labe River. The main sources of PCBs were Skoda car factory at Mlada Boleslav and an industrial dump site upstream of Mlada Boleslav. The contamination of Sumava Lakes was described as a result of atmospheric transport to non-industrialised areas. The lakes are located in South-West Bohemia, a long distance from industrial sources, in a natural park at an altitude of 1 028 - 1 096 m a.s.l.

The concentrations of PCBs were described as Delor 103 and Delor 106 and they are summarised together with HCB, lindan and DDE for all three sampling sites in the Table 3-48

Table 3-48: Concentrations of PCBs and other OCCs in bottom sediments from rivers Labe and Jizera and from Sumava Lakes, 1989 [$ng.g^{-1}$]

Sampling site (numbers of site)	HCB	γ-HCH	DDE	PCBs (low as Delor 103)	PCBs (high as Delor 106)
Elbe River (15), 1989	< 1 - 440	ND	< 5 - 205	< 20 - 1 800	50 - 1 900
Jizera River (10), 1990					15 - 450
Sumava Lakes (3), 1986	0.8 - 2.0	0.5 - 1.8	1.0 - 1.6		15 - 40
Hincovo Pleso (High Tatras, Slovakia)	0.9	2.4	1.2		15

3.1.5.3.3 River Rhine

The River Rhine is polluted by many different types of industrial and municipal waste water as well as diffusive inputs from superficial runoff. Some tributaries like Aare, Neckar, Main, Mosel and Ruhr add further quantities of inorganic and organic compounds to the river, so that the highest concentrations were regularly found in the lower Rhine (Brauch, 1993).

In about 30 000 t of pesticides were applied all over West Germany. In Switzerland, France and the Netherlands additional tons of pesticides were used for agriculture and other purposes. A large amount of pesticides were produced in the Rhine basis area, because many chemical plants are located along the river Rhine. In the past there have been number of isolated incidents of organic chemical pollution. A vivid example of this was a spill of endosulfan in 1969 and the Sandoz storehouse fire in 1986, which had severe ecological consequences.

Pesticide, produced within the Rhine basin area, may enter the river by discharges of wastewater from production sites of by accidents (point pollution) and after agricultural application by drainage and infiltration, superficial runoff and precipitation (non-point pollution). Both types of pollution were important for river Rhine quality and led to significantly higher concentrations from time to time.

Little is known about the pesticide pollution in the river Rhine before 1985. The concentrations were relatively low (regularly below 0.1 $\mu g.l^{-1}$ per individual pesticide) and did not provoke special attention. On the other hand these chlorinated substances are strongly absorbed on suspended soils and sediments, so that higher concentrations could not be expected in river Rhine water and blank filtrated water. Many results of pesticide pollution in the river Rhine have been obtained for that period.

Compared to the data of 1986, pesticide concentrations in the river Rhine were much lower in 1987 and 1988. After the Sandoz "shock" (Nov. 1986) the input of highly polluted waste waters effluents from pesticide production sites into the river Rhine was stopped or strongly reduced. In 1986 significantly higher atrazine concentrations could be found in March and November (accidental input by Giby-Geigy). After closing the atrazine production near Basel, higher amounts were observed only in springtime for 1987 and 1988, when atrazine was used for agriculture purposes. The input of metazachlor into the river Rhine was mainly due to wastewater effluents of BASF AG (point pollution).

It may be concluded that for the period 1986 to 1988 point pollution of individual pesticides from wastewater effluents was the dominant pathway for entering the river. Within that period and afterwards a lot of measures were taken to reduce pesticide discharges by wastewater treatment and/or closing production sites in the Rhine basin area.

Superficial runoff was now the dominant entering pathway for pesticides into the river Rhine. Seasonal fluctuations of atrazine could still be observed each year in June and July. In contrast to earlier results the peak concentrations were quite low. Reasons may be the decrease of atrazine use in agriculture and the lack of point pollution from production sites. This led generally to remarkable lower concentrations in the river Rhine.

3.1.5.3.4 River Danube

The River Danube is one from the most important European rivers. Its riparian area covers 987 300 km^2. The Danube basin is an important agricultural area for the riparian countries. In all of them, the agricultural production strongly relies on the use of pesticides.

During the period of 1995 - 1997, the "Danube Pesticide Regional Study", a project supported by PHARE, was completed (Bratanova et al., 1998). The main objective of the project was to evaluate the risks of pesticide application to humans and the aquatic life in the region and to recommend the adequate legal, management and policy measures to the respective governments. One of the tasks of the project was gathering all available information on the occurrence of pesticide residues in the water

of the Danube ant its tributaries. The data on the occurrence of pesticides in the water were collected from 10 of the Danube riparian countries: Germany, Austria, Slovakia, Hungary, Slovenia, Croatia, Bulgaria, Romania, Moldova and Ukraine. The data from period of 1990 - 1995 were included in the study.

The cumulative number of the analysed pesticides was 77. Residues of 39 of them have been found in the waters. The most positive findings of pesticides (i.e. those over the detection limits of the respective methods) in the Danube water relate to organochlorine pesticides (HCHs, HCB and DDT) and atrazine and its degradation product desethylatrazine. Remarkably high levels and high proportion of positive samples have been found for some chlorophenols.

DDT and lindane data from Romania exceeded by one to two orders of magnitude those from the other countries. Some findings can be episodically high, for example mean concentration of DDT in Danube water from Slovakia was 0.047 $\mu g.l^{-1}$, but findings up to 0.26 $\mu g.l^{-1}$ were reported (Veningerova et al., 1996). It is also interest that lindane and other HCH isomers were detected in two of the nine examined Danube tributaries, both of them on the Romanian teritory (lindane - river Olt, 0.15 $\mu g.l^{-1}$ and river Arges 0.25 $\mu g.l^{-1}$ (Bujis et al., 1992). This would indicate occasional unauthorized uses of organochlorine pesticides in some parts of the region and also suggests Romania as one of the hottest spots for environmental contamination with chlorinated pesticides in the Danube River basin. In other Danube basin countries, the levels of DDT and lindane in the Danube and tributaries were at the order of 10^{-2} $\mu g.l^{-1}$.

Residues of HCB were detected quite frequently in the Danube River (35 % positive samples). Most of the positive findings come from the Slovakian and Bulgarian part of the Danube. As for the changes in the levels of contamination with chlorinated pesticides observed in the last decades, no comprehensive data are available on the whole of the Danube. However, some idea can be obtained on the basis of the results from Bulgaria and Slovakia. Data indicate that the levels of DDT in Bulgarian section of the Danube dropped considerably between the seventies and the nineties i.e. from 0.098 $\mu g.l^{-1}$ in the seventies to below 0.001 $\mu g.l^{-1}$ in the nineties. The levels of lindane in the Bulgarian part did not show any pronounced decreasing trends. The data from the Slovakian part of the Danube indicate a drop off in DDT, γ- and β-HCH concentrations by about 50 % between early seventies and late eighties.

A lot of measurements of PTS were done in all Danube Basin. For example in upper part, the Danube flows through Linz, the provincial capital of Upper Austria, which constitutes an industrial conurbation (steel works, chemical industry) with more than 200 000 inhabitants (Chovanec et al., 1994). The wastewater of Linz and the surrounding regions is collected in the wastewater treatment plant Asten (about 85 000 population equivalents). The water quality of the Traun is primarily influenced by pulp and paper mill effluents as well as dyework effluents (see Tables 3-42 - 3-47).

Sediments and their contamination are also very important and long-term part of Project TOCOEN activities. Sediment samples were collected in the surroundings of industrial sources and in the parts of river and its tributaries where are located important towns. The first broader sampling network in Morava river catchment area was realised in 1992 as a part of European project Chemical Time Bombs. River Morava is one from the most important tributaries of river Danube. This river and some other tributaries in Moravia and Slovakia were included to the first phase of this project (Heinisch et al., 1997; Holoubek, 1993; Holoubek et al., 1994, 1998; Hilscherova et al., 2001). The contamination of Danube River sediments was lower in the first part of 90´s than the contamination of sediments from river Elbe in Bohemia (Nondek and Frolíková, 1991).

A flood disaster took place in all Moravian part of the Czech Republic in July 1997. Agricultural areas and plenty of industrial and municipal landfills located along the River Morava and upstream of the Odra catchment area were flooded. Due to that many types of toxic substances including of PTS could

have entered the surrounding environment. Also sediments from both rivers and its tributaries beds were washed out and re-deposited over flooded areas releasing different toxic substances previously accumulated.

The contents of PTS in rivers of the Czech Republic is regularly monitored last 7 years similarly as in other countries in Danube river catchment area. For example, within the framework of the national monitoring program for water quality more than 3 000 surface water samples taken from Slovak rivers and lakes were analyzed for PCBs in 1989-1997 (Kocan et al. 1999). Surface water and sediment samples were taken from an open effluent canal of the former Slovak PCB manufacturer, the Laborec River (the canal is emptying into it), Zemplinska Sirava Lake (a large water reservoir serving for flood-control, irrigation and recreational purposes supplied from the Laborec and several Vihorlat mountain streams), Ondava River and Domasa Lake (the latter two are situated in the control area of the Stropkov District). Based on those findings, one can estimate that at least tonnes of PCBs are still adsorbed in the sediments of the effluent canal, Zemplinska Sirava and Laborec.

Also quality of drinking waters as far as the contents of PTS is monitored in practically all countries of the region mainly based on EC Directives or WHO limits.

Danube Delta is the largest wetland from Europe (580 000 ha), situated in the southeast of Romania and northwest of the Black Sea (Covaci et al., 2002). The Danube River flows through many European countries, receiving discharges of agricultural, industrial, and urban effluent. At its mouth is the vast wetland system that constitutes the Danube Delta. The delta wetlands perform many important functions contributing to the economical and physical health of the area, not least of which is a part of a filtering system for pollutants. Data about the current contamination status of the lower Danube River and Danube Delta are very scarce. For organic pollutants, no systematic measurements are done in water and fish and thus, no data are available in the literature. Sediments collected in 1994 from the Danube Delta (Winkels et al., 1998) did not contain measurable concentrations of PCBs (< 5 $ng.g^{-1}$). Unfortunately, no measurements of pesticides, the main organochlorine contaminants in Romania (Covaci et al., 2001), were done at that time.

In 2000, PCBs and OCPs were measured in sediments collected at the mouth of the Danube Delta (Fillmann et al., 2002) and it was found that the high concentrations associated with the Danube indicate that the river is a major source of contamination to the Black Sea. In another study, PCBs and OCPs were measured in bird´s eggs collected in 1997 from the Danube Delta (Aurigi et al., 2000). It was found that DDTs are the main contaminants in all samples and that PCBs concentrations are not as low as it might have been thought. The aim of recent study (Covaci et al., 2002) was to evaluate the occurrence of important organic contaminants (PCBs, DDTs, HCHs, HCB, PBDEs) in biota (invertebrates, different species of fish and cormorant tissues) collected from the Danube Delta.

In comparing samples colleted in 1982 and 1997, the contaminant levels were lower in samples of 1997 than those detected during the earlier survey. Such observation was expected since many chlorinated hydrocarbons have been banned by many European and other countries in the past 10 years. Reduces use has, therefore, led to a sharp decrease in the production of organochorines and their subsequent reduction in the environment.

3.1.5.3.5 River Odra

The River Odra is a one of the biggest rivers flowing to the Baltic Sea with the river basin of 118,861 km^2 (Protasowicki et al., 1999). Being the border river, it contains the contamination from Poland, Czech, and Germany e.g. the municipal and industrial wastes from 20 Polish and German cities may be found there. Because the river basin covers also a lot of the agricultural area, the subterranean waters feed it with noticeable amounts of organic matter, harmful and toxic substances. Therefore the Odra waters on the length of 741.9 km are below the 3rd class of purity, according to Polish standards, due to the amount of chemical, physical, and biological contamination.

The sediments in the lower Odra are of various structures. In the port basins of Szczecin as well as in some sections of the river and in the central part of the Szczecin Lagoon typical muddy sediments with rich organic mater exists which amounts to 15 - 20% or more in dry matter. However, in the other parts of the Szczecin Laggon and in the port approach in Swinoujscie some muddy-sandy and sandy sediments exist with a very low amount of organic matter (up to 5%) (Protasowicki et al., 1999).

The Odra River is the main sink of wastewaters from zones of provinces adjacent to the Odra bed and also from provinces of the Odra River catchment area (Wolska et al., 1999). The following main factors may have effect on the quality of water along Odra River:

- Point sources of pollution, wastewater from industry and from urbanised areas (not sufficiently cleaned municipal and industrial wastewater),
- Industrial wastes deposited in landfills located along the Odra River and its basin area – composition of pollutants depends on production profile,
- Municipal wastes with different chemical and biological composition,
- Diffuse sources related to farming and agricultural use of wastewater,
- Wastes from rural areas discharged directly to groundwater, amount and composition of these wastes are difficult to estimate.

Majority of provinces located on catchment area of the upper and middle Odra is characterised by relatively high urbanisation and industrialisation. Specifics of this region are that industry is concentrated in urban centres. Such localisation of industry makes wastewater management easier, and from analytical point of view, simplifies identification of pollutant sources narrowing the spectrum of compounds, which could be looked for in the studied samples.

No systematic investigations of sediments and waters on the pollution level by regulated organic compounds, i.e., polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, volatile organic compounds (VOCs), have been conducted in that region. However, the data concerning the content of these compounds in the Baltic Sea, which can be considerably contaminated by the Odra River, have been recently published. A flood disaster took place in south of Poland in July 1997 similarly as other countries of Central Europe.

These investigations were carried out within the frame of International Odra Project (IOP). Over ninety surface sediment samples in the Odra River estuarine system - from the Oderhaff, the Pomeranian Bight, the Peenestrom, the Greifswald Bodden - and the Arkona Basin between 1994 and 1996 were collected. The contents of polychlorinated dibenzo-p-dioxins, dibenzofurans (PCDDs/Fs) and biphenyls (PCBs), and DDT including their metabolites were determined (Dannenberger and Lerz, 1999). The contents of all investigated organochlorines in the sediments of the western part of Oderhaff (Kleines Haff) were only slightly higher and more homogenously distributed compared to the values of the Pomeranian Bight and the Greifswald Bodden (see Tables 3-42 - 3-47). The distribution and fate of polycyclic aromatic hydrocarbons (PAHs) were investigated in surface sediments and fluffy layer material of the internal and external coastal waters of the Odra river estuary (north-eastern Germany) (Witt and Trost, 1999). The area includes the Odra Lagoon (Oderhaff), the Greifswalder Bodden the Pomeranian Bight, and the Arkona Basin.

A seasonal variation in the PAH levels can be observed in the fluffy layer material from the Odra Lagoon and Pomeranian Bight, with highest concentrations in winter. The influence of the Odra flood could also be measured: The spreading of the Odra flood plume was accompanied by a strong increase in the PAH levels in the fluffy layer samples from the eastern Odra Lagoon and the Pomeranian Bight.

The flood of 1997, as a result of flooding many cites, towns and villages along the Odra and ground water logging of over 500 000 ha of arable land, caused the increase of the contamination of the Odra waters (Protasowicki et al., 1999). Many toxic chemical compounds found the way into the river from flooded rubbish dumps and industrial waste sites. The aim of the present studies was to compare the

heavy metals and polychlorinated hydrocarbons content in the surface sediments taken after the 1997 flood with their level recorded in the earlier studies conducted in area of the Eastern and the Western Odra.

The flood in the Odra River in 1997 has led considerable additional pollution of the Stettin lagoon and the Baltic Sea with contaminated suspended solids (Muller and Wessels, 1999). For some priority substances, the pollutant entries via suspended solids during the flood period are estimated to be approximately 1/3 of the usual annual load. Under the normal conditions of the years 1996 - 1997 the concentrations of organic pollutants in suspended solids at Frankfurt/Oder and at Schwedt were comparable. With one exception of PCBs, which were less remarkable during the floods. The PCBs concentration increases with the factor 3 at the Schwedt site in contrast to Frankfurt. Therefore, at least one PCB source must exist down river from Frankfurt. Since a dilution effect has been observed during the Odra flood regarding PCB, the Warthe River must be considered as a possible PCB source.

From the flood results some general consequences can be deduced with regard to further management measures in the river basin. In order to reduce the load of harmful substances in the Odra river basin it is necessary to improve wastewater purification technologies both in municipal and in industrial plants. Furthermore it would be useful to review and harmonise land uses and landscaping activities on riparian lands and floodplains in the whole river basin in order to limit of contamination under extreme situations. That includes agreements a cultivation plan about vegetation and uses as well as use and storage of harmful substances. Appropriate measures should be organised in action programme of the International commission for the Protection of the Odra River with regard to the adoption of flood protection and warning plan for extreme situations.

On the basis of mentioned above comparison, taking into consideration the glow losses, the following conclusions can be drawn:
- In contrast to earlier studies, in which the content of chloroorganic compounds were found to be comparable in the sediments of both Odra streams, the present studies show that the sediments of Western Odra are less polluted with these contaminants that the sediments of the Eastern Odra;
- In comparison with the 1995 state, the 1997 flood caused the concentration increase of PCBs levels in both arms of the Odra, changes of γ-HCH and Σ DDT content were inverted.

The following conclusions were drawn based on the study evaluating the pollution degree by organic compounds of post-flood sediments in upper and medium course of the Odra:
- The admissible levels of PCBs and pesticides were not exceeded in all examined sites. A slight increase of organochloride pesticides level was found in the region with extensive agriculture.
- The analysis of PAHs content in the investigated samples indicated that in numerous cases the regulated level was exceeded. The power plants, domestic heats, and intensive traffic may be mainly responsible for pollution of the examined sediments.

3.1.5.3.6 Other Baltic Sea rivers

Using the total water discharge to the Baltic Sea via rivers (475 $km^3.yr^{-1}$) and using the median concentrations of 0,7 $ng.l^{-1}$ PCBs; 0,006 $ng.l^{-1}$ of DDTs and 0,1 $ng.l^{-1}$ of HCHs, the river transport results in a yearly amount of 332 kg of PCBs, 2,8 kg of DDts and 47,5 kg of HCHs to the Baltic Sea (Agrell, et al., 1999, 2001). Above-mentioned numbers coincide with the results obtained by the author in the early (Roots, 1981, 1996), estimating that 130 – 570 kg of PCB`s are transported to the Baltic Sea by rivers.

By the data (Shushkin, 1997) main conclusion of the water samples represented 8 points along the Neva River (Russia) and its tributaries at the place of their influx were that, the highest concentration of PCBs is in the mouth of the Okhta River (tributory of the Neva River) – 1,5 $\mu g.l^{-1}$. The high PCB levels are also registered on the Chernaja River. By the data (Khudoley et al., 2001) HCB, HCH and

DDT were found at high concentrations in fish tissues from the River Neva and were dependent on the place od fishing, age and sex of collected fish.

The aim of the project ”PCB, metals and benthic fauna in some rivers draining oil-shale mining areas in the lake Peipsi catchment“ (supported by the Swedish Environmental Protection Agency) was to identify possible local sources of metals and PCB in the Rannapungerja and Mustajõgi catchments in North-East Estonia and the PCB situation in the Russian River Pljussa with similar conditions. The PCB content and the PCB pattern in Pljussa River just downstream Slantsõ clearly indicate leakage from some local source in Slantsõ.

River Daugava (Latvia) was studied by continuous measurements for one year (Nordic Environmental Research Programme, 1999). Water samples were taken continuously between 1991 and 1993 in Poland and in the autumn of 1993 in Sweden. Also the Institute of Meteorology and Water Management in Poland determined the contents of PCBs and OCPs in the Wistula and Odra rivers (Agrell et al., 2001).

The composition and loads of organochlorine pesticides (DDTs, HCB, HCHs, CHLs) and polychlorinated biphenyls (PCBs) transported with the Vistula River waters to the Gulf of Gdansk were measured in 1991-92 (Falandysz et al., 1998, 1999). HCHs were dominating persistent organochlorines quantified in the Vistula River water (Table 3-49). During 12 months period of the study, the total load of DDTs, HCB, HCHs, CHLs and PCBs transported with the Vistula River water to the Gulf of Gdansk was assessed on 11, 0.73, 1 400, 0.38 and 5.0 kg, respectively. There were large monthly fluctuations of OPCs concentration in the Vistula River water with HCHs peaking in August and September 1991.

3.1.5.3.7 Russian rivers

The contribution of gross riverine organochlorine pesticide (OCPs) transport to estuaries of Russian seas and Lake Bajkal was determined to help understand OCPs transboudary transfer and to provide a basis for estimating Russia´s contribution to global pollution by these pesticides (Zhulidov et al., 2000). The official OGNK/GSN data ranks sea/ocean/lake basins in the following order based upon the amounts of total OCPs received from agricultural use: Eastern Arctic > Western Arctic > Pacific > Baltic > Caspian > Azov/Black > Bajkal. A similar ranking was obtained using an independent set of data: Eastern Arctic > Pacific > Caspian > Western Arctic > Baltic > Azov/Black. In terms of riverine flow-associated discharge of HCH isomers estuaries of the Kara, Okhotsk and Beloye (White/Barents seas received more pesticides than other seas. No HCH was discharged to estuaries of the Eastern Siberian and Bering seas. For DDT and its derivative (DDE), estuaries of the Kara, Caspian, Okhotsk and Baltic Seas received the greatest amounts. During our study period (1988 - 1996), HCH transport was more prevalent in the majority of rivers reflecting both the official ban on the use of DDT in the former Soviet Union and the greater popularity of HCH as a pesticide. In general, it appears that Russian rivers play a significant role in OCP contamination of some estuaries of regional seas, especially those of the eastern Arctic basin, such as the Kara Sea.

3.1.5.3.8 Britannia and Ireland

Trends in the concentrations of atrazine, lindane and simazine in the estuary of the River Thames between 1988 and 1997 were examined using linear regression methods to determine whether attempted reductions in pesticide discharges had improved estuarine water quality (Power et al., 1999). Concentrations of all the studied pesticides declined over the period, despite the influences of drought induced reductions in freshwater flow from the Thames catchment. Measures to control pesticide discharges resulted in dramatic reductions (> 90%) of the triazines atrazine and simazine, and a 73% reduction in lindane. Archived reductions in the Thames compare favourably with those recorded for the Humber Estuary. Measured concentrations in the Thames Estuary are now similar to those found

in other UK and European estuaries, suggesting that the Thames estuary is no longer of special concern.

PCDDs/Fs were detected in all sediment samples and the results provide a valuable data set for UK freshwaters (Rose et al., 1994). The results of sediment analysis are summarised in Table 3-45. The general distribution was very wide because of the inclusion of contaminated and background sites, but does reflect the overall frequency distribution of concentrations across England and Wales.

In order places results potentially contaminated sites into context, a number of background sites were also chosen for PCDDs/Fs analysis. If the background sites chosen are representative, the results suggest that in UK rivers the total PCDDs/Fs background concentrations are < 1 000 $pg.g^{-1}$, with a I-TEQ < 6 $pg.g^{-1}$. Whilst the homelogue group and contribution to I-TEQ profiles from these background sites do vary, most show the predominance of OCDF/D and, to a lesser extent, HpCDD. It is possible that the observed PCDD/F in the background river sediments resulted from atmospheric deposition, either onto the catchment of directly onto the water surface, resulting in a profile dominated by higher chlorinate dioxins. Furans were also present in these homologue group profiles.

The analysis of water and sediment samples from both potentially polluted and background areas showed PCDDs/Fs concentrations to be very low. The results from a survey of sediments suggest that the levels present in river sediments across England and Wales may vary by at least a factor of 50, and that the values are comparable to those found in UK soils and to surface sediments in other parts of Europe. The results indicate that the background PCDDs/Fs total concentrations in river sediment in England and Wales may originate primarily from direct deposition and indirect catchment runoff of atmospherically derived PCDDs/Fs.

In general, levels of PCDDs/Fs in river sediments sampled were higher in industrial and urban areas. Agricultural sites showed low level despite the use of pesticides. In several cases, samples taken above discharge points appeared to be higher than those downstream, indicating that unidentified sources may be present. These observations indicate that sources of PCDDs/Fs to rivers are not necessary the readily identifiable ones, and emphasise the difficulty of identifying and defining sources.

3.1.5.3.9 Lakes

Semivolatile organochlorine compounds (OCs) such as PCBs, HCHs, HCB, and DDTs are ubiquitous in the planet. Atmospheric transport in one of the most efficient and rapid ways for the transfer of these persistent organic pollutants to remote sites. Cold sites may also be encountered in temperature areas, namely in the high mountain regions. Lakes are ideal ecosystems for the study of the atmospherically transported OC burden in these cold environments (Fernandez et al., 1999). Accordingly, high mountain lakes in Europe have been selected for study. These lakes are distributed among the main mountain ranges (Alps, Pyrenees, Tatra Mountains, Scandinavia, Iberian Peninsula, Ireland and Scotland - sites between 430 - 2800 m above sea level). Sedimentary composition of PAH in these lakes has been examined. OC were analysed in fish from 18 o these lakes and sediments in eight of them. Both average concentrations show a significant dependence of the LVC with altitude.

Polycyclic aromatic hydrocarbons (PAHs) were measured in superficial sediments from several high altitude mountain lakes for assessment of contemporary background PAH pollution levels in Europe (Fernandez et al., 1999, 2002). Location of the lakes ranged from western to Eastern Europe (see Table 3-60), all studied lakes were oligotropic with low total organic carbon (TOC) in the waters. The parent PAH mixtures were very uniform regardless of lake location, lake characteristics, and PAH load. The PAH profile was dominated by parent compounds, from phenanthrene to coronene, with a predominance of high molecular weight compounds of cata-condensed structures. The uniform sedimentary PAH profile reflects very well the PAH composition in the atmospheric aerosols collected at these high attitude lakes. The relative proportion of the compounds more labile to photooxidation was low. The PAH distribution indicates that the PAH mixtures are not significantly modified by the

water column processes. The PAH profiles in sediments correspond to airborne combustion mixtures refractory to photooxidation and chemical degradation.

PAH concentrations detected in most central European Lakes are intermediate between contaminated sites near to urban/industrial centres (values of thousand $ng.g^{-1}$) and remote marine or lacustrine areas (a few hundred $ng.g^{-1}$). Lakes from Tatra Mountains have PAH levels similar or exceeding the concentrations reported for sediments near to urban suggesting atmospheric transport of PAHs to these environments is very significant.

PCBs, HCHs, DDTs, HCB and endosulfans were measured in waters from three European remote mountain lakes (Alps and Caledonian mountain from Region III and Pyrenee) (Vilanova et al., 2002). High HCHs concentrations were measured in the Alps (and also in Pyrennes), which was being among the highest recorded in continental waters. The levels of other determined pollutants were low in comparison with other continental waters.

From determined HCHs, the most abundant isomer in Alpine lake was γ-HCH. These high levels of HCHs are close to the highest concentrations described for lacustrine waters. These results are surprising for such remote sites that only receive atmospheric input. The dominance of γ–isomer is in agreement with the accepted HCH product in the present European legislation. The higher content of α-HCH in Caledonian lake could reflect the influence of HCH distributions accumulated in northern latitudes as consequence of the widespread use of technical mixtures in the past, which were characterized by high proportions of the α–isomer (Breivik et al., 1999).

These trends were confirmed also by measurements of bulk deposition concentrations of PCBs, HCHs, HCB and endosulfans in these remote European high mountains areas. The compounds of present use in agriculture, namely endosulfans and γ-HCH, exhibit large differences in mean deposition fluxes between the evaluated sites. In contrast, the compounds whose use is now banned exhibit a more uniform geographic distribution of deposition fluxes for α-HCH, PCBs and HCB (Carrera et al., 2002). Both compounds of present and past use exhibit a clear seasonal pattern, with higher deposition in the warm periods, which is consistent with enhanced volatilization at higher temperatures, In the case of the agricultural pesticides it may also reflect higher use during application periods.

PCDDs/Fs were measured in 16 sections of sediment core from a freshwater lake in rural England (Green et al., 2001), Esthwaite Water, Cumbria, U.K. (54°21´N, 3°00´W). This is a small, eutrophic, seasonally anoxic lake in rural England. The lake is remote from large residential or industrial conurbations but receives a small amount of treated domestic sewage. Each section represented 10 yr of deposition. Concentrations greater than the limit of detection were observed for most homologues in all samples. Local industries such as mining, quarrying, charcoal burning, and iron smelting appear to have had a minor impact on the PCDDs/Fs deposition in the lake. Since 1900, two major peaks in PCDDs/Fs input to the lake were evident. The first, reaching a maximum in the 1930s, had an unusual homologue pattern dominated by high molecular weight PCDFs, and the source of this input is unknown. The second, with a maximum in the 1970s, is in keeping with previously reported time trends for Europe and North America. Pre-1900, the TCDD/F isomer pattern was dominated by dimerization products of 2,4-dichlorophenol. Despite detailed knowledge of the catchment and of industry in the surrounding area, the identity of some sources and the contribution of other known sources remain unclear for each era. This indicates that there remain significant gaps in our understanding of PCDD/F sources and undermines our ability to predict future trends in PCDD/F emissions.

The historical trends in the concentrations of toxaphene, its component homologue groups, and individual chlorobornane congeners, were determined in a dated sediment core from a mountain lake, Lochbagar, in Scotland, U.K., representing the first such profiles outside of North America (Rose et al., 2001). The study has used the lake sediments of the U.K. mountain lake, remote from areas of

toxaphene production and use, as a natural archive. Lochnagar (56°57.48´N, 3°13.08´W) is remote corrie lake in the Grampian Mountains of Scotland lying in the center of a granitic massif at an altitude of 785m. Toxaphene has been neither used nor produced in the U.K., and while some production was undertaken in France and Germany (1955 - 1990, main production in the early 1980s (Saleh, 1991), much of this was exported to Eastern Europe and Cuba (Heinish et al., 1994). Therefore, Lochnagar and its sediment record are ideally placed to monitor the long-range transport and historical deposition of this pollutant to an area of Europe remote from any direct treatment.

The profile of total toxaphene showed a bimodal distribution with maxima in the mid-1970s and early 1990s unlike the unimodal PCB profile (maximum 1973) in the same core. The earlier toxaphene peak shows agreement with the U.S. source curve and therefore may correspond to modelled global patterns while the later peak may be due to long-range transport from eastern and southern Europe or from still lower latitudes. Sediment toxaphene concentrations (14 $ng.g^{-1}$ dry wt (dw) at surface; 40 $ng.g^{-1}$ dw at maximum) and accumulation rates (surface 0.42 ng cm^{-2} yr^{-1}; maximum 1.6 ng cm^{-2} yr^{-1}) were considerably higher than levels in untreated sites in the Great Lakes region and the Canadian Arctic and are equivalent to those reported for the Great Lakes themselves where there have been additional riverine inputs.

Prior to 1960, total concentrations were low but uniformate all analyse sediment levels. A dramatic increase in concentration occurred in the 1960s, stabilizing for a period between the mind-1960s and the mind-1980s before reaching a peak in 1990 and the declining to the sediment surface. The East German toxaphene production data reported by Heinisch et al. (1994) can also be used as an indicator of European sources although, as noted previously, much of the production was exported. To our knowledge, there are no toxaphene sediment profiles outside of North America against which to compare our data.

The sediment record of total PCBs was also studies for the same Lochnagar sediment core. PCB concentrations begin to increase in levels dated to the mid-1930s and undergo a large increase during the 1960s. This increase coincides very well with the known production of PCBs in the U.K. (Harrad et al., 1994; Gevao et al., 1997; Kidd et al., 1995). Unlike the toxaphene profile, PCBs show a more uniform distribution with depth between 1960 and the mid-1990s. The PCB profiles in dated sediment cores collected in remote lakes in Northern Finland (68 - 69° N) also show post-1950 deposition of PCBs with maximum in the 1970s (Vartianen et al., 1996). A peat core from an ombrotropic bog in northwest England also showed maximum PCBs in slices dated to the late 1960s and an approximately 50% decline in concentrations between 1970 and 1990 (Sanders et al., 1992).

The Groser Arbersee is a glacial cirque near Bayerisch-Eisentein on the Bavarian Forest, south east Germany (Bruckmeier et al., 1997). Since the Middle Ages, mining and smelting of iron-ores, and glass production, were important sources of gaseous emissions in this region. The Groser Arbersee has been acidified due to acid atmospheric deposition from local sources before industrialisation, and from an increase in transboundary acidifying pollutants in the 20th century. There are no direct discharges into the lake, which is fed by a catchment of 2.58 km^2.

PCB concentrations increased between 1946 and 1972 with corresponding increase of I-TEQ between 1951 - 1972. Their peak concentrations in 1968 - 1972 were 19 times background in 1884 - 1890. PCB concentrations have decreased since but, even in 1991 - 1993, they were still 15 times higher than background. Although PCBs were detected in deep slices (1884 - 1990) they do not exceed blank levels. Therefore contaminations during extraction and clean-up procedure are responsible. Trends in lake sediments reflect these changes in commercial production and use.

PCDDs/Fs increased slightly in the late 19th century and by 1911 - 1918 concentrations were 14 times higher than background in 1865 - 1872. I-TEQ increased in the early 20th century prior to a strong increase in PCDDs/Fs concentration, which occurred after 1950. Peak concentrations in 1977 - 1981

reached 266 times background, but have since declined by 33% in PCDDs and 19% PCDFs. In contrast, I-TEQ peaked later in 1981 - 1985, reflecting variable patterns among the homologues.

A marked increase in PCDDs/Fs concentrations in the 1950s has also found elsewhere but a prior increase in I-TEQ suggests that other sources were important for the release of dioxins into the environment before the production of chlororganics; the most likely is the burning of fossil fuels. There was also indicated by the homologue profiles in 1911 - 1918 which were dominated by low chlorinated furans similar to those of soot derived from coal and wood burning. Additionally, high proportion OCDD suggest that other sources, such as local glass production and metal smelting industries, might have been involved.

PCDDs/Fs were detected in sediments from the 17th to 19th Century onwards with toxic equivalents (I-TEQ) below 1 pg.g^{-1}. Sediments at this time were dominated by OCDD in Herrenwieser See, comparable with results from 8000-year-old marine sediments and 19th Century sediments from Green Lake (New York). In contrast, in Huzenbacher See, OCDF dominated in the 18th Century, but OCDD dominated in the 19th Century. TCDF dominated the old sediments from Schutmsee. Furans predominated at Wildsee in sediments deposited in the 19th and the early 20th century.

Together, these data show that adjaced lakes in the Black Forest indicate consistently that contamination by PCDDs/Fs occurred prior to the industrial use of chlorophenols and even from early in the industrialization of Germany. However, subsequent variations between lakes in temporal trends, homologue patterns, and apparent PCDDs/Fs sources indicate that local variability can confound attempts that records from single locations may be unrepresentative. This likely to be an important lesson for other locations where cost and logistical considerations often limit paleolimnological studies to individual lakes.

The contamination of various Estonian water bodies with PAHs has been studied since 1972 (Veldre and Karlova, 2002). The 62 Estonian small lakes were investigated at all seasons of a two year period. These lakes were selected to characterize lakes of different economical use and of various regions. This investigation has shown that Estonian small lakes were not highly polluted with BaP.

Lake Vättern in southern Sweden is a large oligotrophic lake with high surface to catchment area ratio (ca. 0.4) and a water residence time of 60 years (Lindell et al, 2001). The lake combines sensitivity to atmospheric PTS pollution with general susceptibility for effects of PTS and slow concentration decline. The series, from the 1960s until 1996, of PCBs and DDT in fish and data on TCDD in sediment of Lake Vättern were presented and compared to other large lakes. Oligotrophic clear lakes are important ecosystems for monitoring POPs in biota.

3.1.5.3.10 Freshwater biota

The use of bioindicators and bioaccumulators is very common in various POPs monitoring and research programmes and studies. The examples of using in Germany were described above. Also in some other countries these methods are very frequently used, such as Czech or Slovak Republic (Kocan et al., 1999; Hajslova et al., 1997; Gregor and Hajslova, 1998). The purpose of these studies was to determine the characteristic patterns of persistent organochlorine contaminants in several fresh water fish species.

Example of these types of studies concerning to the determination of indicator and DL PCBs is shown in Table 3-63 (Gregor and Hajslova, 1998). Following samples of pooled fish (fillets, skin removed) collected in autumn 1997 were analysed: (i) barbel caught in Elbe river, locality Hrensko - close to the German border; yellow eel, from the same sampling site; roach caught in Skalica river, locality downstream from Rozmital and roach caught in Skalice river upstream from Rozmital.

12 years ago, a serious breakdown pollution by Delor 103 (Czechoslovakia name of PCBs- containing technical PCBs mixture with 48 %, w/w, chlorine) occurred at the locality Rozmital. Observed values indicate unequivocally continuing high PCBs input at sampling site downstream from Rozmital. Ten-fold higher total TEQs were found in fish living here compared to that collected upstream. The concentrations of non-ortho and mono-ortho substituted PCBs determined in barbel from Elbe river even exceeded values reported for some freshwater fish (pike-perch, perch) collected in seriously polluted Rhine, Meuse and their side-rivers. Hence, considering results obtained for barbel from Czech part of Elbe, may be assigned among the strongest PCB-contaminated waters in Europe (Table 3-63).

High levels of dioxins and dioxin-like PCBs in eel from Dutch freshwater were reported in a screening of Dutch fishery products (van Leeuwen et al., 2002). To protect the Dutch citizens from the intake of high levels of dioxins by consumption of contaminated eel, a Dutch maximum residue limit (MRL) for eel was set at 8 pg PCDDs/Fs-TEQ.g^{-1} ww. Following the establishment of this Dutch MRL and anticipating the new European MRL for dioxins and furans in fish (4 g PCDDs/Fs-TEQ.g^{-1} ww), an extensive survey was carried out on PCB and dioxin contamination of eel from the Netherlands.

Levels in farmed and imported eel are significantly lower those in the highest wild eel samples and none of farmed and imported eel (mostly farmed) exceed the EU MRL. The current MRL only accounts for the PCDDs/Fs-TEQ whereas for these samples PCBs are the main contributing compounds (61-97 %) to the total dioxin toxicity (total TEQ). In this respect, the EU MRL does not satisfy for protection of consumers.

3.1.5.3.11 References

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Table 3-42: DDTs in rivers

Area	Sampling sites	Duration	Frequency of measurements	Typical range [pg.l^{-1}; pg.g^{-1}]	Comments	References
North Sea						
Elbe						

Czech part	200	1987 - 1990		DDE: < 5 - 205		Nondek and Frolikova (1991)
	7 42 samples	From 1988	One times per year	4 480 (280 – 58 200)	Košetice, small stream, southern part of CR, middle European PTS background site (DDT + DDE + DDD)	Holoubek et al., 2002 Vana et al., 2001
	16 16 samples	2001	2001	5 990 (1 170 – 17 600)	Beroun, Berounka River, a tributary of Vltava River, central part of CR, industrial agglomeration (industrial, agricultural and rural sites) (DDT + DDE + DDD)	Holoubek et al., 2002
Germany, Elbe and its tributary	Schmilka, km 4.1	1993 – 1998	Monthly	14 – 2 250	Time series for the course of the ΣDDTs constituent profiles in sedimented suspended matter from 6 sampling points in the river Elbe and one sampling point each in the Schwarze Elster, Mulde and Saale. Arithmetic means of all monthly samples/year. Biotic samples such as breams or eels were also analysed	Heinisch and Kettrup (2001)
	Zehren, km 89.6	1994 – 1998		20 – 1 394		
	Magdeburg, Km 318.1	1994 – 1999		32 – 2 352		
	Cumlosen, km 470,0	1994 – 1998		3 – 1 426		
	Schnackenburg, km 474.5	1988 – 1998		7 – 1 411		
	Bunthaus, km 609.8	1988 – 1998		5 – 2 195		
	Saale/ Grossrosengburg	1994 – 1999		20 – 261		
	Mulde/Dessau	1994 – 1999		74 – 27 700		
	Schwarze Elster Gorsdorf	1994 – 1999		1 – 4 620		
Baltic Sea						
Wistula (PL)				60	N=31	Agrell et al (2001)
Odra (PL)				170	N=24	
Mörrum (S)				40	N=11	
Ume				20	N=9	
- in all cases – concentrations in river water (median)						
Eastern Odra	12			DDT: 400 – 3 200 DDD: 700 – 1 800 DDE: 1 100 – 5 800 ΣDDT: 1 500 – 8 100	Sediments after floods	***1.1.1.1 Protasowicki et al. (1999)***
Western Odra	11			DDT: ND – 4 000 DDD: 400 – 4 100 DDE: 1 300 – 5 600 ΣDDT: 2 800 – 9 700		
Wistula		1991 - 1992		DDT: 3.4 – 91 (26) DDD: 43 – 570 (170) DDE: 57 – 170 (100) ΣDDT: 120 – 840 (310)	water	Falandysz et al. (1998, 1999)
Black Sea						

Danube					Danube Pesticide Regional Study	
River Morava	7 21 samples	1993, 1996-8, 2001	1996 1997 2001	4 000 (500 – 47 100)	Zlín, Drevnice River – tributary of Morava River, eastern part of CR, industrial agglomeration (industrial, agricultural and rural sites) (DDT + DDE + DDD)	Holoubek et al., 2002
Upper Danube and tributaries, Austria	4	1 campaign 1993		ND	Also contents in aquatic mosses were measured (ND – 1 800)	Chovanec et al. (1994)

Table 3-43: HCB in rivers

Area	Sampling sites	Duration	Frequency of measurements	Typical range [pg.l^{-1}; pg.g^{-1}]	Comments	References
North Sea						
Elbe						
Czech part	200	1987 - 1990		< 1 - 440		Nondek and Frolikova (1991)
	7 42 samples	From 1988	One times per year	390 (40 – 78 100)	Košetice, small stream,	Holoubek et al., 2002 Vana et al., 2001
	16 16 samples	2001	2001	90 (240 – 2 320	Beroun, Berounka River, a tributary of Vltava River	Holoubek et al., 2002
Baltic Sea						
Wistula		1991 - 1992		7,6 - 52	water	Falandysz et al. (1998, 1999)
Black Sea						
Danube					Danube Pesticide Regional Study	
River Morava	7 21 samples	1993, 1996-8, 2001	1996 1997 2001	1 500 (300 – 9 400)	Zlín, Drevnice River – tributary of Morava River	Holoubek et al., 2002
Upper Danube and tributaries, Austria	4	1 campaign 1995 ?		ND - 600	Also contents in aquatic mosses were measured (700 – 4 700)	Chovanec et al. (1994)

Table 3-44: PCBs in rivers

Area/River	Sampling sites	Duration	Frequency of measurements	Typical range [pg.l^{-1}; pg.g^{-1}]	Comments	References
North Sea						
Czech part	7 42 samples	From 1988	One times per year	2. 570 (930 – 7 070)	Košetice, small stream (7 congeners)	Holoubek et al., 2002 Vana et al., 2001
	16 16 samples	2001	2001	14 900 (4 760 – 114 800)	Beroun, Berounka River, a tributary of Vltava River (7 congeners)	Holoubek et al., 2002
Germany, Elbe and its tributary	Schmilka, km 4.1	1993 – 1998	Monthly	36 – 836	Time series for the course of the ΣPCBs constituent profiles in sedimented suspended matter from 6 sampling points in the river Elbe and one sampling point each in the Schwarze Elster, Mulde and Saale. Arithmetic	Heinisch and Kettrup, 2001.
	Zehren, km 89.6	1994 – 1998		11 – 298		
	Magdeburg, km 318.1	1994 – 1999		17 – 403		
	Cumlosen, km 470,0	1994 – 1998		7 – 489		
	Schnackenburg, km 474.5	1987 – 1998		10 – 275		

	Bunthaus, km 609.8	1987 – 1998		3 – 322	Saale. Arithmetic means of all monthly samples/year. Biotic samples such as breams or eels were also analysed	
	Seemannshoff, km 629.9	1987 – 1998		3 – 172		
	Blankensee, km 634.3	1987 – 1993		4 – 164		
	Graurerort, km 660.5	1988 – 1998		2 – 103		
	Cuxhaven, km 725.2	1988 - 1998		1 – 44		
	Saale/ Grossrosengburg	1994 – 1999		5 – 128		
	Mulde/Dessau	1994 – 1999		7 – 127		
	Schwarze Elster Gorsdorf	1994 – 1999		5 - 148		
Baltic Sea						
Daugava (La)				500 – 7 400	N=12	Agrell et al (2001)
Wistula (PL)				610	N=31	
Odra (PL)				1 440	N=24	
Mörrum (S)				720	N=11	
Ume				210	N=9	
- in all cases – concentrations in river water (median)						
Odra - estuary		1994, 1996		< 130 – 9 550	23 congeners; sediments	Dannenberger and Lerz (1999)
Eastern Odra	12			DDT: 400 – 3 200 DDD: 700 – 1 800 DDE: 1 100 – 5 800 ΣDDT: 1 500 – 8 100	Sediments after floods	***1.1.1.2 Protasowicki et al., (1999)***
Western Odra	11			DDT: ND – 4 000 DDD: 400 – 4 100 DDE: 1 300 – 5 600 ΣDDT: 2 800 – 9 700		
Wistula		1991 - 1992		120 – 300 (190)	water	Falandysz et al. (1998, 1999)
Black Sea						
Danube					Danube Pesticide Regional Study	
River Morava	7 21 samples	1993, 1996-8, 2001	1996 1997 2001	37 800 (2 600 – 143 100)	Zlín, Drevnice River – tributary of Morava River (7 congeners)	Holoubek et al., 2002
Upper Danube and tributaries, Austria	4	1 campaign 1995 ?		1 850 – 2 290	Also contents in aquatic mosses were measured (ND – 1 630)	Chovanec et al. (1996)
Tributaries in Slovakia		1989 – 1997		5 – 30 (average with maximum > 1 000)	3000 samples	Kočan (2001)

Table 3-45: PCDDs/Fs in rivers

Area	Sampling sites	Duration	Frequency of measurements	Typical range [pg.l^{-1}; pg.g^{-1}]	Comments	References
North Sea						

Rivers, UK	36	1993	One campaign	PCDDs/Fs: 300 – 16 000 (median: 3 258) TEQ: 2 – 120 (16.7) Background: PCDDs/Fs: 300 - 400 TEQ: 20 - 94	Rivers in England, Wales	Rose et al., 1994
Czech part	16 16 samples	2001	2001	200.1 (30.3 – 1 105) 1.83 (0.21 – 11.2)	Beroun, Berounka River, a tributary of Vltava River	Holoubek et al., 2002
Elbe	5	1990 - 1991		PCDDs/Fs: 2 143 – 15 760 211 – 75 000	River Hamburg - harbour	Weber; Gotz in Rose
Baltic Sea						
Odra - estuary		1994, 1996		PCDDs: 13 – 2 991 PCDFs: 2.5 - 820	Sediments	Dannenberger and Lerz (1999)
Black Sea						
Danube					Danube Pesticide Regional Study	
River Morava	7 21 samples	1993, 1996-8, 2001	1996 1997 2001	110.0 (60.8 – 722.5) 1.9 (0.9 – 5.6)	Zlín, Drevnice River – tributary of Morava River	Holoubek et al., 2002
Upper Danube and tributaries, Austria	4	1 campaign 1992		PCDDs: 76 - 225 PCDFs: 41 – 71 PCDDs/Fs: 117 – 326 TEQ: 1.25 – 3.69		Ref: in Rose

Table 3-46: HCHs in rivers

Area	Sampling sites	Duration	Frequency of measurements	Typical range [pg.l^{-1}; pg.g^{-1}]	Comments	References
North Sea						
Germany, Elbe and its tributary	Schmilka, km 4.1	1993 – 1998	Monthly	3 – 54	Time series for the course of the ΣHCHs constituent profiles in sedimented suspended matter from 6 sampling points in the river Elbe and one sampling point each in the Schwarze Elster, Mulde and Saale. Arithmetic means of all monthly samples/year. Biotic samples such as breams or eels were also analysed	Heinisch and Kettrup (2001.)
	Zehren, km 89.6	1994 – 1998		1 – 54		
	Magdeburg, km 318.1	1994 – 1999		4 – 1 513		
	Cumlosen, km 470,0	1994 – 1998		1 – 75		
	Schnackenburg, km 474.5	1987 – 1998		3 – 245		
	Bunthaus, km 609.8	1987 – 1998		1 - 84		
	Seemannshoff, km 629.9	1987 – 1998		1 – 56		
	Blankensee, km 634.3	1987 – 1993		3 – 51		
	Graurerort, km 660.5	1988 – 1998		2 – 40		
	Cuxhaven, km 725.2	1988 - 1998		1 – 26		
	Saale/ Grossrosengburg	1994 – 1999		77 – 3 342		
	Mulde/Dessau	1994 – 1999		2 – 38		
	Schwarze Elster Gorsdorf	1994 – 1999		1 - 93		
Czech part	7 42 samples	From 1988	One times per year	410 (40 – 4 090)	Košetice, small stream, southern part of CR (4 isomers)	Holoubek et al., 2002 Vana et al., 2001

	16 16 samples	2001	2001	340 (150 – 1 210)	Beroun, Berounka River, a tributary of Vltava River (4 isomers)	Holoubek et al., 2002
Baltic Sea						
Wistula (PL)				140	N=31	Agrell et al. (2001)
Odra (PL)				100	N=24	
Mörrum (S)				300	N=11	
Ume				110	N=9	
- in all cases – concentrations in river water (median)						
Eastern Odra	12			γ: 800 – 4 200	Sediments after floods	***1.1.1.3 Protasowicki et al. (1999)***
Western Odra	11			γ: 400 – 2 100		
Pistula		1991 - 1992		α: 410 – 310 000 (median: 1 400) β: 200 – 39 000 (650) γ: 930 – 63 000 (1 800) ΣHCHs: 1 600 – 410 000 (4 200)	water	Falandysz et al. (1998, 1999).
Black Sea						
Danube					Danube Pesticide Regional Study	
River Morava	7 21 samples	1993, 1996-8, 2001	1996 1997 2001	200 (0 – 3 100)	Zlín, Drevnice River – tributary of Morava River	Holoubek et al., 2002
Upper Danube and tributaries, Austria	4	1 campaign 1995 ?		γ – 200 – 310	Also contents in aquatic mosses were measured (1 800 – 3 800)	Chovanec et sal. (1994)

Table 3-47: PAHs in rivers

Area	Sampling sites	Duration	Frequency of measurements	Typical range [pg.l^{-1}; ng.g^{-1}]	Comments	References
North Sea						
Czech part	7 42 samples	From 1988	One times per year	175.3 (18.6 – 559.2)	Košetice, small stream, southern part of CR (16 US EPA)	Holoubek et al., 2002 Vana et al., 2001
	16 16 samples	2001	2001	2 602 (95.4 – 9 829)	Beroun, Berounka River, a tributary of Vltava River (16 US EPA)	Holoubek et al., 2002
Baltic Sea						
Odra lagoon – open sea area				5 – 1 070	Sediments	Witt and Trost (1999)
Black Sea						
Danube					Danube Pesticide Regional Study	
River Morava	7 21 samples	1993, 1996-8, 2001	1996 1997 2001	8 001 (635.5 – 30 232)	Zlín, Drevnice River – tributary of Morava River, eastern part of CR	Holoubek et al., 2002
Upper Danube and tributaries, Austria	4	1 campaign 1995 ?		396 – 1 101	Also contents in aquatic mosses were measured (232 – 479) 18 PAHs (15 USEPA – no NAP + BeP, TRI, COR	Chovanec et al. (1994)

Danube Estuary				1 596 (477 - 5 612) 355 (287 - 422)	Suspended particulate matter, XX PAHs Dissolved phase, XX PAHs	Maldonado…
Dniepr and Dniester Estuaries				1 609 104 - 5 521 183	Suspended particulate matter, XX PAHs Dissolved phase, XX PAHs	
Danube Estuary				355 287 - 422	Subsurficial water	
Odessa depression				183		
Offshore Constantza				455		

Table 3-48: The concentrations of organochlorine pesticides and PCB in Vistula River water collected at the Kiezmark site near the city of Gdansk [pg.l^{-1}]

Compound	Median	Mean and S.D.	Range
Trans-chlordan	9.1	9.8 ± 5.6	< 4.0 - 19
Cis-chlordan	3.9	4.5 ± 3.6	< 4.0 - 9.1
Trans-nonachlor	3.6	4.9 ± 3.6	< 4.0 - 9.6
Heptachlor	5.5	6.1 ± 5.1	2.1 - 20
CHLs	12	15 ± 13	2.6 - 40

Table 3-53: DDTs in lakes

Table 3-54: HCB in lakes

Table 3-55: Toxaphen in lakes

Table 3-56: PCBs in lakes

Area	Sampling sites	Duration	Frequency of measurements	Typical range [pg.g^{-1}]	Comments	References
Remote Lakes						
Germany, Groser Arbersee, Bavarian Forest				PCBs7: 1884-1890: 1 734 1940-1946: 4 200 1946-1951: 15 784 1951-1957: 19 058 1957-1963: 24 174 1963-1968: 26 692	 1968-1972: 32 029 1972-1977: 27 554 1977-1981: 25 395 1981-1985: 25 023 1985-1991: 27 341 1991-1993: 25 553	Bruckmeier et al. (1997)
Latvia, 4 rural lakes				Perch: 180 – 2 400	[ng.g^{-1}] ??	Ott ??

Table 3-57: PCDDs/Fs in lakes

Area	Sampling sites	Frequency of measurements	Typical range		Comments	References
Germany, Groser Arbersee, Bavarian Forest		One campaign	PCDDs/Fs: 1884-1890: 1940-1946: 1946-1951: 1951-1957: 1957-1963: 1963-1968:	 1968-1972: 1972-1977: 1977-1981: 1981-1985: 1985-1991: 1991-1993	:	Bruckmeier et al. (1997)
Germany, 4 lakes in northern Black Forest	Herrenswieser See	One campaign	PCDDs/Fs: 17th Cent.: 238 18th Cent.: 270 1886-1927: 430 1927-1960: 1 154 1960-1982: 7 079 1982-1992: 18 388	TEQ: 0.4 0.5 4 17 110 229		Jüttner et al. (1997)

	Schurmsee		18th Cent.: 317 19th Cent.: 268 1946-1965: 537 1965-1979: 423 1979-1987: 1 564 1987-1992: 3 010	0.1 0.4 9 7 23 31		
	Wildsee		Early19th Cent.: 489 1850-1892: 483 1892-1930: 1 371 1930-1964: 8 029 1964-1985: 16 490 1985-1992: 13 559	8 9 25 130 205 157		
	Huzenbacher See		18th Cent.: 758 19th Cent.: 136 1882-1903: 455 1903-1934: 153 1961-1983: 19 743 1983-1992: 8 996	1 0.2 2 0.7 90 69		
UK	4	One campaign	Sediments: PCDDs/Fs: 590-4500 TEQ: 6-92 Fish: PCDDs/Fs: 100-800 TEQ: 1-20	4 remote lakes, England (2), North Ireland, Scotland, fish samples were also analyzed		Rose and McKay (1996)

Table 3-58: HCHs in lakes

Table 3.59: PAHs in lakes

Area	Sampling sites	Duration	Frequency of measurements	Typical range [ng.g^{-1}]	Comments	References
High Altitude Mountain Lakes						
West and Central Europe	5		One campaign	260 – 2 900 (260 - 910) 44 - 150 (38-130)	PAHs, sediments PAHs, fluxes [μg.m^{-2} yr^{-1}]	Fernandez et al., 1999
East Europe	2		One campaign	13 000 - 18 000 (11 000 - 16 000) 960 - 1 700 (820 - 1 500)	PAHs, sediments PAHs, fluxes [μg.m^{-2} yr^{-1}]	

Sum as PAHpyr (21 PAHs); In brackets – sum of phenanthrene + fluoranthene + pyrene + benz(a)anthracene + chrysene + benzofluoranthenes + benzo(e)pyrene + benzo(a)pyrene + indeno(1,2,3-cd)pyrene + benzo(ghi)perylene

3.1.6 Terrestrial ecosystems

3.1.6.1 Introduction

Soils are natural sinks for persistent and lipophilic compounds, which adsorb to the organic carbon of the soil and, once adsorbed, remain relatively immobile (Buckley-Golder et al., 1999). Soil is a typical accumulating matrix with a long memory; in other words, PTS inputs received in the past will remain and, due to the very long half-lives of these substances in soils, there is hardly any clearance. Soils can receive inputs of environmental pollutants *via* different pathways of which the most important are: atmospheric deposition, application of sewage sludge or composts, spills, erosion from nearby contaminated areas. Once PTS contamination is detected in soils, a historic evaluation has to be performed to determine which might have been the predominant input pathway (sometimes pattern analysis might provide further evidence). In general, it is difficult to determine when a soil contamination occurred. The concentrations in soil tend to reflect the baseline contamination of a region. Thus, urban areas exhibit higher concentrations than rural.

3.1.6.2 Regional and subregional activities

Most data are available for dioxin concentrations in soils, as a number of intensive surveys have been carried out. In almost all countries a broad range of dioxin concentrations was detected, as illustrated in Table 3-60, with the lowest concentrations below 1 pg I-TEQ.g^{-1} d.m. and the highest around 100 pg I-TEQ.g^{-1} d.m. In the Netherlands, particularly, most soil samples have been taken in the neighbourhood of municipal solid waste incinerators, where concentrations up to 252 pg I-TEQ.g^{-1} d.m. have been detected.

In contaminated locations measured concentrations range from several hundred to around 100 000 pg I-TEQ.g^{-1} d.m. The highest concentrations reported are shown in the last column of Table 3-60. As the extent of measurement programmes varies considerably from one country to another, it is not possible to identify any individual country with dioxin concentrations in soils, which are significantly higher or lower than any other.

Table 3-60: Summary of dioxin concentrations in soil from EU Member States (pg TEQ.g^{-1} d.m.)

	Other types	Forest	Pasture	Arable	Rural	Contamin.*
Austria		<1-64	1.6-14			332
Belgium	2.7-8.9				2.1-2.3	
Finland						>90,000
Germany		10-30	<1-30	<1-25	1-5	30,000
Ireland	<1-8.6	4.8	<1-13			
Luxembourg	1.8-20	6.0			1.4	
The Netherlands					2.2-16	98,000
Sweden					<1	11,446
United Kingdom	<1-87				<1-20	1,585

* maximum measured concentration at contaminated sites

Contemporary soil samples from 46 sites across the UK and 12 sites in Norway have been analysed for a range of PCBs congeners (Lead et al., 1997, Meijer et al., 2002). Results show spatial differences, in terms of concentration and congener profile. The difference is partly caused by an increased proportion of the mid-molecular weight congeners in the samples from Norway. The soils from southern Norway and the UK contained similar amounts of PCBs per unit area; those from northern Norway contained lesser amounts. Archived soils (1951-1974) from the UK sites have also been analysed and the results show increasing concentrations of these compounds up to the late 1960s/early 1970s, after which there has been a substantial decline. This temporal trend is in accordance with that reported in previous studies. However, it is possible that some of the archived samples were contaminated in the process of air-drying. Due to this contamination artifact, it is not possible to ascertain whether the scale of the observed temporal differences truly reflect changes in the environment.

3.1.6.3 National monitoring programmes

A lot of monitoring and research projects, which were focused on soil contamination of PTS were performed during last ten years in CEE countries. For example, the Czech National Agricultural Institute for Supervision and Testing Pesticides has realised the programme of monitoring on agricultural soil in the network of 190 representative monitoring plots on arable land, grassland and special crops since 1992 (Sanka, 2001). On selected monitoring plots atmospheric deposition is monitored simultaneously in one-month period. On the special subsystem of 27 monitoring plots, designed in highly polluted areas, parameters of pollution are investigated (level of pollution, sources, translocation in soil profile, transfer to plants). Since the agricultural soil monitoring serves as a tool for risk evaluation of agricultural production contamination, samples of different crops from contaminated plots (27) and reference plots (22) are taken and analysed for risk elements contents each year (See Tables 3-61, 3-62, 3-63 and 3-66).

Long-term project is carried out in the area of observatory of Czech Hydrometeorological Institute in Kosetice, south Bohemia. This observatory is a part of few international scientific programmes (EMEP, GAW). This locality is a background area of Project TOCOEN (Holoubek et al., 1990, Holoubek et al., 1994b; Vana et al., 2001). The soil samples are collected from 1988, 8 soil sampling sites are located in this area with the frequency 1 times per year. The polycyclic aromatic hydrocarbons (PAHs), some types of chlorinated pesticides (OCPs), polychlorinated biphenyls (PCBs) and in some cases polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/Fs) are determined, too (Tables 3-61 – 3-66).

The loads of agriculturally used soils of the Czech Republic with monocyclic aromatic hydrocarbons (BTX), polycyclic aromatic hydrocarbons (PAHs), organic chlorinated compounds (OCCs) and petroleum hydrocarbons (PHs) have been investigated (560 soil samples) (Podlesakova et al., 1998) – see Table 3-61 - 3-66.

Background values for heavy metals, PAHs and PCBs in the soils of Bulgaria were determined (Atanasov et al., 2001). Also soil samples from arable and forest areas in South Bulgaria were also collected and analysed for the presence of priority organic pollutants (PAHs, PCBs, OCPs) (Shegunova et al, 2001). The main pesticides found were DDE, DDD and DDT. Similarly, the assessment of the quality of contaminated soils in Romania, was given by Dumitru (2001). Maximum values of level of contamination obtained are shown in Tables 3-61 and 3-66. PAHs were determined in moldovian soils (Teyrytze et al., 2001). The project was performed in the context of a german-moldovian cooperation project on harmonization of analytical methods for international use and was aimed to get an overview over soil contamination. The sampling sites (77 samples) were chosen to cover different land utilization and expected contamination. At every site different soil depth were sampled (Table 3-66).

The levels of HCH in soils of the Slovak Republic were described by Schlosserova (1993). Few, very broad campaigns (1984, 1987-89) were performed (1 711 samples of soils and agricultural products). The value of latter campaign showed that the contents of HCHs had decreased about thirty times in comparison to the samples studied in years 1986-89 (Table 3-65).

3.1.6.4 Soil contamination - research projects and pilot studies

Soil samples were collected in 1994 from various sites in a former Soviet army base localised near the town of Swinoujscie in the north-western corner of Poland and the possible contamination with PCBs was investigated (Falandysz et al, 1997). Elevated concentrations of PCBs in soil in a former military (mainly air) grounds were observed in US base in Veitnam and in the surroundings of many former Soviet army bases in Poland, former Czechoslovakia, former GDR and former Soviet Union. The former Soviet Union has two own PCB formulations - Trichlorodiphenyl (with 41 % of chlorine content and average number of chlorine atoms per biphenyl molecule is 3) and Sovol (53 % of chlorine and 5 chlorine atoms per biphenyl molecule).

Surface soil and sediment samples collected from the cities of Krakow, Katowice and Chorzow city in southern part of Poland in 1993 - 1994 were analysed for residue levels of hexachlorobenzene (HCB), isomers of hexachlorocyclohexane (α-, β-, γ-HCH), and DDT and its metabolites (DDD and DDE), chlordane compounds (CHLs) and polychlorinated biphenyls (PCBs) in order to evaluate their concentrations and distribution (Falandysz et al., 2000). The soil from the city of Katowice is relatively more polluted mainly by PCBs, but also by the other organochlorines. Both the soil in the cities of Krakow and Katowice are more polluted by organochlorines than soil from many other places in Poland.

The distribution and accumulation of PAHs in Estonian soil as well as PAH profiles have been investigated in areas with different anthropogenic pollution such as the city of Tallinn, the towns of Pärnu and Kohtla-Järve and some rural areas (Trapido, 1999). The main source of PAHs in Tallinn,

especially in its centre is increasing transport and overloaded transport system. These problems were discussed also in chapter 3.1.2

The first information, concerning to the levels of contamination of soil in former Czechoslovakia were published in the 1992 (Holoubek et al., 1992). In the time of early 90´ many potential sources of these harmful compounds have existed in Czechoslovakia, many of them were unknown or little known. Soil samples were collected from TOCOEN model sites (background area Kosetice, the surroundings of industrial sources – waste incinerators, various types of chemical industry) and some other places (the surroundings of Bratislava MWI, factory for preparing precoated gravel in North Bohemia (Holoubek et al., 1994a) (See Tables 3-61 - 3-66).

Substance distribution patterns of DDT, DDE, DDD, DDMU, and of α, β, γ, δ, ε–HCH as well as the IUPAC congeners of PCBs in aquatic and terrestrial ecosystems may give hints as to the kind of input (i.e. the perpetrator) as well as dating of the process. Heinisch and Kettrup (1997) demonstrated it on examples such as the distribution pattern of DDT metabolites after massive applications in GDR forests in 1983/4 compared with earlier applications and the distribution pattern of HCH isomers in the surroundings of factories or as consequences of lindane applications.

The applications in former GDR had the consequences with level of contamination in the former Czechoslovakia and we can describe very useful tool for interpretation of history and state of contamination (Heinisch et al., 1997a,b,c). More than 20 years after the worldwide ban of DDT there are still increased contamination levels in different matrices. Using a simple substance distribution pattern of DDT parent substance and metabolites it is possible to get hints as to the source.

In 1983/4 on the territory of the former GDR 260 000 ha of forests were treated with high amounts of DDT/lindane preparations from aircraft to combat the black-arched moth (*Lymanthria monacha*). Before that, in 1975 a stepwise ban for DDT was passed, which mainly worked well. The levels of Σ DDTs and also the percentage of the parent substance DDT usually decreased after banning. This may be judged as a hint for the fact that from 1983 on there was new DDT input into the region. The impact of this new impact was possible to detect not only in the region of applications but also round whole the former GDR and also in former Czechoslovakia or still in Czech Republic, 15 years after. Other border-crossing co-treatments have been registered in the former Czechoslovakia, now the Czech Republic. The Table 3-67 describes higher levels Σ DDTs residues with high percentages of DDT in soil samples from the boundary mountain and decreasing levels if we are coming from the former neighbour, the former GDR towards the inner parts of Czech Republic and south border mountains (Sumava Mountains). This trend is evident in the levels of Σ DDTs and mainly the percentages of the parent substance markedly decrease that means the Σ DDTs residues must be of older origin. Σ DDTs residues and the percentage of the parent substance are particularly low in the south of the Czech Republic, in the Sumava Mountains as well as in the area of CHMI/TOCOEN regional background observatory Kosetice.

Table 3-67: Σ DDTs and percentages of the parent substance DDT in soil samples from the Czech Republic [$ng.g^{-1}$]

Sampling site	DDT	DDE	DDD	Σ DDTs	% DDT in Σ DDTs*	References
Mumlava, Krkonose, 1 190 m, 1995	33	8	na	41	80	Holoubek et al., 1996; see Chapter 10.5, too
Pudlava, Krkonose, 1 140 m, 1995	179	70	na	249	72	
Paseracky chodnicek, 1 310 m, 1995	99	36	na	135	73	
Jedlova, Luzicke hory, 710 m, 1995	302	84	na	386	78	
Lesna, Krusne hory, 800 m, 1995	2 390	795	na	3 185	75	
Nacetin, Krusne hory, 710 m, 1995	4 013	1 164	na	5 177	78	
Usti nad Labem, M, 1995	1 133	1	1	1 135	100	Podlesakova, 1996
Teplice, M, 1995	1 207	146	256	1 609	75 (89)	

Karlovy Vary, M, 1995	398	122	36	556	72 (77)	
Sokolov, M, 1995	522	209	40	771	68 (71)	
Cheb, M, 1995	264	167	25	456	58 (61)	
Kladno, M, 1995	63	53	7	123	51 (54)	
Praha, M, 1995	1 044	1 054	1	2 099	49 (50)	
Mnisek pod Brdy, M, 1995	651	245	4	900	72 (73)	
Pribram, M, 1995	28	31	1	60	47 (47)	
Boubin, Sumava, 1995	11	7	na	18	61	Holoubek et al., 1996
Cesky Krumlov, M, 1995	1	1	1	3	33 (50)	Podlesakova, 1996
Prachatice, M, 1995	1	1	1	3	33 (50)	
Kosetice, 1995	0.2	9	0.2	1.3	15	Vana et al., 2001

M – maximal value from 5 – 60 samples

* number without parantheses – original number of Heinisch and Kettrup, in parantheses - Σ DDTs DDT + DDE – same values for all samples from various authors

The measurements of PCBs and OCPs contents in soil samples from Slovakia were part of very unique study concerning the environmental and human population load in an area contaminated with PCBs (Kocan et al., 1999). As far as soil contamination – see more details in the Chapter Hot spots. A summary of results from measurements of soil samples is described in the Table 3-68. The estimation of content of PCBs in soils in Slovakia based on the higher level of background contamination (used area of Slovakia and 20 cm to soil layer) is round 50 tons as a result of using of PCBs in Slovakia and long-range transport from other countries.

Table 3-68: Summary of concentrations of PCBs and OCPs in soils [ng.g^{-1} d.w.]. Study of environmental and human exposure load in the area contaminated with PCBs (Kocan et al., 1999)

Pollutants	Dumps (n=6)	Producers of precoated gravel (n=8)	District Michalovce (n=11)	District Stropkov (n=4)
Σ PCBs	170 - 8 600	43 - 53 000 000	1.5 - 28	3.6 - 9.2
HCB	< 0.2 - 3.9	< 0.2 - 8.9	0.028 - 3.7	0.57 - 5.1
DDT + DDE	< 0.009 - 1 080	1.1 – 20	0.65 - 51	1.5 - 490

The estimation of content of PCBs in soils in Slovakia based on the higher level of background contamination (used area of Slovakia and 20 cm to soil layer) is round 50 tons as a result of using of PCBs in Slovakia and long-range transport from other countries.

Very complex review of contemporary information on the concentrations, burdens and fate of PAHs was published by Maliszewska-Kordybach (1999). The widespread occurrence of PAHs is largely due to their formation and release in all processes of incomplete combustion of organic materials. Changes in their qualitative distribution suggest that the sources of PAHs shifted from biomass burning to fossil fuels combustion in last 200 years. Air contributes in very small degree (< 0.5%) to the total PAH burden in the environment even though all PAHs released in the natural and anthropogenic combustion processes enter the atmosphere (Table 3-69). The atmosphere is not a repository and collector of PAHs but more likely a transporter, dilutor and reactor.

Table 3-69: Partition of some hydrophobic PTS in natural environments

PTS	Percent of total					
	Soil	Freshwater sediment	Water	Air	Vegetation	Biota
Σ PAH	94.4	5.4	< 0.01	0.1	0.1	< 0.01
BaP	92.9	7.1	< 0.01	< 0.01	< 0.01	< 0.01
PCB	89.2	9.9	0.3	0.5	-	0.1

Mean contents of PAHs in urban soils are within the range of about 1 000 - 3 000 ng.g^{-1} but values of 30 000 to 50 000 ng.g^{-1} were found in some locations. The average PAHs level in rural European soils is rather uniform with median values of about 300 - 400 ng.g^{-1} (Table 3-66).

The evaluation the content of PAHs in arable soils in Poland with special focus on the agricultural areas exposed to anthropogenic stress was performed as a part of country-wide Agricultural Soils Monitoring Programme in the years 1995 - 1997 (Maliszewska-Kordybach and Terelak, 1998). For the evaluation of the influence of sampling point location on PAHs content - which was one of the aims of the study – sample population was divided into four groups similar to those identified in Bavaria and to five levels of PAHs content in soil (soil classes) (Table 3-70).

Table 3-70: Criteria for evaluation of soil based on PAHs contents

Contents of Σ PAHs in soil (soil classes) [ng.g^{-1}]		**Samples location**	
< 200		R	Rural location, far from industrial activities
200 - 1 000	200 ng.g^{-1} - corresponding to Dutch background value for the model soil with 10 % OM	RC	Rural location, close (5 - 20 km) to industrial activity and peripheral areas of towns
1 000 - 3 000	1 000 ng.g^{-1} - corresponding to Danish ecotoxicological soil quality criterion	K	Location within the influence of traffic routes
3 000 - 10 000	3 000 ng.g^{-1} - corresponding to German precautionary value for soil with OM < 8%	I	Location within the direct surrounding area (< 5 km) of industrial sites
> 10 000	10 000 ng.g^{-1} - corresponding to German (Baden-Wurtemberg) plant protection (PP) level		

Some of the PTS were either produced in the Leipzig-Halle region in East Germany, or from by- or waste products of various chemical manufacturing processes. Furthermore, pesticide formulations containing p,p´-DDT and lindane were partly used in agriculture and forestry until the 1980s, and are still found in the forest due to their persistence. In East Germany, various chemical factories could be HCH emitters. Lindane and industrial HCHs were produced by three companies, Berlin-Chemie until 1971, Fahlberg-List until 1981, and Chemie-Kombinat Bitterfeld until 1982. In addition, HCH can be emitted by gas-evolving hazardous waste dumps, such as those in the areas of Bitterfeld (Antonie landfill) and Magdeburg (Enden hazardous waste dump), as well as by wood processing, cable-scrapping and incineration in smelting plants.

Concentrations of selected PTS (PCBs, HCHs, DDTs, HCB) in soil from different Romanian locations (Covaci et., 2001). Soil samples from Iassy were compared with soil samples collected from different locations all over Romania, which includes various types of sites (rural, urban, industrial and near waste incineration facilities, plus one near OLTCHIM factory). A comparison of concentrations of POPs in soils from different types of sites revealed that highest concentrations were found near industrial sites, especially near an organochlorine producing factory (OLTCHIM –Rm. Vilcea). Except for DDTs, all POPs were significantly higher than in other locations, exceeding the official norms. Even after more than 10 years from the DDT ban, DDTs concentrations in soil were significantly higher at rural sites, sometimes close to the actual tolerance limits for agricultural purposes.

Study of evidence for the presence of PCDDs/Fs in the environment prior to 1900 and on their temporal trends was performed in UK (Alcock et al., 1998). The background levels of PCDDs/Fs in Danish soil, the investigation of regional and geographical differences and the influence of sources, were studied in Denmark (Vikelsøe, 2002).

Table 3-XX: Aggregated data concerning to PTS soil contamination in selected region sof the Czech Republic – results of monitoring a research project of Project TOCOEN (Toxic Organic COmpounds in the ENvironment) {median; (minimum - maximum); n = number of samples; * ongoing projects}

Subproject Characteristic of sampling sites	Number of sampling sites	Duration	PAHs (16 USEPA)	PCBs (7 indicator congeners)	HCHs (4 isomers)	DDTs (DDT + DDE + DDD)	HCB	PCDDs/Fs	TEQ	DLPCBs (77+126+169)	TEQ DL PCBs
			[ng.g^{-1}]					[pg.g^{-1}]			
Košetice, Central European PTS background locality (EMEP)	9	1988-2001*	244.3 (5.8 – 5 412) n = 87	4.19 (0.07 – 116) n = 63	0.59 (0.02 – 182) n = 82	3.6 (0.20 – 294) n = 88	0.55 (0.04 – 9.18) n = 99				
	5	1998-2001*						87.11 (22.8 – 1 241) n = 9	1.3 (0.3 – 16.4) n = 9	7.91 (3.05 – 234.2) n = 9	0.25 (0.08 – 5.24) n = 9
Zlín, industrial agglomeration (industrial, agricultural and background sampling sites)	17	1993	3 145 (220 – 22 025) n = 62	16.47 (1.1 – 345.8) n = 63	0.89 (0.22 – 8.51) n = 63	9.39 (0.72 – 1 018) n = 63	3.28 (0.02 – 44.2) n = 63	307.1 (75.3 – 2 238) n = 10	2.42 (1.27 – 4.45) n = 10	53.4 (6.59 – 84.3) n = 10	0.78 (0.16 – 1.94) n = 10
	29	1997-2000									
	5	2001									
Beroun, industrial agglomeration (industrial, agricultural and background sampling sites) (smaller than previous)	25	2001	523.9 (123.1 – 6 778) n = 25	6.87 (4.36 – 29.2) n = 25	1.03 (0.34 – 1.62) n = 25	8.8 (2.19 – 216) n = 25	2.54 (0.54 – 10 295) n = 25	276.2 (98.3 – 1 279) n = 25	1.82 (0.97 – 7.11) n = 25	40.76 (11.2 – 158.7) n = 25	0.52 (0.19 – 2..92) n = 25
Mokrá, the vicinity of industrial source	12	1998-2001*	283.0 (29.0 – 2 953) n = 120	4.11 (1.78 – 27.5) n = 120	0.74 (0.11 – 64.7) n = 120	14.45 (0.80 – 6 120) n = 120	0.75 (0.06 – 8.39) n = 120				
	6	2000-2001*						61.2 (42.2 – 703.5) n = 12	0.78 (0.42 – 13.7) n = 12	11.97 (3.04 – 172.6) n = 12	0.29 (0.11 – 4.08) n = 12
Boarder mountains, background sites without local sources affected by LRT only	14	1994-1995, 1998-2001	3 213 (242 – 8 188) n = 23	26.2 (7.9 – 82.8) n = 21	1.34 (0.22 – 5.78) n = 15	55.0 (6.08 – 1 908) n = 21	2.21 (0.47 – 11.9) n = 21	1 900 (624.5 – 8 383) n = 23	28.5 (11.2 – 141.6) n = 23	242.6 (0.18 – 575) n = 15	6.4 (0 – 12.01) n = 15
Highways, the surroundings of main Czech highways	112	1999	192.8 (6.8 – 10 776) n = 60	3.9 (1.14 – 227.3) n = 45	1.18 (0.17 – 14.6) n = 45	12.88 (0.43 – 356.5) n = 45	0.92 (0.05 – 6.6) n = 45	NA	NA	NA	NA

3.1.6.5 High-mountain ecosystems, using of needles as a bioindicator

Many recent studies have used vegetation which bioaccumulates organic pollutants for monitoring studies (Larsen et al., 1985; Reischl et al., 1989; Moser et al., 1991; Kylin 1994; Simonich and Hites, 1995). Vegetation has been used to indicate ubiquitous pollutant contamination levels. In order to determine the general contamination level of cities, countries, and continents, many samples from variety of locations are required in order to minimise the effect of point sources and overcome the inherent variability of samples from the same size. Vegetation integrates contamination over time, and vegetation samples are much easier to collect than air samples, especially in remote locations. Vegetation has been used to identify point sources of organic pollutants, to determine regional contamination within cities, countries, and continents, and to determine the global contamination of organic pollutants (Simonich and Hites, 1995).

Many studies have monitored the atmospheric deposition of both heavy metals and organic pollutants by epiphytic mosses (Oehme et al., 1985). Mosses do not have a root system, so that the uptake of nutritive substances and pollutants therefore occurs exclusively via the atmosphere. The annual rate of growth is easily detectable, which allows the determination of air pollutants collected during one growth period.

As biomonitors are also frequently used the outer waxy surfaces of pine needles, kale or grass, which absorb atmospheric lipophilic pollutants and serve as an excellent monitoring system for many of PTS (Buckley-Golder et al., 1999; Weiss et al., 1998, 2000; Calamari et al., 1991, 1994; Simonich et Hites, 1995; Holoubek et al., 2000). The advantage of biomonitors, such as pine needles, is that they are widely spread over Europe and samples can be easily obtained. As there is a database of

measurements taken from a wide range of locations over long periods of time, the analytical results from different locations or years can be compared. However, a linear correlation between PTS concentrations in pine needles, or any other vegetation, and the high volume samplers or deposition samples cannot be established. The concentrations in biomonitors reflect the ambient air concentrations during the time of exposure (growth period) of the plant. With pine needles, accumulating effects over several years can be determined.

Vegetation has been used by many countries to monitor ambient air concentrations. The use of these biomonitors was found useful for both routine programmes on a long-term basis and to identify potential hotspots around point sources of emissions. The use of kale was successfully implemented around a steel producing plant in Luxembourg, where mean concentrations up to 106 pg I-TEQ.g^{-1} d.m. were detected; in Germany 12.6 pg I-TEQ.g^{-1} d.m. were determined close to combustion sources. In Austria, spruce needles were used as biomonitors: the background concentrations were in a very narrow range between 0.3 and 1.9 pg I-TEQ.g^{-1} d.m. Normally, baseline concentrations were around 0.5 pg I-TEQ.g^{-1} d.m. in rural areas and around 1-1.7 pg I-TEQ.g^{-1} d.m. in urban areas. Studies from Bavaria and Hesse in Germany reported that mean dioxin concentrations in pine needle ranged from 0.53 to 1.64 pg I-TEQ.g^{-1} d.m. However, in the neighbourhood of the Brixlegg copper reclamation plant in Austria, between 51 and 86 pg I-TEQ.g^{-1} were determined. In Welsh Rye grass, which is typically exposed for four weeks during the summer, concentrations were between 0.5 and 1 pg I-TEQ.g^{-1} d.m. However, as mentioned above, a linear correlation between dioxin concentrations in vegetation and the high volume air samplers or deposition samples cannot be established.

One part of the Czech TOCOEN project activities is focused on the investigation selected PBT compounds (PAHs, PCBs, OCPs, PCDDs/Fs) in the air, soils and needles from sampling sites located in Czech boundary high-mountain ecosystems (Holoubek et al., 1994c, 1998a, b). Sampling sites were located in the boundary mountain and samples were selected during five sampling campaigns in 1994, 1995, 1996, 1998, 2001 (Tables 3-66 - 3-71). Concentrations of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and phenols were determined in samples of topsoil (horizon A), Scots pine (*Pinus sylvestris*) needles and lichen thalii *Hypogymnia physodes* (Migaszewski, 1999) in the highest parts of the Holy Cross Mts.

To test the hypothesis that the pine needles is a suitable monitoring matrix and to determine the extent of the DDT event(s) of 1983 - 84, the samples that been collected during the period July - September 1986 were analyzed (Eriksson et al., 1989). These samples were collected along a transect running from the south-west to the north-east of Western Europe, the detection of the prevailing winds in most of the study area. The sample trees were selected to reflect rural and remote rather than urban or industrial conditions.

The moss and pine needle samples were collected from the field sites of Project TOCOEN (Holoubek et al., 1990a) - from the surroundings of two industrial factories (The Coal and Gas Fuel Company Vresova (in the period 1991 – 1993), and DEZA Valasske Mezirici (1990 – 1991) (Holoubek et al., 1991), and from a background site at the Kosetice observatory (1988 - up to date) (Holoubek et al., 2000, 2001; Vaňa et al., 1997, 2001). A study of the spatial distribution and mixture of PAHs in pine needles sampled across the UK (Tremolada et al., 1996) showed that phenathrene was the predominant compound in PAH mixtures. This predominance was not observed in needles from CR. The detection of PAHs in all of the PAHs analysed in the moss and needle samples from those regional background site can be – similarly as for example in UK (Tremolada et al., 1996) - interpreted as evidence for widespread diffusive PAH contamination throughout the troposphere, which is supplemented in some areas by elevated inputs. Evidence for widespread diffusive inputs and environmental occurrence of PAHs in both countries (CR and UK) has been published previously (Holoubek et al., 1990b, Holoubek et al., 1991, Tremolada et al., 1996).

A series of papers by Kylin and co-workers (Kylin et al., 1994; Strachan et al., 1994; Eriksson et al., 1989; Jensen et al., 1992) has outlined the use of Scots pine (P. Sylvestris L.) needles to determine the

regional contamination of organochlorines in Europe. Calamari et al. (1994) used pine needles to determine regional contamination of DDT, HCHs and HCB in Europe. Samples were collected from Italy, Holland, Austria, Czechoslovakia, Finland, and Greece. The measured needle organochlorine concentrations were compared to previous studies in other European countries. These authors suggested that the organochlorine distribution pattern, or "fingerprint", in pine needles from a given country is dependent on use of the compounds in that country and on its socioeconomic conditions.

As Lead and co-workers clearly described (Lead et al., 1996), the various plant species are ideal biomonitors. They play an important role in the global cycling of POPs since they cover over 80 % of the earth´s land surface, the surface area of plants is generally much greater than the area of the ground they cover, and the vegetation has a high lipid fraction which is likely to accumulate lipophilic persistent organic compounds.

Persistent organochlorine compounds (OCPs, PCBs, PCDDs/Fs) in spruce needles from Western Finland (Sinkkonen et al., 1995). The concentrations of α-HCH, lindane, DDT, DDE, and HCBz were on the same level as those measured by Jensen et al. (1992) in pine needles collected 1986 across Europe. Reischl et al.(1987). Have reported on somewhat higher concentrations in spruce needles collected from a rural area in Northern Bavaria. The study of the pathway of benzo(a)pyrene (BaP) migration from bulk deposition to soil and vegetation, with special emphasis on the forest ecosystem, was performed in Lithunia (Milukaite, 1998). 25 remote forest sites from all over Austria and located far away from settlements, factories and public roads were investigated (Weiss et al., 1998, 2000). All sites in the Alps are located several hundred meters above the bottom of the valley. Three exposed alpine mountains sites situated at one slope but at different altitudes (altitude profile) were included to investigate the influence of altitude on the concentrations detected (Weiss et al., 1996; 1998a; Horstmann and McLachlan, 1998). Scots pine (*Pinus sylvestris* L.) bark samples were collected at two field sites (Neuglobsow, Rösa) and in different years between 1987 and 1996 in the east of Germany (Schulz et al., 1999).

3.1.6.6 Terrestrial wildlife

An important part of the programme the German Environmnetal Specimen Bank is focused on the terrestrial ecosystems especially in the areas of the national parks of mud flats in Schelswig-Holstein and Lower Sacony (North Sea) and the areas of Sarland and the Halle/Leipzig/Bitterfeld as urban-industrialized regions (Kettrup et al.). For screening purposes individual samples were also collected in the National Parks of Berchtesgaden and Bavarian Forest in order to determine individual differences in biology and pollution exposure of similar specimens.

Soil samples, earthworms (*Lumbricus terrestris* and *Allolobophora longa*), and deer livers (*Capreolus capreolus*) as well as in city dove eggs (Columbia livia f. domestica) were analysed for the PTS under list of SC contents in these model regions.

The concentrations of organochlororine insecticides and PCBs were measured in eggs, brains, livers, carcasses and stomac contents (wet weight) and lipids of house sparrow (Passer domesticus) and tree sparrow (Passer montanus) nestlings in 1988 - 1989, and in 1995 only in brains of mature and one-year birds (Niewiadowska et al., 1998). The study was conducted in suburban areas of Warsaw characterized by small farms and houses surrounded by gardens and fields. These fields were treated with DDT in 1950s and 1960s. In Poland concentrations of DDT and its derivatives in animal tissues have declined 10 - 20 fold since 1975. It was widely used in years 1955 - 1975 to fight against the Colorado beetle. It was banned from retail trade in 1971 and withdrawn from use by 1974.

The contamination of whole bodies and brains of house sparrow (Passer domesticus) and tree sparrow (Passer montanus) as indicators of contamination with organochlorine pesticides and PCBs were studied in rural and suburban areas near Warshaw (Pinowski et al., 1999). Between 1950s and 1975, both study areas were treated with DDT in an effort to combat the Colorado beetle.

3.1.6.7 Cow´s milk

Cows' milk has been used by several countries as a biomonitor for ambient air contamination around potential dioxin point sources. Based on experiences from The Netherlands and Germany, cows' milk concentrations around 1 to 3 pg I-TEQ.g^{-1} fat should be considered as background for highly industrialised and densely populated countries. Both countries have set upper limits for the marketing of cows' milk, which are at 5 and 6 pg I-TEQ.g^{-1} fat, respectively. The German regulation states that if dioxin concentrations above 3 pg I-TEQ.g^{-1} fat are detected, such concentrations should not be considered as background; a nearby dioxin source should be identified and, if possible, eliminated. In view of these experiences and guidelines, the numbers in Table 3-71 show data from hotspots that have been identified and subsequently monitored in Austria. The case of the Brixlegg copper reclamation plant in Austria revealed a severe problem for the farmers in the neighbourhood. In Austria, it was more than five years before the dioxin concentrations returned to background levels. The surveys performed in Ireland were designed to obtain a general overview on concentrations in cows' milk and did not target any point source. All concentrations were very low, based on general European data for dairy products.

Table 3-71: Summary cows' milk concentrations as biomonitors around potential dioxin point-sources from EU Member States [pg TEQ.g^{-1} fat]

	Austria	Ireland
Source	Copper reclamation plant	General surveys, no point source
Range	5-69.5	0.13-1.5

To assess the presence of PCDDs/Fs in the Irish environment, the Environmental Protection Agency (EPA) of Ireland conducted a study on the levels of PCDD/Fs in cow's milk in 1995 (Hamm et al., 2001). It was found that I-TEQs in Irish cow's milk samples from so-called background stations were lower than e.g. in other European countries.

When comparing the PCDD/F TEQs of the Irish cow's milk samples from the current study with those of 1995, it can be seen that the low PCDD/F level found in 1995 is confirmed by the year-2000 data. As can be seen from Table 3-72, the range of values is even slightly lower in the background samples from 2000. I-TEQs are used for comparison since the older data were calculated by using I-TEFs. Compared to recent cow's milk data from other European countries (e.g. France, Germany, Spain) the dioxin levels of Irish cow's milk are still in the lowest range. The same seems to be true for the total TEQ when including the dioxin-like PCBs.

Table 3-72: Comparison of the 1995 and 2000 PCDD/F data of Irish cow's milk from background locations

Year of sampling	Minimum [pg I-TEQ.g^{-1} fat]	Maximum [pg I-TEQ.g^{-1} fat]	Median [pg I-TEQ.g^{-1} fat]	Mean [pg I-TEQ.g^{-1} fat]
1995 (n=20)	0.14	0.50	0.21	0.23
2000 (n=24)	0.09	0.35	0.20	0.20

3.1.6.8 Sewage sludge

In Austria and Germany, sewage sludge for application in agriculture has to be analysed for dioxins and comply with legal limit values. These countries have established a maximum permissible concentration of 100 pg I-TEQ per g dry matter for sewage sludge applied to agricultural land. Additional data were available from Denmark, and the UK. As can be seen from Table 3-73, in general, the concentrations ranged from below 1 pg I-TEQ.g^{-1} d.m. to around 200 pg I-TEQ.g^{-1} d.m, with levels in Germany reaching over 1 000 pg TEQ.g^{-1} d.m. Average concentrations of dioxin in sewage sludge are quite similar for each country, lying between 15 and 40 pg I-TEQ.g^{-1} d.m. These

findings indicate that similar sources are responsible for the contamination in sludge. The results, mainly from Germany and Sweden, revealed that "normal" effluents from households, especially from washing machines, could explain these results. Additional inputs can originate from dishwashers but also run-off from streets and from roofs. Industrial inputs, where untreated effluents enter the municipal sewer systems, can cause very high contamination in sewage sludge. In such cases, more than 1 000 pg I-TEQ.g^{-1} d.m. have been detected.

Table 3-73: Summary of sewage sludge concentrations from EU Member States [pg TEQ.g^{-1} d.m.]

Country	Austria	Denmark	Germany	Sweden	UK
Range	8.1-38	0.7-55	0.7-1,207	0.02-115	9-192
Average	14.5	21	20-40	20	

3.1.6.9 References

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Table 3-66: DDTs in soils [ng.g^{-1} d.m.]

Country	Sampling sites	Duration	Typical range					Comments	References
			Near the sources	Urban/ industrial	Rural	Background	Others		
Austria	Remote forest				n.d. - 22 (n=25)				Weiss (1998)
	Remote forest (pine needles)				n.d. – 2.38 (n=24)				Weiss (1998)
	Pine needles				2.3 – 8.2				Calamari et. al. (1994)
Bulgaria	Various	1999					DDE - 5.1 - 386.3 DDD - 0.96 - 68.8 DDT - 4.3 - 495.8	Arable and forest soils	Shegunova et al., 2001
Czech R.	Various						1.3 - 5 177		Holoubek et al. (2000)
	Agricultural 27 contaminated plots, 22 reference plots	from 1992					35.7 - mean 12.2 - median 22.7 - mean 7.5 - median	plough layer subsoil	Sanka, 2001
	Pine needles				12.1 - 112				Calamari et. al. (1994)
Finland	Pine needles				0.7 – 1.0				Calamari et. al. (1994)
Netherland	Pine needles				2.5 – 5.6				Calamari et.

s									al. (1994)
Poland	Katowice			23 -260					Falandysz et al. (2000)
	Krakow			4.3 - 4300					Falandysz et al. (2000)
Romania	Various						85 - 2460		Dumitru
	Various (n=46)	2000	79.9 Ramnicu Valcea/near OLTICHIM factory	113.1±151.8 - urban n=13 71.5±35.9 - industrial n=2	226.9±157.2 n=7	3.5-119.5 35.5±42.9 Issay, n=20	100.7±120.4 waste soils n=4	6 isomers	Covaci et al. (2001)
Slovakia	Various						1 - 2073		Schlosserova (1993)
	Various						0.65 - 490		Kocan et al. (1999a,b)

Table 3-67: HCB in soils [ng.g^{-1} d.m.]

Country	Sampling sites	Duration	Typical range					Comments	References
			Near the sources	Urban/industrial	Rural	Background	Others		
Austria	Remote forest				n.d. – 1.85 (n=25)				Weiss (1998)
	Remote forest (pine needles)				0.34 – 1.06 (n=24)				Weiss (1998)
	Pine needles				4 - 17				Calamari et. al. (1994)
Czech R.									
	Agricultural 27 contaminated plots, 22 reference plots	from 1992					2.26 - mean 1.74 - median 1.59 - mean < 1.0 - median	plough layer subsoil	Sanka, 2001
	Pine needles				4.6 - 30				Calamari et. al. (1994)
Finland	Pine needls						0.21 – 0.73		Sinkkonen et al. (1995)
	Pine needles				2 – 2.8				Calamari et. al. (1994)
Netherlands	Pine needles				3.2 – 4.3				Calamari et. al. (1994)
Poland	Katowice			0.46 - 30					Falandysz et al. (2000)
	Krakow			0.19 – 9.9					Falandysz et al. (2000)
Romania	Various (n=46)	2000	337.4 Ramnicu Valcea/near OLTICHIM factory	1.9±2.1 - urban n=13 0.9±0.8 – industrial, n=2	0.30±0.11 n=7	ND-0.18 0.07±0.02 Issay, n=20	0.9±0.6 waste soils n=4		Covaci et al. (2001)
Slovakia	Various						3.9 - 1609		Schlosserova (1993)
	Various						<0.05 – 8.9		Kocan et al. (1999a,b)

Table 3-68: PCBs [ng.g^{-1} d.m.]

Country	Sampling sites	Duration	Typical range					Comments	References
			Near the sources	Urban/ind	Rural	Background	Others		
Austria	Remote forest				0.2 – 7.5 (n=25)				Weiss (1998)

	Remote forest (pine needles)				n.d. – 0.4 (n=24)				Weiss (1998)
Bulgaria	96 soils	1999				1			Atanasov et al., 2001
	Various	1999					below LOD	Arable and forest soils	Shegunova et al.
Czech R.									
	Agricultural 27 contaminated plots, 22 reference plots	from 1992					7.0 - mean 1.5 - median 3.3 - mean 1.5 - median	plough layer subsoil 6 congeners	Sanka, 2001
Germany	Various						12 - 46		Krauss et al. (2000)
Norway	Various						6.1 – 52.1		Lead et al. (1996)
Poland	Swinoujscie		32 - 3400						Falandysz et al. (1997)
	Katowice			67 - 870					Falandysz et al. (2000)
	Krakow			4.6 - 110					Falandysz et al. (2000)
Romania	Various (n=46)	2000	722.2 Ramnicu Valcea/near OLTICHIM factory	57.3±41.0 - urban n=13 23.1±17.3 - industrial n=2	4.0±2.5 n=7	1.8-8.5 3.5±1.6 Issay, n=20	63.2±35.3 waste soils n=4	19 congeners	Covaci et al. (2001)
Slovakia	Various						10 - 560		Schlosserova (1993)
	Various		53000 µg g^{-1}		35 000		400 – 5800 (landfill)		Kocan et al. (1999a,b)
UK	Various						1.1 – 1600 (n=46)		Lead et al. (1997)

Table 3-69: PCDD/Fs in soils [pg TEQ.g^{-1} d.m.]

Country	Sampling sites	Duration	Typical range					Comments	References
			Near the sources	Urban/ind	Rural	Background	Others		
Austria	Various		332		1-64			Rural inc. Forest/pasture	Buckley-Golder et al., (1999)
	Remote forest				106 – 2676 (n=25)				Weiss (1997)
	Remote forest (pine needles)				14.3 – 168 (n=24)				Weiss (1997)
Belgium	Various				2.1-8.9				Buckley-Golder et al., (1999)
Czech R.			See Table						Holoubek et al., 2002
	Agricultural 27 contaminated plots, 22 reference plots	from 1992					35.7 - mean 12.2 - median 22.7 - mean 7.5 - median	plough layer subsoil	Sanka, 2001

Denmark	Newly ploughed fields or grass fields, or grass lawn in parks or garden	Fall 2001	Topsoil near to sources – 0.25-3 pg I-TEQ.g^{-1} The background level 0.20 pg I-TEQ.g^{-1} The mean of exposed zone 0.18 pg I-TEQ.g^{-1}					representative for agriculture, park, or garden soil; no direct contamination from ash, sludge or chemicals, sampling depth 0-10 cm	Vikelsøe, 2002
Finland	Various		>90 000						Buckley-Golder et al., (1999)
Germany	Various		30 000		1-30			Rural inc. Forest, pasture, arable	Buckley-Golder et al., (1999)
	Soil – 2 502 samples		Median below 20 pg I-TEQ.g^{-1} dm. Soil all types – median – 4 pg I-TEQ.g^{-1} dm, 90 percentile – 26 pg I-TEQ.g^{-1} dm Organic layers - median – 17 pg I-TEQ.g^{-1} dm, 90 percentile – 43 pg I-TEQ.g^{-1} dm Top soils - median – 3 pg I-TEQ.g^{-1} dm, 90 percentile – 16 pg I-TEQ.g^{-1} dm						Fiedler et al., 2002
Ireland	Various				1-13			Rural inc. Forst, pasture	Buckley-Golder et al., (1999)
Luxemburg	Various				1.8-20			Rural inc. Forest	Buckley-Golder et al., (1999)
Netherlands	Various		98000		2.2-16				Buckley-Golder et al., (1999)
Russian F.	Bashkortostan		Khimprom (200 m) (n=4) 207.2 ± 10.7	n=32 3.24 ± 0.73	n=67 0.25 ± 0.15	Game reserve national parks n=5 0.15 ± 0.1			Amirova, 2002
			Khimprom Soil: 0.99 – 10.04 Wall plaste scrapes: 1.54 – 6.60						
	Republic Komi		Near silicate plants: 0.5 Oil refinery: 1.19	1.96 – 2.9	0.27			City Ukchta	
	Chuvash Republic		Khimprom: 0.7 – 0.8 (n=5)		0.24				
Sweden	Various		11 446		<1				Buckley-Golder et al., (1999)
UK	Various		1 585		<1-87				Buckley-Golder et al., (1999)
	Various			4 800 - 87 000	800 - 18 000				HMIP (1994)

Table 3-70: HCHs in soils [ng.g^{-1} d.m.]

Country	Sampling sites	Duration	Typical range					Comments	References
			Near the sources	Urban/ ind	Rural	Background	Others		

Austria	Remote forest				0.6 – 6.6 (n=25)				Weiss (1998)
	Remote forest (pine needles)				2.8 – 9.7 (n=24)				Weiss (1998)
	Pine needles				11 - 51				Calamari et. al. (1994)
Czech R.			See Table						Holoubek et al., 2002
	Pine needles				15 - 87				Calamari et. al. (1994)
Finland	Pine needles						0.4 – 1.71		Sinkkonen et al. (1995)
	Pine needles				2.2 – 4.0				Calamari et. al. (1994)
Netherlands	Pine needles				9.5 - 26				Calamari et. al. (1994)
Poland	Katowice			1.1 - 11					Falandysz et al. (2000)
	Krakow			0.36 - 110					Falandysz et al. (2000)
Romania	Various						34 - 800		Dumitru
	Various (n=46)	2000	2 584.8 Ramnicu Valcea/near OLTICHIM factory	29.17±27.4 - urban n=13 6.5±1.6 - industrial n=2	28.4±33.7 n=7	0.7-7.3 1.9±1.7 Issay, n=20		α–, β–, γ–	Covaci et al. (2001)
Slovakia	Agricultural						mean - 25 9 9 10.9 - 16.8	1986 - 89 n = 337 1991 - 92 n = 152 1992 - 93 n = 396 1987 - 89 - gardens in the vicinity of the formel HCH producer	Schlosserova (1993) Holoubek et al. (2000)

Table 3-71: PAHs in soils [ng.g^{-1} d.m.]

Country	Sampling sites	Duration	Typical range				Comments	References
			Urban/ind	Rural	Background	Others		
Austria	Remote forest			68 - 1342 (n=25)				Weiss (1998)
	Remote forest (pine needles)			15.3 - 261 (n=24)				Weiss (1998)
Bulgaria	96 soils	1999			2 - 22			Atanasov et al., 2001
	Various	1999				36 - 68	Arable and forest soils	Shegunova et al.
Czech R.	Various		170-45 750 (n=99)			0-350 BaP only (n=145)		Maliszewska-Kordybach (1999).
	Brno (Urban)		170 – 45 750 (n=54)					Sanka et al. (1995)
	Brno (Urban)		369 – 5 078 (n=13)					Holoubek et al. (1994)
	Agricultural 27 contaminated plots, 22 reference plots	from 1992				1 066.0 - mean 594.6 - median 591.7 - mean 256.7 - median	plough layer subsoil 16 PAHs	Sanka, 2001
			See Table					Holoubek et al., 2002
	Mosses		<0.3 – 16 700		<0.3 - 4700			Holoubek et al. (1990)

	Pine needles		<0.3 – 18 590		<0.3 – 19 250			Holoubek et al. (1990)
Estonia	Tallin, Pärno, Kohtla-Järve (Urban)		2240 – 12 390	100				Trapido (1999)
Germany	Bavaria (Others)					321 (mean, n=85)		Maliszewska-Kordybach (1999).
	Borhover (Rural)			69 – 19 260 (n=60)				
	Bonn/Stalberg (Urban)		356-28 900 (n=49)					
	Various					841 – 9 272		Krauss et al. (2000)
	Bonn					430 – 1 780		Tebaay et al. (1993)
Poland	Lublin		70-2 787 (n=136) (median=196 , mean=248					Maliszewska-Kordybach (1999)
	Wilkow			81-645 (n=56)				
	Various urban				72-29 000 (n=59)			
	West-north-east part					110-4 122 (n=80) (median=346, mean=520		
	Arable, n=216					75 - 11 391 Mean=520, median=294		
Moldova	77 samples					Mean - 241.3 Median - 88.2	Different soil depth	Teyrytze et al., 2001
Russian F.	Ostashkov (Rural)			60 (mean, n=52)				Maliszewska-Kordybach (1999)
	Chelyabinsk (Urban)		109-1 815 (n=23)					
Slovakia	Various					210 - 12254		Schlosserova (1993)
Switzerland	Bern		4 800 (n=19)					Maliszewska-Kordybach (1999)
UK	Various					20 - 7400		Cousins et al. (1997)
	Various		4240 (n=60)	187 (mean, n=30)		106-6400 (n=46)		Maliszewska-Kordybach (1999).
	Pine needles					19 – 3090		Tremolada et al. (1996)

3.1.7 Hot spots

3.1.7.1 Introduction

The sources and environmental levels of the PTSs in the countries of Central and Eastern Europe are broadly described in the State-of-the-Art Report (Holoubek et al., 2000). The first complex descriptions of the state of environmental pollution with PTS types of compounds in Central and Eastern European countries (CEECs), was prepared by Heinisch et al. (1994,1997a,b,c).

Special attention must be given to obsolete PTS pesticides. This problem poses the greatest danger to the environment and people, which is brought about by chemization of agriculture in the CEE countries. The countries have not solved the safe storage of pesticides and other chemicals classified as hazardous and they have little information concerning the quantity of pesticide and chemical (e.g. PCBs) waste. Many of the CEE countries have no special sites for the storage of hazardous waste or installations in which these types of chemicals could be safely disposed of by combustion or non-combustion processes. In Poland, the stockpile of obsolete pesticides is estimated to be about 60 000 tonnes – about 10 000 t in tombs, 25 000 t in storehouses and about 25 000 t at farms round the country (Stobiecki, 1998). The 1996 inventory of banned organochlorine pesticides stockpiles in

Bulgaria showed about 35 t, which is relative high quantity for the small territory of Bulgaria (Tasheva, 1998). There are 15 000 t or 22 000 000 t stockpiles in Ukraine mostly containing pesticides (Kundiev, 1997). The situation with obsolete organochlorine pesticides might be similar in other CEE countries.

In some countries of the region (e.g. in Bulgaria) it was recognized that PBT pesticides in environmental media decreased on such levels that no further systematic monitoring is needed (Tasheva, 1998). Different situation was observed in Rumania (PHARE, 1997; Bratanova et al., 1998; Toader and Chitimiea, 1998) where still relatively high concentrations of DDT and other chlorinated pesticides are found in water and sediments. In the Slovakia, measured data has shown high human exposure to HCB from unknown sources (UNEP, 1999; Kocan et al, 1994, 1996, 1998).

Some pesticides from the UN-ECE POP list, have never been used in many countries from this region (aldrin, chlordane, mirex, heptachlor, toxaphen). Their use was banned or restricted. Hungary was among the first countries in the world, which banned or severely restricted chlorinated pesticides already in 1966 (UNEP, 1999).

Main sources of PCDDs/Fs in the region are typical for industrialized countries - they are formed as by-products, mainly in chemical industry - production of chlorophenols and their derivatives (former Czechoslovakia, USSR, former East Germany, Poland, probably Romania), processes in which chlorinated catalysts and solvents are used; pulp and paper production - bleaching based on chlorine treatment, metallurgical production - if metal chlorides are used, magnesium production, metal scrap recycling; municipal, hospital, hazardous and industrial waste incineration; solid fossil fuel combustion (coal, wood, peat), internal-combustion engine operation - leaded petrol use with the addition of chlorinated compounds; dry distillation (dry cleaning of clothes); fires (forest, agriculture, buildings).

3.1.7.2 Former USSR

The highest levels of atmospheric air pollution with polycyclic aromatic hydrocarbons (PAHs) are found in cities where the world`s largest aluminium and steel plants are located: Shelekhov, Novokyznetsk, Bratsk, Magnitogorsk, Nizny Tagil, Krasnoyarsk, Chelyabinsk and some others, where the PAH content in the air amounts to 5 – 15 $ng.m^{-3}$ (Kurlyansky, 1997). By the data (Milyaev, 1997), total emissions of benzo(a)pyrene in Russia in 1991 and 1992 were 174.863 ($t.y^{-1}$) and 89.408 ($t.y^{-1}$) respectively.

Ten thousands of tonnes of DDT and HCH were used in the USSR in the period of 1950s-80s. DDT was being used even almost 20 years after its ban (Fedorov, 1999; Fedorov,Yablokov, 1999, Kundiev, 1997).

The pollution by dioxins and dioxin-like compounds are especially serious in the cities of (1) former chemical weapons production (Novocheboksarsk, Volgograd, Dzerdzinsk, Chapaevsk, Berezniki, Novomoscowsk, etc.), (2) former PCB production and capacitors filled with PCBs (Dzerdzinsk, Novomoscowsk, Serpukhov, etc.), and (3) the manufcture of organochlorine pesticides (Ufa, Chapaevsk, Volgograd, Novocheboksarsk, Dzerdzinsk, Vulnary, etc.) (Fedorov, 1999; Fedorov, Yablokov, 1999).

In Russia, PCBs were produced from 1939 to 1989-1993 mainly at plants “Orgsteklo” (Dzerdzinsk) and “ Orgsynthesis” (Novomoscowsk) under three trademarks: Sovol (a mixture of tetra- and pentachlorinated PCBs used as a plasticiser in paints and varnishes, total 1939-1993 production was 52 500 t; Sovtol (Sovol mixed with 1,2,4-trichlorobenzene mostly in a ratio of 9:1, then called Sovtol-10, used in transformers, total 1939-1990 production – 57 000 t) and TCB (mixed isomers of trichlorobiphenyl used in capacitors, total 1968-1990 production – 70 000 t (AMAP, Report, 2000).

It was shown that the most contaminated are the Central, Ural and North-Western Russian economic regions. Ufa, Shchelkovo, Noginsk, Chapayevsk and Dzerzhinsk (where chemical plants using chlorophenols operate) are characterized by increased dioxin levels in the environment (Danilina, 1997). It was estimated that in 1995 dioxin emissions in the areas of Chapayevsk, Dzersinsk and Ufa were 740 g, 480 g and 900 g respectively (Kurlyanski, 1997). Dioxin air pollution also may have other sources. High dioxin concentrations were observed in workmen´s settlement in Chapaevsk and other sites outside of plant. The origins of this dioxin contamination are most likely atmospheric transport and deposition from the plant territory. High PCB levels were found in soil samples taken in 1988 the vicinity of a capacitor plant in Serpuchov: 2 km to the north from the plant concentration was up to 35.7 ppm, and at 0,3 km to the south - up to 11 000 ppm. There is a serious dioxin pollution of water sources in the towns, including Belaya River with tributaries in Ufa, Chapayevka River in Chapayevsk (and the Volga) and others.

The main source of dioxin contamination in Ufa is the plant Khimprom. For 55 years of the plant operation several chloroorganic products containing dioxins as by-products have been manufactured at large scale – 2,4-D, 2,4,5-trichlorphenol (TCP) and other chlorophenols. In 1964-1967, there was the production of butyl ester of 2,4,5- trichlorophenoxyacetic acid (50-60 tons per month). During the production 128 cases of chloracne at workers. Industrial buildings where these chemicals were produced still exist and they remain hazardous in terms of dioxin pollution. This situation is similar to that of in the Czech Republic (see further). The production rate of 2,4,5-TCP and 2,4,5-trichlorphenolate of copper in 1962-1987 was 100-120 tons and 35 tons per year respectively. Samples of technical 2,4,5-TCP contained up to 0.65 ppm of 2,3,7,8-TCDD. Such a long period of producing dioxin hazardous products resulted in pollution of the Khimprom plant territory. Soil samples from the plant territory contain dioxin from 0.4 to 10 ppb including the soil at the depth of several meters. The highest pollution was found in the samples taken near a chlororganic waste incinerator that had been a source of dioxin emission for a long time. The territory of the industrial waste landfill site is an area of extreme pollution. Thus in bottom sediment of the pond formed by ground waters from the plant and landfill site territory the concentration of 200 ppb was found. Analyses of human milk samples taken in towns villages of the region showed the highest levels in samples from Ufa and from neighbouring (about 100 km) Blagoveshchensk (25.9-27.1 pg TEQ.g^{-1}). This is most probably due to transfer of pollution from the chemical plants to the town. Increased PCDDs/Fs level in milk samples from Iglinsky and Sterlitamaksky (21.9 and 26.7 pg TEQ.g^{-1}) districts are accounted for by their location in the vicinity of industrial centres.

3.1.7.3 PCBs in Slovakia

PCBs called Delor (Delotherm, Hydelor) were produced in the Chemko chemical plant in Strazske (Michalovce District) in eastern Slovakia from 1959 to 1984. These formulations were used as a dielectric fluid in power capacitors produced in a Czech electrotechnical factory (ZEZ Zamberk) and transformers produced also in the Czech Republic, as a filling in heat-exchanging and hydraulic systems and as an additive to synthetic paints. Officially 21 482 tonnes of PCBs were produced: 9 869 tonnes, i.e. 46 percent, was exported mainly to former East Germany and the rest, i.e. 11 613 t was used inside former Czechoslovakia [Kocan et al. 1998]. There was an attempt to manufacture polychlorinated terphenyls in Chemko. About 35 t were produced of which about 30 t were used at glue production for furniture industry. Production devices as well as those for the PCB production corroded to a large extent resulting in leakage of a reaction mixture.

It has been estimated that in addition to the amount produced about 1 600 t of PCB waste were generated during the production. A part of the Chemko PCB waste entered the environment mainly via the factory effluent canal causing the contamination of the Laborec River and Zemplinska Sirava Lake. Another part could lie at a Chemko landfill site in a form of contaminated soil mixed with miscellaneous production waste. The rest, that is about 1 000 t, is stored in store-houses situated on the territory of the factory including lots of drums that were collected in 1992 in a forest area above the Chemko factory. There is an ongoing project dealing with the non-combustion disposal of the waste. It

should be noticed that during the production a part of the distillation residues was mixed with heavy oil and used as fuel in a factory heating plant. About 115 t of unsold and used PCBs stored at Chemko were burned in the 1970/80s in Slovakia's cement kilns.

PCB formulations are still used in Slovakia in closed systems. According to questionnaires sent in 1997 to PCB users, the PCBs are used only in power capacitors which are located at transformer and switchgear units. In 2001, another inventory aimed at PCBs still used in running equipment has launched in Slovakia. Devices, e.g. capacitors or transformers recognized to contain PCBs will be labeled and registered in order to be easily identified when POP disposal will start. There is little information on the present use of PCBs in heat exchanging systems which were an important source of environmental contamination with PCBs in the past. Lots of heat exchangers around Slovakia used PCB fluids (e.g. facilities preparing asphalted gravel for road construction). Several years ago some companies managing those facilities collected used PCBs and ensured their disposal abroad by incineration. Contaminated soil however has not been removed. Up to 1 000 t of PCBs could be encased in power capacitors that are still in use or disabled and stored at their users.

Analyses showed that the highest PCB levels were found in a muddy part of an effluent canal flowing from the Chemko factory (mean 3 000 ppm, dry weight). No doubt that the polluted effluent canal emptying into the Laborec River has caused its contamination (3.9 ppm behind vs 0.052 ppm in front of the confluence). The Zemplinska Sirava Lake (33.5 km^2 in surface area) that is partly filled from the Laborec contained several hundred times higher PCB levels if compared with a similar lake in a control area (1.7 to 3.1 ppm vs 0.007 to 0.01 ppm). The control area was the Stropkov district about 60 km upwind and upstream far from Chemko in Strazske. Based on those findings, one can estimate that at least tonnes of PCBs are still adsorbed in the sediments of the effluent canal, Zemplinska Sirava and Laborec (Kocan et al. 1999, 2001, Petrik et al. 2001b).

Samples were taken from an upper soil layer near the disposal sites of the PCB manufacturer (Chemko), agricultural fields in the districts of Michalovce (polluted area) and Stropkov (control area), and at several plants around Slovakia preparing gravel coated with asphalt formerly using PCBs in their heat-exchangers. PCB levels in the soil samples taken from the agricultural fields near some towns and villages were considerably lower (on average 0.008 ppm) than those taken from the neighbourhood of the disposal sites and plants mixing asphalt and gravel. Those plants situated often close to quarries, i.e. in mountains on rocky ground, have been preparing asphalted gravel to be used for road construction. It is known that because of the untightness in heat-exchanging systems filled with PCBs hundreds of tonnes of PCBs leaked from those systems. PCB concentrations peaked at 53 000 ppm in a soil sample taken under one of the heat-exchangers. However, high PCB levels were also observed in agricultural (35 and 38 ppm) or forest soil (3.9 and 7.5 ppm) taken near those plants. As soil from the vicinity of the major Chemko landfill site, which could be contaminated by air transported particles only, contained increased PCB levels (0.4 to 5.8 ppm), it is likely that this dump may contain large quantities of PCBs. Similarly PCB waste might be present in the municipal dump of Michalovce (district town) since increased PCB concentrations were found in a sample collected close to the dump (0.17 ppm) (Kocan et al. 1999, 2001).

Likewise the sediment, fish from the Michalovce waters contained much higher PCB levels than those from the control area. The maximum lipid adjusted value peaked even at 900 ppm. It was confirmed that predatory fishes are more exposed than fishes feeding on plankton or benthic food. It was observed that the environmental pollution of the Michalovce District with PCBs has reflected in the exposure of forest and field wildlife, as well.

Higher PCB content found in some foods available in the polluted district of Michalovce in particular that coming from locally raised animals has evidently caused increased exposure of the human population of that district. Average PCB concentration of 4.2 ppm in blood lipids taken from the human general population long-term living in the Michalovce District was 3.5-times higher than that in the control Stropkov area (1.2 ppm). People eating foods coming from animals kept on small family

farms at their houses and fed mainly with local feed contained significantly higher PCB levels in their blood serum lipids. While average 8.6 ppm was found in the blood lipids of the former Chemko workers the blood lipids of fishermen consuming fish from Laborec and Zemplinska Sirava contained even 11.2 ppm on average (the max value was 60 ppm; the highest level found in the blood lipids of a fisherman outside the study was 230 ppm).

Within the 2nd round of the WHO-coordinated exposure study on the levels of PCBs, PCDDs and PCDFs in human milk running in 1993 it was shown that PCB content in samples coming from the area of former PCB production in Slovakia and an area of PCB application (paint industry) in the Czech Republic were 3—25-times higher than levels in samples from other European countries. Dioxin levels were similar to the European average although PCDF contribution was dominating because of high PCB exposure (WHO/ECEH 1996).

3.1.7.4 Spolana Neratovice in the Czech Republic

The chemical factory of Spolana Neratovice is situated approximately 25 km north of Prague at the Elbe River. It produced in the period of 1965-68 the chlorine herbicide 2,4,5-T and chlorinated phenols. A part of 2,4,5-T was even exported to the USA and was applied as the component of "Agent Orange" within the Vietnam war. During the production due to breaking technological conditions, a huge amount of dioxins (in particular, the most toxic 2,3,7,8-TCDD) was formed and former factory buildings containing products, intermediates, installations, etc. belong currently to the most dioxin-contaminated sites on the globe. Moreover, soil in the factory is highly contaminated with organochlorine pesticides produced there, as well. The 2,4,5-T and chlorophenols production was stopped in 1968 when about 80 cases of occupational diseases developed (55 workers were hospitalized mainly with severe chloracne manifestations and porphyria) (Pazderova-Vejlupkova et al., 1981, Pelclova et al., 2001).

Chemical analysis proved an extremely a high degree of the contamination of waste products stored in production buildings, building walls and floors, air, soil and ground water. The highest concentration of dioxins (over 24 ppm of 2378-TCDD) was measured in the residues of chemical substances. It is assumed that there are tons of that waste stored in the buildings. The immediate toxic impact of dioxins in the air of the contaminated buildings was proven by a rabbit experiment in the 1970s. Rabbits in cages were located in the buildings to be exposed only to dioxin-contaminated air. The rabbits started to died on the 7th day of the experiment. Autopsy showed a significant damage of the liver, lung and kidney.

The Spolana factory including some of the dioxin-contaminated buildings were flooded in 2002 and one can expect dioxin release into agricultural fields and Elbe River and its sediment. An extend of environmental contamination shall be mapped in detail without delay as well as to start with the definitive solution of dioxin-contaminated buildings and soil in their vicinity in Spolana Neratovice (Zemek and Kocan, 1991, Kocan et al., 1991).

3.1.7.5 Bitterfeld

Besides the Buna-Werke, the chemical enterprise Chemiekombinat Bitterfelf (CKB) was the most important production and processing site of organochlorine substances in the former GDR. In 1980s, not only di-, tri- and tetrachloromethane and trichloroethane were produced in amounts of 10 000-20 000 $t.y^{-1}$, but also 73 000 t technical HCHs were synthesized in 1967-1982 and processed to 5 500 t of lindane. In the same period, estimated 50 000 t DDT were synthesized at the CKB. Especially problematically was the yield of very high amounts of waste products like hexa- and pentachloroethane and the above all the “ballast isomers” α–, β–, δ– and ε–HCH. These persistent and toxic substances were disposed of in former brown coal mines.

This procedure has led to environmental burdens because not only in the immediate vicinity of the CKB, but also in the river Mulde, directly influenced by the CKB, partially up to the present DDT and HCH may be found in the sediments and fishes. Comparisons with two other rivers from the region have been documented in Heinisch et al. (2001).

Time series of the course of DDTs and HCHs contents in monthly sediment samples of the rivers Mulde, Saale and Elbe in Saxony-Anhalt are shown in Table 3-74.

Table 3-74: Sediment contents of DDTs and HCHs in monthly collected sediment samples from the rivers Mulde, Saale and Elbe, Saxony-Anhalt (arithmetic means of all samples per year)

Year	Contents of Σ DDTs [ppb]			Contents of Σ HCHs [ppb]		
	Mulde/ Dessau	Elbe/ Magdeburg	Saale/ Gr. Rosenb.	Mulde/ Dessau	Elbe/ Magdeburg	Saale/ Gr. Rosenb.
1994	4 840	305	100	410	40	20
1995	1 590	290	90	855	230	15
1996	2 170	485	75	1 356	10	< 5
1997	445	225	70	235	20	< 5
1998	835	275	80	965	30	10
1999	1 040	285	65	970	25	10
Σ DDTs = Σ DDT + DDE + DDD (2,4´ isomers); Σ α– + β– + γ– + δ– + ε–HCH						

Especially the aquatic sediment represents a sink and slowly flowing source for the substances. The presence of partially strongly enhanced HCH and DDT concentrations in the vicinity of the CKB could be found in earthworms (*Lumbricus terrestris),* city dove eggs *(Colomba livia),* deer livers *(Capreolus capreolus)* and pine shoots *(Pinus sylvestris)* as late as in the ninetees.

3.1.7.7 References

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