# An Assessment of Environmental and Aquatic Ecosystem Contamination by Persistent Organochlorine Pollutants (POPs) in the Russian Federation

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**Global EnvironmentMonitoring System (GEMS)**

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# Abstract

*Persistent organochlorine pollutants* (POPs) are among a general class of slowly degrading, bioaccumulative xenobiotic compounds that have become ubiquitous contaminants of global ecosystems during the twentieth century. Like most industrialized countries, Russia and the former Soviet Union [FSU] produced and used certain POPs in appreciable quantity, but accounts of environmental contamination in Russia and the FSU republics have only emerged slowly since the disintegration of the FSU. This report reviews what is known about production, usage and general environmental occurrence of selected POPs, and examines some particular data sets and case studies that characterize POPs contamination in particular Russian aquatic systems. Discussion focuses mainly on the insecticides DDT and HCH; and the industrial contaminants PCBs and PCDD/Fs (dioxins and furans). DDT -and HCH were - widely used for agriculture and other purposes since the 1950s. While usage and environmental occurrence have broadly declined since the 1960s and 1970s, lindane (y-HCH) usage may be increasing and there is evidence of recent DDT usage. From the 1930s, the FSU produced about 125 Kt PCBs. There is serious environmental contamination near one production plant, and likely at others. There is also evidence of lower level, but widespread environmental contamination most likely due to insecure disposal of old electrical equipment. Amongst other sources, PCDD/Fs released unintentionally by chemical plants, pulp mills and chlorophenolic wood preservative usage at timber yards may pose locally significant risks. There is reason to suspect that heavy usage of contaminated herbicides and other agrochemicals in some regions of southern Russia may have caused widespread PCDD/F pollution; however, this remains to be confirmed by environmental measurements. Studies in specific aquatic ecosystems show that sediments in Lake Ladoga in northwestern Russia have PCB and PCDD/F contamination similar to that seen in Scandinavian water bodies. In the adjacent North Dvina River basin, indications are contradictory as river sediments have amongst the lowest PCDD/F levels ever reported despite evidence that several of Russia's largest pulp mills may be releasing appreciable PCDD/Fs. The ecosystem of Lake Baikal, widely considered to be the world's cleanest large lake, appears to be ultra sensitive to low inputs of POPs, and once contaminated make take centuries to cleanse itself. Although air, soil, sediment and water contamination are modest, the Baikal seal at the top of the food web has DDT and total PCB burdens second only to Baltic ringed seals, and appears to accumulate dioxin-like PCBs at appreciably greater levels than found in Baltic seals. The Sea of Azov likely suffers high pollution DDT, HCH, PCBs, and potentially by PCDD/Fs. Taken together, the current fragmentary information suggests that POPs contamination of Russian aquatic systems ranges from modest to potentially grave. PCBs may pose the greatest future risks as the current stocks are unknown, and there appear to be no policies to ensure the secure disposal of old electrical equipment.

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# Units and Reporting Conventions

## Time

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| s | second | | | | | | | | | |
| d | day | | | | | | | | | |
| a | annum | = | 1 | year | | | | | | |

## Distance

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| mm | millimetre | = | $10.^{3}$ | m | | | | | | |
| cm | centimetre | = | 10'2 | m | = | 10 mm | | | | |
| m | metre | | | | | | | | | |
| km | kilometre | = | $10^{3}$ | m | | | | | | |

## Area

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $m^{2}$ | square metre | | | | | | | | | |
| ha | hectare | = | $10^{4}$ | $m^{2}$ | | | | | | |
| $km^{2}$ | square kilometre | = | $10^{6}$ | $m^{2}$ | = | $10^{2}$ ha | | | | |

## Volume

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| L | liter | = | 10'3 | $m^{3}$ | | | | | | |
| $m^{3}$ | cubic metre | | | | | | | | | |
| $km^{3}$ | cubic kilometre | = | $10^{9}$ | $m^{3}$ | = | 1 | teralitre | | | |

## Mass

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| fg | femtogram | = | $10-^{15}$ | 9 | | | | | | |
| pg | picogram | = | $10-^{12}$ | 9 | | | | | | |
| ng | nanogram | = | $10-^{9}$ | 9 | | | | | | |
| ~g | microgram | = | 10-6 | 9 | | | | | | |
| mg | milligram | = | $10-^{3}$ | 9 | | | | | | |
| g | gram | | $10^{3}$ | | | | | | | |
| kg | kilogram | = | | 9 | | | | | | |
| t | tonne | = | $10^{3}$ | kg | = | $10^{6}$ | 9 | | | |
| Kt | kilotonne | = | $10^{3}$ | t | = | $10^{6}$ | kg | = | $10^{9}$ | 9 |
| Mt | megatonne | = | $10^{6}$ | t | = | $10^{9}$ | kg | = | $10^{12}$ | 9 |

## Pesticide Composition

| | |
|---|---|
| ai | active ingredient; used to denote mass of active chemical present in a pesticide formulation exclusive of dispersants, emulsifiers and other nominally inactive ingredients. |

## Reporting Bases: Solid Media

| | |
|---|---|
| WW | wet or fresh weight (mass strictly) before standard drying |
| dw | dry weight after standard drying |
| Iw | lipid or fat weight after normalizing to lipid content of sample |

## Large Numbers

As listed below, North American definitions of numbers greater than 1 million have been used herein:

| | |
|---|---|
| million | 1,000,000 |
| billion | 1,000,000,000 |
| trillion | 1,000,000,000,000 |
| quadrillion | 1,000,000,000,000,000 |

## MassNolume [MIV] to Mass/Mass [M/M] conversions for fluid concentration data

To directly compare mass ***I*** volume [MN] water concentrations with mass ***I*** mass [M/M] solid media (soil, sediment, biological tissue) concentrations, the water concentrations can be expressed approximately on an M/M basis for dilute aqueous solutions by noting that the density of freshwater is about 1,000 *g/L.* Therefore,

1 *mg/L* R: 1 mg *11* ,000 g R: 1 1 *J.l9/g*
J..L9/L R: 1 J..Lg *11* ,000 g R: 1 1 *ng/g*
ng/L R: 1 ng *11* ,000 g R: 1 pg/L 1 pg/g
R: 1 pg *11,000* g R: 1 *fg/g*

The approximation holds for typical freshwaters. The conversion can be adjusted for seawater using the standard seawater density of 1035.5 *g/L*

*MN* ground level air concentrations, e.g., *ng/m*$^3$, can be approximately converted to M/M concentrations using the standard sea level air density of 1.023 *kg/m*$^3$ at 15C.

## Mass / Mass [M/M] Units: ppm, ppb, ppt, ppq

The expression of M/M chemical concentrations as parts-per-million [ppm], parts-per-billion [ppb], parts-per-trillion [ppt], and parts-per-quadrillion [ppq], is a North American convention that has been deliberately avoided because of the potential confusion arising from the different definitions of large numbers greater than 1 million outside of North America.

# Notes on Russia

In the post-Soviet era, the two abbreviations listed below are now widely seen in literature on Russia and the former USSR:

- **FSU** - former Soviet Union,

- **NIS-** Newly Independent States, Le., the 15 former republics of the USSR.

The 89 internal political divisions of the Russian Federation are a source of much confusion to non-Russians. The main divisions are:

1. **Oblast** - Usually translated as *region,* occasionally as *province.* Oblast is retained herein to avoid confusion with generic usage of the word region. There are 49 Oblasts.

2. **Republic** - There were 21 Republics before the succession of Chechnya which now calls itself the Republic of Ichkeriya. Republics are nominally ethnically based.

3. **Kray** - Usually translated as *territory.* There are 6 Krays.

4. **Okrug** - Usually translated as *autonomous area;* however, the 10 Okrugs seem to be affiliated with or subservient to the aforementioned primary units. Okrugs appear to be ethnically based.

In addition, there are two ***federal** cities:* Moscow and S1. Petersburg, and one ***autonomous** oblast.*

# Chapter 1 Introduction

Since the advent of chlorine-based industrial chemistry about the 1920s, and particularly since World War II, *persistent organic pollutants* (POPs), which include such notoriously familiar chemicals as DDT, PCBs, and dioxins, have become widely dispersed throughout global ecosystems. By the 1990s, POPs were recognized as ubiquitous global contaminants and international efforts were organized to assess the status of these chemicals. In late 1995, the POPs threat to the marine environment was formally recognized by more than 100 countries in the **Washington Declaration on Protecting the Marine Environment from Land-based Activities** that included a call for "the development of a global, legally-binding instrument on persistent organic pollutants (POPS)"[1]. Under UNEP, a process has been initiated for scientific assessment of 12 specific POPs known as the *"dirty dozen".* The Washington Declaration also recognized "the need for regular reviews of the state of the world's marine and freshwater environments".

This report attempts to assess the status of POPs in aquatic systems in the Russian Federation. POPs production, usage and environmental contamination are now reasonably understood for much of the world, but knowledge of POPs contamination in Russia and the republics of the *former Soviet Union* [FSU] has only begun to emerge slowly since the disintegration of the FSU. This report focuses almost exclusively Russia, but occasional mention of the fifteen FSU republics or Newly Independent States [NIS] is unavoidable. Most POPs were produced and released during the Soviet regime when Russia and the NIS were formally unified.

While numerous accounts of environmental conditions in Russia and the FSU have emerged in the post-Soviet era, reliable accounts of POPs are few. Initial plans for a broad review of POPs contamination in aquatic systems were stalled by poor data availability and quality, circumstances that were compounded by limited and contradictory background information. Where POPs data are available, it can be exceedingly difficult to judge their reliability.

A solid foundation of reliable information on environmental conditions is essential for the identification of problems and the formulation of appropriate corrective actions. Consequently, this project adopted the more modest goals of summarizing what was known about the POPs of major global concern, and of reviewing several POPs data sets and geographically focused case studies. The result is a preliminary assessment that should help to characterize the dimensions of POPs contamination in Russia's environmental and aquatic ecosystems systems and to plan further action. The report

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[1] UNEP press release, November 7, 1995. See also UNEP/IRTPC WWIN pages regarding IFCS meetings on POPs, Manila, Philippines, 17- 22 June 1996, http://irptc.unep.ch/pops/manila/manexp10.html.

complements other good information that has now begun to emerge such as the relevant parts of the recent *State of the Arctic Environment Report* (AMAP, 1997).

## 1.1 POPs

Before proceeding, it is helpful to establish which POPs are addressed in the present report. These are listed in Table 1.1. The set is slightly modified from the UNEP *dirty dozen* list to include HCH because usage and environmental contamination are prevalent across Russia, and to exclude aldrin, endrin, and mirex because no data were available. This is mostly the same set of POPs considered in the AMAP Arctic assessment.

The *Persistent* ***Organochlorine*** *Pollutants* in Table 1.1 fall broadly in two classes: (1) pesticides, and (2) industrial contaminants. Of the pesticides, the two insecticides DOT and HCH receive most attention because they have been most heavily used and have ubiquitous environmental data. Amongst the many industrial POPs-class contaminants that might be considered, PCBs and PCDD/Fs are by far the most notorious. For convenience, PCDDs and PCDFs, are mostly treated jointly and collectively abbreviated PCDD/Fs.

Readers lacking a good understanding of these POPs can find informative accounts of these chemicals in (IARC, 1985; WHO, 1984a; WHO, 1984b; WHO, 1984c; WHO, 1989a; WHO, 1989b; WHO, 1989c; WHO, 1991a; WHO, 1991b; WHO, 1993). The recent Arctic assessment report (AMAP, 1997) has a chapter on POPs with a very good introductory level treatment of their ecological significance, and numerous findings concerning POPs occurrence in Arctic Russia.

Table 1.1 Study POPs list.

| | |
|---|---|
| DDT | insecticide |
| hexachlorocyclohexane (HCH) | insecticide |
| chlordane | insecticide |
| heptachlor | insecticide |
| dieldrin | insecticide |
| hexachlorobenzene (HCB) | fungicide / industrial contaminant |
| polychlorobiphenyls (PCBs) | industrial contaminant |
| polychlorodibenzo-p-dioxins (PC DDs) | industrial contaminant |
| polychlorodibenzofurans (PCDFs) | industrial contaminant |

## 1.2 Report Outline

The original intent of this review was to perform a broad assessment of POPs contamination in the aquatic systems of the Russian Federation using monitoring and survey data for aquatic systems obtained by Russian agencies. All that became available were some terse summary reports of historical pesticide monitoring activity and a report of the 1993 dioxin survey in the North Dvina watershed. A search of scientific literature uncovered a modest set of reports on POPs-related studies in Russia and the FSU. Mostly, these concerned Lake Baikal, but there were scattered studies on miscellaneous aspects of historical POPs usage and environmental contamination.

Taken together, the available material reveals that, other than for Lake Baikal, the degree of POPs contamination in the Russian environment remains poorly understood. Despite having collected voluminous data on DDT and HCH concentrations in surface waters and sediments for decades, there has been little effort to assess the ecological impacts that these POPs have had on the Russian environment. For the industrial POPs, there have been almost no investigations of any kind until the 1990s.

Because information is generally lacking, fragmentary, or contradictory, the goals of this report became:

- to synthesize a broad overview of what is known about the major POPs including information on production, usage and general environmental occurrence,
- to review in detail some data sets and case studies that characterize contamination by certain POPs in particular Russian aquatic systems.

The synopsis of POPs was organized by the two major operational classes: insecticides, and industrial POPs. The review of insecticides considers (a) historical production and usage, (b) recent geographic occurrence patterns of DDT and HCH in Russian surface waters, and (c) a modest synoptic assessment of DDT and HCH in some Russian and FSU soils contrasted against international data. The review of PCDD/Fs and PCBs follows a similar pattern, except that PCDD/Fs are neither produced nor used intentionally, and the soil assessment is limited to PCBs.

The three case studies review investigations of (i) insecticides and industrial POPs in the Lake Baikal ecosystem, (ii) PCBs and PCDD/Fs in Lake Ladoga sediments, and (iii) PCDD/Fs in the North (Severnaya) Dvina River watershed.

Effectively, the review of Lake Baikal studies forms the centre piece of this report. The series of investigations conducted since the early 1990s represent the most comprehensive assembly of POPs data for any aquatic ecosystem in Russia. The findings of these studies of POPs in particular Baikal environmental compartments are summarized with emphasis on the ecological linkages and the implications of POPs contamination. Beyond the immediate relevance to Baikal, and perhaps more importantly, these studies provide outstanding examples of the conceptual approach and the kinds of high quality data that are required to assess the occurrence and environmental impacts of POPs on aquatic ecosystems elsewhere in Russia.

The review of PCBs and PCDD/Fs in Lake Ladoga sediments reassesses two small surveys that were limited by the observation of incomplete sets of PCB and PCDD/F congeners. The available data are scaled up to permit approximate assessment of the contamination in Ladoga sediments against other geographic locations. It was of particular interest to obtain estimates of sediment PCDD/F content that could be compared with river sediment data in the adjacent North Dvina system.

The North Dvina case study rigorously reviews the results of the 1993 exploratory survey undertaken to characterize potential PCDD/F pollution by some of Russia's largest pulp producers. Some questions are raised about the representativeness of the 1993 survey and some overlooked aspects of two PCDD/F sources are uncovered.

Chapter 2 functions as the *executive summary* found in many reports.

# Chapter 2 Summary

This chapter summarizes the salient findings presented the main chapters of the report, along with certain recommendations for future action.

## 2.1 POPs Insecticide Summary

### 2.1.1 Historical Production and Usage of POPs Insecticides

POPs insecticides were produced and used in appreciable quantities in the Russian Federation and the FSU republics from the 1950s to at least the late 1980s. The major compounds used were DOT, crude HCH and PCC (polychlorocamphene or toxaphene). Despite a nominal ban on DOT in 1971, production and usage continued until the late 1980s or early 1990s. In the Russian Federation, crude HCH production and usage appear to have been superseded by y-HCH (lindane) in the early 1990s. PCC production and usage seem to have been curtailed at some point in the 1980s. It is unclear if PCC is still produced.

The extent of historical production and usage of the common cyclodienes (aldrin, dieldrin, endrin, heptachlor, chlordane) is not known. A compound known as *dihydroheptachlor* was being used in the early 1990s. This is not identical to what is commonly known as heptachlor elsewhere in the world, but may be closely related.

The main plant for production of DOT, HCH and presumably other organochlorine pesticides is located at Chapayevsk near the city of Samara in the central Volga basin. Plant emissions considerably polluted the Chapayevka River with DOT and HCH.

Some references suggest that DOT analogue *dicofol* (kelthane) is used in Russia. If production methods are primitive, the dicofol will be contaminated with DOT and will be an ongoing source of DOT release to the environment.

The monitoring program for pesticides in Russia's surface waters analyzes for HCB at certain sites. This suggests that HCB may have been, and perhaps may still be, produced and used explicitly as a fungicide.

POPs pesticide usage varied considerably across the FSU. Historically, it seems that most DOT, crude HCH and pce were applied in southern regions of the FSU where most agricultural activity occurs. Agricultural usage was particularly heavy in Moldova, parts of the Ukraine, the Northern Caucasus region of Russia (including lands draining to the Black Sea, Sea of Azov and Caspian Sea), and the Central Asian republics with territories draining to the Aral Sea. Less intensive, but widespread agricultural usage of DOT and HCH occurred across the Volga River watershed and the steppe lands of southern Siberia and northern Kazakhstan.

Non-agricultural usage of POPs insecticides to control disease-bearing and nuisance insects seems to have been appreciable. Reports claim that DOT was used for 16 years (late 1960s to mid 1980s) to combat tick-borne encephalitis in Siberia's Kemerovo Oblast. DOT and other insecticides may have seen similar usage elsewhere. Tick-borne encephalitis is endemic to eastern Europe and southern Siberia, and Japanese encephalitis occurs in the southern maritime territories of far eastern Russia. Historically, DOT and HCH may also have been used for malaria control in southern regions of the FSU.

Unless there are unreported insect-borne diseases endemic to northern Russia, DOT, HCH and other insecticides have likely been used there to present times for control of nuisance insects (e.g., mosquitoes, black flies) on the Kola Peninsula, in the environs of Norilsk, and possibly elsewhere.

It does not appear that non-agricultural usage of POPs insecticides has been included in the available accounts of historical usage, and the accounting of agricultural usage may be incomplete.

### 2.1.2 POPs Insecticides in Surface Waters and Sediments

A national agency has monitored the occurrence of DOT, HCH and other pesticides in surface waters and sediments of the FSU, and since 1993, in the Russian Federation. Historical accounts indicate that DOT and HCH were observed at high levels in surface waters across the FSU during the 1960s and 1970s when active usage was great, but have since declined as active usage has declined.

The most recent report (Roshydromet, 1994) available for inspection tersely summarizes data obtained in 1993. This report is difficult to interpret due to excessive data reduction, crude statistical treatment, questionable handling of results below analytical detection limits, inadequate detail concerning field and analytical methodology, and inadequate geographic detail. *The summary statistics for DDT and metabolites in water samples given in the annual summary reports* of *the federal monitoring agency are unreliable.* Due to low analytical resolution (detection thresholds of 50 ng/L), few detections and inappropriate statistical methods, it is impossible to ascertain what resemblance DOT summary statistics given in the 1993 annual summary report bear to actual DOT levels in Russian rivers and streams.

Useful information from the 1993 report of the federal monitoring agency concerning HCH in water samples, and HCH and DOT in sediments is summarized below. Sediment sampling was limited and not broadly representative.

Table 2.1 LHCH summary for five administrative regions, 1993.

| Region | t Mean concentration | *Min% ;:::5 | Probable territory |
|---|---|---|---|
| Omsk | 110-115 | 62 | territories of the upper Ob River basin drained by the Irtysh River and its affluents the Ishym and Tobol rivers |
| Privolzhskoye | 49-55 | 46 | roughly the lower third of the Volga River basin |
| Krasnoyarsk | 26-31 | 46 | may represent all the Yenesei River basin excluding the Angara River tributary lands in Irkutsk Oblast, plus several independent Arctic rivers including the Pyasina, Taymir and Khatanga |
| Zabaikalsk | 12-19 | 35 | upper Amur, and possibly central and lower Amur basin |
| Northern | 9-16 | 39 | likely Barents and White Sea drainage excluding Kola Peninsula |

t mean concentration range by assuming 0 or detection limit (5 ng/L) for non-detections.

* lower limit of possible percentage of samples with detectable ( ~ 5 ng/L) LHCH calculated as the maximum of individual percentage of a-HCH or y-HCH ~ 5 *ng/L.*

### 2.1.2.1 **HCH in Surface Waters**

In 1993, relatively water soluble a-HCH and y-HCH were widely detected above the measurement threshold of 5 ng/L in surface waters across the Russian Federation. With some exceptions, the geographic patterns of occurrence mirror the mapping of HCH usage by Li et al. (1996). Broadly, these HCHs are prevalent at perceptible levels[2] across southern Russia, but only sporadically evident across northern Russia.

In decreasing order, the greatest HCH occurrence was observed in the following five administrative regions of the federal agency listed in Table 2.1. Waters of Omsk region have unequivocally the highest HCH contamination. Omsk region compromises mainly steppe lands on the frontier with Kazakhstan. Waters in the main river channels entering from Kazakhstan are likely already contaminated with HCH. HCHs likely do not occur uniformly at the reported mean levels over the potentially vast Krasnoyarsk and Zabaikalsk administrative regions.

---

[2] Perceptible levels are defined for the present purpose by the detection of least one HCH isomer in 35% or more samples and mean concentrations of 'LHCH = a-HCH + y-HCH > 10 *ng/L.*

Table 2.2 $\Sigma$HCH[a] summary by major watershed, 1993.

River

15

Eastern Arctic

37

Ob

Eastern Arctic

12

Yenesei

Eastern Arctic

28

Pyasina

Pacific

27

Amur

47

Caspian Sea

[c] Min % ≥ 5

Terek

Caspian Sea

Volga

Caspian Sea

Ural

[b] Mean concentration ng/L

29 29 67

Hydrographic basin

31 19 26 71

5

5

[a] LHCH = a.-HCH + y-HCH except for Ob and Volga basins where LHCH = a.-HCH + p-HCH + y-HCH. [b] mean concentrations by assuming 0 concentration for non-detections.

[c] lower limit of possible percentage of samples with detectable ( ~ 5 ng/L) LHCH calculated as the maximum of individual percentage of a.-HCH or y-HCH ~ 5 *ng/L.*

Table 2.2 lists summaries from the 1993 annual report for river basins with the greatest occurrence and mean concentrations of :LHCH = a-HCH + y-HCH. *These are mean concentrations for all samples collected in the river basins, not the concentrations observed* at *the rivers' outlets.* Precisely the same 1993 summary data for the subset of Arctic rivers were incorrectly interpreted in the recent Arctic assessment (AMAP, 1997; see graph page 82) as representing water concentrations at Arctic river outlets to the Arctic Ocean.

*For the Db watershed, the concentration* of 55 *ng/L represents mainly Omsk region rivers and streams* on *the northern frontier with Kazakhstan, not the lower reaches* of *the Db main branch where it enters the Arctic.* The greater part of the Ob basin including the lower reaches is represented by the Western Siberian region of the federal monitoring agency. That region's mean :LHCH concentration was in the range 2-12 ng/L. Unless there has been appreciable HCH usage associated with the settlements and resource development activities in the lower Ob basin, mean :LHCH concentration of Ob waters near the outlet to the Ob Gulf is likely < 10 ng/L.

The Pyasina River basin, with the second highest HCH concentration, originates in the low Arctic. The likely source of HCH in the Pyasina River is high usage in the environs of the Norilsk smelter complex in the upper reaches of the Pyasina.

Unless there has been appreciable HCH usage associated with settlements and resource developments in the lower Yenesei basin, the mean concentration of 15 ng/L for the Yenesei basin may represent mainly upstream reaches in southern Siberia.

### 2.1.2.2 HCH in Sediments

Three sites in River Chapayevka, apparently downstream of the insecticide plant, had mean LHCH = a-HCH + y-HCH of 12-27 *ng/g.* Data for 1990-1993 given at one site show a shift in 1993 to dominance by y-HCH from earlier dominance bya-HCH. This likely reflects conversion from crude HCH to lindane (y-HCH) production.

HCHs were prevalent in sediments of small watercourses and canals discharging to the lower Don River and Don estuary of the Sea of Azov. Mean LHCH concentrations at nine sites ranged from 0.2-88 *ng/g,* but only three sites had LHCH >10 *ng/g.* At most sites, a-HCH dominated suggesting past and recent crude HCH usage.

Low levels of HCHs, generally < 5 *ng/g,* were found in sediment samples from Murmansk, Northern, Western Siberia, Irkutsk and Ural administrative regions.

### 2.1.2.3 DDT in Sediments

High DOT levels were found at 9-10 sites concentrated in small tributaries or drainage canals of the lower Don River and the Don estuary to the Sea of Azov. Concentrations ranged from 2-700 *ng/g* with a mean of 200 *ng/g.* DOT was mainly unmetabolized suggesting recent usage.

Relatively high levels of DDT were found in 6 sediment samples from 3 sites in Murmansk region. Mean total DDT concentration of all samples was 19 *ng/g,* with 79 *ng/g* at one site (River Rosta) within the city of Murmansk. DDT was mainly *p,p'-DDT* except at the Rosta River site where *p,p'-DDD* was dominant. As conversion to *p,p'_* ODD can be rapid, Murmansk region sediment data generally suggest that DDT usage was recent.

### 2.1.3 DOT and HCH in Soils

DOT and HCH concentrations in some Russian and FSU soils are contrasted against international data in Figure 2.1. The figure key and references are given in Table 2.3. These sites represent soils that likely influence adjacent aquatic systems.

DDT contamination in floodplain soils of Samarkand oasis, the lower Kuban valley and Moscow Oblast was surprisingly high when measured in 1989-1990. Levels rank with DOT observed in agricultural soils of Australia and India where DOT was actively being used. Soils from the southwest periphery of Lake Baikal had perceptibly lower DOT, but levels were higher than anticipated given the limited agricultural activity in the region. Unmetabolized DDT dominated in Moscow Oblast and Baikal soils indicating recent usage.

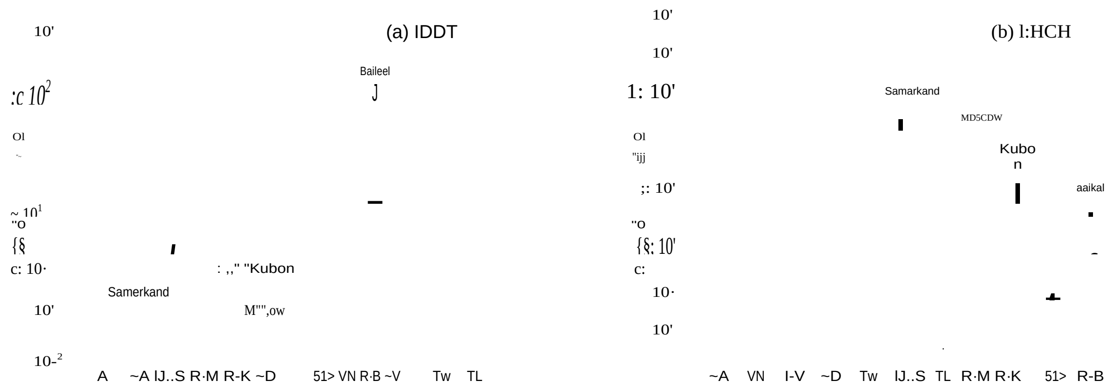

Figure 2.1 DDT and HCH in FSU soils - global comparisons.

Table 2.3 Key and references for Figure 2.1; DDT and HCH in FSU soils - global comparisons.

| | |
|---|---|
| A | Australia - 9 tropical fruit and vegetable soils of NSW from 1987 (Wan et al., 1989). |
| I-A | India - 56 agricultural soils from across India from 1988-89 (Kawano et al., 1992). |
| I-V | India -19 paddy soils, Vellar River basin, Tamil Nadu, 1987-89 (Ramesh et al., 1991). |
| I-D | India - 25 urban Delhi soils collected in 1988-89 (Nair and Pillai, 1992). |
| R-B | Russia, southwest Lake Baikal - (Iwata et al., 1995), see chapter 5. |
| R-K | Russia, Kuban low plain - (Galiulin and Bashkin, 1996), see chapter 3. |
| R-M | Russia, Moscow Oblast - (Galiulin and Bashkin, 1996), see chapter 3. |
| Sp | Spain - 10 Guadalquivir River valley soils from 1990 (Hernandez et al., 1992). |
| TL | Thailand -15 mainly paddy soils from 1989-90 (Thao et al., 1993). |
| Tw | Taiwan -14 agricultural and roadside soils from 1990 (Thao et al., 1993). |
| U-S | Uzbekistan, Sarnarkand oasis - (Galiulin and Bashkin, 1996), see chapter 3. |
| VN | Vietnam - 25 agricultural and upland soils from 1990 (Thao et al., 1993). |

Concentrations of HCH in Russian and Uzbekistani soils were relatively Iowan a global scale, but HCH is generally not found in soils at high levels except where active usage has been high as in southeast Asia. In Baikal soils, 13-HCH accounted for about 50% of I;HCH - a legacy of past crude HCH usage. HCH may persist mainly as 13HCH for some time in areas where crude HCH usage was high.

### 2.1.4 Other POPs Pesticide Data

The recent Arctic assessment (AMAP, 1997) has reported various observations of POPs insecticides in northern Russia. Sediments from 18 remote northern lakes had DDT concentrations mostly at < 1 *ng/g.* These levels rank at the low end of globally observed ranges for freshwater and nearshore marine sediments, and thus likely reflect the background contributed by long range atmospheric transport. Other notable occurrences of DOT and HCH mentioned by AMAP were mainly on the Kola Peninsula or near the Norilsk smelter complex, the same locations identified herein for the presence of HCH and DOT in waters or sediments.

Observations of POPs insecticides are reported elsewhere for Lake Ladoga (negligible) and Lake Baikal (significant in biota).

### 2.1.5 Recommendations for POPs Insecticide Monitoring and Survey

*Unless analytical methodology capable* of *resolving the main DDT species down* to 1 *ng/L or less can be implemented, the continued monitoring* of *DDT species is* a *futile waste* of *resources.* As currently practiced, the monitoring of DDT isomers and metabolites in surface waters is ineffectual and uninformative due to the low resolution of laboratory methods. Judging from the sporadic detections in 1993 data and assuming that DOT production and usage have truly ceased, DDT species may remain observable in water at perceptible frequencies above detection thresholds of 1 ng/L at many sites across Russia for another 5-10 years.

For HCHs, analytical methods should also be upgraded to resolve the main HCH isomers down to 1 ng/L or less.

Measurements of organic matter content (organic carbon, loss on ignition) and clay size fraction should be mandatory for sediment samples that are to be analyzed for nonpolar organic chemicals such as POPs insecticides.

Monitoring of fish, fish-eating birds, seals or other biota near the top of freshwater and marine food webs should be considered for DDT and other bioaccumulative POPs. The Lake Baikal studies exemplify the kinds of data that should be obtained.

Pesticide monitoring in aquatic systems should be coordinated with pesticide usage and soil contamination survey activities. Pesticide usage surveys should endeavor to include all pesticide usage, agricultural and non-agricultural.

### 2.1.5.1 **Reporting Practices**

Considering the volume of data collected, the annual reports of the federal monitoring agency are at best marginally informative, and at worst, misleading. The current summary reports suffer from excessive data reduction, crude statistical treatment, questionable handling of results below analytical detection limits, inadequate detail concerning field and analytical methodology, and inadequate geographic detail.

More rigorous statistical methods should be applied to data summary, time trend assessment, and intersite comparison. As necessary, rigorous methods should be applied to the treatment of data sets containing sample results reported below detection thresholds. The excessive tendency to report extreme concentrations and exceedences of dubious environmental criteria (Le., *Maximum Acceptable Concentrations* or MACs) should be severely restrained, in favour of more reliable characterizations of central tendency (mean, geometric mean, and median) and dispersion (standard deviation, or for lognormal data, confidence bands).

The current practice of gross data lumping by vast administrative regions and river basins often severely distorts the geographic patterns of pesticide occurrence in surface waters. Monitoring sites should be classified by drainage area, predominant land use types, hydroclimatic regimes, ecoregions or other important determinants of water quality. Monitoring data could then be organized by classes that more accurately reflect the prevailing geographic patterns of pesticide usage and occurrence.

As an alternative to the current terse and largely uninformative annual reports, the agency should consider developing river or hydrographic basin oriented reports over longer time frames (e.g., 3-5 years of recent records) with greater attention to historical, hydrologic and geographic context.

## 2.2 Industrial POPs - PCDD/Fs

As in other developed countries, Russia likely has a multiplicity of combustion and chemical sources that generate dioxins and furans. As yet, knowledge of emissions and ambient environmental contamination is minimal.

### 2.2.1 Chemical Industry **Sources**

A short list of chemical plants known or thought to have produced PCDD/F contaminated products and emissions was given by Fedorov (1993, see Section 4.1.4.1, Table 4.4 herein). Atmospheric emissions and wastewater discharges may have contaminated local ecosystems in the vicinity of the chemical plants, while contaminated products were likely dispersed widely across the FSU.

PCDD/Fs are likely also released at numerous metallurgical works, electrolytic chlorine fabrication plants and other industrial facilities in Russia. As PCBs are generally contaminated with PCDD/Fs, insecure disposal of PCBs can be another source of PCDD/Fs. Currently, the PCDD/F content of Russian PCBs is not known.

Current evidence of PCDD/F contamination by chemical plants is limited to (1) a study in the Belaya River system showing what appears to be significant contamination downstream of chemical plants in Sterlitamak and Ufa, (2) a few samples from the Arkhangelsk pulp mill complex at Novodvinsk suggesting that the chlorine fabrication plant is a significant local source, and (3) an unconfirmable report by an activist group that claims the Dzerzhinsk environment has been severely polluted by local chemical plants. Chloracne cases reported in workers at chemical plants in Ufa, Dzerzh"insk, and Chapayevsk affirm that these are probable sources of PCDD/F contamination to the local environments, but little is known about potential emissions from other facilities.

### 2.2.2 **Forest Industry Sources**

Russia has a large pulp and paper industry with about 30-35 primary pulp producers and 130 enterprises producing paper and paperboard products. About 10-12 major pulp producers dominate the industry. Most pulp mills are in northwestern Russia, mainly in the Baltic and White Sea drainage basins with some in the upper Volga watershed. There are at least three large pulp mills in the upper reaches of the Yenesei River basin (Angara River - Lake Baikal system), and a few smaller plants in the far eastern maritime territories.

Controls on atmospheric and wastewater emissions are minimal. Some pulp mills operate within large timber industry complexes that produce other wood products. Beyond the usual emission sources, large complexes may have chlorine fabrication plants, black liquor boilers, scrap incinerators, electrical generating stations and other facilities that may generate PCDD/Fs. Some plants producing unbleached pulp may be generating PCDD/Fs if raw process waters are chlorinated at intake and mechanical pulping is followed by a cooking stage.

Current evidence that Russia's pulp mills emit significant PCDD/Fs is limited and contradictory. A cursory survey in the North Dvina basin showed that the major pulp mills there had potential to release significant PCDD/Fs, but that PCDD/F pollution was minimal in a potentially unrepresentative sampling of river sediments. Better characterization of potential mass emissions from Russia's major pulp mills is required. Then if warranted, any further aquatic surveys of aquatic systems could more precisely focus on downstream areas most likely to be affected. There is also limited evidence that a small unbleached pulp mill (Pitkyaranta) is releasing PCDD/Fs to northern Lake Ladoga. A sample of four Lake Baikal seals had somewhat elevated concentrations of PCDD/Fs that likely originated mainly from the pulp mills at Baikalsk and Selenginsk.

PCDD/F contamination may be locally significant near timber yards where there has been long standing application of chlorophenolic wood preservatives. Asoil sample from the apparently large Lenin woodworking complex near Arkhangelsk city yielded 77 *pg/g* I-TEQ (International or NATO toxic equivalency) that rivaled the highest level observed in pulp mill sludges in the North Dvina survey. Russia likely has many similar timber treatment facilities located near surface water courses. Currently, there is little information available on the PCDD/F content, the usage patterns and the quantities of chlorophenolic wood preservatives deployed in Russia.

### 2.2.3 PCDD/F Pollution by Contaminated Pesticides

From 1961 to 1988, the Khimprom chemical plant at Ufa produced herbicides (2,4,5T; 2,4,5-TCP; Cu salt of 2,4,5-TCP; 2,4-D; and others) that were contaminated with PCDD/Fs. From Ufa, herbicides were distributed to other plants for further processing and regional distribution. There may be significant local PCDD/F contamination at the processing plants, and in soils subjected to herbicide applications. Amongst other areas, the 1992 State Report on the Environment for the Russian Federation considered dioxin pollution to be a threat in the Kuban rice growing zone, the Sea of Azov and the lower Volga. Recent reports suggest that a variety of contaminated organochlorine insecticides and herbicides that were applied at high rates in the Aral Sea basin may be at least partly responsible for potentially severe PCDD/F contamination problems that are now being identified there. As most of the same chemicals were likely applied at high rates in southern Russia, similarly severe PCDD/F contamination may have occurred there also. If historical pesticide usage data warrant, investigations of PCDD/F occurrence in the environments of the Kuban . valley, Sea of Azov, the lower Volga and other watersheds should be conducted.

## 2.3 Industrial POPs - PCBs

### 2.3.1 Production and Deployment of PCBs in the FSU

Historically two varieties of PCBs were produced: *Sovol* and *Trichlorodiphenyl* that are roughly comparable to Aroclors 1254 and 1242 respectively. To about 1990, cumulative production of Sovol was about 100 Kt, while that of TCD was about 25 Kt. By the early 1990s, TCD production had ceased, but about 500 *t1a* Sovol were still being produced. TCD was used primarily in closed systems. but Sovol was also used for a long time in open systems including sealants, paints, plasticizers, plastics and wire insulation.

PCBs were produced at a main plant in Dzerzhinsk, and at a smaller facility in Novomoskovsk. Electrical transformers and capacitors were manufactured at plants in Serpukhov, Oskemen (Kazakhstan), Kumairi (Armenia), and Chirkchik (Uzbekistan).

There may be significant contamination of the local environments including water courses near all the manufacturing facilities.

*The current standing stocks* of *PCBs in the FSU are unknown.* Thousands of transformers and capacitors were manufactured and dispersed widely to industrial facilities across the FSU. *There appear* to *be* no *official policies or plans* to *ensure secure disposal* of *PCBs and little is known about the fate* of *old PCB-containing electrical equipment.*

### 2.3.2 PCBs in FSU Soils: International Comparisons

PCBs observed in soils of Serpukhov (Moscow Oblast), several agricultural valleys in Moscow Oblast, the Kuban low plain (Krasnodar Oblast), Samarkand oasis (Uzbekistan), and the southwestern periphery of Lake Baikal are contrasted against international data in Figure 2.2. The figure key and references are given in Table 2.4. Generally, these sites represent soils that either influence aquatic systems or are influenced by deposition of PCBs on sediments transported from upstream.

Some Russian soils have PCB contamination that approaches the range seen in severely polluted soils near Taiwanese incinerators. The worst contaminated soils are at Serpukhov where a capacitor plant has operated since the 1950s. Soils R-S1 are valley floodplains downstream of the plant where sediments contaminated by plant wastewater discharges are deposited by spring floods. Atmospheric emissions affect soils R-S2 that lie within a 2.5 km radius of the plant. Soils and sediments near other PCB production and deployment plants listed previously may be similarly contaminated.

The apparent high PCB pollution of irrigated floodplain soils from locations in Moscow Oblast (R-M) is due specifically to some very contaminated samples obtained in the Yakhroma River valley to the northwest of Moscow city. Soils of five other valleys in Moscow Oblast were modestly contaminated (3-38 *ng/g* total PCBs).

The apparent high PCB contamination of lower Kuban River valley soils (R-K) is also the artefact of 3-5 badly polluted samples from a total of 21 samples. However, 19 sediment samples of the Kuban River, the Kuban delta irrigation canals and adjacent inlets of the Azov and Black Seas, showed consistently high PCB contamination (mean *550 ng/g)* that appears to emanate from the city of Krasnodar.

The agricultural soils of Samarkand oasis are mostly modestly contaminated, but some highly contaminated samples are evident. Seven river sediment samples had a mean of 116 *ng/g* total PCBs, and water concentrations in the Zeravshan apparently increased from not detected above Samarkand to >2 J..L9/L at the Kattakurgan reservoir 50-60 km downstream. Thus the local aquatic systems are being appreciably contaminated even if soils are not.

3.

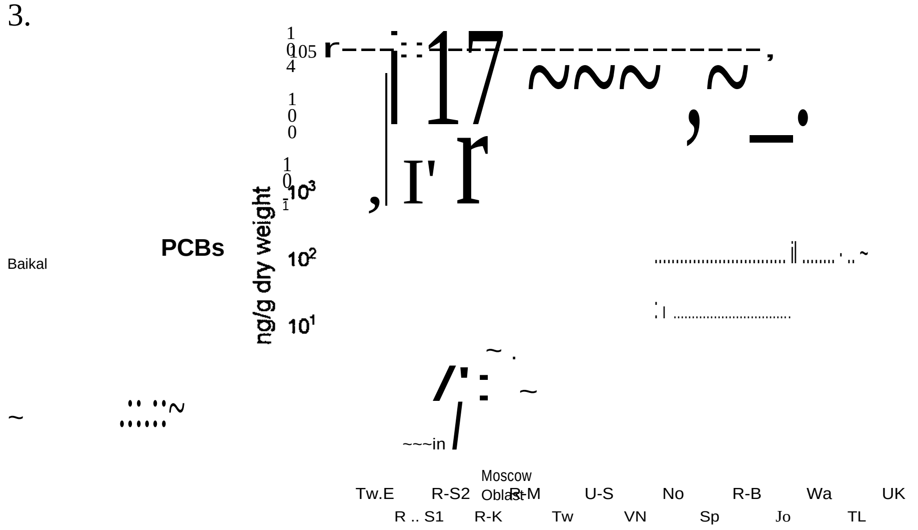

Figure 2.2 PCBs in FSU soils - global comparisons;
MAC is Maximum Acceptable Concentration for Russian Federation.

Table 2.4 Key and references for Figure 2.2; PCBs in FSU soils - global comparisons.

| | |
|---|---|
| Jo | Jordan - 10 rural soils (Alawi and Heidmann, 1991). |
| No | Norway - 12 forest soils (Lead et al., 1997). N.B. 87% organic C content. |
| R-B | Russia, southwest Lake Baikal- 4 soils; (Iwata et al., 1995); see chapter 5. |
| R-K | Russia, Kuban low plain - (Galiulin and Bashkin, 1996); see chapter 4. |
| R-M | Russia, Moscow Oblast - (Galiulin and Bashkin, 1996); see chapter 4. |
| R-S1 | Russia, Serpukhov, Moscow Oblast - valley floodplain soils downstream of capacitor plant wastewater discharges (Bobovnikova et al., 1993). |
| R-S2 | Russia, Serpukhov, Moscow Oblast - soils within 2.5 km of capacitor plant (Bobovnikova et al., 1993). |
| Sp | Spain -10 Guadalquivir River valley soils from 1990 (Hernandez et al., 1992). |
| TL | Thailand -15 mainly paddy soils from 1989-90 (Thao et al., 1993). |
| Tw | Taiwan -14 agricultural and roadside soils from 1990 (Thao et al., 1993). |
| Tw-E | Taiwan, Er-Jen River - 6 waste incinerator soils from 1990 (Huang et al., 1992). |
| UK | UK-10 rural soils (Lead et al., 1997). |
| 'U-S | Uzbekistan, Samarkand oasis - (Galiulin and Bashkin, 1996); see Chapter 4. |
| VN | Vietnam - 25 agricultural and upland soils from 1990 (Thao et al., 1993). |
| Wa | Wales, UK - 42 soils (Jones, 1989). |

The four soils sampled on the southwest margins of Lake Baikal have relatively low PCB contamination. One sample obtained near a coal-fired power plant had marginally high PCB content. While soil concentrations are relatively low, the PCB congener patterns in Lake Baikal waters suggest that local surface runoff is a significant PCB source. As discussed elsewhere, the Lake Baikal ecosystem is extraordinarily sensitive to low inputs of POPs; hence, the Russian soil MAC of 60 ng/g does not appear to be particularly relevant in the Lake Baikal region.

### 2.3.3 PCBs Summary

Evidence suggests that there have been significant environmental releases of PCBs from the substantial stocks produced by Russia and the FSU. Limited environmental data reveal localized areas of high contamination near PCB production and handling facilities, downstream of some urban-industrial centres and on some agricultural lands. Contamination in urban-industrial centres and agricultural lands most likely reflects insecure disposal of old electrical equipment and other PCB laden wastes. Current data are too limited to generalize, but it is likely that the environments of most urban centres with appreciable industrial activity are to some extent polluted. Contamination of agricultural lands is likely limited to lands where sewage sludges and other industrial wastes have been dispersed, and to valley bottom lands where spring floods have deposited contaminated sediments originating from upstream urban-industrial areas.

Vast regions of remote northern and far eastern Russia are likely contaminated at background levels determined by long range atmospheric transport. However, numerous urban, industrial, resource development and military centres scattered across remote Russia may emit appreciable localized PCB contamination. Major rivers draining to the Arctic Ocean likely transport some PCBs from industrial regions in remote southern reaches.

## 2.4 POPs in the Lake Baikal Ecosystem

Lake Baikal is unique among the world's lakes as having the largest volume, one the few species of freshwater seal *(Phoca Siberica* or *nerpa),* and numerous other notable features. In late 1996, UNESCO added Lake Baikal to the list of the World Heritage Sites and declared the protection and conservation of Lake Baikal as one of the responsibilities of humanity. Investigations of POPs contamination in the Baikal ecosystem were prompted by a mass mortality of several thousand seals over 1987-88 due to a morbillivirus, an event similar to epizootics of marine mammals that have occurred in highly contaminated European waters. The results have yielded the most comprehensive set of POPs data available for any Russian aquatic ecosystem, and are particularly important not only to the welfare of Lake Baikal, but as a paradigm for the kind of systematic investigations required for many aquatic ecosystems across Russia that are seriously jeopardized by pollution.

Several factors combine to make the Baikal ecosystem especially vulnerable to POPs contamination. These include Baikal's physical attributes, particularly its enormous water mass and long hydraulic residence time of 350 years, the physicochemical properties of POPs, and a unique ecosystem structure with limited food web linkages. Together these ensure that certain POPs entering Baikal will likely remain there for very long times and that there is extraordinary upward transfer through the food web to the extent that organisms at the top may accumulate some POPs such as dioxin-like PCBs and DDT at levels approaching or exceeding those seen in regions where historical usage of these chemicals has been substantially greater.

Despite its apparent remoteness, the Lake Baikal ecosystem is contaminated to varying degrees with POPs. The leading POPs in water are HCHs and PCBs with mean concentrations about 0.5-1 ng/L, with PCCs and DDT about 10 fold lower, and HCB and chlordanes 3-4 fold lower still. Waters of the southern basin (roughly the lower third of Baikal) have perceptibly higher levels of HCHs, PCBs and DOT suggesting that these derive mainly from regional sources rather than long range atmospheric transport. Regional POPs inputs originate from the sizable Selenga River that enters at the northern extent of the southern basin, local surface drainage and wastewater discharges around the southern basin, and atmospheric emissions from the local drainage area and the Irkutsk Oblast to the west. Waters of the Selenga are contaminated by urban and industrial wastewaters, and agricultural runoff. A large pulp mill, a coal-fired power plant and associated settlements are likely the contaminant sources in the local southern basin catchment. Prevailing westerly winds and topography ensure that atmospheric emissions from heavy industries and chemical plants in Irkutsk and other centres to the west affect Lake Baikal.

### 2.4.1 POPs in Lake Baikal Biota

In global terms, POPs levels observed in the nominally inorganic environmental compartments (air, water, sediment, and soil) of the Baikal ecosystem are relatively low; however, tremendous upward bioamplification through the food web induces such high accumulations in the top members that their health may be at significant risk. These include Baikal seal, and likely other fish-eaters including birds and humans. Recent data show that:

- *POPs contamination in the nerpa (Baikal seal) generally ranks second only* to *that in Baltic seals amongst its nearest relatives (marine and freshwater ringed seals, and the Caspian seal), and is significantly greater than in ringed seals* of *the Svalbard archipelago and the Canadian Arctic.*

Globally, Baltic seals have generally ranked first among seals in POPs contamination which underscores the potential severity of POPs contamination in Baikal seals.

The leading contaminants in nerpa are DDT and PCBs. For mature male seals, DDT levels (mean 64 1-19/g lw) in Baikal nerpa are up to 85 fold higher than in ringed seals of the Canadian Arctic, 25 fold higher than in Svalbard ringed seals, but only about 25% of levels seen in Baltic ringed seals during the 1980s. *Extraordinary net bioconcentration* of *$10^{8}$_$10^{10}$ fold up the Baikal food web renders almost negligible water concentrations* of *DDT into* a *potentially grave ecological threat.*

Comparing males, total PCB concentrations in nerpa (mean 31 I-1g/g lw) rank behind levels seen in Baltic ringed seals during the 1980s, but are up to 35 fold higher than in ringed seals of the Canadian Arctic and 20 fold higher than in Svalbard ringed seals. Recent data for Baltic juvenile and female ringed seals suggest that PCBs in Baltic seals may have declined toward parity with Baikal seals of the same age and sex class. The average bioconcentration from water to seal is about 30 fold lower than for DDT; however, for certain PCBs, bioconcentration may rival or exceed that of DDT species.

Other POPs including PCCs (polychlorocamphenes) and chlordane species also bioconcentrate appreciably from water to seal; however, the concentrations in seal are about two orders of magnitude lower than those of DDT and total PCBs.

### 2.4.2 PCDD/Fs and Dioxin-like PCBs in Baikal Seals

*The* 2,3,7,8- *TCDD equivalency (TEQ) attributable* to *PCBs in Baikal seals* seems *to be appreciably higher than in Baltic seals.* The TEQ of dioxin-like PCBs in Baikal seal blubber gives the best indication of the threat posed by PCBs to Lake Baikal biota. As expected, the TEQ due to PCBs varies appreciably by age and sex classes and the system of toxic equivalence factors (TEFs) applied. Generally, Safe's 1990 TEFs (Safe, 1990) yield the highest TEQs, while the 1994 WHOIIPCS TEFs (Ahlborg et al., 1994) yield the lowest. The latter give slightly higher TEQs than the recently proposed WHO TEFs for mammals, and may give the more valid estimates. In mature males, the Safe 1990 TEFs give a mean TEQ of 4,900 *pglg* (wet weight) versus a mean TEQ of 900 *pglg* for the 1994 WHO/lPCS TEFs. The differences are attributable mainly to the appreciable accumulation of congeners 105, 118 and 156 [3] in Baikal seal, and the varying weights ascribed to these by alternative TEF systems.

PCB TEQ burdens in Baikal nerpa and ringed seals from other locations are contrasted in Figure 2.3. The Baikal seals seem to accumulate significantly more dioxin-like PCBs than Baltic seals which have greater total PCB burdens. On a strictly comparable age and sex class basis, the differences between Baikal seal and Baltic ringed seal are likely smaller as the Baikal data represent a mixed population including mature males, while the Baltic sample comprised predominantly pups and a few mature females. In a limited comparison based on the TEQs attributable to three non-ortho PCBs (77, 126 and 169), Baikal female seals have 5-6 fold higher TEQ than female

[3] IUPAC numbers, see Erickson (1997).

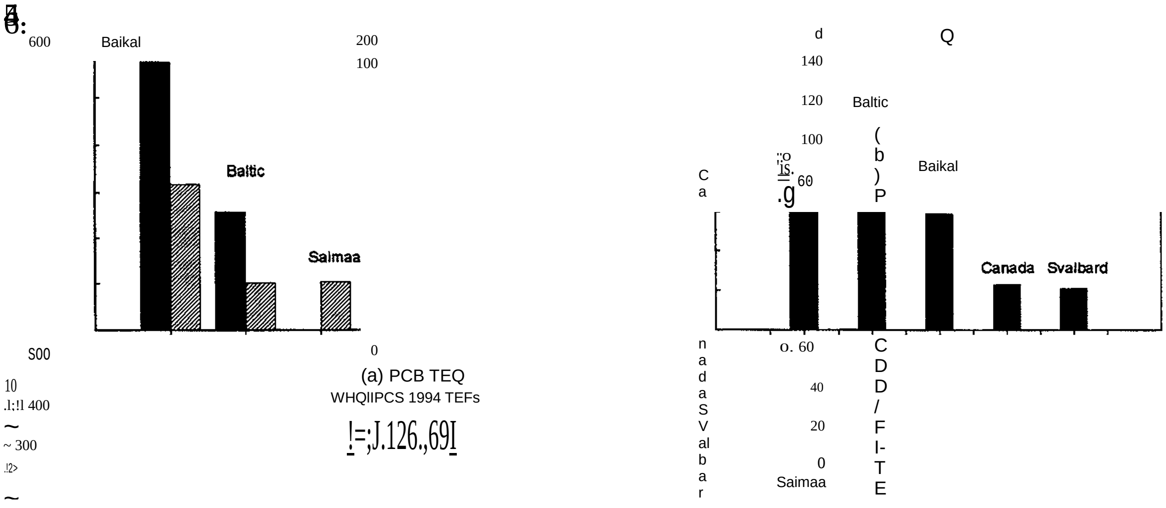

Figure 2.3 TEQ of PCBs and PCDD/Fs in Baikal seal - global comparisons; lumped data for all age and sex classes.

ringed seals of Lake Saimaa and the Gulf of Finland. Compared to ringed seals of the Canadian Arctic, the TEQ determined by the 1994 WHOIIPCS TEFs in Baikal nerpa is 30-35 fold higher than in Canadian Arctic ringed seals. Unlike ringed seals of Svalbard and the Canadian Arctic that have TEQ almost solely attributable to PCB 126, Baikal seals have appreciable TEQ attributable to PCBs 105, 118 and 156.

Limited data for 2,3,7,8-TCDD equivalent burdens of dioxins and furans suggest that Baikal seals are not as contaminated as Baltic and Lake Saimaa ringed seals, but are definitely more contaminated than ringed seals of the Canadian Arctic and Svalbard. The Baikal sample comprises only four seals having a mean I-TEQ of about *60 pg/g* Iw and range 30-90 pg/g Iw. If these data are representative, the TEQ of dioxin-like PCBs overwhelms that due to PCDD/Fs.

### 2.4.3 POPs in Baikal Fish

Baikal fish are contaminated at levels that, for most POPs, rank neither extremely high nor low against available global data. However, fish are an especially important intermediate linkage in the upward transfer of POPs to Baikal seal and likely also to predator birds and humans. Humans should not be overlooked as Baikal has an annual commercial fishery of 13 Kt or more. Bioconcentration from water to fish is a remarkable $10^6$_$10^9$ fold for all POPs considered herein except HCH which concentrates only about $10^4$ fold. DDT, total PCBs, total chlordanes and HCHs amplify further from fish to seal, with DDT concentrating up to 35 fold more in seal. PCCs and HCB decline marginally from fish to seal. Bioconcentration patterns from fish to humans or birds may differ.

The leading contaminants in Baikal fish are PCBs, DOT and PCCs all with mean concentrations in the range of about 1-10 *f.lg/g* lw. Globally, the burden of total PCBs in Baikal fish is about an order lower than in fishes of some heavily industrialized countries, but unequivocally higher than the total PCBs in fishes of numerous low exposure tropical countries that have water concentrations similar to Baikal's.

DOT levels are about 10 fold lower than extremes reported for some tropical countries where DOT has been used copiously until recent times and some industrialized countries where the legacy of high past usage persists. Unmetabolized DOT averaged 56% of total DOT species present confirming indications of water, sediment, and soil data that new DOT inputs into the Baikal environment had occurred before samples were collected in the early 1990s. Some investigators have suggested that the DOT in Baikal originates mainly from remote sources, but the evidence of water, sediment and soil data suggests that local sources cannot be dismissed.

PCC concentrations in Baikal fish rival those of total PCBs and DOT; however, global comparisons show that concentrations are similar to those in fishes from a broad spectrum of North American and northern European waters where long range atmospheric transport is the probable source.

Total chlordanes, heptachlor and HCB all have similar concentrations about 10 fold lower than total PCBs, DOT and PCCs. The total chlordane levels are similar to those in fishes from a broad spectrum of geographic locations where long range atmospheric transport is thought to be the source.

*Unmetabolized heptachlor was found in* a 1993 *sampling* of *Baikal fish* at *levels comparable* to *those in fishes collected from countries where there was active heptachlor and chlordane usage.* This may indicate usage of the Russian pesticide *dihydroheptachlor* for which little information was readily available other than its chemical formula. Degradation of *dihydroheptachlor* to common heptachlor on release to the environment could explain the presence of heptachlor in Baikal fishes and other biota.

*HCB levels in Baikal fish are remarkably high, ranking second only* to *highly contaminated fishes from waters* off *Sydney, Australia.* While uniform surface water concentrations across Lake Baikal suggest that the source is long range atmospheric transport, atmospheric emissions from chemical plants and heavy industries in the Irkutsk Oblast may be regionally significant sources.

### 2.4.4 Some Recommendations for Further Work

Further work is needed to elucidate the sources of POPs to Baikal with a view towards formulating POPs mass budgets and constructing chemical fate models to evaluate the long term behaviour of POPs in Baikal under different remediation scenarios. Data are needed to characterize surface water inflows and outflows, and atmospheric inputs by precipitation and dry deposition. Some data exist for characterizing gas exchange across the air-water interface, but other potential removal processes remain to be elucidated and characterized. Chemical dynamics models developed for Lake Ontario should provide a basic blueprint that could be adapted for Baikal. Attention should probably focus on PCBs and DDT that appear to pose the greatest threats to the Baikal ecosystem.

## 2.5 Lake Ladoga Summary

Available data for Lake Ladoga are limited mainly to sediment data for DDT, PCBs, and PCDD/Fs. The sediment data represent two cores obtained in 1990 and surficial samples obtained at 12 sites in 1993. The cores were collected about 1 km off the towns of Priozersk and Pitkyaranta on the northern margins of Ladoga. Priozersk was the site of an old pulp mill closed in 1986, while a small mill producing unbleached pulp operates in Pitkyaranta. Dating and sectional analyses showed that organic matter and organically bound chlorine content began rising about 1900.

DDT and metabolites were present at 9-14 *ng/g* in the top layer (0-1 cm) of the two cores obtained in 1990. Most DDT was in metabolized form. The 1993 survey found only sub-quantifiable traces of DDT species in surficial samples from a few of 12 sites around the lake. This suggests that DDT contamination decreased from 1990 to 1993.

### 2.5.1 PCBs in Ladoga Sediments

In 1990 and 1993 surveys, measurements were limited to subsets 9 and 17 PCBs; hence, pro-rated *total PCBs* estimates are somewhat uncertain. Over much of the lake, sediments appear to be modestly contaminated by PCBs with typical *total PCBs* concentrations ranging 18-33 *ng/g* with a mean of 26 *ng/g.* The top layers (0-1 cm) of the two 1990 sediment cores and a few 1993 surficial samples show that there are localized areas of higher contamination near Pitkyaranta and Priozersk with *total PCBs* concentrations in the 60-105 *ng/g* range. The samples taken nearest Pitkyaranta likely exceeded Ontario's *Lowest Effect Level* [LEL] guideline of 70 ng/g for total PCBs that should apply broadly to sediments in temperate aquatic systems in the northern hemisphere. The Priozersk sample had total PCBs of 65-75 nglg near the Ontario LEL. Lake Ladoga has not been systematically surveyed and there may be other areas of significant localized contamination.

The composition profiles of the 9 PCBs measured in the 1990 sediment cores suggested that the PCBs were a mixture of Russian *Sovol* and *Trichlorodiphenyl* technical products. The Pitkyaranta core had perceptibly higher PCBs in the top layer (0-1 em) than the second layer (1-4 em) indicating that the PCBs were of recent origin.

Near Priozersk, concentrations were similar through the top 0-4 cm indicating long standing PCB contamination.

Five sites of the 1993 survey were located in Volkhov Bay on the southeast corner of Ladoga where the local land watershed has appreciable urban and industrial activities that may be potential sources of PCBs. Though the 5 Volkhov Bay sites have typical PCB content (mean 25 *ng/g,* range 18-33 *ng/g),* more investigation may be required. Volkhov Bay is shallow with coarse, inorganic sediments. When samples are normalized by organic carbon or clay size fraction, total PCBs at 3-4 of the 5 Volkhov Bay sites rank with the highest concentrations observed in all 12 samples of the 1993 survey. It is possible that PCBs (and other sorptive contaminants) entering Volkhov Bay on fine suspended particles in tributary inflows and direct point source discharges may be swept out of Volkhov Bay into deeper waters before settling.

### 2.5.2 **TEQ of Dioxin-like PCBs in Ladoga Sediments**

The analyses of 1990 sediments included three dioxin-like PCB congeners (105, 118, 180), while the analyses of 1993 sediments included 6 dioxin-like congeners of which only the same three as in the 1990 survey were actually detected.

In the top layers of the two 1990 sediment cores, the calculable TEQ of dioxin-like PCBs was identically 3 pg/g by the Safe 1990 system in both Pitkyaranta and Priozersk sediments, while the WHO/IPCS system yielded identically 1.2 pg/g TEQ.

In 1993, the highest dioxin equivalents due to PCBs were observed in surficial sediments near Pitkyaranta (18 pg/g TEQ), offshore south of Pitkyaranta (10 pg/g TEQ) and at the Syas River inlet to Volkhov Bay (9 pg/g TEQ), all estimated by the Safe 1990 system. Individual congener measurements were not given for 1993 data, only the total TEQs by the Safe 1990 system. However, TEQs by the WHOIIPCS system were estimated to be roughly 40-55% of Safe 1990 TEQs according to ratios observed in the 1990 sediment core data. Thus, for sediments near Pitkyaranta with the highest PCB content, the dioxin equivalents due to PCBs in the 1993 sample would have been in the 7-10 pg/g range if determined by the WHO/IPCS system. These 1993 estimates are 6-8 times higher than determined in the 1990 sediments, despite similar estimates of total PCB concentration. Inconsistencies in field and laboratory methodologies between the 1990 and 1993 surveys may be responsible.

In 1993, the general conditions in Lake Ladoga may have been best represented by the 9 sites remaining after excluding the three most contaminated sites. By the Safe 1990 system, the 9 sites had mean dioxin equivalents due to PCBs of 4.3 pg/g TEQ with range 3-6 pg/g TEQ. By the WHOIIPCS system, these sites would likely have had a mean of about 2 pg/g TEQ with range 1-3 pg/g TEQ.

### 2.5.3 PCDD/Fs in Ladoga Sediments

Nine 2,3,7,S-substituted PCDD/F congeners were measured in the top layers of the two 1990 sediment cores. Comparison with other sediment samples from western Europe and Russia with similar congener profiles, suggests that the 9 PCDD/Fs congeners would represent, *at most,* about one half the TEQ of all seventeen 2,3,7,Ssubstituted congeners. *Minimal estimates* of total TeDD equivalents were respectively about 11 and 7 pg/g I-TEQ for Pitkyaranta and Priozersk in top layer sediments. *Mean estimates* would be about 16 and 10 pg/g I-TEQ respectively, while *upper limit estimates* would be about 2S pg/g I-TEQ at both sites.

The mean estimates of PCDD/F I-TEQ in Priozersk and Pitkyaranta sediments were similar to those reported for most Scandinavian sediments at sites removed from the immediate vicinity of strong PCDD/F sources, about 10 fold higher than in 3 remote lakes from northern Finland, and about 90-1 SO fold higher than in background river sediments in the North Dvina watershed. It seems likely that the PCDD/F contents of sediments near Pitkyaranta and Priozersk are higher than over most of Lake Ladoga; however, a geographically systematic survey of surficial sediments is required to establish the general lake-wide patterns.

Although the Pitkyaranta mill produces unbleached pulp, PCDD/Fs were higher in sediments near Pitkyaranta than near Priozersk. Moreover, the Pitkyaranta sediments had a distinctly different congener profile with perceptibly higher furans than the Priozersk sediments that had composition similar to the broad regional pattern. As observed in some Finnish mills, PCDD/Fs, particularly furans, can be formed by certain unbleached pulping processes where raw process waters were chlorinated at intake to bleach out natural organic matter and control slime formation, and mechanical pulping was followed by a cooking stage. More work is required to determine if this occurs at the Pitkyaranta mill.

### 2.5.4 Biotic Compartments

A comprehensive assessment of POPs contamination in Lake Ladoga awaits more complete data for biota at the top of the food web. Like studies conducted in Lake Baikal, these should include fish, Ladoga seal, and fish-eating birds. Some POPs data for fish and seal were apparently given recently, but the report was unavailable for examination. DDT and y-HCH levels were low in a limited sampling of the eggs of aquatic birds (gulls, terns) from Karelia; however, top predators such as eagles do not yet appear to have been sampled.

## 2.6 Dioxins and Furans in the North Dvina Watershed

Poor health of the region's human population and a mass mortality of starfish on the White Sea coast in 1991 prompted exploratory surveys of PCDD/F and other pollution in the North (Severnaya) Dvina River basin. The North Dvina is the major Russian river draining to the White Sea. PCDD/Fs originate mainly from forest product industries that dominate the regional economy. Three pulp mill complexes - *Syktyvkar, Kot/as* and *Arkhangelsk* [4] (in nearby Novodvinsk) - are amongst Russia's top 10 pulp producers. A fourth mill, *Solombala* (in a precinct of Arkhangelsk city), is smaller, but likely ranks in Russia's top 15 pulp producers. Residual contamination from a defunct pulp mill in Puksa that discharged untreated wastewaters until 1993 may be a persistent problem. The North Dvina watershed also has numerous timber yards and woodworking facilities where localized PCDD/F pollution arising from past and present usage of PCDD/F-contaminated chlorophenolic wood preservatives may be significant.

The region's three largest pulp mills *(Syktyvkar, Kotlas,* and *Arkhangelsk)* function within large timber industry complexes with affiliated operations that may also be PCDD/F generators. These include a chlorine plant in Novodvinsk *(Arkhangelsk),* and plywood, fibreboard and paper board manufacture *(Syktyvkar, Kotlas).* Black liquor boilers, scrap incinerators, and other potential PCDD/F sources are also likely found at these industrial complexes.

The 1993 surveys comprised 36 sediment, soil and pulp mill sludge samples analyzed at the Bavarian Institute of Water Problems (BLW), Munich, Germany, and 27 samples analyzed at the Institute of Evolution and Ecology of Animals (IEMEA), Moscow. The results of all but one sample processed at the IEMEA lab were discarded because, for seven of eight intercomparison split samples, the IEMEA results were 316 fold too high. Most samples processed by IEMEA likely had PCDD/F contents below the reliable analytical resolution of the IEMEA lab.

Superficially, the 22 sediment samples obtained in the 1993 survey suggest that PCDD/F contamination of the North Dvina aquatic system is minimal. A subset of river sediment samples collected some distance from pulp mill sources suggests that regional background PCDD/F contamination is generally below 125 *fg/g* I-TEa with a mean of about 90 *fg/g* I-TEa. *These are amongst the lowest levels ever reported for aquatic sediments.* Samples collected closer to pulp mills show higher levels, but only one sample, collected near the wastewater outfall of the now defunct Puksa mill, with content of 1.8 *pg/g* I-TEa, actually exceeded 1 *pg/g* I-TEa.

There are reasons to be wary of these results. Sampling was cursory and opportunistic, and the usual ancillary data on organic matter content and physical texture of sediments were not reported. Some samples were obtained near river banks

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[4] Syktyvkar, Kotlas and Arkhangelsk are the names of the corporate entities as well as nearest the major urban centres to where the mills are located.

where sediments more likely comprise coarse inorganic materials, and others collected near wastewater outfalls may not have been taken from within the fields of the contaminant plumes. Near Arkhangelsk city, the lower reaches of the North Dvina that are potentially most affected by emissions of the *Arkhangelsk* and *Solombala* pulp mill complexes were represented by only one sample collected near the bank or a sandbar. Contradicting the river sediment data are *PCDD/F contents* of 2-84 *pg/g 1- TEQ observed in four sludge samples from three major pulp mill complexes (Syktyvkar, Arkhangelsk, and Solombala) that demonstrate that region's major pulp producers do have the potential* to *emit appreciable PCDD/Fs.* Thus, it is difficult to judge how well the available river sediment data represent pulp mill emissions of PCDD/Fs, and it is possible that these data may significantly misrepresent the potential PCDD/F releases by the region's major pulp producers.

As there is evidence that the major mills could be strong emitters of PCDD/Fs, further study should concentrate on characterizing the mass emissions of PCDD/Fs via wastewater and atmospheric discharges from the major mills. Where PCDD/F emissions are sufficiently large, further study could be focused on the aquatic systems that are most likely to be affect~d.

Historical and current usage of chlorophenolic wood preservatives is likely the source of significant soil contamination (77 pg/g I-TEQ in one sample) at the Lenin woodworking complex near Arkhangelsk, and likely some pollution at numerous other timber yards and woodworking facilities scattered across the region. Pollution is likely most severe at major timber yards where there has been long standing usage of chlorophenolics. PCDD/F contamination is likely localized to the immediate land and downstream water courses affected by surface runoff. The more mobile chlorophenols may pose problems where downstream surface and groundwaters are extracted for drinking water supplies.

The only other notable source of PCDD/Fs in the North Dvina watershed is the chlorine fabrication plant affiliated with the *Arkhangelsk* complex in Novodvinsk. Furan dominated congener profiles suggest that strong emissions from the plant permeate the local air, soil and pulp sludges. Mass releases remain to be quantified and the effects on local aquatic systems are unclear.

## 2.7 Sea of Azov

Taken together, there are indications of significant contamination by DDT, HCH and PCBs in the lower Don River, the Don estuary, the Kuban valley and adjacent inlets on the Sea of Azov. The region is also cited for potentially significant PCDD/F contamination from high herbicide and other pesticide usage. Consequently, the Sea of Azov watershed may merit special attention.

# Chapter 3 Organochlorine Pesticides

## 3.1 POPs Insecticides in Russia and the FSU

Historical pesticide production and usage in the FSU are not well documented. According to Bridges and Bridges (1996), the production of agrochemicals accelerated about 1953, increased 11 fold by the mid 1980s, and since then seems to have fallen. Feshbach and Friendly (1992) gave the total pesticide usage for the FSU in 1988 as 309 Kt of which about 209 Kt comprised insecticides, and claimed that total usage had fallen 15% from a year earlier. Bridges and Bridges reported what seems to be total usage for the Russian Federation of 150 Kt in 1991, and 43.7 Kt in 1993.

Most pesticides were likely applied across southerly agricultural regions of the FSU, particularly Moldova, Ukraine, the lower Don and Kuban rivers, the Caucasian republics (Armenia, Azerbeijan, Georgia), the lower Volga and the Central Asian republics draining to the Aral Sea (Kazakhstan, Kyrgyzstan, Tajikistan, Turkmenistan, and Uzbekistan). In more northerly regions, pesticides were likely used in agriculture, and may have been applied for public health, forestry, and nuisance insect control.

Though available data are somewhat inconsistent, pesticide usage rates in the FSU seem to have been extraordinarily high. Bridges and Bridges (1996) report that annual mean application rates ranged from 12-17 kg/ha between 1960 and 1990. Peak usage rates in some areas were likely well above average. Without giving dates, Ivanov et al. (1996) reported that mean application rates were 20-25 kg/ha in the irrigated lands draining the Aral Sea, but that the mean FSU rate was only 3 kg/ha, similar to the USA. Without giving actual figures or dates, Feshbach and Friendly (1992) claimed that usage rates in Moldova were 13 times the national average.

By the 1960s, organochlorine insecticides were produced in appreciable quantities and usage was geographically extensive across the FSU. Historically, DOT, HCH, and PCC (polychlorocamphene) which is chemically similar to toxaphene [5], appear to have been the most heavily manufactured and used POPs insecticides. Voldner and Li (1993) estimated cumulative PCC usage from 1970 to about 1990 as >100 Kt[6]. A later report (Voldner and Li, 1995) places cumulative DOT and HCH usage from 1970 to 1990 into the 10-100 Kt range. Li et al. (1996) give crude HCH usage for the FSU 1,674 t in 1980 at which rate the cumulative usage for 20 to 30 years would have been 33-50 K, and crude HCH usage for Ukraine as 240 t in 1990. The FSU portion of the global mapping of a-HCH and y-HCH usage on a 1° x 1° grid by Li et al. (1996) reveals

[5] A complex mixture of chlorinated bornanes and bornenes sometimes denoted as CHB. Herein, PCC denotes pesticide PCC, while PCCs denotes the polychlorocamphenes found in environmental samples.

[6] The maps given by Voldner and Li (1993, 1995) exclude the Aral Sea republics: Kazakhstan, Kyrgyzstan, Tajikistan, Turkmenistan and Uzbekistan where most PCC usage likely occurred.

that most historical HCH usage occurred in the Volga basin and on the steppe lands of southern Siberia and northern Kazakhstan about as far east as Novosibirsk. Similar mappings would be helpful in revealing the geographic patterns of historical DDT, pee, herbicides and other agrochemical usage.

The available literature suggests (but never clearly states) that crude HCH[7] and DDT production were curtailed about 1981-1983. In Russia, lindane (y-HCH) apparently remains permitted for restricted purposes, and usage may be increasing. Chernyak et al. (1995) claim that y-HCH replaced DOT on the Russian Pacific coastal territories. No production or usage figures are available for y-HCH.

The Soviet Union officially banned DOT in 1971, about the time when many developed countries effected severe restrictions on DOT. Judging from fragmentary reports, the Baltic republics may have observed the ban; however, the ban was routinely waived across much of Russia and the southern FSU republics until the late 1980s when production may have finally ceased (Feshbach and Friendly, 1992).

Reports of soil contamination suggest that DDT was most widely used in agriculture. Bridges and Bridges (1996) reported that, about 1990, DDT was present in one half the soils on which fruit and berries are grown, 29% of sunflower fields, and 20% of corn fields. According to Feshbach and Friendly (1992), circa 1990, levels of DOT in about 100,000 $km^2$ of cultivated soils exceeded 'safe' standards[8], and average levels in Azerbeijan, Armenia, Moldova, and Uzbekistan were 2-8 times above the limit. Another report (UNEP, 1992) claimed that in Uzbekistan, DOT levels exceeded standards by 33-46 fold in cereal-growing soils, and 31-46 fold in cotton-growing soils.

DDT and HCH were also likely used for other purposes including public health. Feshbach and Friendly (1992) reported that aerial spraying was conducted for 16 years from the late 1960s in Siberia's Kemerovo Dblast (Db River basin) to control forest ticks that carry encephalitis[9]. As tick-borne encephalitis is endemic to eastern Europe and southern Siberia, DOT and other insecticides may have seen similar use elsewhere in the FSU. These insecticides may also have seen use against mosquitoborne Japanese encephalitis which occurs in southeastern maritime Russia where the first human cases in 30 years have been observed recently. DOT may also have been used to control malaria in the southern FSU republics, particularly in central Asia where there has been a recent resurgence of the disease in Azerbeijan and Tajikistan (Medscape, 1996, CDC 1997). In northerly regions, DOT and HCH may have been used in forestry and nuisance insect (e.g., mosquitoes and black flies) control. A

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[7] Crude technical HCH comprises about 60-70% u-HCH, 5-12% f3-HCH, 10-15% y-HCH, 6-10% o-HCH, 3-4% gHCH and 1-2% other chlorinated compounds. y-HCH is the active insecticidal ingredient. *Undane* is >99% y-HCH. Between crude HCH and lindane, are so-called *fortified* HCH products containing 16-99% y-HCH and reduced percentages of the non-insecticidal isomers.

[8] The maximum allowable concentration (MAC) was 100 *Jl9/g* ca. 1990 (Feshbach and Friendly, 1992).

[9] This is likely what is termed *Russian-Spring-Summer-Encephalitis* in medical sources. The disease is reputed to have a high mortality.

recent report (AMAP, 1997) suggests that DDT, HCH and mixtures of the two may have been used in hospitals against nuisance insects such as cockroaches. If so, domestic usage of these preparations may be common.

Peripheral references in Galiulin and Bashkin (1996b) and Zhulidov et al. (1997) suggest that the DDT analogue *dicofol* (kelthane) may also be produced and used in Russia. Until 1986, dicofol produced in the USA was contaminated with up to 20% DDT (Sericano et aI., 1990) when improved manufacturing reduced DDT contamination to <0.1 %. If Russia were producing dicofol by crude technology, the technical product could be another source of DDT.

It is unclear to what extent that the common cyclodienes (Le., the *drins,* heptachlor, and chlordane) were produced and used. McConnell et al. (1993) claimed that heptachlor was allowed for restricted usage. Unmetabolized heptachlor was found in zooplankton and fish taken in 1993 from Lake Baikal suggesting recent usage in the area (see Chapter 5). A compound designated *dihydroheptachlor* is used in Russia (Roshydromet, 1994; Zhulidov at aI., 1997). This is similar but not identical to what is commonly known as heptachlor elsewhere in the world[10].

Polychlorocamphene (PCC) was manufactured and used heavily in the FSU. A formulation known as *polydophen* (20% DDT and 40% PCC in diesel fuel solvent) was used on cotton crops in central Asia after the nominal banning of DDT in 1971 (McConnell et aI., 1993). While PCC usage was apparently restricted at some point, PCC continued to be recommended into the 1990s as an insecticide for certain field crops (sugar beets, peas, potatoes, mustard, rape and perennial herbs) to be applied as 50% ai formulation at 1.6-3 kg/ha during the sprout stage (McConnell et aI., 1993). The current status of PCC in Russia and the NIS is not known.

HCB analyses are performed on subsets of surface water samples obtained for pesticide monitoring by the Russia federal monitoring agency (Zhulidov et aI., 1997; Roshydromet, 1994). No explanations were offered, but the fact that HCB is monitored suggests that it was, and may still be, produced and used explicitly as a fungicide.

### 3.1.1 Inadvertent PCDD/F Pollution by Contaminated Pesticides

Inadvertent environmental pollution by PCDD/Fs occurring as contaminants in pesticides should be considered. Amongst other areas, the 1992 State Report on the Environment considered dioxin pollution to be a threat in the rice growing zone in the Kuban, the Sea of Azov, the lower Volga and the far east (Feshbach, 1995). From 1961 to 1988, the Khimprom chemical plant at Ufa produced herbicides (2,4,5-T; 2,4,5TCP; Cu salt of 2,4,5-TCP; 2,4-D; and others) that were contaminated with PCDD/Fs.

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[10] The formal chemical name: 2,4,S,6,7,8,8-heptachlor 4,7-endo-methylbicyclo [4,3,0] -S-nonene was given by Zhulidov et al. (1997) for dihydroheptachlor with formula C10H7C17. Heptachlor as known in North America has formula C10HSCI7.

From Ufa, herbicides were distributed to other plants for further processing and distribution. Beyond local contamination at the processing plants, soils subjected to herbicide applications were also dosed with PCDD/Fs.

The herbicides derived from chlorophenolics may be of most concern. These were likely applied mainly in southern Russia, particularly in rice growing areas, and were used heavily in the Aral Sea basin. Recently, an ominous report emerged on the poor health of Kazakhstani children of the Kyzl Orda region citing inordinately high DDT, HCH, PCBs, and HCB observed in blood plasma samples (Jensen et al., 1997) and certain clinical symptoms common to the YusholYu-cheng poisoning victims and their offspring. The authors cite another report (Petreas et al., 1996) of 2,3,7,8-TCDD in Kazakhstani human milk at the extraordinary level of 50 *pg/g* lw. Jensen et al. (1997) conclude that contaminated 2,4,5-T was responsible, while Galiulin and Bashkin (1996a) propose that DDT and PCBs were responsible. Another report (Ivanov et al., 1996) noted that about 30 pesticides in all were used in Aral Sea basin at total annual rates of 20-25 kg/ha. Prominent amongst these was *Saturn,* a herbicide mix that included *chlornitrofen,* a diphenyl ether herbicide used copiously on rice paddies. In Japan, chlornitrofen was found to be contaminated by PCDD/Fs (Ohsaki et al., 1997).

In summary, a variety of contaminated organochlorine insecticides and herbicides that were applied at high rates the Aral Sea basin may have been at least partially responsible for potentially severe PCDD/F contamination problems that are now being identified there. As most of the same chemicals were likely applied at high rates in areas of southern Russia, similarly severe PCDD/F contamination may have occurred there also. If pesticide usage data warrant, investigations of PCDD/F occurrence in the environments of the Kuban valley, Sea of Azov, the lower Volga and other watersheds should be conducted.

Fedorov (1993) has suggested that PCDD/F contamination may also have occurred at the production facility for DDT and HCH located in Chapayevsk near the city of Samara (formerly Kuybyshev) in the central Volga basin.

## 3.2 Surface Water Monitoring of Pesticides

Surface water monitoring of insecticides DDT and HCH began in 1964 in regions where these were being most heavily used (Moldova, Ukraine, Trans-Caucasia, and Central Asia). By 1974, routine surface water monitoring began at 90-100 sites on downstream reaches of major rivers. In addition to DDT and HCH, other non-POPs insecticides and herbicides are monitored according to an evolving priority list.

A terse description of the entire historical pesticide monitoring effort to about 1993 was given by Petrosian et al. (1998), while Zhulidov et al. (1997) review the monitoring program for 1988-1994. Over 1988-1990, coverage across the FSU spanned almost 6,000 sites at which 53,000 samples were collected. The condensed summary by

Petrosian et al. (1998) reveals that during the years of high DOT and HCH usage (1960s and 1970s), high levels were broadly observed in surface waters of the FSU, particularly in southerly regions with greater agricultural activity, and that through the 1980s, observed levels have declined as usage of these chemicals was curtailed. Little regionally specific information can be ascertained at this coarse level of summarization. Petrosian et al. (1998) and Zhulidov et al. (1997) give additional references to regional and river basin oriented studies that may yield more detailed information.

In 1993, it appears that pesticide monitoring in the Russia Federation was formally separated from activities in FSU republics. For 1993, the Russian Federation had about 820 active sites at which 5,350 samples were collected (Roshydromet, 1994).

Although PCC was heavily used in the FSU, there seems to have been little effort to monitor PCC in surface water and other environmental compartments. According to McConnell et al. (1993), PCC is not on the mandatory monitoring list, and is only measured occasionally. It is rather unlikely that PCC could be detected by the analytical methods currently employed.

### 3.2.1 Russian Federation - Summary of 1993 POPs Insecticide Monitoring

For present work, summary statistics for DOT and HCH in major rivers were extracted from the 1993 annual of surface water and sediment monitoring summary report for the Russian Federation (Roshydromet, 1994). These summary data suffer from crude statistical treatment, inadequate detail concerning field and analytical methodology, and questionable handling of results below analytical detection limits, but there is enough information to identify certain regions and watersheds where DOT and HCH continue to be of concern.

In 1993, analyses for HCH and DOT species were performed on about 5,360 samples obtained at 822 *routine* surface water monitoring sites across the Russian Federation (Roshydromet, 1994). From 2-13 samples were obtained at each site, with most sites having 4-7 samples. Additional analyses done at 30 *key* monitoring sites sampled about 4-5 times each. There were also 46 *sediment* monitoring sites where bottom material was sampled 1-5 times, and 6-7 water samples were obtained at 36 of the 46 sediment sites. Narrative descriptions indicate that there is appreciable geographic overlap among routine, key and sediment monitoring sites, but it is unclear how many sites in any set are identical or in near proximity to sites in the other two sets. It appears that water samples collected at the 46 *key* sites (132) and 36 *sediment* sites (248) were not included in the *routine* water monitoring summaries.

The most commonly analyzed chemical species in all monitoring regimes were o,HCH; y-HCH; *p,p'-DDT* and p,p'-DDE which were done on nearly all samples. p-HCH and *p,p'-DDD* were measured far less frequently (p-HCH on 614 samples at 99 routine sites, and *p,p'-DDD* on 341 samples at 64 routine sites). At routine sites, there were also 73 analyses for HCB (hexachlorobenzene) and 240 for *dihydroheptachlor.*

### 3.2.2 Limitations of the 1993 Summary Report

The 1993 annual report suffers from excessive reduction of a large, spatially extensive data set. The omission of crucial geographical and technical information makes it difficult to extract geographically and quantitatively meaningful information. Data are summarized geographically at three levels: (1) by 20 administrative regions of the federal monitoring agency from which field operations are organized, (2) by more than 30 hydrologic divisions (major river basins, or aggregates of contiguous small rivers and streams such the Kola Peninsula), and (3) by 10 greater hydrographic units (oceanographic watersheds for open river systems).

At no level of geographic aggregation is it indicated what drainage area or predominant upstream land use classes are represented by the sites contained therein. Thus, summary data in the 1993 report may often represent indeterminate mixtures of watershed classes that misrepresent conditions over the greater watershed. For example, a preponderance of sites in small agricultural watersheds where pesticides are applied heavily could dramatically overwhelm fewer sites distributed along the main channels of large rivers, or across sparsely populated northerly catchments.

Generally, the most detailed data summary is given for the administrative regions. The 20 administrative regions of the federal monitoring service are listed in Table 3.1 with the major hydrographic and river basins thought to be within the territories administered by each office. These latter indications are merely educated guesses that may be subject to errors and omissions. The only administrative regions with reasonably unambiguous correspondence to distinct hydrologic divisions are Murmansk (Kola Peninsula), Sakhalin Island, and Kamchatka.

The administrative regions and hydrologic divisions are not hierarchical. Administrative districts sprawl across major hydrologic divisions, and vice versa. Also, the monitoring agency's administrative regions of are not generally identical to political administrative divisions of the Russian Federation. Without maps or georeferenced site lists, the extent of territories and rivers basins within monitoring agency administrative regions is impossible to ascertain accurately.

Some regions may be very large. While the Omsk region is limited to territories of Irtysh River affluent of the Ob River along the frontier with Kazakhstan, the Western Siberia region may span the entire territories of the main Ob branch from headwaters in the Altay Republic on the frontier with Kazakhstan to the Arctic Ocean. If Krasnoyarsk region corresponds spatially to the Krasnoyarsk- Kray, it may have responsibility for all the Yenesei River exclusive of the Irkutsk Oblast, and several independent low Arctic rivers including the Pyasina, Taymir and Khatanga. Krasnoyarsk region may also have responsibility for Yenesei headwaters in the Tuva and Khakassia Republics to the south and west of Krasnoyarsk Kray.

Table 3.1 Administrative regions of the federal environmental monitoring agency and likely hydrographic and river basins within these regions.

| Region | Hydrographic basin | Major basin | Rivers / geographic unit |
|---|---|---|---|
| Northwest | Baltic Sea | Baltic | Neva, Luga, Narva, Daugava |
| Murmansk | Western Arctic | Barents Sea | Kola Peninsula |
| Northern | Western Arctic | Barents Sea | Onega, Severnaya Dvina, Mezen, Pechora |
| Omsk | Eastern Arctic | Ob | Irtysh, Ishym |
| Western Siberia | Eastern Arctic | Ob | Ob excluding Irtysh |
| Krasnoyarsk | Eastern Arctic | Yenesei | Yenesei excluding Angara lands in Irkutsk Oblast |
| Irkutsk | Eastern Arctic | Yenesei | Angara, L. Baikal, upper Lena |
| Yakutsk | Eastern Arctic | Lena | central/upper Lena |
| Tiksi | Eastern Arctic | Lena | lower Lena, Omoloy, Yima |
| Central Chernozem | Black / Caspian Sea | Volga / Don / Dniepr | Dniepr, Oka, Don |
| North Caucasus | Black / Caspian Sea | | lower Don, Kuban, Kuma |
| Upper Volga | Caspian Sea | Volga | |
| Moscow | Caspian Sea | Volga | Moscow |
| Bashkirsk t | Caspian Sea | Volga | Kama |
| Privolzhskoye | Caspian Sea | Volga | lower Volga |
| Urals | Caspian Sea | Ural | Ural |
| Zabaikalsk | Pacific | Amur | upper Amur |
| Far Eastern | Pacific | | lower Amur, Primorsky Kray |
| Sakhalin | Pacific | | Sakhalin Island |
| Kamchatka | Pacific | | Kamchatka Peninsula |

t Bashkirsk is another common name for the Republic of Bashkortostan.

### 3.2.3 Analytical and Statistical Issues

The 1993 report defines analytical *trace* level limits as 5 ng/L (a.-HCH, y-HCH), 50 ng/L (DOT,. DOE), and 10 ng/L (ODD). For routine monitoring data, it appears that these trace limits were used to distinguish detections from non-detections. For socalled *key* monitoring data, percentages of *traces* and *detections* are given separately suggesting that different thresholds may have been used to distinguish traces and detections from fully quantified measurements. Detection thresholds were 10 ng/L for f3-HCH, 20 ng/L for HCB and 5 ng/L for dihydroheptachlor (Zhulidov et al., 1997).

Analytical thresholds of 5 ng/L are marginally adequate for relatively water soluble u-HCH and y-HCH; however, thresholds of 50 ng/L are too high to acceptably characterize DOT species in water. As summarized in the 1993 annual report, the low detection frequency of DOT and metabolites obtained by low resolution analytical methods, compounded with crude statistical summarization predicated on the arbitrary substitution of zeros for non-detections (NOs), likely misrepresents the actual occurrence and significance of DOT in Russian aquatic ecosystems.

An obvious case of misrepresentation occurs with percentages of DOT and DOE measurements that exceed arbitrary *maximum allowable concentrations* (MACs). The MACs are defined identically as 10 ng/L for DOT, DOE and ODD [11]. Because NO sample results are <50 ng/L, it is technically impossible to calculate the percentage of samples exceeding MAC for DOT and DOE. By arbitrarily substituting Os for NOs, the authors of the 1993 annual report have effectively given the percentage of DOT and DOE samples with DOT and DOE content ~50 ng/L, not the percentage of samples exceeding MAC. For each HCH isomer, the MACs are also identically 10 ng/L. As detection thresholds are 5 ng/L for u-HCH and y-HCH, the reported percentages of samples exceeding MACs for individual HCHs are reliable, but the percentage of samples with "LHCH = u-HCH + y-HCH > 10 ng/L cannot be calculated precisely.

It is never stated precisely what DOT species were measured. Most likely, the *p,p'*-isomers *(p,p'-DDT, p,p'-DDE* and *p,p'-DDD)* were measured in water and sediments. However, it is unclear, and seems unlikely, that *o,p'* -isomers were determined in water or sediments. While *a,p'-DDT* is likely the only a,p'-isomer that might be found in water at perceptible frequency, all a,p'-isomers could be present in sediments.

### 3.2.4 HCH Regional Summary

A regional summary for "LHCH = u-HCH + y-HCH is given in Table 3.2. The table illustrates the implications of assuming different numerical values between zero and detection threshold (5 ng/L) for samples reporting undetected u-HCH or y-HCH. The effects of arbitrary numerical substitution are not great if roughly 45% or more samples have detectable u-HCH or y-HCH and "LHCH > 25 ng/L. Relative uncertainty in mean concentrations becomes proportionately greater as the percentage of samples with detectable u-HCH or y-HCH falls below 40% and "LHCH < 20 *ng/L.*

The three regions with leading HCH occurrence in water samples- Omsk, Privolzhskoye, and Krasnoyarsk - generally conform to the geographic distribution of historical HCH usage mapped by Li et al. (1996). The waters of the Omsk region have unequivocally the highest levels of HCH contamination with at least 38 of 40 sites

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[11] Russian legislation apparently specifies zero presence of DDT and HCH in water samples. As zero concentrations are physically impossible for POPs class chemicals in surface waters, the monitoring agency has arbitrarily specified unofficial MACs of 10 ng/L for DDT and HCH species in water.

having detectable a-HCH or y-HCH; at least 46% of samples having LHCH > 10 ng/L; and overall mean concentration of 110-115 ng/L. At least one sample had LHCH > 1 /lg/L (maximum reported y-HCH was 1.7 j..lg/L). Omsk region likely comprises mostly agricultural steppe lands on the southern frontier with Kazakhstan. The main channel waters of several major Ob River tributaries (Tobol, Ishym, and Irtysh) entering from Kazakhstan likely carry HCHs that originated there.

After Omsk, Privolzhskoye region, which likely spans the mid and lower reaches of the Volga basin, has widespread HCH contamination (70 of 85 sites) but a lower regional mean concentration of 49-55 ng/L LHCH. The region includes sites on the River Chapayevka that receives waste discharges from the HCH production plant located near the city of Chapayevsk. The 1993 Omsk region maxima for a-HCH and yHCH (1.8 and 4.2 /lg/L respectively) occurred in River Chapayevka samples. If River Chapayevka data were removed from the Privolzhskoye region data set, the regional mean concentration should decline perceptibly, but widespread regional contamination would likely remain evident.

After Privolzhskoye, Krasnoyarsk region has widespread HCH contamination (41 of 47 sites), and a regional mean concentration of 26-31 ng/L LHCH. Reported 1993 maxima for a-HCH and y-HCH are both about 100 ng/L indicating that the severity of contamination at the most polluted sites is perceptibly lower than in Omsk or Privolzhskoye regions.

The next three regions: Zabaikalsk, Northern, and Central Chernozem, could be considered to have widespread but marginal contamination by HCHs. At least 60-80% of sites reported detectable LHCH, and regional mean concentrations are at or nor far above MAC. After these, eight regions (Yakutsk, North Caucasus, Murmansk, West Siberia, Upper Volga, Bashkirsk, Northwest, Far Eastern) show mild HCH pollution with regional mean concentrations likely in the 1-9 ng/L range. Lastly, six regions (Moscow, Urals, Irkutsk, Tiksi, Kamchatka, and Sakhalin) show nil contamination of HCH isomers above the 5 ng/L detection threshold.

In addition to the main HCH isomers, there were 13 detections in 614 13-HCH determinations at 99 sites in three regions. The 13-HCH occurred mostly in Western Siberia region at five of 57 sites that had 2 detections each. One site (River Inya, a tributary of the Tom River) in Kemerovo Oblast yielded 1.4 /lg/L 13-HCH. Crude HCH may have been used in the district along with DOT to combat tick-borne encephalitis.

### 3.2.5 HCH Major Watershed Summary

Table 3.3 gives a summary of 1993 HCH data reorganized by major watershed. The estimates of LHCH mass flux are intended to indicate roughly the potential for delivery of LHCH to coastal waters.

Table 3.2 LHCH a summary by administrative regions, 1993.

| Region | mean concentration b ng/L | | | | C Min | d M. | sites | e Min |
|---|---|---|---|---|---|---|---|---|
| | | | | n | | In | | |
| | | | | | %:2:5 | %> 10 | | %sites |
| | a | *1/2* DL | DL | | | | | |
| Omsk | 111 | 113 | 115 | 311 | 62 | 46 | 40 | 98 |
| Privolzhskoye | 49 | 52 | 55 | 847 | 46 | 36 | 85 | 82 |
| Krasnoyarsk | 26 | 29 | 31 | 251 | 46 | 42 | 47 | 87 |
| Zabaikalsk | 12 | 16 | 19 | 280 | 35 | 24 | 62 | 77 |
| Northern | 9 | 12 | 16 | 207 | 39 | 17 | 42 | 79 |
| Central Chemozem | 6 | 10 | 14 | 1,027 | 19 | 6 | 79 | 62 |
| Yakutsk | 4 | 9 | 13 | 93 | 14 | 14 | 18 | 50 |
| North Caucasus | 3 | 8 | 12 | 674 | 11 | 5 | 98 | 26 |
| Murmansk | 3 | 7 | 12 | 161 | 14 | 8 | 29 | 55 |
| West Siberia | 2 | 7 | 12 | 380 | 9 | 6 | 57 | 35 |
| Upper Volga | 2 | 7 | 11 | 378 | 6 | 3 | 99 | 20 |
| Bashkirsk | 3 | 7 | 11 | 73 | 27 | 10 | 11 | 72 |
| Northwest | 2 | 7 | 11 | 165 | 14 | 6 | 55 | 27 |
| Far Eastern | 1 | 6 | 11 | 105 | 6 | 3 | 11 | 18 |
| Moscow | a | 5 | 10 | 141 | 1 | a | 26 | 8 |
| Irkutsk | a | 5 | 10 | 51 | a | a | 22 | a |
| Kamchatka | a | 5 | 10 | 18 | a | a | 9 | a |
| Sakhalin | a | 5 | 10 | 141 | a | a | 23 | a |
| Ural | a | 5 | 10 | 12 | a | a | 3 | a |
| Tiksi | a | 5 | 10 | 44 | a | a | 6 | a |
| Mean *1* total | 12 | 16 | 20 | 5,359 | 22 | 15 | 822 | 48 |

[a] LHCH = u-HCH + y-HCH.

[b] Mean LHCH concentrations obtained from separately determined u-HCH and y-HCH assuming non-detections = 0, *1/2* or 1 times detection threshold of 5 *ng/L.*

[C] Lower limit of possible percentage of samples with detectable ( ~ 5 ng/L) LHCH defined as the maximum percentage detected of either u-HCH or y-HCH.

[d] Lower limit of possible percentage of samples exceeding MAC ( > 10 ng/L) for LHCH defined as the maximum percentage exceeding MAC of either u-HCH or y-HCH.

[e] Lower limit of possible percentage of sites with detectable ( ~ 5 ng/L) LHCH defined as the maximum percentage detected of either u-HCH or y-HCH.

For large watersheds, the LHCH annual mass flux estimates are likely too high because the concentration data seem biased to remote headwater source areas. Moreover, the geographic distribution of historical HCH usage (Li et al., 1996) strongly suggests that this should be the case. In particular, LHCH flux from the Ob, Yenesei, and Volga rivers may be grossly exaggerated. The mean concentration of 55 ng/L

given for the Ob watershed is roughly the average of concentrations reported in Table 3.2 for the Omsk and West Siberia regions. Using the West Siberia mean concentration of 7 ng/L yields an annual flux to the Arctic Ocean of only 2,800 kg. The mean concentration of 15 ng/L given for the Yenesei watershed is roughly the average of mean concentrations reported for the Krasnoyarsk and Irkutsk regions. Using the· Irkutsk mean concentration of 5 ng/L yields an annual flux of only 1,640 kg to the Arctic Ocean from the Yenesei River. As the mapping by Li et al. (1996) suggests more geographically uniform historical HCH usage in the Volga watershed, HCH fluxes from the lower Volga may not be so exaggerated.

The reliability of the potentially high HCH flux from the Amur River is impossible to determine without further investigation. The mean concentration of 12 *ng/L* is identical to that reported for Zabaikalsk administrative region which may represent mainly headwater sites in Chita Oblast. There are sizable areas of land with agricultural potential in eastern Chita Oblast, southeastern Amur Oblast (mid Amur basin) and Primorsky Kray (Ussuri River watershed) where HCH may have been used. Appreciable HCH in the lower Amur River may also originate from the Sungari River (Chinese *Songhua Jiang)* that drains northern Manchuria, the most heavily populated and agricultural sub-basin of the Amur system[12]. The mapping of global HCH usage by Li et al. (1996) shows that there was significant crude HCH usage in Manchuria. Although China banned crude HCH usage about 1983, perceptible residues may continue to leach from Chinese territory. The Ussuri River (Chinese *Wusuli Jiang)* drains lands of both Russia and China where HCH may have been used.

Extraordinarily high mean concentration and potential river flux are reported for the Pyasina watershed located in the Arctic east of the lower Yenesei River. The Pyasina River basin is sparsely inhabited other than in the environs of the large copper-nickelplatinum smeltering centre at Norilsk (pop. -170,000). The city lies about 100 km east of the main channel of the lower Yenesei, and just south of the tree line in the upper Pyasina basin. Agriculture at this latitude ($69^0$ N) is unlikely, but it is conceivable that HCH has been used for nuisance insect (mosquito, black fly) control. If so, it seems likely that the high HCH concentration reported for the Pyasina watershed reflects mainly monitoring sites near Norilsk.

Otherwise, the highest HCH concentrations occurred in river systems draining to the Caspian Sea. The Russian Ural River basin is adjacent to the Omsk region territories of the upper Ob-Irtysh system along the frontier with Kazakhstan. Despite sites in Upper Volga, Bashkirsk, and parts of other regions, the relatively high mean concentration for the Volga basin is most likely determined by monitoring sites on the lower Volga system in Privolzhskoye region, particularly on the River Chapayevka where the HCH manufacturing plant is located.

[12] 50,000,000 or more residents of Heilongjiang and Jilin provinces may reside within the Songhua basin.

Table 3.3 LHCH summary by major watershed, 1993.

| | | | LHCH[a] | |
|---|---|---|---|---|
| River | Hydrographic basin | [b] Annual discharge km$^3$ | [c] Mean concentration ng/L | Annual mass flux kg |
| Neva | Baltic Sea | 80 | 3 | 239 |
| Kola Peninsula t | Western Arctic | 18 | 3 | 53 |
| Onega | Western Arctic | 16 | 6 | 94 |
| S. Dvina | Western Arctic | 102 | 8 | 819 |
| Mezen | Western Arctic | 27 | 6 | 164 |
| Pechora | Western Arctic | 132 | 4 | 530 |
| Ob | Eastern Arctic | 399 | 55 | 21,947 |
| Yenesei | Eastern Arctic | 591 | 15 | 8,871 |
| Pyasina | Eastern Arctic | 49 | 37 | 1,798 |
| Lena | Eastern Arctic | 520 | 5 | 2,600 |
| Kolyma | Eastern Arctic | 120 | 3 | 360 |
| Amur | Pacific | 338 | 12 | 4,057 |
| Dniepr | Black Sea | 12 | 3 | 36 |
| Don | Black Sea | 25 | 2 | 50 |
| Kuban | Black Sea | 11 | 2 | 23 |
| Terek | Caspian Sea | 1 | 28 | 30 |
| Volga | Caspian Sea | 231 | 27 | 6,224 |
| Ural | Caspian Sea | 10 | 47 | 461 |

14
15
7
19
2
6
71

[d] Min %:2:5

19

14 47 31 39 26

29 29 67 15 10

[a] LHCH = cx.-HCH + y-HCH except for Ob and Volga basins where LHCH = cx.-HCH + ~-HCH + y-HCH.

[b] Annual discharge near outlet except: (1) Dniepr estimated for roughly 25% of basin in Russian territory, (2) Terek at mid basin, (3) Ural at Kazakhstan frontier.

[c] Mean concentrations by assuming 0 concentration for non-detections; there were insufficient data given in

Roshydromet (1994) to consider other possibilities. Mean *concentrations are for all samples obtained the watershed, not sites* at *the rivers' outlets.*

[d] Lower limit of possible percentage of samples with detectable ( ~ 5 ng/L) LHCH defined as the maximum percentage detected of either cx.-HCH or y-HCH.

[t] Estimate for streams of Kola Peninsula; mean concentration and percentage detections are average for White Sea and Barents Sea drainage given in Roshydromet (1994).

The Terek River is on the Trans-Caucasian isthmus between the Sea of Azov and the Caspian Sea. Other sites in the area draining eastward to the lower Don and Sea of Azov (Don, Kuban, and some small tributaries) and the River Kuma draining to the Caspian Sea had low (1-4 ng/L) mean LHCH concentrations.

Mean LHCH concentrations of 6-8 ng/L for the Onega, North Dvina and Mezen watersheds draining to the western Arctic are relatively low, but higher than anticipated. This suggests there is some ongoing HCH usage in the watersheds, likely in agriculture and possibly as general purpose insecticide against nuisance insects. The Neva basin summary data for 1993 suggests that a few sporadic occurrences of HCHs were observed. For 1995, authorities of Leningrad Oblast reported no occurrences of HCH above a detection threshold of 1 *ng/L* (Lencompriroda, 1997).

### 3.2.6 HCH at *Key* and *Sediment* Monitoring Sites

For the 30 *key* monitoring sites, the overall detection rates of a-HCH and y-HCH (40-43% of 132 samples) were about the same as observed at *routine* monitoring sites. The mean concentration of LHCH = a-HCH + y-HCH was 17 *ng/L,* somewhat lower than the highest regional and watershed mean concentrations seen at *routine* monitoring sites, but greater than in most regions or watersheds. The highest concentrations (52 *ng/L)* were observed in the Irtysh River at Tobolsk (Ob basin, Omsk region) and in the Kuma River at Vladimirovka (Caspian Sea basin, Northern Caucasus region). In 4-5 samples from River Chapayevka, the highest concentrations were 34 *ng/L* a-HCH and 32 *ng/L* y-HCH, both appreciably lower than the extremes recorded in the *routine* samples (1. 79 ~*g/L* a-HCH, 4.2 ~*g/L* y-HCH).

In water samples collected at 36 *sediment* monitoring sites, the main HCH isomers had a gross detection frequency of 34%, perceptibly lower than observed at *key* and *routine* sites. However, the overall result is skewed by 90% detection in 58 samples from four sites in Privolzhskoye region, at least two of which were on River Chapayevka. Outside of Privolzhskoye region, the main HCH isomers were detected in only 17% of samples. Data were not summarized other than by detection frequencies, and it is unclear why additional samples where collected at many of these sites.

HCH concentrations in sediment samples are more informative. Three sites in the River Chapayevka, apparently downstream of the insecticide plant, had mean LHCH = a-HCH + y-HCH concentrations of 12-27 *ng/g* for 4-5 sediment samples each. y-HCH isomer was dominant at both sites. Annual data for 1990-1993 given for one site, suggest that 1993 marked a significant shift in composition to dominance by y-HCH from earlier dominance by a-HCH. This may correspond to increased production of lindane (y-HCH). f3-HCH was evidently not measured at any River Chapayevka sites.

HCHs also were prevalent in sediments collected in small watercourses discharging to the lower Don River and Don estuary. Mean LHCH concentrations for 3-4 samples at each of 9 sites ranged from 0.2 to 88 *ng/g,* but only three had LHCH > 10 *ng/g.* At most sites, LHCH composition was dominated by a-HCH suggesting past and recent crude HCH usage in the district. Despite these indications, f3-HCH was not measured. There were no HCH detections in 29 water samples from 5 sites. Because a-HCH and y-HCH are more likely to be found in water than in sediment, the water and sediment sample data appear to be inconsistent for the lower Don sites.

Otherwise, sediment samples from Murmansk, Northern, Western Siberia, Irkutsk and Ural regions showed mean LHCH concentrations of 0.5-2.4 *ng/g* with a few results > 5 *ng/g.* No f3-HCH detections were recorded in 37 samples from 18 sites in 4 regions. No a-HCH or y-HCH detections were observed in 27 sediment samples from 9 sites in Sakhalin and Krasnoyarsk regions.

### **3.2.7** DOT Summary

A regional summary for *LDDT* = *p,p'-DDT* + *p,p'-DDE* at routine monitoring sites is given in Table 3.4. The effects of the low resolution measurements are illustrated by assuming different numerical values between 0 and detection threshold (50 ng/L) for samples reporting undetected *p,p'-DDT* or *p,p'-DDE.* The mean concentrations obtained by assuming Os for ND sample results give the lower limits of the true regional averages. Due to the detection thresholds of 50 ng/L for *p,p'-DDT* and *p,p'-DDE,* the upper limits on average *LDDT* concentrations are 100-108 ng/L for all regions. The true regional averages are likely closer to the lower limits in the table, but there is no way of obtaining better estimates without better analytical methods capable of resolving DDT species down to 1 ng/L or better. Typical guidelines for aquatic life protection in temperate northern waters for *LDDT*[13] are in the range 1-3 ng/L (MacDonald, 1994). It is very likely, that many sites will have total DOT exceeding 3 ng/L, particularly in regions registering some DDT and DDE detections above the 50 ng/L threshold.

Superficially, waters of Moscow and Omsk regions seem most contaminated with DDT, but apparent differences amongst regions may be spurious. Because there were only 95 detections of *p,p'-DDT* at 66 sites and 13 of *p,p'-DDE* at 14 sites for all Russia, differences amongst regional averages depend on sites with 1-2 measurements above 50 ng/L. Generally, extrema are more likely to be erroneous or atypical samples that do not reliably indicate central tendencies.

The best that can be concluded from the 1993 regional summary is that there are weak indications that DDT occurrence in surface waters is more prevalent in Moscow and Omsk regions. In Moscow region, there was 1 detection of *p,p'-DDT* at each of 10 sites with an average detected concentration of 169 ng/L, while in Omsk region there were 23 detections of *p,p'-DDT* at 13 sites with an average of 95 ng/L per detection, plus 3 detections of *p,p'-DDE* at 3 sites with an average of 104 ng/L per detection. Central Chernozem region had 32 detections of *p,p'-DDT* at 17 sites with an average of 97 ng/L per detection.

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[13] Usually determined as LOOT = *p,p'-DDT* + *D,p'-DDT* + *p,p'-DDE* + *p,p'-DDD.*

Table 3.4 LDDT[a] summary by administrative regions, 1993.

| Region | mean concentration b ng/L | | | | C Miri | sites | dM· |
|---|---|---|---|---|---|---|---|
| | | | | n | %~50 | | In %sites |
| | 0 | *1/2* DL | DL | | | | |
| Moscow | 12 | 60 | 108 | 141 | 7.1 | 26 | 39 |
| Omsk | 8 | 56 | 104 | 311 | 7.4 | 40 | 33 |
| Northwestern | 6 | 55 | 103 | 165 | 4.8 | 55 | 13 |
| West Siberia | 3 | 53 | 103 | 380 | 0.5 | 57 | 2 |
| Central Chernozem | 3 | 52 | 101 | 1,029 | 3.1 | 79 | 22 |
| Far Eastern | 3 | 52 | 101 | 105 | 3.8 | 11 | 18 |
| North Caucasus | 2 | 52 | 101 | 670 | 1.3 | 96 | 9 |
| Privolzhskoye | 1 | 51 | 101 | 847 | 0.7 | 85 | 7 |
| Upper Volga | 0 | 50 | 100 | 378 | 0.3 | 99 | 1 |
| 11 regions | 0 | 50 | 100 | 1,329 | 0 | 271 | 0 |
| Mean *I* total | 2 | 49 | 96 | 5,355 | 1.8 | 819 | 8 |

[a] *LDDT* = *p,P'-DDT* + *p,P'-DDE.*

[b] mean ~DDT concentrations obtained from separately determined *p,p'-DDT* and p,p'-DDE assuming non-detections = 0, *1/2* or 1 times detection threshold of 50 *ng/L.*

[c] lower limit of possible percentage of samples with detectable ( ~ 50 ng/L) *LDDT* calculated as the maximum of individual percentage detected of *p,p'-DDT* and p,p'-DDE; as p,p'-DDE detections are about *1/6 p,p'-DDT* detections, these percentages are identical to % *p,p'-DDT* ~ 50 *ng/L.*

[d] lower limit of possible percentage of sites with samples with detectable ( ~ 50 ng/L) *LDDT* calculated as the maximum of individual percentage of sites with detected *p,p'-DDT* and p,p'-DDE; as p,p'-DDE detections are about *1/6 p,P'-DDT* detections, these percentages are identical to % of sites where *p,P'-DDT* was detected.

For other regions, the available data may not be particularly meaningful. For example, West Siberia region ranks fourth in mean concentration only because of two detections of *p,p'-DDT* at one site, one sample of which yielded *p,p'-DDT* of 1.11 J.lg/L, the highest concentration observed across Russia. Removing the site places West Siberia near the bottom of the ranking. Northwestern and Far Eastern regions rank relatively high, but again the rankings depend on a few samples at a few sites.

The Western Siberian site yielding the high *p,P/-DOT* concentration of *1.111lg*$^{/L}$ was in the Kemerovo Oblast (Kemerovo city on River Iskitimka, a tributary of the Tom River, Ob watershed) where DDT was used to combat tick-borne encephalitis. More detections might be observed if higher resolution analytical methods were employed.

### 3.2.8 DOT Major Watershed Summary

Like HCH, DOT was summarized by major watersheds, but meaningful conclusions cannot be derived from this approach. The low watershed mean concentrations (0-7 ng/L) derived by assuming non-detections to be zero depend on relatively few detections (from nil to 7%) above the 50 ng/L measurement threshold for DOT species.

As summarized in Roshydromet (1994), DOT data at the 30 *key* monitoring sites yield little useful information. Superficially, detections of *p,p'-DDT* and p,p'-DDE seem to be perceptibly higher than at *routine* monitoring sites; however, the definition of a detection appears to differ from that used for summarizing routine data. The highest *p,p'-DDT* measurement (90 ng/L) was found in the Ussuri River headwaters at Novomikhailovka, Primorsky Kray. This at least suggests that there has been DOT usage in the far eastern maritime territories.

In *water samples* collected at 36 *sediment* monitoring sites, *p,p'-DDT* and *p,p/*DOE were detected on 6-7% of samples. However, 10 detections (about 60% of all detections) occurred in 58 samples from three of four sites in Privolzhskoye region, at least two of which were on River Chapayevka, site of the DOT production plant.

The *sediment samples* collected at 46 *sediment* monitoring sites yield somewhat different findings. Either *p,p'-DDT* or p,p'-DDE was detected on at least 75% of 38 samples from 10 sites in North Caucasus region. At least 9 of the 10 sites are small tributaries or canals discharging to the lower Don River or the Don estuary from within Rostov Oblast. LOOT = *p,p'-DDT* + p,p'-DDE concentrations for the 9 sites had mean 204 ng/g and range 1.6-698 ng/g. More importantly, *p,p'-DDT* comprised 58-92% of LOOT composition. Though the full complement of DOT species was not measured, the evidence strongly suggests that there had been recent DOT usage. Oddly, there was only 1 detection of DOT in 29 water samples collected at these sites.

High levels of DOT were also detected in 6 sediment samples from 3 sites in Murmansk region. The mean LOOT = *p,p'-DDT* + p,p'-DDE + *p,p'-DDD* concentration for all samples was 19 ng/g, while mean LOOT for one site within the city of Murmansk (River Rosta) was 79 ng/g. For all samples, *p,p'-DDT* contributes an average of 56% to *LOOT* composition. For the Rosta River site, *p,p'-DDD* contributes 54%. As the conversion to *p,p'-DDD* can be rapid, Murmansk region sediment data generally suggest recent DOT usage in the area.

Lower DOT levels were seen in sediments of the Ural and Privolzhskoye regions. In Ural region, DOT was found in one sample from each of 3 sites. Mean LOOT = *p,p/*DOT + p,p'-DDE + *p,p'-DDD* was 1.6 ng/g, and most was in metabolized form. In 18 samples from 4 sites in Privolzhskoye region, *p,p'* -DOT or *p,p/* -DOE were apparently detected in only 2 samples from 1 site. Oddly, DOT was found more frequently in water samples from Privolzhskoye region. No DOT species were detected in 63 samples from 26 sites in Northern, Western Siberia, Krasnoyarsk, Irkutsk and Sakhalin regions.

## 3.3 Galiulin-Bashkin 1989-1990 Soil-Sediment Survey

Surveys conducted over 1989-1990 of soils, sediments and surface waters of irrigated agricultural lands in Moscow, Kuban (Krasnodar) and Samarkand (Uzbekistan) regions by Galiulin and Bashkin (1996b) yields considerable insight into the varying degrees of regional contamination by DOT, HCH and PCBs. The PCB data obtained in these surveys are summarized in Chapter 4. The studies are of great relevance to aquatic ecosystem contamination by agricultural runoff as the sites were generally on riparian floodplains. Moreover, irrigation often entails surface or subsurface drains that enhance the transfer of agricultural chemicals into watercourses. A further report (Galiulin and Bashkin, 1996a) that apparently considers the potential pollution due to PCDD/Fs present in the pesticides and PCBs was unavailable for inspection.

The general features of the survey are summarized in Table 3.5. Samples were analyzed for four HCH isomers *(a-, J3-, y-,* 8-) and three DOT species (DOT, DOE, ODD; apparently only for *p,P/-isomers).* Detection thresholds were 2 *ng/L* in water and 50 *pg/g* in soil and sediments, much better than those of the Russian federal agency.

Table 3.5 General summary of 3 region Galiulin-Bashkin 1989-91 soil survey.

| | Moscow | Kuban | Samarkand |
|---|---|---|---|
| Soil / sediment type | light silt loam | loamy sand, light clay | clay loam, silty clay loam |
| % total C soil | 0.6-32.8 | 0.5-2.4 | 0.3-2.1 |
| % total C sediment | 1.7-3.1 | 0.5-4.7 | 0.2-0.6 |
| Pesticide usage kg/ha | 2-4 | 4-6 | 8-10 |
| Soil samples | 33 soils:<br>28 cabbage, 3 carrot, 2 fodder beet | 21 soils:<br>10 rice, 5 vineyards, 2 orchards, 3 cabbage, 1 winter wheat | 71 soils:<br>57 cotton, 8 tobacco, 5 vineyards, 1 orchard |
| Water samples | 6 | 2 | 8 |
| Sediment samples | 3 | 19 | 7 |

### 3.3.1 Moscow Oblast

Soils were sampled in Moscow Oblast (area 47,000 km$^2$) surrounding the city of Moscow with a population of about 8,700,000 including Moscow city. The region lies within the upper Volga basin, specifically parts of the Oka River and several of its affluents (Moscow, Klyazma, Yakhroma, and Istra rivers). Samples were obtained from fields on river valley floodplains of six districts in the region. Soils were mostly siltyloams, but evidently, some muck soils with high organic carbon content were sampled.

Table 3.6 DDT and HCH in Moscow Oblast soils *(ng/g), 1989-1990.*

| River | LDDT | | | LHCH | |
|---|---|---|---|---|---|
| | mean | range | %DDT | mean | range |
| Klyazma | 595 | 9-1 ,180 | 97 | t12.5 | |
| Yakhroma | 266 | 27-742 | 63 | 22.1 | 17-27 |
| Moscow | 187 | 0.1-701 | 89 | 6.8 | 2.5-16 |
| aka | 43 | 1-103 | 83 | 2.3 | 0.2-9 |
| Istra | 42 | 10-74 | 0 | :j:nd | |
| mean | 226 | | 66 | 8.7 | |
| MAC§ | 100 | | | 100 | |

t one sample only; :j: reported zero interpreted as not detected. § maximum allowable concentration.

Survey data are summarized in Table 3.6 by five river units (the Moscow River was sampled above and below the city). Significant OOT usage was evident at all sites, and HCH usage at all sites except the Istra River fields. LOOT levels at the Moscow, Yakhroma and Klyazma sites rival those seen in India (e.g., Kawano et aI., 1992), the world's leading OOT consumer. In 1989-1990, the OOT usage had been very recent as indicated by the high percentage of unmetabolized OOT in four of the five catchments. These indications of recent usage and strong contamination in 1989-1990 would explain the relatively high detection frequency and mean concentration observed by the routine monitoring program of the federal agency in 1993 as described earlier.

While LHCH levels are not especially high compared to southeast Asia where HCH is heavily used (e.g., Kawano at aI., 1992; Thao et aI., 1993), usage is nonetheless evident. Regrettably, the investigators did not give isomeric compositions. [3-HCH is the most persistent, most bioaccumulative, and potentially most toxic isomer (WHO, 1991 a). Though Russia has apparently shifted to y-HCH production, it is desirable to ascertain the lingering effects of historic crude HCH usage, as [3-HCH may remain long after the more volatile a-HCH and y-HCH have dissipated.

In the six surface water samples representing rivers and reservoirs, HCH and OOT levels were very high. DOT (likely LOOT but not clearly specified) ranged from 46 to 760 ng/L, while LHCH = a-HCH + y-HCH ranged narrowly from 134-143 ng/L. The OOT results are consistent with federal monitoring results for Moscow region in 1993, but the federal agency observed only 2 detections of HCH isomers in 141 samples from 26 stream sites in Moscow region. Even if HCH usage ceased after 1990, it seems surprising that HCHs were not detected more frequently in 1993.

The limited results of three sediment samples may not be typical of Moscow Oblast water courses. There was only one sample with complete OOT species analyses that yielded about 120 *ng/g* LOOT with about 80-85% in unmetabolized form.

### 3.3.2 Kuban Valley

The sampling area corresponded to the Kuban low plain in the lower Kuban River watershed in the southwest corner of Krasnodar Kray. The survey area represents about 20% of the Kray's 76,000 km$^2$ area. The near subtropical climate of the agricultural areas is not especially humid, but wet agriculture is supported by the relatively high runoff of the Kuban River that drains the north slopes of the Caucasus Mountains where rainfall is perceptibly higher.

Soils were sampled in the Kuban valley below Krasnodar city, in the Kuban delta, and on the land spit separating the Sea of Azov from the Black Sea. Water and sediment samples were collected from the reservoir above Krasnodar city and otherwise over the same area. Sediment sample coverage is particularly good including 4 samples in the reservoir and river, 5 from the extensive irrigation canal network on the delta, 7 from Sea of Azov inlets, and 3 from Black Sea inlets.

Kuban soil survey data are summarized by crop type in Table 3.7. DOT pollution is evident in all samples except perhaps one orchard soil for which only a low ODD analysis of 0.7 *ng/g* was obtained. One orchard soil had extraordinarily high LOOT of 2.2 *j..Lg/g.* In most samples, DOT was in predominantly metabolized forms. HCH was only detected in three soil samples, and surprisingly, in no rice fields. In Asia, HCH has been widely used against rice pests.

Sediment data are summarized in Table 3.8. DOT contamination appears to be confined to the irrigation canals of the Kuban delta and the inlets of the adjacent seas where levels are generally about 10 fold lower than in district soils. Curiously, HCH was detected in neither rice soils nor irrigation canal sediments which are generally confined to the Kuban delta, but were detected in the sediments of 7 Sea of Azov inlets that are the immediate recipients of discharges from the Kuban delta channels.

Table 3.7 DOT and HCH in Kuban valley soils *(ng/g), 1989-1990.*

| Crop | LOOT | | | LHCH | |
|---|---|---|---|---|---|
| | mean | range | %DDT | mean | range |
| rice | 116 | 12.5-363 | 41 | t nd | nd |
| wheat | 121 | | 0 | 33 | |
| cabbage | 121 | 12-197 | 67 | nd | nd |
| vineyard | 47 | 3-94 | 27 | +16 | |
| orchard | § 1,983 | 0.7-2,187 | 39 | *10 | |
| mean * | 223 | | 39 | 4 | |

**t** reported 0 interpreted as not detected; * one sample only; § one sample only for DOT and DOE, two for ODD; * mean of available samples, not crop class means.

Table 3.8 DOT and HCH in Kuban valley sediments *(ng/g), 1989-1990.*

| water body | LOOT | | | LHCH | |
|---|---|---|---|---|---|
| | mean | range | %DDT | mean | range |
| river sites | 8 | | 6 | t nd | nd |
| irrigation canals | 28 | 14-28 | 30 | nd | nd |
| Azov Sea | :1:24 | 15-33 | 20 | 43 | 3.6-92 |
| Black Sea | § 43 | 41-46 | 45 | nd | nd |
| mean * | 24 | | 23 | 16 | |

t reported zero interpreted as not detected; :I: one sample only for ODD, 7 for DOT and DOE; § one sample only for DOT and ODD, 3 for DOE; * mean of available samples.

The results of the two water samples yield some additional information but cannot be interpreted as generally representative. In at least one of the two samples, *LDDT* reached 21.3 J..l9/L, 92% as DDT. This would likely indicate a sample collected near a locale of recent DDT application.

### 3.3.3 Samarkand Oasis

Samarkand (pop. 360,000) is the second city of Uzbekistan and capital of Samarkand *wi/oyat* (administrative district). The city lies in the valley of the Zeravshan River, an affluent of the Amu Darya. The soil sampling program mirrors the regional agriculture practice that is dominated by cotton cultivation with some fruit, vegetables and tobacco. Sampling was conducted in the agricultural valley lands from upstream of Samarkand city to the Kattakurgan reservoir about 50-60 km downstream.

Soil survey data are summarized in Table 3.9 by crop class. DOT has clearly been used in the area, particularly on cotton. About 30% of cotton field samples exceeded 100 ng/g, and recent DDT usage was indicated at almost one half of 57 samples. Four of five orchard soils also had high DOT, in predominantly metabolized forms. Modest HCH contamination is widespread.

The reported findings for the eight water samples are vague and contradictory. DDT, DDE and y-HCH were detected, but exact values were not given. Concentrations of individual species were all apparently in the range 2-74 ng/L.

For the seven sediment samples, the mean *LDDT* concentration was 50 *ng/g.* The variability was not indicated, nor was the proportion of unmetabolized DDT. HCH was not mentioned suggesting that no detections of HCH species were observed.

Table 3.9 DDT and HCH in Samarkand oasis soils *(ng/g), 1989-1990.*

| Crop | LDDT | | | LHCH | |
|---|---|---|---|---|---|
| | mean | range | %DDT | mean | range |
| cotton | 327 | 3-1,715 | 49 | 18.6 | 2-64 |
| tobacco | 74 | 25-158 | 30 | 14.5 | 13-16 |
| vineyard | 70 | 28-157 | 19 | 28.8 | 14-70 |
| orchard | 426 | | 24 | nd | nd |
| mean * | 282 | | 44 | 18.6 | |

t reported 0 interpreted as not detected; :I: one sample only; § one sample only for DDT and DDE, two for DDD; * mean of available samples, not crop class means.

### 3.3.4 Summary

The survey data for all three regions are summarized in Table 3.10. DOT levels are generally high in all three regions. Due to the influence of cotton fields, Samarkand soils have somewhat higher DOT than Moscow or Kuban regions. HCH levels are generally low across all regions, and marginally higher in Samarkand region.

Table 3.10 Summary of Galiulin-Baskin soil-sediment surveys *(ng/g), 1989-1990.*

| region | LDDT | | | LHCH | |
|---|---|---|---|---|---|
| | mean | range | %DDT | mean | range |
| Moscow - soil | 226 | 0.1-1,180 | 66 | 8.7 | nd-27 |
| Kuban - soil | 223 | 0.7-2,187 | 39 | 4.1 | nd-33 |
| Kuban - sediment | 24 | 8-46 | 23 | 16.0 | nd-92 |
| Samarkand - soil | 282 | 3-1,715 | 44 | 18.6 | 2-70 |

## 3.4 AMAP Findings on POPs Insecticides in the Russian Arctic

The chapter on POPs contamination in the recent Arctic Monitoring and Assessment Programme report (AMAP, 1997) discusses various organochlorine insecticide data obtained the Russian Arctic, but gives no references. Particular findings concerning POPs insecticides in the Russian Arctic include:

- The AMAP report gives a comparative diagram of Arctic river HCH concentrations on page 82 that shows the Russia rivers, particularly the Ob, Yenesei and Pyasina to have extraordinarily concentrations. The plotted concentrations are precisely the mean watershed concentrations given in the annual summary report of pesticide monitoring in Russian surface waters for 1993 (Roshyromet, 1994). As pointed out in Section 3.2.5, the watershed summary data are heavily biased to data collected in remote southern headwater reaches. *For the Ob basin, the concentration of 55 ng/L mainly represents Omsk region rivers and streams on the northern frontier with Kazakhstan, not the lower reaches of the Ob main branch where it enters the Arctic.* The Pyasina River with the second highest HCH concentrations (37 ng/L) originates in the low Arctic unlike the major Russian Arctic Rivers. The probable source of HCH is high usage in the environs of the Norilsk smelter complex in the upper reaches of the Pyasina basin. There appears to be little activity elsewhere in the Pyasina basin; hence, HCH concentrations in the lower Pyasina where it enters the Arctic Ocean may be much lower if only due to dilution downstream of Norilsk. To some degree, similar circumstances likely prevail for all Russian Arctic rivers except for streams on the Kola Peninsula where points of HCH application would not be far upstream of the surrounding seas.

- The AMAP report cites DOT concentrations of 5 ng/L for the Ob River. This is also the Ob watershed average given in (Roshydromet, 1994). As pointed out earlier, *water sample summary data for DDT generated by the Russian monitoring agency should be discarded as unreliable. Due to low analytical resolution (detection thresholds of 50 ng/L), few detections above threshold and inappropriate statistical methods, it is impossible to ascertain if the DDT summary statistics given in the 1993 annual summary report bear any resemblance to actual DDT levels in Russian rivers.*

- HCH concentrations in air collected in the Lena River delta between March and December 1993 were similar levels to samples obtained at Canadian Arctic sites. Precipitation samples collected from the Taymir Peninsula and Laptev Sea during August 1994, and snow samples collected from the Taymir Peninsula during May 1995 had about 10 times higher DOT than in the Canadian Arctic; however, sample contamination is considered a possibility.

- Water samples from two lakes on the Taymir Peninsula had high levels of HCH and DOT, but no actual data were given. If these lakes are near Norilsk, they may not be typical of more remote sites.

- DOT was determined in bottom sediments from at least 18 Russian Arctic lakes, including 14 spread across Siberia, and 4 east of Siberia in the Mezen and Pechora watersheds (if they were located precisely on a small map). Sediments in 9 of 15 Siberian lakes had DOT <0.25 *ng/g,* and at 4 others were in the 0.25-1 *ng/g* range.

- Suspended particulate samples in unspecified Russian Arctic rivers allegedly have levels of DOT 10-100 fold higher than observed in Canadian and Norwegian rivers. Concentrations of DDT up to 2.8 J.,.lg/g were apparently reported; however, AMAP acknowledges that these results require independent confirmation. Relatively high DOT levels (-80 *ng/g* maximum) were observed in sediments of small streams draining Murmansk area where DOT may have been used for nuisance insect control, but levels on suspended particulates >1 J.,.lg/g seem unlikely unless samples were obtained in the near downstream vicinity of recent DOT applications.

- HCH and HCB concentrations measured in caribou and reindeer livers are remarkably uniform across the Canadian and Russia Arctic. However, levels of DOT are higher in Russia than elsewhere for reindeer and ground-feeding animals such as lemming, ptarmigan and brant (but how much so was not stated).

- Marine sediments were collected at more than 50 sites along the Russian Arctic coast from the White Sea to eastern Siberia. HCHs and HCB were reported to be higher in the gulfs and estuaries than offshore, but no actual data were given.

- Harp seals from waters of western Russia (generally Barents and White Seas) and the Yenesei Gulf have similar DOT levels as seals from the Norwegian Sea. These Russian seals have DOT concentrations 2-3 fold higher than harp seals of Alaska, the Canadian Arctic, Greenland, Iceland and Svalbard.

- Human maternal blood plasma samples from Nikel (Kola Peninsula), Salekhard (lower Ob River) and Norilsk (upper Pyasina River) were analyzed for DOT, ~-HCH, chlordane, and HCB. Plasma of Nikel mothers had relatively high DOT and extremely high ~-HCH indicating usage of DOT and crude HCH in the area.

- DOT, HCH, chlordane and HCB were reported for human milk sampled over 19931996 at four western Russian Arctic urban centres: Murmansk and Monchegorsk (Kola Peninsula), and Arkhangelsk and Severodvinsk (North Dvina River delta). The DOT levels are marginally lower than observed by Schecter et al. (1990a) in a limited 1988-1989 survey of mothers from four southern Siberian centres (Novosibirsk, Irkutsk, Baikalsk, Kachug), and from 3-6 fold higher than .a sampling of mothers from Troms0, Norway in 1993. The percentage of unmetabolized DDT in mothers milk of the western Russian Arctic ranged from 12-17%, while that in southern Siberian mothers milk ranged from 20-30% indicating that southern Siberian mothers had been exposed to more recent DOT applications prior to sampling. The HCH content of mothers milk from the western Russian Arctic averaged 33% of that observed in southern Siberian mothers over 1988-1989, but was 14-25 fold higher than in mothers milk of Troms0, Norway. The HCB content of mothers milk from the western Russian Arctic averaged 44% of that observed southern Siberian mothers over 1988-1989, but was 2.4-3.3 fold higher than in mothers milk of Troms0, Norway.

## 3.5 The Role of Atmospheric Transport POPs to Remote Areas

Zhulidov et al. (1997) have suggested that there is significant POPs pesticide contamination in aquatic systems of remote regions of northern and eastern Russia, and that long range atmospheric transport is the main source of POPs pesticides to these systems. The authors specifically cite the North Dvina, Ob, Yenesei and Amur watersheds, but offer no evidence to support their assertion.

There is little doubt that atmospheric transport from southern regions is the main source of POPs over vast northern areas with little human activity. The recent Arctic assessment gave a map showing that sediments of 18 remote lakes across Arctic Russia had DOT concentrations mostly <1 ng/g. These levels rank at the low end of globally observed ranges for freshwater and nearshore marine sediments, and thus likely reflect the background contributed by long range transport.

In contrast, reports of relatively high DOT and HCH levels in the Russian Arctic have consistently been either (1) for areas where there is considerable human activity, (2) in large rivers and coastal zones that receive waters from remote regions to the south, or (3) the coastal waters off east Asia where a-HCH concentrations increase along a northerly gradient (Iwata, et al., 1993; Chernyak, et al., 1995) to the Chukchi Sea. There is evidence that POPs insecticides have been released in northern and eastern Russia for agriculture and disease-bearing insect control, and possibly for forestry management and nuisance insect control. DDT and HCH levels seen in surface waters and sediments of the Kola Peninsula and the Pyasina River basin are far too high to be explained by long range transport. Both areas have sizable concentrations of human population. The increasing a-HCH concentrations in seawaters northward along the east Asian coast are likely driven by atmospheric transport from southeastern Asia and cold condensation (Wania and Mackay; 1993, 1995) or other deposition as air masses move northeastward from southeast Asia where HCH is heavily used. Given the prevailing westerly atmospheric circulation patterns over continental Russia, it is questionable how far this effect extends inland into continental Russia.

In order to establish the significance of long range atmospheric transport of POPs to remote areas, it will be necessary to clearly distinguish local and regional POPs releases from those contributed by long range atmospheric transport. The available accounts of historical POPs insecticide usage in Russia and the FSU (Voldner and Li, 1995; Li et al., 1996; based on reports by Kundiev and Kagan, 1993a,b) may not have captured all agricultural usage, and may have missed most non-agricultural usage. For example, the maps given by Li et al. (1996) show no HCH usage in either the Norilsk or Lake Baikal regions where water quality data clearly indicate that HCH has been used. It would be premature to conclude that POPs occurrence in remote northern and eastern regions is solely attributable to long range atmospheric sources.

# Chapter 4 Dioxins, Furans and PCBs

This chapter briefly reviews what is known about sources of PCDD/Fs and PCBs in Russia and the FSU, and studies on environmental contamination of humans and soils that provide some context for evaluating PCBs and PCDD/Fs in aquatic ecosystems. The specific findings of PCBs and PCDD/Fs in the Russian Arctic from the recent Arctic assessment report (AMAP, 1997) are itemized in point form. Supplementary information on environmental risk assessment of PCDD/Fs and PCBs is given in Appendix A.

## 4.1 PCDD/Fs in the Russian Environment

Concerns about environmental contamination by PCDD/Fs emerged in the FSU during the early 1990s. According to Feshbach[14] (1995), the 1992 *State Report on the Environment* considered dioxin pollution to be a threat in several Russian cities, the rice growing zone in the Kuban, the Sea of Azov, the lower Volga and the far east. The cities of Ufa and Chapayevsk were cited for soil and air contamination well above prescribed guidelines[15]. Recently, a report attributed to Greenpeace (McLaren, 1997), cited Dzerzhinsk as Russia's *"dirtiest'* city alleging that women have *"unusually large"* amounts of PCDD/Fs in their breast milk, and that PCDD/Fs in sewage and snow indicate the presence of active sources. The original report was unavailable for inspection and these activist accounts may be more enthusiastic than scientific.

As in other developed countries, Russia has a multiplicity of combustion and industrial sources that generate dioxins and furans. Major sources likely include chemical plants, pulp mills and metallurgical complexes. Other significant atmospheric emitters include waste incinerators, motor vehicles burning leaded fuel with halogenated additives, coal-fired electrical generating stations using coal with high chloride content, cement plants, and wood burning. There are, as yet, few waste incinerators[16]. In 1995, about 60% of the gasoline consumed in Russia was leaded (Miller and Badkhen, 1997).

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[14] Feshbach mis-identifies dioxin as a "chlorinated hydrocarbon insecticide widely employed in the FSU."

[15] *2.15 pg/m*$^3$ for air, and 130 *fg/g* for soil according to Bridges and Bridges (1996). Presumably these are for total sample TEa of2,3,7,8-substituted congeners.

[16] According to Brydges and Brydges (1996), Russia incinerates only 2-5% of its wastes. According to Gluszynski and Kruszewska (1996) Russia had only 6 known operational [Moscow (2), Vladivostock, Sochi, Pyatigor, and Murmansk] and one inactive municipal waste incinerators; however, there were plans to build more, and proposals to import industrial wastes from western Europe for incineration in Russia. Existing Russian incinerators apparently lack pollution control technology used in the west; hence, air emissions, including PCDD/Fs are thought to be more severe.

### 4.1.1 Chemical Industry Sources

Fedorov (1993) gave a short list of chemical plants known or thought to have produced PCDD/F contaminated products and emissions (Table 4.1). At plants in Chapayevsk, Dzerzhinsk and Ufa, chloracne cases were recorded among workers, while at others, PCDD/Fs have been measured at certain stages of production processes. Thus, there are reasonable grounds to suspect that human and more general environmental contamination has occurred. Atmospheric emissions and wastewater discharges from these plants may have contaminated local ecosystems in the vicinity of the chemical plants. Contaminated products, particularly herbicides, wood preservatives, and PCBs were likely dispersed widely across the FSU. The possibility of significant environmental contamination by contaminated pesticides was discussed in Chapter 3.

Electrolytic chlorine production also generates PCDD/Fs. There are likely many chlorine plants in Russia.

### 4.1.2 Forest Industry Sources

#### 4.1.2.1 Pulp and Paper Industry

Russia has a large pulp and paper industry with about 30-35 primary pulp producers and 130 enterprises producing paper and paperboard products. Controls on atmospheric and wastewater emissions are minimal.

Some pulp plants operate within large timber industry complexes that produce other wood products. In addition to the usual emissions from chlorine bleaching of pulps, some large timber complexes may have chlorine fabrication plants, electrical generating stations, scrap incinerators, black liquor recovery boilers and other activities that generate PCDD/Fs. Some plants producing unbleached pulp may be generating PCDD/Fs if raw intake waters are chlorinated and mechanical pulping is followed by a cooking stage (Kitkunen and Salkinoja-Salonen, 1990). Evidently, chlorination of raw water supplies to prevent slime formation and to bleach out high colour (organic matter) produces chlorophenols that serve as precursors for PCDD/F formation during the cooking stage.

Most pulp plants are concentrated in northwestern Russia, mainly in the Baltic and White Sea drainage basins with a few in the upper Volga watershed. There are at least three large pulp facilities in the upper reaches of the Yenesei River basin (Angara River - Lake Baikal system), and a few smaller plants in the far eastern maritime territories (lower Amur River and Sakhalin Island).

Table 4.1 Cities with chemical plants producing PCDD/F contamination (after Fedorov, 1993).

| City | Plant | Product |
|---|---|---|
| A. Russian Federation | | |
| Ufa<br>Khi<br>mp | rom<br>2,4,5-<br>TCP; Cu | salt of 2,4,5- TCP; 2,4,5- T and derivatives; 2,4-D; trichlorometaphos-3, chemicals for wood preservative formulations, hexachlorobutadiene |
| Dzerzhinsk | Orgsteklo | ropanile vinyl |
| | Synthesis | chloride |
| | Caprolactam | DDT,HCH,TCB,HCB,PCP |
| Chapayevsk | Chemical fertilizer | |
| | plant | epichlorohydrin, vinyl chloride, trichloroethylene |
| Sterlitamak | Caustik | PCBs |
| Novomoskovsk | Orgsynthesis | capacitors filled with PCBs |
| Serpukhov | | trichloroethylene |
| Volgograd | Khimprom | epichlorohydrin, vinyl chloride |
| Zima | Khimprom | trichloroethylene, PCN |
| Usolje-Sibirskoye | Khimprom | decabromodiphenyloxide [a] |
| Slavgorod, Altay Republic | Altaikhimprom | |
| B. FSU republics | | |
| Rubezhnoye, Ukraine | Krasitel | synthetic dyes from Chapayevsk TCB, hexachlorophen from 2,4,5- TCP |
| Pervomayskiy, Ukraine | Khimprom | pesticide formulations from Ufa Cu salt of 2,4,5-TCP |
| Kumairi [b], Armenia | | capacitors filled with PCBs |
| Oskemen [c], Kazakhstan | | capacitors filled with PCBs |
| Chirkchik, Uzbekistan<br>PCB, PCN | | transformers filled with PCB, TCB fluids |

p

[a] possible contamination by polybromodibenzodioxins and furans.

[b] formerly Leninakan.

[c] formerly Ust-Kamenogorsk.

### 4.1.2.2 Wood Preservatives

Historically, pentachlorophenol (PCP) and its salt NaPCP have been used in timber and woodworking industries as a fungicide, an anti-sapstain treatment, and a biocide against wood boring insects and dry rot. Freshly cut logs may be treated to prevent decay during the seasoning process. PCP preparations are commonly contaminated with PCDD/Fs (Alcock and Jones, 1997). PCDD/F residues from contaminated chlorophenolic wood preservatives may be locally significant near timber yards where there has been long standing application of wood preservatives. Surface runoff of contaminated treatment yard soils can lead to PCDD/F contamination of local water courses. In Finland, serious contamination of drinking water supplies by relatively soluble chlorophenols ensued from pollution of groundwaters by from timber treatment yarddrippage (Vartiainen et al., 1995). Russia likely has many similar timber treatment facilities located near surface water courses. Currently, there is little information available on the usage patterns and quantities of wood preservatives deployed historically in Russia.

### 4.1.3 PCDD/Fs in Human Milk and Blood

Data on general human populations suggests that Russia is modestly contaminated with PCDD/Fs. However, blood data unequivocally show significant contamination of an exposed population of Ufa chemical plant workers.

The results for breast milk samples collected in southern Siberia during 1988 and 1989 are shown in Table 4.2, along with global comparative data. The Siberian data are generally similar or lower to levels observed in the USA, significantly lower than observed in industrialized areas of Germany, and higher than rural areas of China. Heavily industrialized areas of Russia west of the Ural mountains may be more contaminated. Schecter et al. (1990a) also reported one sample from Moscow with 1TEQ of 20 *pg/g* lw.

PCDD/F data for human blood samples from Russia and other areas are given in Table 4.3. The general population of Baikalsk shows some contamination, but levels are much less than populations of heavily industrialized western countries.

Ufa is a city of particular concern for its concentration of chemical plants, in particular, the Khimprom plant where numerous cases of chloracne were reported during the 1960s when phenoxy herbicide 2,4,5-T was produced. The Ufa general population is about 30-35% more contaminated than those of Baikalsk and St. Petersburg, but well below populations of USA and Germany. However, office and factory workers showed high contamination even 25 years after exposure. Contaminated soils, sediments and chemical waste dumps in the Ufa area could be an ongoing source of contamination to aquatic systems.

Table 4.2 PCDD/Fs *(pg/g* Iw I-TEa) in human breast milk from Siberia and elsewhere.

| Location | | tn | I-TEa |
|---|---|---|---|
| southern Siberia | Kachug | 4 | 9.3 |
| | Baikalsk | 5 | 10.4 |
| | Novosibirsk | 10 | 11.8 |
| | Irkutsk | 4 | 17.3 |
| | mean | 23 | 12.2 |
| USA | Tennessee | 9 | 14.8 |
| | Binghampton, NY | 22 | 16.7 |
| | Los Angeles, CA | 21 | 16.6 |
| Germany | Rhine-Westphalia | 150 | 26.9 |
| China | rural, unsprayed | 50 | 2.6 |
| | rural, sprayed Na-PCP | 50 | 5.4 |
| South Vietnam | not sprayed | 8 | 13.4 |
| | sprayed with Agent Orange | 9 | 24.4 |

**t** sample size; some data represent pooled samples, others means of individual analyses. References: Schecter et al. (1989; 1990a; 1990c; 1994b).

Table 4.3 PCDD/Fs *(pg/g* Iw I-TEa) in human blood from Russia and elsewhere.

| Location | | tn | mean | min | max |
|---|---|---|---|---|---|
| A. Russia | | | | | |
| Baikalsk | general population | 8 | 18 | | |
| S1. Petersburg | general population | 60 | 17 | | |
| Ufa | general population | 100 | 23 | | |
| Ufa | Khimprom office workers | 2 | 41 | | |
| Ufa | Khimprom factory workers | 7 | 230 | 58 | 355 |
| Ufa | Khimprom factory workers | 5 | 100 | 73 | 132 |
| B. Global data | | | | | |
| USA | New York city, general population | 100 | 41 | | |
| Germany | general population | 102 | 42 | | |
| North Vietnam | Hanoi general population | 82 | 15 | 12 | 18 |
| South Vietnam | 13 urban and rural areas :I: | 383 | 35 | 16 | 77 |
| China | general rural population | 100 | 6 | | |
| | Na-PCP sprayed areas | 126 | 13 | | |

t sample size; some data represent pooled samples, others means of individual analyses.

:t includes 9 or more areas where Agent Orange was sprayed during 1960s.

References: Schecter et al. (1992, 1993, 1994a,b,c).

### 4.1.4 AMAP Findings on PCDD/Fs in the Russian Arctic

The recent Arctic assessment report (AMAP, 1997) notes:

- The large smelter complexes on the Kola Peninsula and at Norilsk in western Siberia, and the coal mining centre of Vorkuta in the Komi Republic are considered probable sources of PCDD/F emissions, but as yet, no surveys have been conducted to establish the degree of contamination,
- Peregrine falcons on the Kola Peninsula have high levels of PCDD/Fs near levels associated with embryonic mortality in other birds.

## 4.2 PCBs in Russia and the FSU

### 4.2.1 Production and Deployment of PCBs in the FSU

Ivanov and Sandell (1992) have indicated that historically two varieties of PCBs were produced: *Sovol* and *Trichlorodiphenyl* [TCD]. At the homologue level, Ivanov and Sandell found the composition of Sovol to be roughly similar to Aroclor 1254, while TCD was roughly comparable to Aroclor 1242. Kannan et al. (1993) obtained the composition of Sovol for more than 60 components, but many are not fully resolved as individual congeners.

Mass production of Sovol began in the late 1930s, and that of TCD in the 1960s. To about 1990, cumulative production of Sovol was about 100 Kt, while that of TCD was about 25 Kt. By the early 1990s, TCD production had ceased due to environmental concerns; however, about 500 *tla* Sovol were still being produced. It is not known if Sovol production continues.

Various mixtures of PCBs and other chemicals, similar to the askarel fluids deployed in North America, were produced in the FSU (Fedorov, 1993). Sovol was mixed with trichlorobenzenes to obtain the *Sovtol* formulations produced from the 1940s to the 1980s. *Nitrosovol* was a mixture of Sovol and napthalenes for arctic applications. *Hexo/s* were mixtures of Sovol and hexachlorobutadiene produced in the 1960s for use in electrical equipment.

The *Orgsteklo* plant at Dzerzhinsk was the FSU's main PCB production facility (Fedorov, 1993). Dzerzhinsk is located east of Moscow on the Oka River just upstream of its confluence with the Volga. PCBs were also produced on smaller scale at the *Orgsynthesis* plant at Novomoskovsk in the Don River headwaters south of Moscow. The deployment of PCBs into electrical capacitors and transformers was conducted in plants at Serpukhov (on the Oka River, southwest of Moscow), Oskemen (formerly UstKamenogorsk, on the Irtysh River in northeastern Kazakhstan), Kumairi (formerly Leninakan, Armenia), and Chirkchik (Uzbekistan).

The deployment and fate of FSU PCB stocks remains to be elucidated. Most were likely used in closed electrical equipment and hydraulic systems. Thousands of transformers were manufactured, and every major metallurgical and machine manufacturing facility would have had hundreds (Fedorov, 1993). Even more capacitors were produced. Little is known of the locations where these were deployed nor of the fate of old electrical equipment. TCD was used primarily in closed systems, but Sovol was also used for a long time in open systems including sealants, paints, plasticizers, plastics and wire insulation (Ivanov and Sandell, 1992).

### 4.2.2 Serpukhov Survey

In the late 1980s, Bobovnikova et al. (1993) examined the PCB content of environmental compartments near the capacitor plant at Serpukhov which is located on a small tributary of the Oka River in Moscow Oblast south of Moscow city. The plant, which had operated for about 35 years, polluted the local environment via air emissions and wastewater discharges.

Samples of air, snow, soil, human breast milk, and locally grown vegetables and eggs were collected in 1987-1988. Soil and snow data observed in radial patterns around the capacitor plant are given in Table 4.4. The PCB content of the soils sampled in the radial zones would represent the effects of atmospheric deposition. By most standards, these soils have relatively high PCB levels. The floodplain soils are on valley bottom lands downstream of the capacitor plant. During spring floods, contaminated sediments are deposited on these lands which are used by local citizenry for vegetable cultivation. Floodplain soils are severely contaminated with PCBs.

Table 4.4 PCBs in soils and snow at Serpukhov .

| Zone | soil *(J.lg/g)* | | | . snow (1l9/L) | | |
|---|---|---|---|---|---|---|
| km range | Mean | Min | Max | Mean | Min | Max |
| 0.1-0.35 | 1.5 | 0.39 | 4.70 | 5.40 | 0.58 | 67.0 |
| 0.4-0.6 | 1.0 | 0.26 | 1.96 | 3.00 | 0.42 | 8.0 |
| 0.65-2.5 | 0.9 | 0.80 | 1.86 | 0.91 | 0.16 | 1.2 |
| mean | 1.1 | | | 3.10 | | |
| floodplain t | | 10.00 | 60.00 | | | |

t floodplain affected by plant wastewater discharges.

The breast milk samples from mothers either living or working within 2 km of the plant range from 2,390 J,lg/L (-60-120 *J,lg/g* Iw[17]) for a mother working at the plant down to 20 J,lg/L (-500-1,000 ng/g Iw) for mothers at the periphery of the 2 km zone.

## 4.2.3 Galiulin-Bashkin Soil-Sediment Survey 1989-1990

PCB analyses were included in a 1989-1990 survey of pesticide content in soils, sediments and surface waters of irrigated agricultural lands in Moscow, Kuban (Krasnodar) and Samarkand (Uzbekistan) regions by Galiulin and Bashkin (1996b). Survey details were given in Chapter 3. As the soils studied were on riparian floodplains, the results are particularly relevant to aquatic ecosystem contamination.

Soil types and sample sizes are summarized in Table 4.5. Samples were analyzed for five PCB homologues (mono, tetra, penta, hexa, hepta) that were evidently summed to obtain *total PCBs* (this partial total denoted as LPCBs hereafter in this section). Detection thresholds were 2 ng/L in water and 50 pg/g in soil and sediments.

Table 4.5 Soil types and sample sizes of Galiulin-Bashkin 1989-90 survey.

| | Moscow | Kuban | Samarkand |
|---|---|---|---|
| Soil / sediment type | light silt loam | loamy sand, light clay | clay loam, silty clay loam |
| Soil samples | 33 | 21 | 71 |
| Water samples | 6 | 2 | 8 |
| Sediment samples | 3 | 19 | 7 |

### 4.2.3.1 Moscow Oblast

The survey area corresponds to the Moscow Oblast (area 47,000 km$^2$) that lies within the upper Volga watershed. Regional soils are apparently treated with municipal and industrial sewage sludges that may contain PCBs. The region has potentially more industrial sources of PCB emissions than the other two regions, but pollution controls are believed to be better. Six districts on river valley floodplains of the Oka River and several tributaries (Moscow, Klyazma, Yakhroma, and Istra rivers) were sampled. Most soils were silty-Ioams, but evidently, some peat muck soils with high organic carbon content were included.

[17] Assuming that a liter of milk had 1000 9 mass and typical fat content of 2-4%.

Table 4.6 PCBs in Moscow Oblast soils *(ng/g), 1989-1990*.

| River valley | mean | range |
|---|---|---|
| Klyazma | t16 | |
| Yakhroma | 707 | 10-1,404 |
| Moscow | 21 | 16-26 |
| Oka | 17 | 3-32 |
| Istra | 26 | 12-38 |
| mean | 157 | |
| MAC§ | 60 | |

t one sample only; § maximum allowable concentration.

Survey data for six districts are summarized in Table 4.6 by five river units (the Moscow River was sampled above and below the city). PCBs are clearly present and greater than in some western European countries (e.g., see Jones, 1989; Lead et al., 1997, for UK and Norway). At least a few samples in the Yakhroma catchment showed levels in the lower range seen at severely contaminated sites (e.g., Huang et al., 1992). The investigators do not explain the abnormally high concentrations. In three sediment samples from unspecified locations, PCBs levels were only 6.6-7.5 ng/g.

### 4.2.3.2 **Kuban Valley**

The sampling area corresponds to the lower Kuban River watershed in the southwest corner of Krasnodar Kray. Soils were sampled in the Kuban valley below Krasnodar city, in the Kuban delta, and on the land spit separating the Sea of Azov from the Black Sea. Water and sediment samples were collected from the reservoir above Krasnodar city and otherwise over the same area as soil samples. Sediment sample coverage is good with 4 samples in the reservoir and river, 5 from the extensive irrigation canal network on the delta, 7 Sea of Azov inlets, and 3 Black Sea inlets.

Kuban soil survey data are summarized by crop type in Table 4.7. At least 3 samples (and perhaps 2-3 others) showed very high levels of PCB contamination of >500 ng/g up to a maximum of 2.5 *119/g.* Galiulin and Bashkin attribute this contamination to air emissions from industries, but unless these fields are adjacent to waste incinerators the explanation seems unlikely. The land application of PCB contaminated sewage sludges is a more plausible explanation but others are possible. The remaining 14-15 samples had PCBs ranging from 6-66 *ng/g* with mean of about *30 ng/g.* This indicates widespread, but modest contamination.

Table 4.7 PCBs in Kuban valley soils *(ng/g), 1989-1990.*

| Crop type | mean | range |
|---|---|---|
| rice | 31 | EH>1 |
| wheat | 588 | |
| cabbage | 13 | 9-17 |
| vineyard | 929 | 66-2,466 |
| orchard | :1:688 | |
| mean * | 314 | |

:I: one sample only; * mean of available samples, not crop means.

Sediment data are summarized in Table 4.8. The PCB levels observed in all sediments are remarkably high and approach the degree of contamination observed at certain highly contaminated sites (e.g., Miyata et al., 1988; Huang et al., 1992). The higher concentrations in river samples suggest that contamination emanates from the city of Krasnodar. As a city of nearly 650,000 servicing a predominantly agricultural district, the sources are not immediately obvious. Insecure disposal of old electrical equipment is a potential explanation. PCBs were also detected in at least one of only two available water samples at 30 ng/L comprising exclusively tetra-PCBs.

Table 4.8 PCBs in Kuban valley sediments *(ng/g), 1989-1990.*

| | mean. | range |
|---|---|---|
| river sites | 949 | 74-1,978 |
| irrigation canals | 477 | 51-1,727 |
| Azov Sea | 408 | 57-1,137 |
| Black Sea | 496 | 155-836 |
| mean * | 554 | |

* mean of available samples.

### 4.2.3.3 Samarkand Oasis

Sampling was conducted in the agricultural valley lands of the Zeravshan River from upstream of Samarkand city to the Kattakurgan reservoir about 50-60 km downstream. Soil data are summarized in Table 4.9 by crop class. Modest PCB contamination is widespread. Some cotton field samples had significant PCB contamination.

For PCBs in river water, separate mean concentrations were reported for the five measured homologues. These sum to give mean LPCBs as 2.2 *IJ.g/L.* However, back calculations using the reported mean percentages that each homologue contributes to LPCBs, give mean LPCBs concentrations ranging from 1.5 1J.9/L to 8.8 1J.9/L rather than an approximately constant value near 2.2 *1J.9/L.* Thus, there is some inconsistency in the reported data. Another remark suggests that LPCBs increased longitudinally from not detected upstream of Samarkand to 2.51J.g/L at the Kattakurgan reservoir 50-60 km downstream. The best that can be concluded from this is that there are signs that significant PCB contamination is introduced into the Zeravshan River on its passage by the city of Samarkand and downstream towards Kattakurgan. For the 7 sediment samples, the mean LPCBs concentration was 116 ng/g.

Table 4.9 PCBs in Samarkand oasis soils (ng/g), 1989-1990.

| crop type | mean | range |
|---|---|---|
| cotton | 28 | 0.1-433 |
| tobacco | 33 | 6-71 |
| vineyard | 16 | 2-33 |
| orchard | 68 | |
| mean * | 28 | |

* mean of available samples, not crop class means.

Table 4.10 Summary of Galiulin-Baskin survey PCB data (ng/g) for 1989-1990.

| region | mean | range |
|---|---|---|
| Moscow | 157 | 3.2-1,404 |
| Kuban - soil | 314 | 6.0-2,466 |
| Kuban - sediment | 554 | 51-1,978 |
| Samarkand | 28 | 0.1-433 |

### 4.2.3.4 Summary

Survey data for all three regions are summarized in Table 4.10. PCBs are unequivocally the highest in Kuban region. Relative to Kuban region soils, Moscow region soils average about 50% lower, while Samarkand oasis soils average about an order of magnitude lower PCB concentrations.

### 4.2.4 AMAP Findings on PCBs in the Russian Arctic

The recent Arctic assessment report (AMAP, 1997) notes:

- Precipitation samples collected from the Taymir Peninsula and Laptev Sea during August 1994, and snow samples collected from the Taymir Peninsula during May 1995 had about 10 times higher PCBs than in the Canadian Arctic; however, sample contamination is considered a possibility.

- PCB levels in lichens at three sites across Arctic Siberia were perceptibly higher than in Canadian Arctic lichens. In contrast, PCBs in mosses from 5 Arctic sites across Russia were remarkably low vis-a-vis levels observed in Scandinavia.

- Levels of PCBs in reindeer and ground-feeding animals such as lemming, ptarmigan and brant are higher in Russia than elsewhere (but how much so is unclear).

- Suspended particulate samples in unspecified Russian Arctic rivers have levels of PCBs 10-100 fold higher than observed in Canadian and Norwegian rivers. Concentrations of PCBs up to 27 *Ilg/g* were apparently observed; however, AMAP acknowledges that these results require independent confirmation.

- Water samples from two lakes on the Taymir Peninsula had relatively high levels of PCBs (> 1 ng/L), but no actual data were reported. If these lakes are near Norilsk, they may not be typical of more remote sites.

- PCBs were determined in bottom sediments from at least 19 Russian Arctic lakes. These include 15 spread across Siberia and 4 east of Siberia in the Mezen and Pechora watersheds (if they were located precisely on the small maps in the report). There may be a few others on the Kola Peninsula. Sediments in 12 of 15 Siberian lakes had PCBs <2 *ng/g,* while sediments at two lakes had PCBs in the 2-7 *ng/g* range, and one lake's sediments had PCBs in the 15-25 *ng/g* range. The latter lake is located near Norilsk if the map is correct.

- In a survey of marine sediments collected at more than 50 sites along the Russian Arctic coast from the White Sea to eastern Siberia, the majority of samples had PCBs <0.5 *ng/g,* but numerous samples in the White Sea and the outlets of the

Pechora, Db and Yenesei Rivers had PCB content in the 5-9 *ng/g* range. PCBs were generally higher in the gulfs and estuaries than offshore.

- Harp seals from waters of western Russian waters (generally Barents and White Seas) and western Siberia (Yenesei Gulf) have similar PCB levels as seals from Norwegian Sea. Russian harp seals have PCB concentrations 2-3 fold higher than harp seals of Alaska, the Canadian Arctic, Greenland, Iceland and Svalbard.

- Human maternal blood plasma samples from Nikel (Kola Peninsula), Salekhard (lower Db River) and Norilsk (upper Pyasina River) were analyzed for PCBs as part of a circumpolar survey. Blood of Nikel and Salekhard residents had PCB content near the survey median concentration. Blood of Norilsk residents had 50% higher PCBs than Nikel and Salekhard residents. That is about the same as observed in northern Sweden, but perceptibly lower than observed in northern Quebec and northwestern Greenland.

- The PCB content of human milk observed over 1993-1996 was given for six Arctic urban centres: Murmansk and Monchegorsk (Kola Peninsula), Arkhangelsk and Severodvinsk (Severnaya Dvina delta), and Salekhard and Norilsk (western Siberia). Levels were relatively uniform in the range 406-535 *ng/g* Iw. These are about the same levels as observed by Schecter et al. (1990a) in a limited 1988-1989 survey of mothers from four southern Siberian centres (Novosibirsk, Irkut$k, Baikalsk, Kachug). Contrasted against other countries (Schecter et al., 1994d), southern Siberian mothers had higher PCBs than mothers of Bangkok, Thailand, similar PCBs to a small sample from Binghampton, New York, USA, and about 15-25% of the PCBs burden seen in mothers of the former West Germany.

## 4.3 Other PCB and PCDD/F Data Sources

Several studies of aquatic systems that included PCB or PCDD/F data analyses were reviewed by Petrosian et al. (1998), but serious consideration of this material in the present context was precluded by probable errors in measurement units in the draft copy that was available for inspection. The final copy or the original source reports cited therein may have the correct data. Studies of particular interest are listed below.

- Studies of PCDD/F contamination in water and sediments have been conducted in the Belaya River system from upstream of Sterlitamak to downstream of Ufa. As noted earlier (Table 4.1), both Sterlitamak and Ufa are major production centres for organochlorine chemicals where PCDD/F contamination is considered likely. The reported river water concentrations are so high (1-22 *Jl9/L* TEQ by an unspecified toxic equivalency system) that they cannot be accepted without corroboration. Samples obtained in certain stream sites below Sterlitamak and Ufa were high relative other data, suggesting that PCDD/Fs are emitted in both cities.

- PCB contamination of bottom sediments and fish tissue from the Scheksna River near Cherepovets seems to be significant. Cherepovets is located north of Moscow in Vologda Oblast where the Scheksna River (an upper Volga headwater stream) enters the Rybinsk reservoir. The city is a sizable industrial centre with steel works, chemical plants and other industries.

- PCB contamination has been investigated in the Irtysh River below Qskemen, Kazakhstan, where there is a capacitor plant. As no data were given, the degree of PCB contamination cannot be assessed.

- PCBs were allegedly found in some aquatic systems of the Buryatia Republic. As no data were given, the degree of PCB contamination cannot be assessed.

# Chapter 5 Lake Baikal Ecosystem

## 5.1 Lake Baikal

Lake Baikal is unique among lakes. It is the deepest, the largest in volume having about 20% of the world's freshwater, and the world's oldest lake at circa 20 million years. Baikal has a unique ecosystem with 1,500 or more indigenous plants and animals. Most notable are Baikal freshwater seals *(Phoca siberica)* or *nerpa,* relatives of marine ringed seals, and the *omul,* an endemic whitefish. The lake has about 230 Kt fish with an annual commercial fishery of about 13 Kt[18] (ILEC, 1996) that would provide a route for human bioaccumulation of POPs. Kucklick et al. (1994) describe the ecosystem food web as structurally comparable to Lake Superior, but note that the presence of the *nerpa* also renders it similar to Arctic marine ecosystems. In late 1996, UNESCO included Lake Baikal in the list of the World Heritage Sites and declared the protection and conservation of Lake Baikal as one of the responsibilities of humanity.

Lake Baikal receives inflow from the three large tributaries listed in Table 5.1 and over 300 smaller streams. The lake has three major basins (southern, central, and northern) of roughly comparable area. Most of the drainage area lies to the east and south of the lake. The main tributary, the Selenga, enters on the southeast side and drains a sizable area of Mongolia[19]. The Selenga delta roughly defines the northern limit of the southern basin. The only outflow is by the Angara River at the southwestern end of the lake. The Angara ultimately forms the largest affluent of the Yenesei River.

The human population in the Russian administrative districts (Irkutsk Oblast, Buryatia Republic, and Chita Oblast) of the greater Baikal region is about 5 million, but only 1-2 million likely reside within in the Baikal watershed proper. The Mongolian part of the watershed may have as many as one million mainly concentrated in the capital city of Ulan Bator and several smaller urban centres.

Remote location protected Baikal waters from pollution until industry arrived in the late 1950s when construction of a bleached cellulose pulp mill began at Baikalsk at the south end of the lake. Near Baikalsk is a coal-fired powerplant at Slyudyanka. Influent waters of the Selenga are contaminated by Ulan Bator and other cities Mongolia; UlanUde, the capital city of the Buratiya Republic that borders the west and south sides of Baikal; and another pulp mill at Selenginsk near the head of the Selenga delta[20].

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[18] ILEe data are for 1946-1955; Irkutsk State Univ. claims the commercial catch is 60 Kt (ISU, 1997). [19] The drainage area within Mongolia is likely at least 180,000 km$^2$.

[20] Informal reports suggest that the Selenginsk pulp mill may no longer be discharging wastewaters.

Table 5.1 Lake Baikal facts.

| | | |
|---|---|---|
| Latitude range | 52° - 56° | N |
| Longitude range | 104 ° - 110° | E |
| altitude | 456 | m |
| Length | 635 | km |
| Maximum width | 80 | km |
| Shoreline length | 2,000 | km |
| Volume | 23,015 | $km^3$ |
| Surface area | 31,468 | $km^2$ |
| Maximum depth | 1,741 | m |
| Mean depth | 731 | m |
| Visibility (Secchi depth) | up to 40 | m |
| Basin area - total | t 540,000 | $km^2$ |
| Basin area - Russia | 320,000 | $km^2$ |
| Mean annual outflow - Angara River | 65.3 | $km^2$ |
| Mean annual inflow from largest tributaries: | | |
| Selenga River | 31.0 | $km^3$ |
| Upper Angara River | 8.3 | $km^3$ |
| Barguzin River | 4.4 | $km^3$ |
| Mean hydraulic residence time | 350 | yr |
| Ice cover formation / breakup | early January | May |
| Age | >20,000,000 | yr |
| Indigenous species | >1,500 | |
| Top aquatic predator | Baikal seal | *Phoca siberica* |

t Some reports give the basin area as 557,000 $km^2$.

Due to prevailing westerly winds and topography, air pollution from heavy industries and chemical plants in Irkutsk Oblast to the west of Baikal affects the southern lake basin. The capital city, Irkutsk, located 60 km downstream on the Angara River, has a large hydroelectric plant, a pulp mill, and an aluminum smelter. Consequently, there may be considerable old PCB-containing electrical equipment in the region. Evidently, fly ashes from Irkutsk industries easily reach Baikal, and the pulp mill at Baikalsk emits considerable aerosols (van Malderen et al., 1996; Jambers and van Grieken, 1997).

Among numerous centres west of Irkutsk on the Trans-Siberian Railway, Usolje-Sibirskoye and Zima have Khimprom chemical plants producing trichloroethylene, PCNs (polychlorinated napthalenes), PVC, and epichlorohydrin (Fedorov, 1993). These plants may be sources of dioxins, furans, HCB and other chemicals that reach Baikal by atmospheric transport.

Evidence to be discussed below shows that certain organochlorine insecticides (DDT, HCH) were likely applied in the limited agriculture (potatoes, beets, and livestock) conducted near Irkutsk and Baikalsk. POPs insecticides may also have been used upstream of Ulan-Ude where the Selenga valley broadens into a sizable area that appears to be suitable for livestock, grain and field crop agriculture. DDT and other insecticides may have been used against tick-borne encephalitis that is endemic in Baikal region forests.

## 5.2 POPs Data Availability in the Baikal Region

Concerns about the pollution of Baikal intensified after the mass mortality of several thousand seals over 1987-89 due to a morbillivirus. The event prompted investigations into potential catalytic mechanisms that has yielded good, basic data on POPs contamination of Baikal ecosystem compartments including air, water, sediments and biota. These investigations and their results are described in following subsections.

Other studies that merit consideration include: analysis of PCDD/Fs and PCDEs (polychlorodiphenyl ethers) in a single male Baikal seal taken in 1992 (Koistinen et al., 1995); and sediment samples from the vicinity of the Baikalsk pulp mill outfall that were analyzed for total organochlorines by Maatela et al. (1990). Recently, Tarasova et al. (1997) reported PCDD/Fs observed in three Baikal seals. According to Nakata et al. (1995) earlier reports by Bobovnikova et al. (1985,1989) give some data for organochlorines in Baikal seal. These were unavailable for review. PCBs were allegedly found in surface waters of the Buryatia Republic (Petrosian, 1998), likely near Ulan-Ude, but no data were given.

### 5.2.1 US investigations

On a Lake Baikal cruise in June 1991, US investigators gathered 19 air samples, 7 high volume water samples, 10 low volume water samples, and fish samples of two species[21]. Samples were analyzed for PCBs, DOT, HCH, heptachlor, chlordane, HCB and pees (toxaphene). The fish were analyzed as 2 replicates of the composited specimens of the 2 species. The results of these exploratory investigations are given in Kucklick et al. (1993, 1994) and McConnell et al. (1993, 1996).

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[21] 35 sculpin *(Comephorus dybowski/)* and 2 omul *(Coregomus autumna/is migratorius).*

During August 25 to September 81993, a second expedition (Kucklick et al., 1996) obtained 7 high volume water samples, 3 zooplankton samples, pooled samples of a macroplankter and benthic amphipods, 17 fish of 3 species[22] and 7 seals. Water samples were analyzed only for PCBs, HCB and some conventional parameters, while biota were analyzed for the full suite of POPs done in 1991. The objective was to trace POPs transfers upward through the Baikal food web.

### 5.2.2 Japanese investigations

Another series of investigations were launched by Japanese investigators in 1992. A cruise from May 14 to June 1, provided 16 water samples, 6 air samples, 6 sediment samples, 35 fish from 5 species, and 58 seals 23. There were also four soil samples from Irkutsk and Baikalsk agricultural fields. All environmental media were analyzed for PCBs, HCH, DOT, and chlordanes. HCB analyses were performed only on the nominally inorganic matrices (air, water, soil, and sediment). Results for the latter were presented by Iwata et al. (1995). Nakata et al. (1995, 1997) gave detailed accounts of fish-to-seal bioaccumulation for the four core POPs (total PCBs, DOT, HCH and chlordanes), and in the second paper, for more than 40 PCB congeners 24.

### 5.2.3 Human Milk and Foodstuffs

POPs present in human tissues in the Baikal region should partially reflect diet derived from local agriculture and the Baikal commercial fishery, and thus give some confirmation of regional POPs pollution. There are limited data on POPs in human milk (Schecter et al., 1990a) and in foodstuffs (Schecter et al., 1990b) from Baikalsk, Irkutsk, and Kachug. Kachug is a settlement in the Lena River basin near Lake Baikal and should represent smaller outlying settlements within the Baikal watershed. The human milk samples were from mothers in Baikalsk *(n=5),* Irkutsk *(n=4),* and Kachug *(n=4).* The foodstuff samples are limited to single samples of pork and butter from Baikalsk, and cow milk cream from Irkutsk.

Schecter et al. (1990a) also analyzed the human milk samples from Baikalsk, Irkutsk, and Kachug for the 17 toxic PCDD/Fs, and later reported PCDD/Fs in the blood of 8 Baikalsk residents (Schecter et al., 1992). These data were discussed in Chapter 4, Section 4.1.3.

---

22 4 *Comephorus dybowskii,* 6 *Comephorus baikalensis* (another sculpin), and 7omul.

23 Fish: 8 *Comephorus baikalensis,* 10 *Comephorus dybowskii,* 10 *Cottocomephorus grewiinki,* 6 *Cottocomephorus inermis,* and 2 unknown. Seals: 17 juveniles, 16 mature male, and 25 mature female.

241n the study of PCB congeners (Nakata et al., 1997), reduced sets of the original samples were analyzed: 23 fish of three species, and 40 seals (15 juvenile, 18 mature female, and 8 mature male).

## 5.3 POPs in Baikal Ecosystem Compartments

This section integrates the available data sources to ascertain the dominant POPs in the various environmental compartments of the Baikal ecosystem. The results are summarized graphically by environmental compartments in Figure 5.1. Notes on the construction of the figures are given in Section 5.9 at the end of this chapter.

### 5.3.1 Water

As shown in Figure 5.1 a, POPs concentrations in Baikal waters are very low. Only PCBs and LHCH = a-HCH + y-HCH have been observed above 1 ng/L. The water samples collected by Kucklick and McConnell (Kucklick et aI., 1994, 1996; McConnell et aI., 1996) in June 1991 and August 1993 showed roughly 5-10 times higher concentrations than those collected by Iwata et al. (1995) in May 1992. Iwata et al. (1995) suggested that differences might be due to their having sampled during ice break-up in May, while Kucklick and colleagues sampled after ice break-up and appreciable snowmelt and spring surface runoff had entered the lake. Roughly 6070% of annual precipitation on the region occurs from June to September during which time inputs of POPs by surface runoff from active land surfaces could be significant. If POPs insecticides were still being used at the time, active spraying and dusting would likely have begun during June. Regardless of cause, the differences in water concentrations among surveys are relatively small compared to the differences between concentrations in water and other environmental compartments.

All contaminants shown on Figure 5.1 a likely have remote atmospheric sources, but only PCBs, HCH, and DOT and HCB likely have significant local sources. Iwata et al. (1995) observed the highest concentrations of HCHs and PCBs to occur near the SelengcfRiver delta and the southwest end of the lake near Baikalsk, Slyudyanka, and the Angara River outlet. By comparing the PCB con'gener profiles observed in Baikal waters with those observed in Lake Superior which receives primarily atmospheric inputs, McConnell et al. (1996) concluded that local surface runoff was a significant source of PCBs. The air data shown in Figure 5.1 e also implicate Irkutsk as a probable local source of atmospheric deposition onto Baikal. McConnell et al. also observed that the congener composition of the PCBs in Baikal waters resembled a mixture of Russian *Sovol* and *Trichlorodiphenyl* products.

Local surface runoff and atmospheric inputs are also likely major sources of HCHs to Lake Baikal's southern basin. McConnell et al. (1996) reported three samples from the Selenga River with LHCH = a-HCH + y-HCH concentrations of 4-5 ng/L, the highest observed amongst all studies. This HCH may have originated in Russia or upstream in Mongolia. They also found LHCH of 3.5 ng/L in a single sample of Angara River waters. This may have represented local runoff into the Angara River rather than Baikal outflow waters.

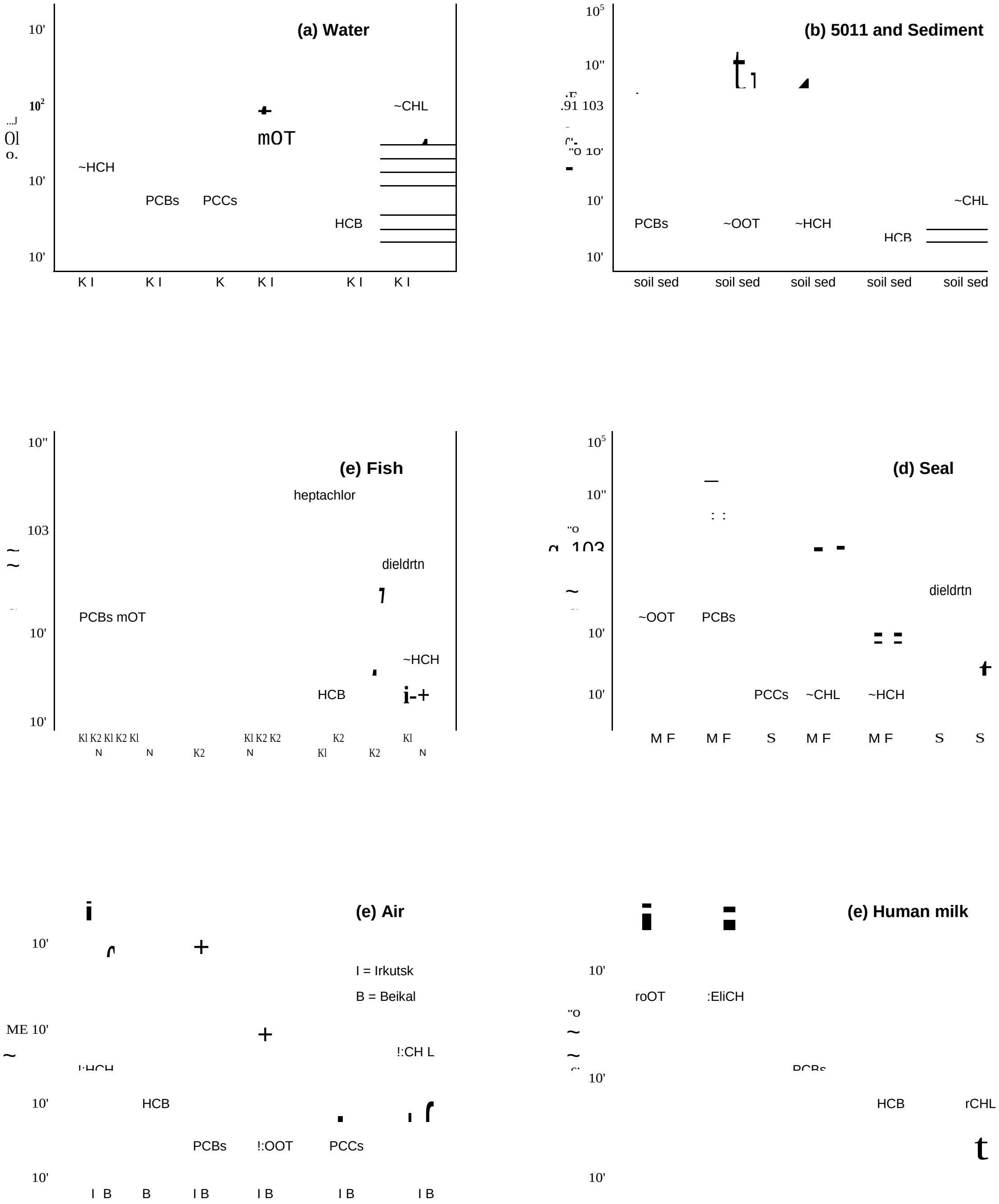

**Figure 5.1 POPs compared within Baikal environ.mental compartments; Notes: (a) K are lumped 1991 and 1993 surface water data reported by Kucklick et al. (1994, 1996) and McConnell et al. (1996); I are 1992 water data from Iwata et al. (1995), (c) K1 are 1991 and K2 are 1993 fish data from Kucklick et al. (1994,1996); N are 1992 fish data from Nakata et al. (1995); (d) M and F are male and female seal data from Nakata et al. (1995); (e) I and B are Irkutsk and Baikal air data from McConnell et al. (1996).**

DOT also likely originates from local sources. In 1991, water samples obtained by Kucklick et al. (1994), concentrations were greater in the southern basin and 50-80% of DOT was in unmetabolized forms indicating recent usage. Air data (Figure 5.1 e) implicates Irkutsk as a local of atmospheric inputs. Data obtained by Iwata et al. (1995) in 1992 suggest that water concentrations were more evenly distributed across the lake. This would further suggest that atmospheric inputs were significant; however, the mid and northern basins were not well sampled. The Selenga River has yet to be rigorously sampled and may be a significant DDT source.

Surface water concentrations HCB and chlordanes were more evenly distributed across Lake Baikal suggesting that these derived mainly from atmospheric sources. The PCCs also likely originate from remote sources, but some could have originated from usage for the limited purposes still permitted in the late 1980s, if such usage occurred. Some chlordanes could have derived from local usage of dihydroheptachlor if that compound belongs to the heptachlor-chlordane family.

### 5.3.2 Soil and Sediment

The measured POPs in soil and sediment samples have the same order of concentrations: PCBs> LOOT> LHCH > HCB > LCHL. PCBs observed in four soil samples from agricultural fields in the Baikalsk-Irkutsk area likely reflect contamination from industrial sources, while the OOT and HCH concentrations likely reflect past and recent usage. The HCB might be partly attributable to impurities in the other POPs used in the region, including insecticides and the *Sovtol* technical mixture of PCBs and trichlorobenzenes (Iwata et al., 1995). HCB may also originate from both local and remote atmospheric sources.

Among soil samples, the maximum concentrations of HCH and OOT were observed in one potato field sample. Unmetabolized ODT *(p,p'-DOT* + o,p'-OOT) comprised at least 57% of LOOT, indicating relatively recent usage. In both soils and sediments, recalcitrant J3-HCH is the dominant HCH isomer at 50% or more of LHCH. As J3-HCH is the least volatile HCH isomer, its presence indicates that crude technical HCH has been used in the Baikal region.

Except for chlordanes, soils are clearly more contaminated than sediments. Levels of PCBs, LOOT, and LHCH are about 15 fold higher in soils, while HCB is about 10 fold higher. Iwata et al. (1995) observed the expected positive correlations between POPs concentrations and the organic carbon content of sediments. The highest concentrations in sediments were found in a sample affected by discharges from the Slyudyanka coal-fired power plant.

Maatela et al. (1990) analyzed sediment samples from the vicinity of the Baikalsk pulp mill outfall and along the coast near Baikalsk for organic matter (as LOI, loss-on-ignition) and organically bound chlorine[25] (OCI). These measurements give indirect evidence that the Baikalsk mill uses chlorine and likely discharges PCDD/Fs and other chlorinated organic chemicals to Baikal. Mill effluents are discharged after treatment via two outfall pipes that extend over an underwater canyon that penetrates the submerged nearshore terrace near the mill. Samples from the canyon near the outfalls had the highest LOI and the highest OCI. When OCI was normalized to LOI, the effects of mill effluents appeared to extend eastward along the coast

### 5.3.3 **Fish and Seal**

In fish, the general order of contamination is PCBs ~ *LDDT* ~ PCCs > LCHL > heptachlor ~ HCB > dieldrin> LHCH as shown in Figure 5.1 c. PCBs, DDT and PCCs are present at practically the same levels, while chlordanes, heptachlor and HCB (in 1993) are present at about one order of magnitude lower.

The limited sampling by Kucklick et al. (1994) and the greater sampling of 5 species by Nakata et al. (1995) gave much the same results, while the late August - early September 1993 samples of Kucklick et al. (1996) have perceptibly higher levels of PCBs, DDT, PCCs, HCB and chlordanes. Rather than significant increases in pollution by these chemicals from 1991 to 1993, the increased concentrations may reflect typical seasonal differences in the POPs burdens of fish between early spring and late summer.

The data shown on Figure 5.1 c are lumped for all fish species observed within each survey. Where given, detailed data indicate that there are likely real differences in POPs content amongst species. Omul appear to accumulate most POPs more than other species, but 1993 data of Kucklick et al. (1996) suggest that sculpin C. *Baika/ensis* had greater DDT and PCCs. Such differences are not important for present purposes.

Heptachlor and dieldrin were measured for the first time in the 1993 fish samples. Heptachlor can be metabolized rapidly to heptachlor epoxide which has been observed to be the dominant species in fish in several studies (Tanabe et al., 1991; Kannan et al., 1994). In 1991 samples, Kucklick et al. (1994) had observed heptachlor epoxide but were unable to reliably quantify it with their particular analytical methodology, while in 1993 samples, Kucklick et al. (1996) were unable to detect the compound. In zooplankton and benthic amphipods, heptachlor was dominant amongst the related heptachlor-chlordane compounds.

In seal, POPs are neatly ordered by magnitude as PCBs> LOOT> PCCs > LCHL > LHCH > dieldrin> HCB. ODT and PCBs are clearly dominant. Heptachlor is no longer evident, apparently metabolized or excreted by the nerpa.

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[25] Obtained by subtracting inorganic chloride from total chlorine measurements.

Male seals accumulate more than females that pass appreciable POPs to offspring on reaching reproductive age at about 7-8 years. Nakata et al. (1995) estimated that females pass about 20% and 14% of their respective DDT and PCBs burdens to offspring. Though less evident, recalcitrant isomers and metabolites of HCH (B-HCH) and chlordane (oxychlordane, trans-nonachlor, and cis-nonachlor) also pass from mother to pup.

There are differences in chemical species composition between fish and seals. In fish, unmetabolized DDT *(p,p'-DDT + o,p'-DDT),* ranges from 49-74% with a mean of about 56%, suggesting that the DDT was of recent origin. In male seal, unmetabolized DDT was 33% of *LDDT,* while in females the proportion increased to 48%. The females appear to be passing the recalcitrant metabolite *p,p'-DDE* to offspring in greater proportion than other DDT species.

For fish, the mean HCH speciation is: a-HCH 53%, ~-HCH 31 %, and y-HCH 15%, while in seal, ~-HCH dominates at 70% (male) and 63% (female), with the remainder entirely as a-HCH. Somewhat similarly for chlordanes, fish have little oxychlordane (mean 5-6%), and significant presence of the parent isomers: trans-chlordane 6%, *cis*chlordane 9%, trans-nonachlor 12%, and cis-nonachlor 3%. In contrast, seals have predominantly oxychlordane (male 62%, female 52%), and the remainder comprising almost entirely trans-nonachlor.

### 5.3.4 **Air**

Air data obtained in 1991 and 1992 are shown in Figure 5.1 e with separate summaries for Irkutsk and Lake Baikal. The Baikal data represent 1991 observations by (McConnell et al., 1996) over the lake and at the Listvyanka meteorological station at the exit point of the Angara River composited with the 1992 data reported by Iwata et al. (1995). Here LHCH = a-HCH + y-HCH, and LDDT = *p,p'-DDT* + *o,p'-DDT* + *p,p'*DOE. DDT data of Iwata et al. (1995) were adjusted to approximately include o,p'-OOT which they had not measured, but was found by McConnell and colleagues to be present in significant quantity relative to *p,p'-DOT* and *p,p'-DOE.*

Over Baikal waters, the general order of POPs contamination in air is LHCH > HCB > PCBs> LOOT> PCCs > LCHL. The ranking reflects differences in vapor pressures and the relative strength of local sources including the lake itself. Though there were only 2-3 Irkutsk samples, it seems almo.st certain that Irkutsk is a significant source of HCH, PCBs and DDT. Two Irkutsk measurements had slightly higher PCGs than five from Lake Baikal, but there are too few samples to conclude that a real difference exists. HCB was not measured in Irkutsk air; however, it is possible that industrial sources in Irkutsk and the Khimprom chemical plant to the west in Usolje-Sibirskoye are significant sources. Some additional evidence that Irkutsk is likely a source of HCB is provided by four human milk samples from Irkutsk that are discussed in the next section. It seems unlikely that Irkutsk is a source of chlordane.

### 5.3.5 Human Tissues

DDT and HCH, mostly as *p,p'-DDE* and f3-HCH respectively, are the leading POPs in Baikalsk, Irkutsk and Kachug breast milk samples. The Siberian human milk data of Schecter et al. (1990a) and comparative data are given in Table 5.2. Generally, in southern Siberian mothers, DDT, HCH and HCB levels were higher than observed recently in northwestern Russia (AMAP, 1997) while PCBs were relatively uniform at all locations. HCH levels in southern Siberian milk stood out as almost 3 fold higher than seen recently in northwestern Russia. Moreover, LHCH comprises 92% f3-HCH indicating exposure to crude HCH in southern Siberia. DDT levels were about 20% higher than seen recently in a sampling of urban centres of northwestern Russia (AMAP, 1997), and the samples collected in 1988-1989 indicated more recent exposure prior to sampling. HCB levels were also consistently higher than observed in northwestern Russia, and particularly high in samples from Irkutsk and Kachug.

Globally, DDT and HCH levels in southern Siberian milk were substantially higher than in human milk of western European countries, while HCB levels were similar to those seen in the heavily industrialized former West Germany. Levels of PCBs were only about 15-25% of those seen in mothers of the former West Germany, but 5-6 fold higher than low exposure countries like Thailand and Cambodia (Schecter et al., 1994d). Baikal region samples differ from other countries by the presence of PCB 28 at perceptible levels (6-10% of the total for six congeners). This suggests that the SovietRussian PCB mixture *Trichlorodiphenyl* has been released into the local environment.

Table 5.2 POPs in southern Siberian human milk.

| | Source | | n | $t_{LDDT}$ | %DDT | :j:LHCH | § PCBs | HCB |
|---|---|---|---|---|---|---|---|---|
| Novosibirsk | a | 1988/9 | 10 | 1,757 | 20 | 1,582 | 577 | 181 |
| Irkutsk | a | 1988/9 | 4 | 2,948 | 22 | 3,449 | 542 | 466 |
| Baikalsk | a | 1988/9 | 5 | 1,287 | 23 | 1,150 | 493 | 140 |
| Kachug | a | 1988/9 | 4 | 1,897 | 30 | 1,842 | 301 | 331 |
| South Siberia mean | a | | 23 | 1,862 | 22 | 1,806 | 506 | 242 |
| AMAP mean * | b | 1993/6 | ? | 1,548 | 14 | 657 | 486 | 109 |
| Troms", Norway | b | 1993 | | 328 | 5 | 34 | 383 | 39 |
| West Germany | a | ? | 143 | 802 | 6 | 113 | 2,065 | 356 |

t *LDDT = p,p'-DDT + p,p'-DDE;* Schecter data include o,P'-DDT + o,p'-DDE that are only 1-2% of *LDDT.*

:j: LHCH = a.-HCH + 13-HCH + y-HCH; § total PCBs from Schecter data prorated from measurements of 6 congeners; * for DDT, HCH and HCB - northwestern Russia: Murmansk, Monchegorsk, Severodvinsk and Arkhangelsk; and for PCBs, previous cities plus Salekhard and Norilsk in northwestern Siberia.

References: a. Schecter et al. (1990a); b. AMAP (1997).

### 5.3.5.1 PCDD/Fs in Humans

In southern Siberian human breast milk, Schecter et al. (1990a) found PCOO/Fs at *9-17 pg/g* lw I-TEQ. The maximum concentration (17 *pg/g* lw I-TEQ for four samples from Irkutsk) was similar to U.S. samples (see Chapter 4, Section 4.1.3). PCOO/Fs were observed in the blood of eight Baikalsk residents at 18 *pg/g* lw I-TEQ, about the same level as the general population of St. Petersburg (Schecter et al., 1992; see Chapter 4, Section 4.1.5). These are relatively low levels compared to samples of other western industrial'ized countries. If the Baikalsk pulp mill is emitting appreciable PCOO/Fs, the effects are not evident in the small sampling of Baikalsk human blood.

## 5.4 Bioconcentration Patterns

Magnification tendencies for six POPs among Baikal environmental compartments (Figure 5.2) confirm that the available data exhibit typical patterns. Air and water have the lowest concentrations and biotic compartments have the highest. Soil and sediments are intermediate.

Though there is little complete aquatic ecosystem data to permit broad comparisons, these diagrams suggest that Baikal system is characterized by an extraordinary capacity to biomagnify the concentrations of POPs upward through the food web to the extent that marginal water contamination becomes significant in top level predators. Bioaccumulation among water, fish and seal is compared in the panels of Figure 5.3 that show the log10 *bioconcentration factor* [BCF][26] estimated from the ratios of the lipid normalized concentrations observed in the indicated compartments. The most bioconcentration, from $10^6$-$10^9$ fold, occurs from water-to-fish for LOOT, LCHL, PCCs, HCB, and PCBs, while for LHCH, biomagnification is about 2 orders lower at 14,000-325,000. Amongst the leading contaminants, OOT appears to accumulate 10 fold more than PCBs. Kucklick et al. (1996) explore bioaccumulation patterns among water, fish and intermediate trophic levels in some detail.

As Figure 5.3b reveals, DOT species exhibit unequivocally the greatest amplification from water-to-seal of $10^8$_$10^{10}$ fold. The net water-to-seal amplifications of PCBs and chlordanes are similarly about 30 fold less than OOT amplification.

Relatively small biomagnification occurs from fish-to-seal (Figure 5.3c). OOT species amplify the most with male seals having about 25 fold more LOOT than fish, and females having about 11 fold more. PCBs, chlordanes and HCHs also amplify from fish-to-seal, but there appears to be no significant amplification of dieldrin and PCCs. The nerpa appear to have capacity to eliminate HCB and heptachlor.

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[26] The terms bioaccumulation, bioconcentration and biomagnification are used inconsistently in the literature. Herein, bioconcentration refers specifically to the ratios between environmental compartments of concentrations in biotic compartments are expressed on lipid weight (lw) basis.

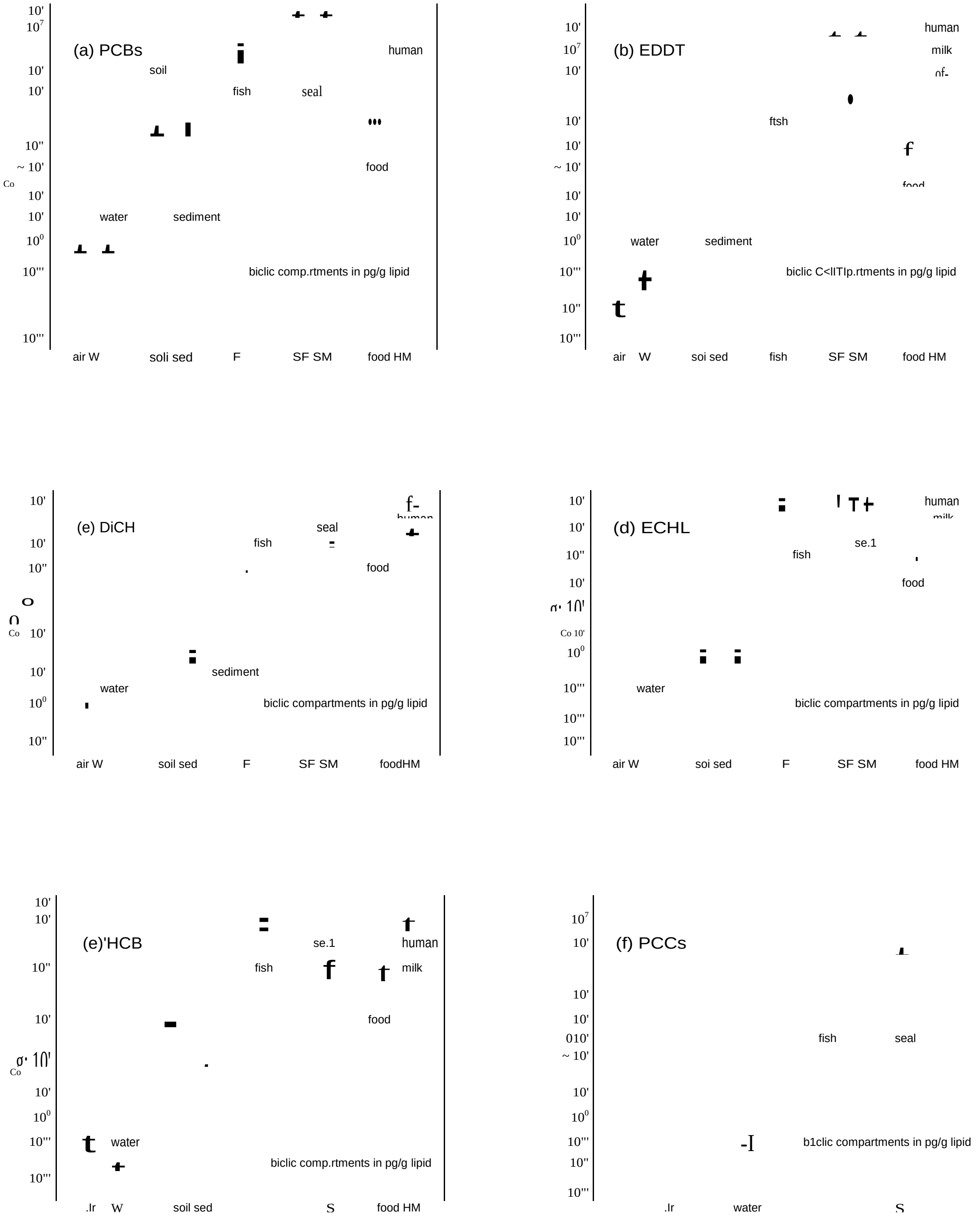

Figure 5.2 Individual POPs distribution across Baikal environmental compartments. Notes: water data: lumped 1991-93 data from Kucklick et al. (1994, 1996), Iwata et al. (1995), McConnell et al. (1996); fish data: lumped 1991-93 data from Kucklick et al. (1994,1996), Iwata et al. (1995); seal data: SF are female and SM are male seal data from Nakata et al. (1995); S are seal data from Kucklick (1996).

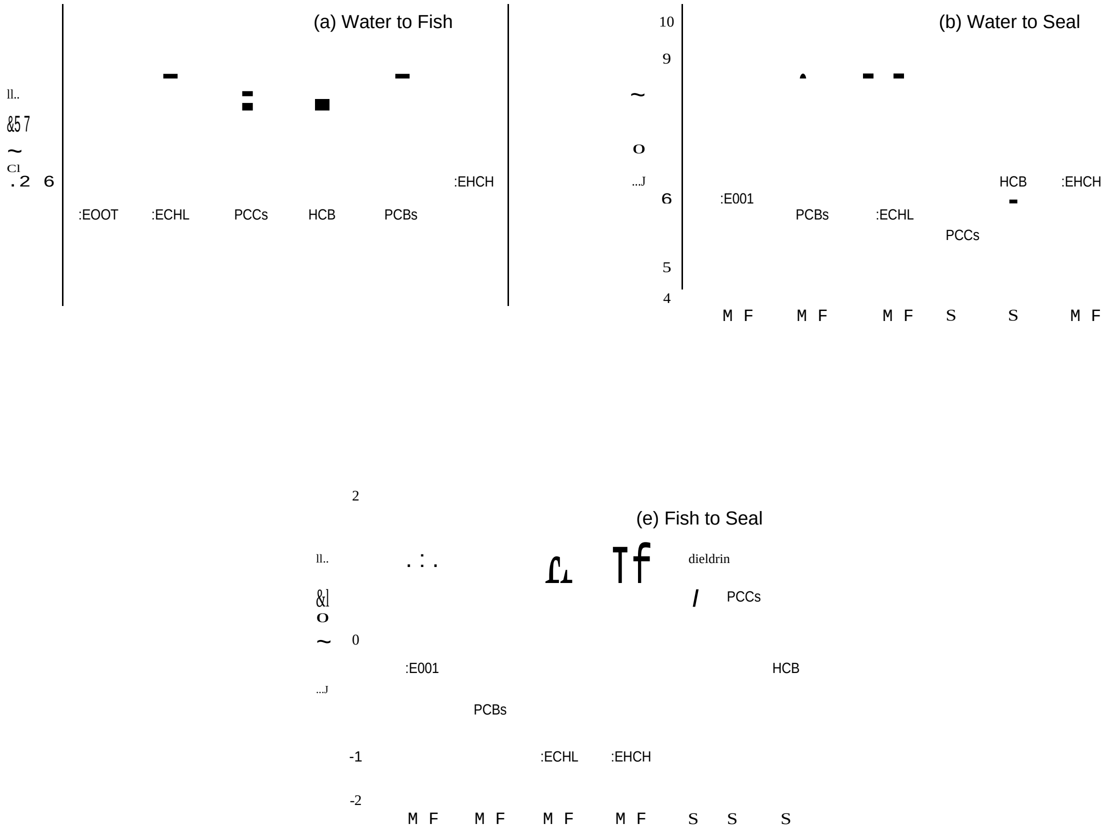

Figure 5.3 Bioconcentration (lipid weight basis) among Baikal water, fish and seal compartments. Calculated from lumped 1991-93 water data from Kucklick et al. (1994, 1996), Iwata et al. (1995), McConnell et al. (1996); lumped 1991-93 fish data from Kucklick et al. (1994,1996), Iwata et al. (1995); and male (M) and female (F) seal data Nakata et al. (1995), except for dieldrin, PCCs and HCB are seal data (S) from Kucklick (1996); see Section 5.9 for notes on calculations.

The net biomagnification of total PCBs masks differential biomagnification amongst PCB congeners. From detailed study of more than 40 PCB congeners in Baikal seal, Nakata et al. (1997) distinguished congeners that were disproportionately accumulative from those that were readily metabolized, and drew conclusions about the metabolic capacity of Baikal seal for particular PCB structures. The most accumulative congeners were PCBs 153 and 138, neither known for dioxin-like toxicity, and PCBs 118 and 180, which are dioxin-like.

## 5.5 Dioxin-like PCB Toxicity in Fish and Seal

The subset of PCBs that exert dioxin-like toxicity is of particular concern in higher aquatic mammals (Tanabe et al., 1987; Tanabe, 1988; Kannan et al., 1989). Nakata et al. (1997) gave concentration data for fish and seal, and estimated dioxin equivalence of certain PCB congeners in seal using the toxic equivalency factors (TEFs) of Safe (1990) augmented with TEFs for PCBs 137,138 and 153 (Table 5.3). The origins of the latter three TEFs are unclear. TEas were given for the average PCB burden of four seal classes: juvenile and mature by sex[27]; however, as sex differences in juveniles are irrelevant, male and female juveniles were grouped for discussion herein.

PCB TEas in seal were recalculated to assess the implications of the alternative TEF systems. The results (Table 5.4, Figure 5.4) show considerable variation by both age/sex class for seal and the assumed TEF system. Mature males clearly have the greatest dioxin-like PCB burden for all TEF systems. The TEFs used by Nakata et al. (1997) yield only marginally greater TEas than Safe's (1990) original system; however, later TEF systems proposed by Safe (1994), Ahlborg, and WHOIIPCS (Ahlborg et al., 1994) all yield substantially lower estimates of dioxin-like PCB toxicity in Baikal seal.

Table 5.3 Toxic equivalency factors for dioxin-like PCBs.

| PCB congener | | | TEF systems t | | |
|---|---|---|---|---|---|
| | Nakata et al., 1997 | Safe 1990 | Safe 1994 | Ahlborg 1992 | WHO/IPCS 1994 |
| 77 | 0.01 | 0.01 | 0.01 | 0.0005 | 0.0005 |
| 126 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| 169 | 0~05 | 0.05 | 0.05 | 0.01 | 0.01 |
| 105 | 0.001 | 0.001 | 0.001 | 0.0001 | 0.0001 |
| 118 | 0.001 | 0.001 | 0.0001 | 0.0001 | 0.0001 |
| 156 | 0.001 | 0.001 | 0.0004 | 0.001 | 0.0005 |
| 137 | 0.00002 | | | | |
| 138 | 0.000002 | | | | |
| 153 | 0.00002 | | | | |
| 180 | 0.00002 | 0.00002 | | | 0.00001 |

**t** Nakata et al. TEFs for PCBs 137, 138 and 153 back calculated from concentration and TEQ data for Baikal seal in Nakata et al. (1997); others from Ahlborg et al. (1994).

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[27] Mean ages were 1.5 years for juveniles, 11 years for mature females, and 16 years for mature males. The age of maturity is about 7-8 years (Nakata et al., 1995).

Table 5.4 TEQs for dioxin-like PCBs in Baikal fish and seal.

| | *L10* PCBs† | TEQs (ng/g wet weight) for alternative TEF systems | | | | |
|---|---|---|---|---|---|---|
| | *nglg* wet weight | Nakata et al. 1997 | Safe 1990 | Safe 1994 | Ahlborg 1992 | WHOIIPCS 1994 |
| Fish | 131 | 92 | 91 | 61 | 41 | 38 |
| Juvenile | 3,070 | 1,387 | 1,363 | 687 | 426 | 388 |
| Female | 6,368 | 2,037 | 1,979 | 1,011 | 632 | 564 |
| Male | 17,787 | 5,060 | 4,893 | 2,183 | 1,025 | 912 |

† sum of 10 PCB congeners listed in Table 5.1.

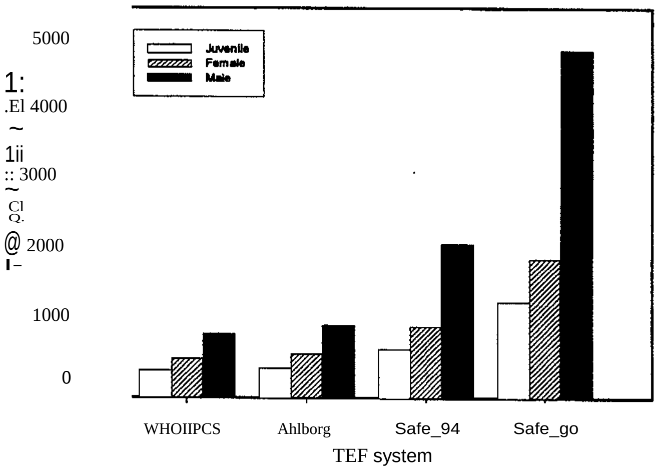

Figure 5.4 PCB TEQs in Baikal seal by alternative toxic equivalency systems.

Among competing TEF systems, the specific PCB contributions to the estimated TEQs can differ appreciably. The relative contributions of the main toxic congeners to the total TEQ estimated by the limiting TEF systems (Safe 1990 and WHOIIPCS) for Baikal seal are illustrated in Figure 5.5. In all age/sex classes, the Safe 1990 system assigns most toxicity to PCB 118 (50%·in juvenile and females, 57% in males), while the WHO/IPCS system assigns most toxicity to PCB 126 (60-63% in juvenile and females, 38% in males). For juveniles and females, the proportional roles of PCBs 118 and 126 are virtually reversed in the two systems. Distinct differences are evident in mature males as the proportional burden of PCB 118 (30%) ranks a close second after PCB 126 in the WHO/IPCS system.

Nakata et al. (1997) explore the metabolic capacity of Baikal seal for more than 40 PCB congeners by various means including their particular toxic equivalency system (essentially Safe 1990). Certain toxicological implications they suggest for dioxin-like PCB congeners in Baikal seal might change somewhat if another TEF system were employed. For fish, WHO/IPCS TEa is about 41 % of Safe 1990 TEa, while for male seal, WHO/IPCS TEa is about 19% of Safe 1990 TEa. This reflects not only the respective abilities of species to metabolize and excrete different congeners, but also the variations in toxicity assigned to dioxin-like congeners by the respective systems.

Also, the list of dioxin-like PCBs in Table 5.3 is not necessarily complete. All systems give TEFs for PCBs 114, 123 and 157, while the Safe 1990 and WHO/IPCS systems also give TEFs for PCBs 167, 170 and 189. In addition, Hong et al. (1993, 1996) used a TEF of 0.004 for non-artho PCB 81 to estimate dioxin-like toxicity in seals and humans. Hong et al.'s (1996) data for harbour seal pups from Puget Sound suggest that for Baikal seal: (1) the Safe 1990 TEas augmented for PCB 81 could increase by 9-12%, and (2) the WHOIIPCS TEas augmented for PCB 81 could increase by 11-20% over values in Table 5.4.

Until consensus is achieved on the most appropriate toxic equivalency systems, it is wise to evaluate dioxin-like PCB toxicity over the range of proposed alternatives, and by age and sex classes. Furthermore, the threat of PCBs should not be assessed solely in terms of dioxin-like toxicity as PCBs in including those without dioxin-like toxicity can induce other toxicological effects including tumor promotion and neurotoxicity (S~fe, 1990).

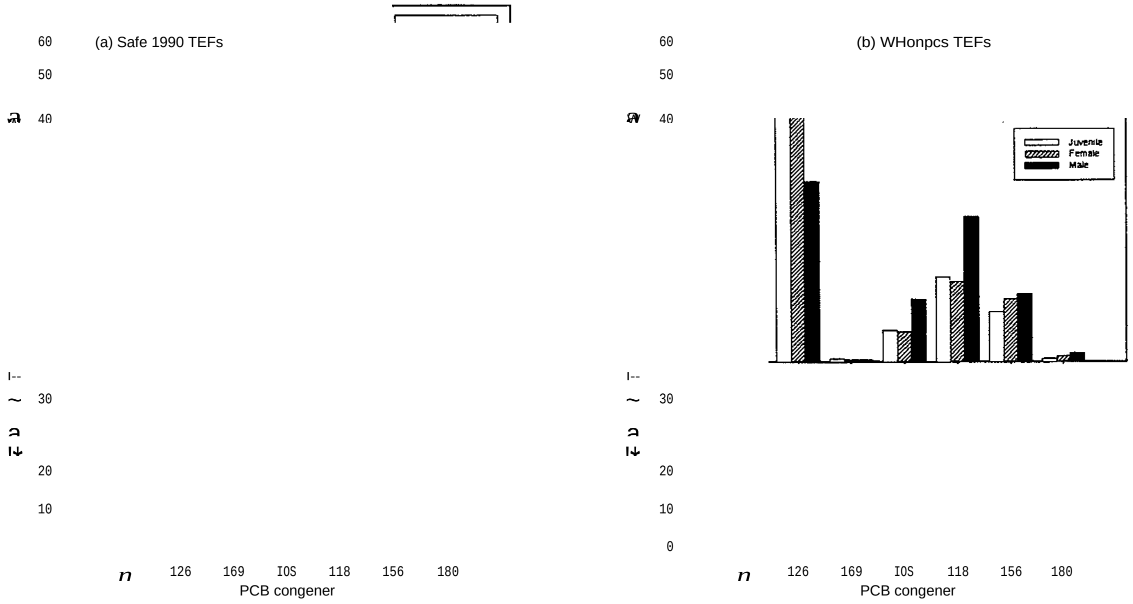

Figure 5.5 PCB TEQs by congener in Baikal seal for Safe 1990 and WHO/IPCS 1994 TEF systems.

## 5.6 PCDD/Fs, *Non-ortho* PCBs and PCDEs in Baikal Seal

Tarasova et al. (1997) gave PCDD/F data for three nerpa and Koistinen et al. (1995) analyzed blubber from a young male nerpa taken in 1992 for PCDD/Fs and PCDEs (polychlorodiphenyl ethers)28. Three' *non-ortho* coplanar PCBs (nos. 77, 126 and 169) were also analyzed in the Koistinen seal. The PCB data (Table 5.5) show that the Koistinen seal was perceptibly less contaminated than all age/sex classes observed by Nakata et al. (1997). Furthermore, the ratio of PCBs 77 to 126 in the Koistinen seal is about 0.7, while for the Nakata seals, the ratio is about 3 for juveniles, 4 for mature females and 6 for mature males. Equivalently, the non-ortho PCBs reported by Nakata and colleagues comprise mostly PCB 77 by mass. Either the Koistinen seal is atypical of the general Baikal population, or laboratory methods are inconsistent. Potential discrepancies due to inaccurate reporting of PCB 77 concentrations are negligible if dioxin equivalency is characterized by the 1994 WHOIIPCS TEF system. Assuming the Koistinen data are correct, if measurements were available for all 1 0 dioxin-like PCBs observed by Nakata et al., the total TEQ in the Koistinen seal could range from 500 (WHO/IPCS) to 1,700 (Safe 1990) pg/g.

PCDD/F data are summarized in Table 5.6 individually for the 6 congeners that contribute >95% of the toxic burden, and cumulatively for all seventeen 2,3,7,8-substituted PCDD/Fs. Again, there are perceptible differences that may reflect inconsistencies in analytical methods. For the Koistinen seal, 60% of the TCDD burden originates from 2,3,7,8-TCDD, while for the 2 mature female Tarasova seals, 60% originates from 2,3,4,7,8-PeCDF. Potential inconsistencies notwithstanding, these results suggest that in Baikal seal, the dioxin equivalency of PCDD/F congeners is relatively small compared to the TEO attributable to dioxin-like PCBs. Bergek et al. (1992) suggested that Baltic seals seemed capable of rapid catabolism or elimination of 2,3,7,8-substituted PCDD/Fs relative to other contaminants such as PCBs and DOT. Baikal nerpa may have similar capacity.

Only about one third of more than 35 PCDE congeners measured in the blubber of the Koistinen seal were detected, generally at low levels. Koistinen et al. (1995) estimated the dioxin-like TEQ attributable to six congeners (PCDE nos. 77, 105, 118, 126, 156, 157) at 10 pg/g lipid. For the present, dioxin-like PCDE contamination in Baikal nerpa appears to be negligible relative to that of PCDD/Fs and PCBs.

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28 PCDEs are a family of 209 double-ringed polychloroaromatics with analogous structures to PCBs and the same congener numbering scheme (Safe, 1991). Non-ortho and mono-ortho PCDEs have been assigned tentative dioxin-like TEFs of 0.001 (Safe, 1990), but the toxicology of PCDEs remains poorly studied. PCDEs were significant contaminants in the particular chlorophenolic wood preservative used heavily in Finland for decades; hence, most available environmental data are for Finland and the Baltic region. PCDEs can be generated by other industrial processes.

Table 5.5 Non-ortho PCBs *(pg/g* wet weight) in Baikal seal blubber; after Koistinen et al. (1995).

| PCB congener<br>Concentration | TEa | Safe *1990/94* | WHO/IPCS 1994 |
|---|---|---|---|
| 77 | 1,860 | 2.2 | 187 |
| 126 | t 44 | 201 | |
| 169 | 3,206 | 0.7 | |
| L3PCB | 13.0 | 186.0 | |
| 1,302 | 186.0 | 0.4 | |

B. Mean *non-ortho* PCB data from Nakata et al. (1997).

| class | mean age (yr) | L3 PCB | TEa<br>Safe *1990/94* | <br>WHO/I PCS 1994 |
|---|---|---|---|---|
| Juvenile | 1.5 | 10,141 | 331 | 251 |
| Female | 11 | 17,700 | 495 | 350 |
| Male | 16 | 26,870 | 599 | 365 |

t PCB 169 <100 *pg/g* lw; assumed value based on PCB *169/126* ratio in data of Nakata et al. (1997).

Table 5.6 PCDD/Fs in Baikal seal blubber *(pg/g* lw).

| congener | I-TEF | specimen | | | |
|---|---|---|---|---|---|
| | | P | F1 | F2 | M |
| 2,3,7,8-TCDD | 1 | 7 | 11 | 13 | 27 |
| 1,2,3,7,8-PeCDD | 0.5 | 13 | 23 | 28 | 5 |
| 1,2,3,6,7,8-HxCDD | 0.1 | 2 | 5 | 9 | 11 |
| 2,3,7,8-TCDF | 0.1 | 10 | 23 | 26 | 51 |
| 1,2,3,7,8-PeCDF | 0.05 | 13 | 24 | 28 | 32 |
| 2,3,4,7,8-PeCDF | 0.5 | 24 | 92 | 120 | 12 |
| sum PCDD/Fs t | | 72 | 184 | 235 | 138 |
| sum I-TEa t | | 28 | 73 | 92 | 43 |
| % PCDD I-TEa | | 51 | 31 | 30 | 71 |
| % PCDF I-TEa | | 49 | 69 | 70 | 30 |

P, F1, and F2 are the 3 month old pup and 2 mature females (10 and 12 years) analyzed by Tarasova et al. (1997); M is the 7 year old male analyzed by Koistinen et al. (1997).

t sums for all 17 2,3,7,8-substituted

## 5.7 External Comparisons

Air, water and sediments appear to be only marginally contaminated with POPs. Kucklick et al. (1994) noted that POPs in Baikal surface waters were at comparable or marginally lower levels than observed in Lake Superior, while Iwata et al. (1995) found Baikal air, water and sediment data to rank at the lower end of the ranges observed in an earlier synoptic survey from across the Asia-Pacific region (Iwata et al., 1994).

### 5.7.1 Fish

Global fish data are shown on Figure 5.6. The most germane reference for comparing Baikal data may be fish from Finland's Teno River that drains northernmost Finland and Norway to the Barents Sea. The Teno River data of Paasivirta et al. (1993) represent composite samples of salmon gathered in 1988 and 1990. POPs in River Teno fish are likely due almost exclusively to long range atmospheric transport.

While the POPs burdens of Baikal fish rank neither extremely high nor low, levels of PCBs and *LDDT* are higher than might be anticipated given the remote location. Levels of PCBs in Baikal fish are in the lower range of those seen in Scandinavian waters that are known for significant PCB contamination. PCB levels are higher than in Teno River [F-T] salmon and fishes from various tropical countries where PCBs did not see appreciable use. DDT levels in Baikal fishes are in the range of fishes from several tropical countries where DDT has been heavily used until recently, and some industrialized countries where the legacy of past DDT usage persists.

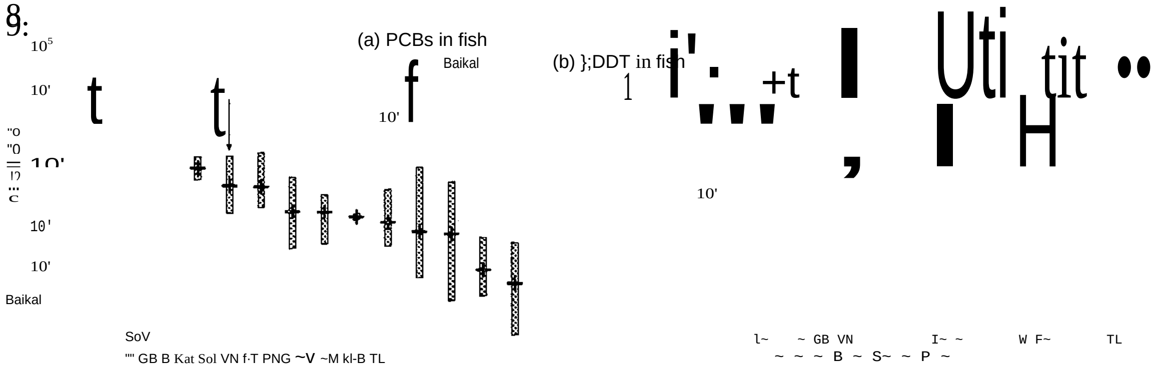

Figure 5.6 POPs in Baikal fish - global comparisons.
See Table 5.7 for figure key and references.

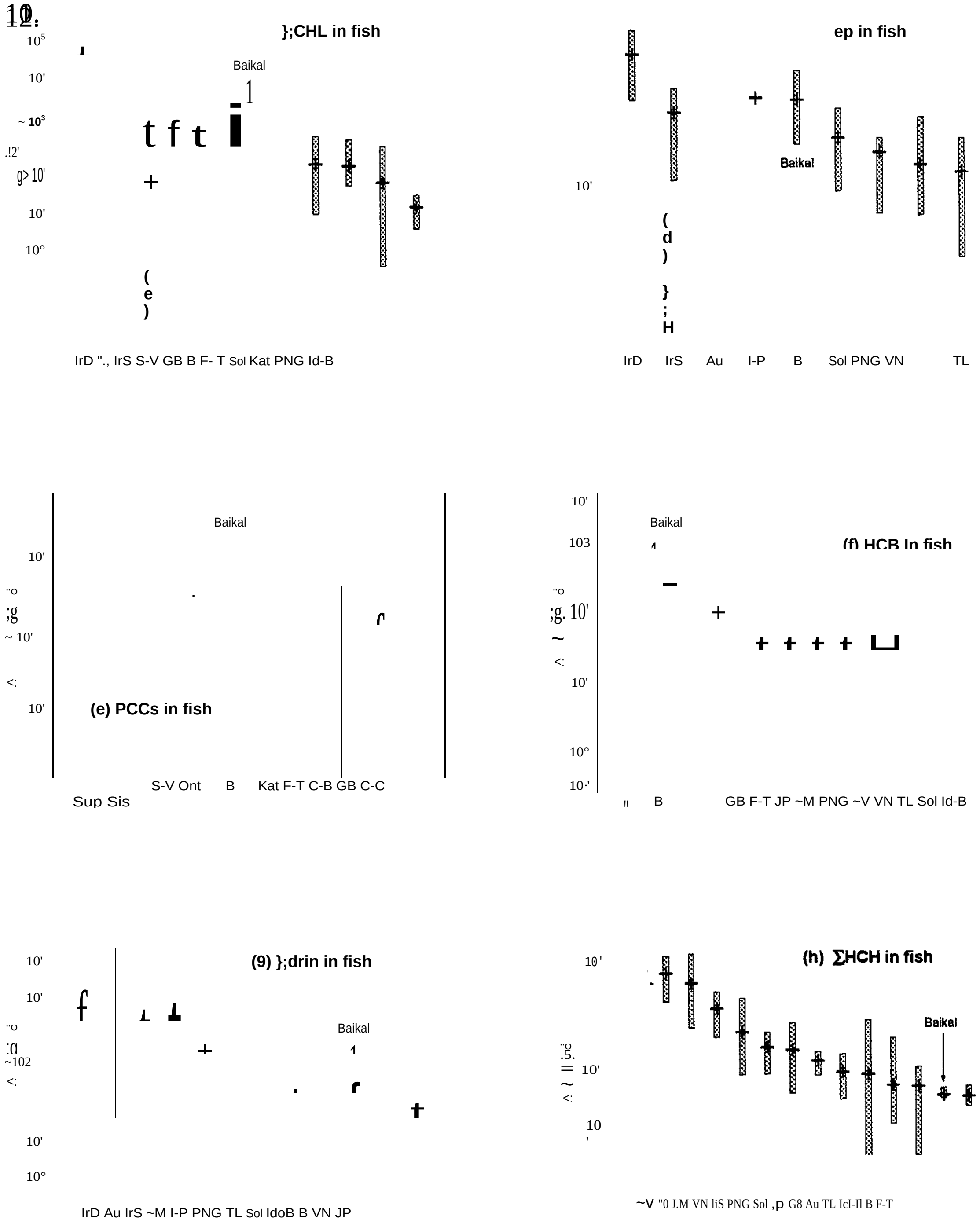

**Figure 5.6 Cont'd. POPs in Baikal fish - glObal comparisons.
See Table 5.7 for figure key and references.**

Table 5.7 Key and sources for Figure 5.6, POPs in Baikal fish - global comparisons.

| | |
|---|---|
| Sup | Great Lakes: Lake Superior - mean ± 2 standard deviations for 1994 lake trout samples (Glassmeyer et al., 1997). |
| Sis | Great Lakes: Siskiwit Lake, Isle Royale, Lake Superior - combined *whole fish* data for lake trout and whitefish netted in 1983 (Swackhamer and Hites, 1988). |
| Ont | Great Lakes: Lake Ontario - mean ± 2 standard deviations for 1994 lake trout samples (Glassmeyer et al., 1997). |
| C-B | Canada: combined data for PCCs in burbot livers gathered at 8 locations from northwestern Ontario to Mackenzie River delta over 1985-88 (Muir et al., 1990). |
| C-C | Canada: combined *whole fish* data forPCCs in arctic char gathered at 6 locations across Canadian Arctic over 1985-87(Muir et al., 1990). |
| F- T | Finland: T eno River, 2 composites of salmon collected 1988 and 1990 (Paasivirta and Rantio, 1993). |
| S-V | Sweden: combined data for salmon, trout and alpine char from Lakes Vattem and Vanem collected in 1979 (Andersson et al., 1988). |
| GB | Baltic Sea: Gulf of Bothnia - combined data for salmon and trout collected 1988-1991 (Paasivirta and Rantio, 1993). |
| Kat | Baltic Sea: Kattegat - combined data for salmon, trout and mackerel collected 1979 . off west coast of Sweden (Andersson et al., 1988). |
| Au | Australia: 37 freshwater and near shore fishes from markets of Sydney, Hobart, and P~rth [1990]; and Brisbane, Townsville and Atherton [1992] (Kannan et al., 1994b): |
| I-P | India: Ganges River near Patna, single composite of four fish species from the gut of 4 Ganges River dolphins collected over 1988-92 (Kannan et al., 1994a). |
| I-V | India: Vellar River near Porto Novo, Tamil Nadu; 28 samples (muscle) of 6 estuarine, mangrove and near shore species collected from 1987-91 (Ramesh et al., 1992). |
| I-M | India: market fish; 42 samples of freshwater and nearshore fishes, and prawn, from fresh fish markets in New Delhi, Bombay, Calcutta, Madras, Porto Novo, and Chidambaram collected December 1989 (Kannan et al., 1992b). |
| Id-B | Indonesia: Bogar area; 5 samples, 199? (Kannan et al., 1995); lipid weights approximated from mean and range of fat % and wet weights. |
| IrD | Iraq: Diyala River near Baghdad; 17 samples mixed freshwater species from 1984 (Al-Omar et al., 1986); l;CHL = *trans-* + *cis-* + oxychlordane. |
| IrS | Iraq: Shatt ai-Arab River; 16 samples *Tenualosa ilisha* (muscle tissue) from 1984 (DouAbul et al., 1987); l;CHL =. *trans-* + *cis-* + oxychlordane; l;HCH = sum of measured ~-and y-HCH, and estimated a-HCH. |
| JP | Japan: 1 sample each of 2 species of cultured fish from markets of Fukuoka, Kyushu 1992-93 (Nakagawa et al., 1995) .. |

Table 5.7 Cont'd. Key and sources for Figure 5.6, POPs in Baikal fish - global comparisons.

| | |
|---|---|
| PNG | Papua New Guinea: 9 samples of 2 species from Port Moresby markets 1990 (Kannan et aI., 1994b). |
| Sol | Solomon Islands: 10 samples of 3 species from Honiara markets Aug - Sep 1990 (Kannan et aI., 1994b). |
| TL | Thailand: 15 samples of 5 species from Bangkok markets Dec 1989 - Jan 1990 (Tanabe et aI., 1991); due to numerous typographical errors in Table 2 Tanabe et aI., fat weights were approximated as necessary from wet weights and fat % in Table 1 Tanabe et al. |
| VN | Vietnam: 11 samples of freshwater and nearshore fishes from Hanoi, Phu Loc Lake [Hue area], and Duyen Hai [Ho Chi Minh] 1990-91 (Kannan et aI., 1992a). |

Unless otherwise indicated LHCH = a-HCH + j3-HCH + y-HCH; *LOOT = p,p'-DDT + o,p'-DDT + P,P'*DOE + *p,p'-DDD;* I:drin = aldrin + dieldrin; I:CHL = trans-chlordane + cis-chlordane + trans-nonachlor + cis-nonachlor; LHEP = heptachlor + heptachlor epoxide.

Chlordane levels in Baikal fish rank within the range observed in a broad spectrum of geographic locales suggesting that the chlordane in Lake Baikal may be mainly derived from long range atmospheric transport. In contrast, the heptachlor levels reported for Baikal fish rank with fish from several countries (Iraq, Australia, India) where there has been appreciable heptachlor or chlordane use in until at least the early 1990s. Consequently, there is reason to suspect that heptachlor has seen recent use in the Baikal watershed. This heptachlor may have originated from *dihydroheptachlor.* Furthermore, if there are chlordane constituents in the technical *dihydroheptachlor,* these may contribute to the chlordanes found in Lake Baikal.

PCCs, .. which rival DDT and PCBs as the leading POP in Baikal fish, are present at concentrations similar to those in fishes from a broad spectrum of North American and northern European waters. This suggests that PCCs in Baikal originate from atmospheric transport.

Baikal fish stand out as having high concentrations of HCB second only to fish from the vicinity of Sydney, Australia. The even distribution of HCB in Baikal surface waters suggests that the HCB originates from remote air emissions, but local industrial emissions from Irkutsk and Usolje-Sibirskoye could be significant regional sources. As noted in Section 5.3.5, human milk samples from Irkutsk and Kachug had particularly high HCB levels suggestive of local contamination.

Levels of both dieldrin and HCHs rank near the low end of the global spectrum. Dieldrin is remarkably persistent, and the dieldrin in Baikal fish may be the legacy of usage in the remote past. Generally, HCHs do not accumulate appreciably in fish unless there is regionally significant active usage or copious past usage of crude HCH has left significant residues of the persistent f3-HCH isomer.

### 5.7.2 **Seal**

The Baikal seal is likely best compared with related species including marine ringed seal, freshwater ringed seals (Lakes Saimaa and Ladoga), and the Caspian seal. In a comparison of Baltic seals, Blomkvist et al. (1992) found that ringed seals had DDT and PCB burdens intermediate between harbour seals with least contamination and grey seals with the most. However, Bergek et al. (1992) found for PCDD/Fs that Baltic ringed seals were perceptibly more contaminated than harbour and grey seals.

Table 5.8 gives available POPs data for Baikal seal and its nearest pinniped relatives from various geographic locations. Contaminant levels in Baikal seal are surprisingly high given the low levels of POPs observed in air, water and sediments. For DDT and PCBs, Baikal seals rank after the highly contaminated Baltic ringed seals, but are undeniably more contaminated than ringed seals of Svalbard archipelago and the Canadian Arctic (Figure 5.7). Levels of chlordanes and PCCs in Baikal seal are much less than Baltic ringed seal, and similar to Canadian ringed seal, while contamination by HCB and HCHs is minimal.

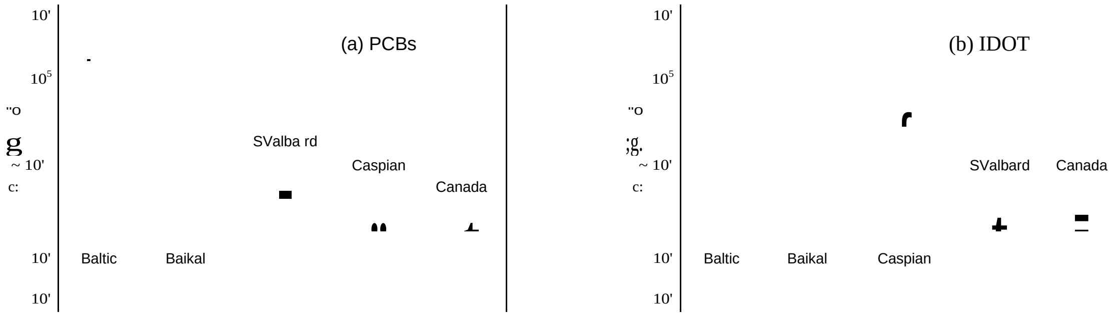

Figure 5.7 PCBs and DOT in Baikal seal- global comparisons; lumped data for all age and sex classes.

PCB contamination in Baikal seal is further contrasted against other ringed seals in Table 5.9 that gives data for the few cases where dioxin-like congeners have been determined. Figure 5.8a contrasts the PCB TEQs of Baikal seal against other seals for lumped data of all age and classes. The Baikal seal is unequivocally much more contaminated than Svalbard and Inukjuaq (East Hudson Bay) ringed seals. The Inukjuaq seals are considered contaminated relative to other Canadian Arctic ringed seals. By Safe's 1990 TEFs, the toxic burdens of Baikal females and females are respectively 50-100 and 175-250 fold higher than Svalbard and Inukjuaq ringed seals, while by WHO/IPCS TEFs, the toxic burdens of Baikal females and females are respectively 20-30 and 30-50 fold higher.

Table 5.8 POPs (j..tg/g Iw) in Baikal seal - global comparisons.

| species [a] | location | date | n | sex [b] | age [c] | }:DDT | PCBs | }:CHL | }:HCH | PCCs | HCB | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BS | Baikal | 1992 | 16 | M | M | 64 | 31 | 1.0 | 0.089 | | | 1 |
| | | 1992 | 25 | F | M | 22 | 13 | 0.47 | 0.055 | | | 1 |
| | | 1992 | 17 | M&F | J | 17 | 6.7 | 0.52 | 0.090 | | | 1 |
| | | 1993 | 7 | M&F | J&M | 16 | 8.3 | 0.48 | | 0.89 | 0.009 | 2 |
| RS | Svalbard | 1986 | 7 | M&F | J&M | 1.66[d] | 2.38[e] | | 0.14 | | 0.021 | 3,4 |
| | | 198?f | 11 | M&F | U | 1.23 | 1.67[e] | | 0.097 | | 0.027 | 5 |
| | | 1990 | 8 | M | J&M | 2.40[d] | 1.72 | | | | | 6 |
| | | 1990 | 5 | F | J&M | 1.69[d] | 1.13 | | | | | 6 |
| RS | Baltic | 1980/8 | 10 | U | J | 16 | 19 | 1.1 | | 2.7 | | 7,8 |
| | | 1980/8 | 5 | M | M | 250 | 225 | 11 | | 14 | | 7,8 |
| | | 1991/2 | 14 | M&F | J&M | | 15[9] | | | | | 9 |
| RS | Canadian Arctic | 1983/91 | 96 | M&F | J&M | | | | | | 0.021 h. | 10,11 |
| RS[i] | | 1983/91 | 101 | M | J&M | 0.74 | 0.87 | 0.58 | 0.27 | 0.38 | | 11,12,13 |
| RS[i] | | 1983/91 | 75 | F | J&M | 0.47 | 0.58 | 0.43 | 0.25 | 0.32 | | 11 ,12,13 |
| CS | Caspian Sea | 1977 | k5 | U | U | 38 | 1.9 | | | 2.9 | | 14 |
| CS | | 1993 | 1 | M | U | 6.83 | 1.36 | | 0.30 | 0.008 | 0.0065 | 15 |

a BS = Baikal seal, RS = Ringed seal, CS = Caspian seal; b U = unknown, M = male, F= female; C U = unknown, M = mature, J = juvenile; d pro-rated to approximate 1:00T = *p,p'-OOT* + p,p'-OOE + p,p'-OOO; e pro-rated from sum of specific congener measurements according to mean data given in ref. 6; f likely late 1980s; 9 mean for 14 seals (mostly pups, ~ Mature F, no mature M) pro-rated from sum of 9 congeners according to ratio observed in (1997); h pooled mean of 14 means for 10 locations; J pooled mean of means for 10/9 (M/F) locations across Canadian Arctic; wet weight data from refs. 11 and 12 converted to lipid weight using 88% mean blubber fat content from refs. 9 and 10; k homogenate of 5 blubber samples of unknown age/sex.

References: 1. Nakata et al. (1995), 2. Kucklick et al. (1996), 3. Oehme et al. (1988), 4. Oehme et al. (1990), 5. Luckas et al. (1990), 6. Oaelemans et al. (1993), 7. Blomkvist et al. (1992), 8. Andersson and Wartanian (1992), 9. Koistinen et al. (1997). 10. Norstrom et al. (1990), 11. Muir et al. (1995), 12. Muir et al. (1988),13. Muir et al. (1992), 14. Andersson et al. (1988), 15. Vetter et al. (1995).

Table 5.9 Total PCBs and PCB TEas t (wet weight basis) in Baikal seal - global comparisons.

| | | | | TEF system | | | |
|---|---|---|---|---|---|---|---|
| | | | | Safe 1990 | | WHO/IPCS | |
| species | location | class | total PCBs f.Lg/g | TEa *pg/g* | t %126 | TEa *pg/g* | %126 |
| BS | Baikal | J | 5 | 1,363 | 18 | 388 | 63 |
| BS | Baikal | F | 10 | 1,979 | 17 | 564 | 60 |
| BS | Baikal | M | 26 | 4,893 | 7 | 912 | 38 |
| RS | Baltic | M&F | §12 | 1,084 | 10 | 257 | 41 |
| RS | Svalbard | M&F | 1.4 | 19 | 94 | 18 | 100 |
| RS | Hudson Bay | F | 1.3 | 20 | 92 | 19 | 98 |
| RS | Hudson Bay | M | 1.2 | 28 | 91 | 26 | 98 |

**t** % TEa due to PCB 126; BS = Baikal seal; RS = ringed seal.

:j: TEa for Baikal and Baltic seal from PCBs (77,126,169,105,118,156,180); for Svalbard and Hudson Bay seals only *non-ortho* PCBs, mainly PCB 126, contribute.

§ Represents 14 Gulf of Finland RS [1 pups < 1 yr.; 4 juveniles 1-3 yr., 3 mature F) found dead in *1991/2;* total PCBs pro-rated from sum of 9 congeners by ratio observed in Baikal.

References: Baikal - Nakata et al. (1997); Baltic - Koistinen et al. (1997); Svalbard - Daelemans et al. (1993) adjusted to approximate wet weight; Hudson Bay (Inukjuaq) - Muir et al. (1995).

Also, there is a striking difference in the relative role of PCB 126. In Svalbard and Inukjuaq seals, virtually all PCB dioxin-like toxicity is attributable to PCB 126; hence, there is I'ittle difference in TEQ estimates by whatever system is employed. As shown previously for Baikal seal, other dioxin-like PCB congeners are present in sufficient amounts that the various proposed TEF systems yield appreciably different results.

Table 5.10 compares the burden of *non-ortho* coplanar PCBs (nos. 77,126,169) in Baikal seals with 14 seals from the Baltic (Koistinen et aL, 1997), four seals from Lake Saimaa seals Koistinen et al. (1995), and a single Baikal specimen (Koistinen et aL, 1995). These data re-affirm earlier observations that analytical inconsistencies, particularly for PCB 77, may affect the results reported by different investigators. Nakata et al. (1997) report PCB 77 concentrations that are appreciably greater than PCB 126 concentrations, while Koistinen (1995,1997) and others (Daelemans et al., 1993; Muir et al., 1995) report PCB 77 concentrations that are significantly lower than PCB 126 concentrations. Again, characterizing the TCDD equivalency of dioxin-like PCBs by the 1994 WHOIIPCS TEFs minimizes the potential effects of inaccurate PCB 77 measurements. Accordingly, Baikal seals have appreciably greater 2,3,7,8-TCDD equivalents due to PCBs than has been observed elsewhere. This is shown for lumped age and sex class data in Figure 5.8a.

Table 5.10 Non-ortho PCBs and TEQs in Baikal and Lake Saimaa seals.

| species | location | class | $L3^{PCB}$<br>§ pg/g | t<br>R~tio<br>77:126 | Safe 1990/94<br>TEQ<br>pg/g | WHOIIPCS<br>TEQ<br>pg/g |
|---|---|---|---|---|---|---|
| BS | Baikal | J | 10,140 | 3.0 | 331 | 251 |
| BS | Baikal | F | 17,700 | 4.1 | 495 | 350 |
| BS | Baikal | M | 26,870 | 6.6 | 599 | 365 |
| BS | Baikal | aM | 3,210 | 0.7 | 201 | 187 |
| RS | G. Finland | b P/J/F | 1,430 | 0.3 | 108 | 103 |
| RS | L. Saimaa | c P/F | 1,680 | 0.6 | 113 | 106 |

TEF system

BS = Baikal seal; RS = ringed seal. L3 PCB = PCB nos. 77 + 126 + 169. t ratio of PCB 77 to PCB 126. § wet weight basis.

[a] 7 yr. male from 1993 analyzed by Koistinen et al. (1995).

[b] 14 Gulf of Finland RS (7 pups < 1 yr.; 4 juveniles 1-3 yr., 3 mature F) found dead in *1991/2.*

[c] 2 pups of 3-4 months; 2 mature F.

References: Lake Baikal (Nakata et al., 1997); Gulf of Finland (Koistinen et al., 1997); Lake Saimaa (Koistinen et al., 1995).

14.

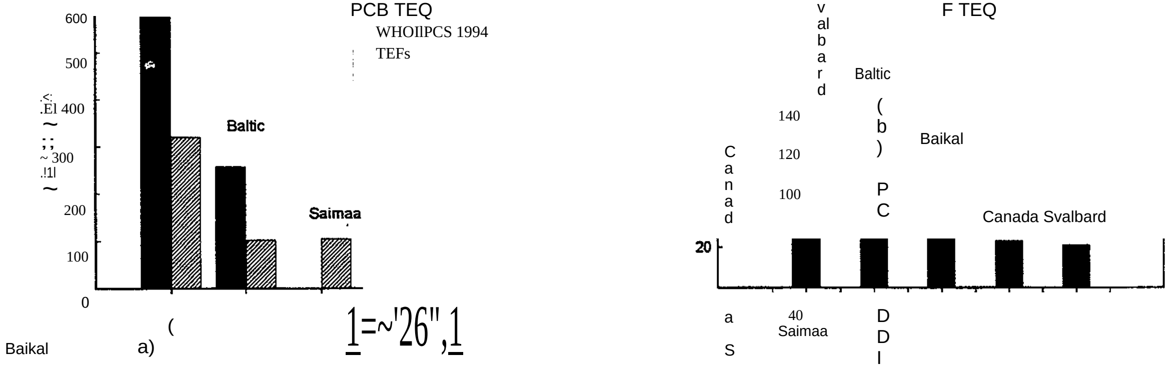

Figure 5.8 TEQs of PCBs and PCDD/Fs in Baikal seal - global comparisons; lumped data for all age and sex classes.

Despite inconsistencies in observed age/sex classes and potential discrepancies in laboratory methods, it appears that Baltic ringed seals likely have higher total PCB mass concentrations, but that Baikal nerpa accumulate disproportionately more dioxinlike PCBs.

Table 5.11 gives the PCDD/F burden in I-TEa for Baikal and related seals from other waters. The estimated I-TEas derive mostly from five congeners: 2378-TCDD, 12378-PeCDD, 123678-HxCDD, 2378-TCDF and 23478-PeCDF. Together these usually account for 95% or more of the 2,3,7,8-TCDD equivalent in ringed seals. Baikal seals are represented by the four seals analyzed by Koistinen et al. (1995) and Tarasova et al. (1997). As the data set is small and some differences in congener profiles are evident that may reflect analytical inconsistencies between the reporting laboratories, the Baikal data must be regarded as tentative for the time being.

Lumped PCDD/F data for Baikal and other seals are shown in Figure 5.8b. The 2,3,7,8-TCDD burden of Baikal seals seems to be perceptibly lower than Baltic and Lake Saimaa ringed seals, but distinctly higher than ringed seals of Svalbard and the Canadian Arctic. The TEa of dioxin-like PCBs estimated by the most conservative 1994 WHO/IPCS TEFs, appears to overwhelm the TEa of PCDD/Fs in Baikal seal. While PCDD/Fs may be less of a threat to Baikal seal, further study of PCDD/F pollution in Baikal may be warranted as the available data are rather tentative and seals may not be the best indicator of PCDD/F contamination.

## 5.8 Considerations for Constructing POPs Mass Budgets for Baikal

The construction of POPs mass budgets for Lake Baikal would help address the many questions that remain concerning the future occurrence and persistence of POPs in the Lake Baikal ecosystem. Dynamic chemical mass balance models developed for Lake Ontario (Mackay, 1990; Mackay et al., 1994) offer a reasonably simple paradigm that might be adapted to Lake Baikal using available ecosystem models (e.g., Silow, 1995). With 4-5 months of ice cover on the lake and snow accumulation in the watershed, the efforts by Wania (1997) to model POPs behaviour in snow packs merit consideration. Currently, data are inadequate to estimate POPs mass budgets, but crude estimates of some components can be developed to stimulate further discussion.

### 5.8.1 Surface Water Components

The POPs content of the Lake Baikal water mass and the annual POPs mass outputs to the Angara River were estimated as in Table 5.12. The water concentrations are composited lake surface water data from Kucklick et al. (1994), Iwata et al. (1995), McConnell et al. (1996) and Kucklick efal. (1996). The contaminant mass estimate for Baikal assumes that the lake is thoroughly mixed and that the surface samples represent the entire water body.

Table 5.11 PCDD/Fs in Baikal seal - global comparisons.

| | | | | | | I-TEQ *pg/g* lw | | | |
|---|---|---|---|---|---|---|---|---|---|
| species . a | location | date | *n* | sex b | age c | mean | min | max | ref |
| BS | Baikal | 1992 | 1 | M | M | 43 | | | 1 |
| BS | Baikal | *1994/5* | 3 | F | J&M | 65 | 28 | 93 | 2 |
| RS | Canadian Arctic | *1984/6* | 85 | M&F | J&M | d 23 | d$_4$ | d 48 | 3 |
| RS | Svalbard | 1981 | :1:$_{10}$ | M | M | 28 | 26 | 31 | 4 |
| RS | Svalbard | 1981 | t$_4$ | F | M | e$_{15}$ | e 11 | e$_{18}$ | 4 |
| RS | Svalbard | 1981 | t$_2$ | M&F | J | e 11 | a$_8$ | e$_{15}$ | 4 |
| RS | Svalbard | 1986 | 7 | M&F | J&M | 13 | 5 | 30 | 5,6 |
| RS | f Arctic Ocean | 1987" | t$_5$ | M&F | M | 26 | | | 4 |
| RS | Baltic | *1986n* | :1:$_{10}$ | M&F | J | 9 147 | 72 | 221 | 4 |
| RS | Baltic | 1980s | 10 | U | J | 66 | | | 7 |
| RS | Baltic | 1980s | 5 | M | M | 171 | | | 7 |
| RS | Baltic | *1991/2* | h$_{14}$ | M&F | J&M | 64 | 44 | 146 | 8 |
| RS | L. Saimaa | 1992 | 4 | U&F | J&M | 136 | 96 | 250 | 1 |

:j: 2 homogenates of 5 specimens each; t homogenate of *n* specimens; a BS = Baikal seal, RS = Ringed seal; b U = unknown, M = male, F= female; C U = unknown, M =. mature, J = juvenile; d statistics for 12 group means from 9 locations; e mean, min and max assuming *1/2,* 0 and detection limit respectively for undetected congeners; f off northern Norway; 9 condition of blubber (56-65% fat) suggests starvation;

h 11 juveniles (7 < 1 yr., 4 1-3 yrs., 3 mature F).

References: 1. Koistinen et al. (1995), 2. Tarasova et al. (1997), 3. Norstrom et al. (1990), 4. Signert et al. (1989), 5. Oehme et al. (1988), 6. Oehme et al. (1990), 7. Sergek et al. (1992), 8. Koistinen et al. (1997).

As rough as the estimates in Table 5.12 may be, it is immediately obvious that there are likely substantial reservoirs of some POPs such as PCBs and HCHs resident in the Baikal water mass. Moreover, losses via the Angara River are small at about 0.3% annually. This directly reflects the long hydraulic residence time of 350 years. If contaminant inputs ceased, it could take that long for Baikal to cleanse itself. The process could be accelerated by volatilization losses to the atmosphere, burial in deep sediments, and other removal processes. Nonetheless, once Baikal becomes contaminated with POPs, its immense volume ensures that recovery may require centuries.

Table 5.12 POPs in Lake Baikal water and estimated annual flux to Angara River.

| | Water concentration (pg/L) | | | Mass in Lake Baikal water (t) | | | Flux to Angara River (kg/a) | | |
|---|---|---|---|---|---|---|---|---|---|
| | Mean | Min | Max | Mean | . Min | Max | Mean | Min | Max |
| LHCH | 799 | 56 | 1,740 | 18.4 | 1.29 | 40.0 | 52 | 3.6 | 113 |
| PCBs | 488 | 18 | 1,870 | 11.2 | 0.41 | 43.0 | 32 | 1.2 | 122 |
| PCCs | 64 | 34 | 143 | 1.5 | 0.78 | 3.3 | 4 | 2.2 | 9 |
| LDDT | 47 | 2 | 120 | 1.1 | 0.04 | 2.8 | 3 | 0.1 | 8 |
| LCHL | 15 | 1 | 54 | 0.3 | 0.02 | 1.2 | 1 | 0.1 | 4 |
| HCB | 17 | 7 | 28 | 0.4 | 0.16 | 0.6 | 1 | 0.5 | 2 |

Actual mass outflows may vary somewhat from the estimates given in Table 5.12. For DOT, HCH and PCBs, the mass fluxes to the Angara River may be closer to the maximum estimates as water concentrations for these POPs are generally higher in the southern basin. McConnell et al. (1996) observed LHCH = a-HCH + y-HCH for a single sample in the Angara River mouth at 3.5 *ng/L.* This translates to an annual outflux of 228 kg at the mean annual Angara discharge of 65 km$^3$. The difference between the single Angara sample and the lake surface samples may represent mainly local HCH inp~ts at the southwest corner of Baikal near the Angara outlet.

McConnell et al. (1996) also reported LHCH as 4-5 *ng/L* for three samples in the Selenga River. These concentrations translate into annual LHCH inputs of 129-156 kg at the Selenga River mean annual discharge of 31 km$^3$ into Baikal. As the Selenga represents only about half the surface water inflows to Baikal, the influx of LHCH by rivers will be higher.

### 5.8.2 **Gas Exchange Across the Air-Water Interface**

Both Iwata et al. (1995) and McConnell et al. (1996) used their air and water data to estimate the gaseous exchange of POPs across Lake Baikal's water surface. Their estimates for mean windspeed of 5 *m/s* extrapolated to the whole lake surface for a seven month ice-free season are given.in Table 5.13. The estimates are likely crude as they depend strongly on air concentrations, temperatures (air and water) and wind speeds that can be highly variable. The estimates of Iwata et al. (1995) are for water temperatures of 0-2.4C encountered in late May, while the estimates by McConnell et al. (1993, 1996) for June water and air temperatures of 3.5C and 12C respectively. At peak air and water temperatures during July and August, conditions should favour increased volatilization losses or lower influx rates.

The figures in Table 5.13 give an indication of those POPs for which volatilization is a viable removal process, and those for which gas exchange tends to reinforce the POPs mass in the lake. The data suggest that considerable HCH will enter the lake by gas exchange, and that considerable HCB and lower chlorinated PCBs in the lake will be lost to the atmosphere. However, certain higher chlorinated PCBs, including some with dioxin-like toxicity, may tend to accumulate in the lake if other removal processes are small relative to the cumulative inputs of snowmelt, surface runoff, and wet and dry deposition. This also may be the case for PCCs and DOT.

Table 5.13 POPs gas exchange (kg) across the Baikal air-water interface for a seven month open water season; negative values denote volatilization losses.

Iwata et al.
McConnell et al.

an

-
28
2
-320

PCBs
HCB
l:CHL [a]
PCCs
l:PCBs [b]
l:DDT[c]
l:HCH [d],
min

-215
-
-12
3
17
4
16
-
2
7
6
4
913

-29 161 43

8
1
2,81
9

18 738
max

me

References: Iwata et al. (1995); McConnell et at (1996).

[a] l:CHL = trans-chlordane + cis-chlordane + trans-nonachlor. [b] l:PCBs = sum nos. 87, 99,105,129,132,138,153,178,180.

[c] *LOOT* = *p,p'-DDT* + *a,p'-DDT* + p,p'-DDE. [d] LHCH = a.-HCH + 'Y-HCH.

## 5.9 Notes on Construction of Figures 5.1, 5.2 and 5.3

Studies by Kucklick et al. (1994, 1996), McConnell et al. (1996) and Iwata et al. (1995) were not perfectly consistent in analytical methods and reported summary statistics. Developing the numerical summary data presented on the graphics required certain arbitrary adjustments and manipulations of reported data to achieve approximate consistency. Generally, the underlying trends are so dominant that uncertainties concerning the precise numerical values have negligible effect on the outcome.

In water and air, LHCH = c:x.-HCH + y-HCH; otherwise LHCH = c:x.-HCH + f3-HCH + y-HCH. Total DOT concentrations in water were adjusted as necessary to approximate *LOOT* = *p,p'-DDT* + *a,p'-DDT* + *p,p'*DOE + *p,p'-DDD.* Total chlordanes in water, soil and sediments were adjusted as necessary to approximate LCHL =

trans-chlordane + cis-chlordane + *trans-nonachlor* + cis-nonachlor using average compositions for water and sediments observed by Iwata et al. (1994). Total chlordane in fish and seal were adjusted as necessary to approximate LCHL = trans-chlordane + cis-chlordane + trans-nonachlor + cis-nonachlor + oxychlordane using average compositions observed by Nakata et al. (1995).

To satisfy plotting software requirements for a central statistic, when only a range was given, the central statistic was taken as the geometric mean of the maximum and minimum. Summary statistics for water from Kucklick et al. (1994) were summed for dissolved and particulate fractions and averaged over the results for the two different analytical methods that gave somewhat different results. Chemical species reported as below detection threshold was estimated by pro-rating proportions from higher resolution data where avail~ble, and otherwise as 1/2 detection threshold. Summary statistics for water from Iwata et al. (1995) were obtained by scaling individual data from Figure 2.

Schecter et al. (1990a,b) analyzed foodstuff and human milk samples for HCB, HCHs, DOTs, PCBs and chlordanes. PCB analyses were confined to six congeners (IUPAC nos. 28, 52, 101, 138 and 153). The sum of the six was pro-rated to estimate total PCBs using the multiplier of 2.71 based on the human milk extract analyzed by Safe et al. (1985). Schecter and colleagues gave only three chlordane species: trans-nonachlor, oxychlordane and heptachlor epoxide. The sum of these is not strictly compatible with the chlordane components measured in other environmental media, but these should comprise most of the chlordane-heptachlor species present; hence, no attempt was made to adjust the totals.

Male and female seal data from Nakata et al. (1995) represent juveniles and mature members of each sex. Generic seal summary data from Kucklick et al. (1996) represent 4 juveniles, 3 mature females and a 7 year-old male yielding a net representation similar to the average of juveniles and mature females reported by Nakata et al. (1995).

For Figure 5.2, air, water and fish data from all sources were lumped within the respective compartments.

The determination of bioconcentration factors for Figure 5.3 is unavoidably arbitrary. The rule used to determine typical bioconcentration factors is reasonably consistent and avoids the extreme ranges obtained by dividi'ng an extreme minimum concentration (e.g., a water concentration below detection arbitrarily taken as 1/2 detection threshold) into the maximum concentration that may represent an unusually contaminated fish or seal; or conversely dividing an usually dirty water sample concentration into an unusually clean fish or seal sample. For determining bioconcentration factors, the minimum, central statistic (mean or geometric mean), and maximum of numerator medium (Le., fish or seal) were divided by: the central statiStic of the denominator medium (Le., water or fish); and the central statistic of the numerator medium (Le., fish or seal) was divided by the minimum, central statistic and maximum of denominator medium (Le., water or fish). Then minimum, average (over logarithms) and maximum of all results were taken. The resulting average is close to the estimate obtained by dividing compartmental averages, and the spread should represent the majority of fish and seal exclusive of extremes.

# Chapter 6 Lake Ladoga

## 6.1 Lake Ladoga ~ Neva River Wate~shed Description

The Neva River is the largest tributary of the Baltic Sea yielding mean annual discharge of 80 km$^3$ from a catchment of about 283,000 km$^2$. The Neva River itself is only a short 74 km channel that drains Lake Ladoga (Russian *Ladozhskoye* Ozero) , Europe's largest lake, to the Gulf of Finland at St. Petersburg. About 220,000 km$^2$ (78%) of the Neva system lies in Russia, and the remainder in Finland.

Basic Lake Ladoga facts are given in Table 6.1. The main affluents of Ladoga are the Vuoksi River entering from Finland, and the Svir River that drains Lake Onega (Russian *Onezhskoye Ozero;* 1,989 km\ Europe's second largest lake. Southern affluents of Ladoga include the Syas and Volkhov Rivers that discharge to Volkhov Bay on the southwest corner of the lake. The Volkhov and its upper tributary the Lovat extend southward to about 55° 30' N draining lands that are increasingly agricultural. The deepest waters of Ladoga are found at the northern end of the lake to the west and south of Valamo (Valaam) Island, while a broad zone of shallow water <25 m depth extends across the southern end of the lake, including Volkhov Bay.

Table 6.1 Lake Ladoga facts.

| | | |
|---|---|---|
| Latitude range | 59° 54'- 61 ° 47' | N |
| Longitude range | 29° 47' - 32° 58' | E |
| Volume | 908 | km$^3$ |
| Surface area | 18,390 | km$^2$ |
| Maximum depth | 230 | m |
| Mean depth | 51 | m |
| Shoreline length | 1,570 | km |
| Basin area - total | 280,000 | km$^2$ |
| Basin area - local | 70,120 | km$^2$ |
| Mean annual outflow - Neva River | 79.1 | km$^3$ |
| Mean hydraulic residence time | 12.3 | yr |
| Ice cover formation / breakup | January | May |

Table 6.2 Industrial facilities in the immediate Lake Ladoga watershed (after Ristola et aL, 1996)

| Location | Products | Wastewater characteristics | | | |
|---|---|---|---|---|---|
| | | Treatment | Volume<br>$10^6$ $m^3$ / a | Load<br>*tla* | |
| Svetogorsk | -bleached and unbleached pulp<br>-paper products | -mechanical and biological | 80 | AOX[t]<br>BODs:!: | 1,000<br>800 |
| Priozersk | -sulphite pulp mill | -closed 1986 | | | |
| Pitkyaranta | -unbleached pulp and paper | -mechanical and biological<br>-none for barking house and lime kiln | 18 | BODs | 800 |
| Lyaskelya | -unbleached paper | none | 7 | NA § | NA |
| Syasstroi | -bleached and unbleached pulp<br>-board and paper products | -mechanical and biological | 66 | AOX<br>BODs | 500<br>1,100 |
| Volkhov | aluminum, soda, potassium ash | -settling ponds | NA | BODs | 22 |

t AOX = adsorbable organohalogens; :!: BODs = 5 day biochemical oxygen demand; § NA = not available.

The La,ke Ladoga ecosystem has one of the world's few freshwater seal species, *Phoca hispida ladogensis,* a type of ringed seal (Sipil~ et al. 1996). There are 10,00012,000 Ladoga seals whose position at the top of the aquatic food web renders Ladoga comparable to Lake Baikal. Upstream in the Vuoksi River system, there is also a small, endangered population of freshwater ringed seals in Lake Saimaa, Finland. Ladoga supports a significant fishery with an estimated catch of 8 Kt in 1986 (ILEC, 1987), and is the source of raw drinking water supplies drawn from the Neva for the residents of St. Petersburg and the surrounding Leningrad Oblast.

St. Petersburg and environs have about 6 million inhabitants. Excluding major upstream watersheds, the immediate 70,120 km$^2$ catchment of Lake Ladoga has a population approaching 1 million; while the 51,540 km$^2$ Lake Onega watershed has about 500,000 (ILEC, 1997). The major urban centres of the greater watershed are Petrozavodsk (pop. 280,000) on Lake Onega and Novgorod (pop. 235,000) upstream on the Volkhov River. Otherwise, there are numerous small urban centres in the . Ladoga watershed with populations of 10,000-50,000. Generally, most communities discharge urban and industrial wastewaters with inadequate treatment.

Over the much of the Neva watershed, particularly the greater part that lies north of about 60° N (roughly the latitude of S1. Petersburg), land cover is predominantly forested, and forest products industries are prominent in the regional economy. The Neva basin has numerous pulp and paper mills. Those in the immediate vicinity of Lake Ladoga are listed in Table 6.2. In production capacity, the Svetogorsk mill on the Vuoksi River near the Finnish frontier ranks with the top 11 Russian pulp producers (>250 KUa), however, production was below 200 KUa for 1993-1995 (RINACO, 1996a,b,c). The Syasstroi mill has low capacity «50 KUa) .. No data were found for the mills at Pitkyaranta and Lyaskelya, but these are thought to be relatively small facilities. Discharges from Finnish mills on the Vuoksi system may have residual effects on Lake Ladoga. Emissions from the large mill at Kondopoga upstream on Lake Onega likely have negligible influence on Lake Ladoga.

The Ladoga watershed also likely has many woodworking facilities including sawmills and timber yards where chlorophenolic wood preservatives may have been used. Other industrial sources of contamination in the region include a small aluminum smelter at Volkhov on the south side of the lake. The great concentration of industry in S1. Petersburg may contribute contaminants to Ladoga via atmospheric emissions.

Agriculture in the watershed also contributes nutrients and other contaminants to surface water systems. Specifically, the organochlorine insecticides DOT and HCH likely have had historical us~ge on field crops and in livestock operations. These POPs may have been used in forestry management and for mosquito control.

## 6.2 Lake Ladoga POPs Data

Rivers and streams of the Neva-Ladoga watershed are monitored for DOT, HCH and other pesticides under a national program as discussed in Chapter 4. For 1993, monitoring showed only sporadic detections of HCHs and DOTs above detection thresholds of 5 ng/L and 50 ng/L respectively. For 1995, Leningrad Oblast authorities (Lencompriroda, 1997) reported no detections of HCHs above 1 ng/L, and DOT occurrences above detection threshold of 30 ng/L only in single samples from each of the Vuoksi, Volkhov, and Syas rivers. These results suggest that inputs of HCH and DOT from Ladoga tributaries are low.

Two studies offer limited POPs data for Lake Ladoga sediments. A comprehensive assessment awaits more complete data for Ladoga environmental compartments including biota at the top of the food web. Similar to studies conducted in Lake Baikal, these should include fish, Ladoga seal, and fish-eating birds. Some POPs data for fish and seal were apparently presented by Kostamo et al. (1996), but the report was unavailable for examination. Medvedev and Markova (1995) observed low DOT and yHCH levels in a limited sampling of the eggs of aquatic bird (gulls, terns) from Karelia; however, top predators such as eagles donot yet appear to have been sampled.

## 6.3 Study 1 - Priozersk and Pitkyaranta Sediment Cores

In 1990, Sarkka, et al. (1993) analyzed two sediment cores obtained near Priozersk (Kakisalmi), the site of the sulphite mill closed in 1986, and Pitkyaranta where a mill producing unbleached pulp continues to operate. Priozersk is on the northwest corner of Ladoga, while Pitkyaranta is at the north end of the lake. The cores were collected about 2 km offshore from mill sites. Chemical analyses included total and extractable organochlorines, free and bound chlorophenols, HCB, HCHs, DDTs, oxychlordane, heptachlor, 9 PCB congeners, 9 of the toxic 17 PCDD/F congeners, some other chlorohydrocarbons anticipated in pulp and paper mill effluents, and organic matter (loss on ignition) content.

Dating and sectional analysis of the cores shows that sediment deposition rates, organic matter content and organochlorine content all began increasing after about 1900. The Priozersk core shows a dramatic rise in organically bound chlorine between 1920 and 1940 that may signal the establishment of the pulp mill abandoned in 1986. The Pitkyaranta core shows a more gradual rise since 1900.

Detailed data for the top layers of each core [0-1 cm, and 1-4 cm] showed perceptible DDT, PCBs and PCDD/Fs that are discussed below. Otherwise, there were only marginal traces of HCB, a-HCH, y-HCH, heptachlor and oxychlordane at or below detection levels [0.5 *ng/g* dw]. These latter results likely indicate the trace residuals of historical usage or recent long range atmospheric inputs. As sediment is not the best environmental matrix for examining HCB and HCHs, further analyses of water and biotic media may be more informative.

### 6.3.1 DDT

The DDT levels reported for Ladoga sediments are low, but nonetheless, indicative of past and possibly recent usage of DDT in the basin. It appears that only the *p,p'*isomers were measured. In sediments, the *o,p'-isomers* can also be present; hence, the true Ladoga LDDT levels may be somewhat higher.

The Priozersk sediments had significant fractions of unmetabolized DDT [%DDT in Table 6.3] suggesting that there had been recent usage. The Pitkyaranta sediments have low %ODT; however, this may not be indicative of remote past usage, as DDD is the dominant isomer. Under appropriate .anaerobic conditions, metabolism to 000 can occur rapidly, and thus effectively confound the interpretation of the *DDTI* LDOT ratio. While it is unclear whether the ODD at Pitkyaranta was created in stream channels of the local watershed, or in the depths of Lake Ladoga, there are clearly different processes affecting the composition of DOT found in sediments at Pitkyaranta and Priozersk.

Table 6.3 DOT *(ng/g* dw) in Lake Ladoga sediments, 1990 (after Sarkka et al., 1993).

| | Pitkyaranta | | Priozersk | |
|---|---|---|---|---|
| | 0-1 em | 1-4 em | 0-1 em | 1-4 em |
| central layer date | 1990 | 1983 | 1990 | 1968 |
| LOI % t | 20.5 | 11.0 | §NA | 10.3 |
| IOOT :j: | 14 | 11 | 9 | 11 |
| %DDT | 7 | 5 | 33 | 59 |
| %000 | 57 | 59 | 33 | 27 |
| %DDE | 36 | 36 | 33 | 14 |

t Loss-on-ignition (approximate organic matter content); § NA = not available. :j: IOOT = *p,p'-DOT* + p,p'-DDE + *p,p'-DDD.*

## 6.3.2 **PCBs**

Sarkka et al. (1993) analyzed the 9 PCB congeners listed in Table 6.4 in the top layers of Ladoga sediments. Also given are the sums of the 9 congeners calculated assuming non-detections were 1/2 the detection limits, and estimates of total PCBs assuming that the PCBs originated from particular commercial mixtures. The pro-rating multipliers used to obtain the total PCB estimates are derived from compositional data given by Schulz et al. (1989) for common Aroclor and Clophen commercial mixtures . . The validity of these prorated estimates is discussed in the next section. The arbitrary assumption of 1/2 detection limit for non-detections is only of much consequence for the Pitkyaranta sediments at 1-4 cm depth for which the sum of 9 congeners could range from 3.5-5.5 ng/g depending on what value is-assumed on the possible range of 0-0.5 ng/g for non-detections. The data suggest that the release of PCBs in Lake Ladoga near Pitkyaranta is a recent phenomenon.

Estimates of dioxin-like toxicity according to Safe's (1990) toxic equivalency factors are also given for the sediments. These derive only from PCBs 105, 118 and 180[29]. PCB TEQs appear low, but there is little to compare them with. If the interim WHOIIPCS TEFs (Ahlborg et al., 1994) are used, the estimated TEQs are reduced to 40-55% of the figures in Table 6.4.

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[29] While the various proposed systems give TEFs for up to 13 congeners, the other 10 are not usually observable in nominally inorganic environmental compartments (water, sediments, air), as they are present at only negligible levels in commercial PCBs. Due to appreciable biomagnification, they may be observable in higher members of ecological food webs.

Table 6.4 PCBs *(ng/g* dw) in Lake Ladoga sediment cores (after Siirkkii et al., 1993).

| Congener | Pitkyaranta | | Priozersk | |
|---|---|---|---|---|
| IUPAC no. | 0-1 cm | 1-4 cm | 0-1 cm | 1-4 cm |
| 8 | <0.5 | <0.5 | <0.5 | 2.5 |
| 28 | 8 | <0.5 | 8 | 5.5 |
| 52 | 3 | <0.5 | 2 | <0.5 |
| 101 | 1 | 0.5 | 2 | 0.5 |
| 105 | 1 | 0.5 | 1 | 2.5 |
| 118 | 2 | 0.5 | 2 | 3.5 |
| 138 | 4 | 1.0 | 2 | 3.0 |
| 153 | 2 | 1.0 | 2 | 3.0 |
| 180 | 1 | <0.5 | 1 | 0.5 |
| L 9 congeners t | 22.3 | 4.5 | 20.3 | 21.3 |
| TEQ * (Safe 1990) | 3.0 | 1.0 | 3.0 | 6.0 |
| TEQ * (WHO/IPCS) | 1.2 | 0.6 | 1.2 | 2.9 |
| Total PCBs: as Aroclor 1242 a | 95 | 19 | 86 | 91 |
| Total PCBs: as *1242/1254* mix b | 80 | 16 | 73 | 76 |
| Total PCBs: as Aroclor 1254 c | 69 | 14 | 63 | 66 |
| Total PCBs: as ~Iophen A60 d | 76 | 15 | 69 | 73 |

t using *1/2* detection limit for non-detect data where necessary; * for PCBs 105, 118, and 180

Pro-rating multipliers: a Aroclor 1242 - 4.27; b Aroclor 1242/1254 50:50 mix - 3.60;

c d

Aroclor 1254 - 3.11: Clophen A60 - 3.41.

#### 6.3.2.1 Total PCB Estimates

If the composition profile of 9 PCBs observed by Sarkka et al. (1993) is a reliable indicator, the PCBs in Ladoga sediments were likely a mixture of Russian *Sovol* and *Trichlorodiphenyl* which Ivanov and Sandell (1992) describe as similar to Aroclors 1254 and 1242 respectively. The higher chlorinated congeners (PCBs 52 to 180) have a profile similar to Russian *Sovol* as described by Kannan et al. (1993). Sarkka et al. (1993) suggest that the occurrence of PCB 28 at levels higher than expected from *Sovol* indicates the presence of *Trichlorodiphenyl.* Examination of the congener profiles observed in Ladoga sediments vis-a-vis the profiles in Aroclors 1242 and 1254 reveals that neither well describes the Ladoga sediments, nor does any simple mixture of the two. Nonetheless, estimating total PCBs by assuming that the Ladoga sediment PCBs were derived from either Aroclor 1242 or Aroclor 1254 approximately bounds the potential range of total PCBs in the sediments.

Table 6.4 also gives total PCBs estimated from the sum of 9 congeners as if Clophen A60 were the parent mixture. Sarkka et al. (1993) also gave estimates of total PCBs "quantitated as Clophen A60", but these differ from the estimates given in Table 6.4, and furthermore, are inconsistent with the specific congener measurements. In two of four cases, Sarkka et al. gave "total PCB" estimates lower than the sum of the 9 measured congeners. Using their mysterious Clophen A60 total PCB estimates, the authors calculate mean total PCBs of 20 ng/g for Ladoga sediments and conclude that Ladoga sediments are only lightly contaminated. However, *the present analysis suggests that mean total PCBs in the most recent top layer sediments of 1990 were in the 65-95 ng/g range.*

In sediments, PCBs exhibit a *weathered* congener profile that reflects the relative loss of lower chlorinated congeners and enrichment of higher congeners as compared to typical commercial mixtures. The lower congeners are more hydrophilic, more readily volatilized and more readily biodegraded. Given typical *weathering* tendencies observed in sediments, the most plausible total PCB levels were more likely in the 6380 ng/g range ascribed to Aroclor 1254 and a 50:50 mix of Aroclors 1242 and 1254. While this is far below the total PCBs levels seen in heavily contaminated environments, these samples hover near Ontario's *Lowest Effect Level* [LEL] guideline of 70 ng/g for total PCBs that should apply broadly to sediments in temperate aquatic systems in the northern hemisphere (see Appendix A, Section A.2.2). Judgement of the significance of these PCBs to Ladoga ecological systems should be reserved until data are obtained for fish, seal and fish-eating birds at the top of the Ladoga food web.

### 6.3.3 **PCDD/Fs**

PCDD/F data and toxicity estimates expressed in I-TEQ for the 9 measured congeners in the Ladoga sediments are given Table 6.5. These limited data tentatively reveal that Ladoga is moderately contaminated with dioxins and furans. As discussed below, the total toxicity for all 17 toxic PCDD/F congeners in the Ladoga samples likely would have been *at least* 2 fold greater than that in the measured 9 congeners. Thus, the Ladoga samples have *at least* 60-120 fold greater toxicity than Severnaya Dvina watershed background sediments for which mean and upper limit background concentrations defined were only 90 and 125 *fg/g* respectively.

The site near the former sulphite pulp mill at Priozersk shows only 50-60% of the PCDD/F contamination seen at the site near Pitkyaranta where a mill produces unbleached pulp. The relative PCDD/F congener profiles of the Priozersk sediments (mean of 0-1 and 1-4 cm layers) are contrasted against other regional data from Finland (Vartiainen et al., 1997), and Russia (North Dvina) in Figure 6.1. The Priozersk sediments have composition somewhat similar to North Dvina River (background and most non-background sites) and remote Finnish lake sediments suggesting that the Priozersk sediments have the broad regional background signal modified by local PCDD/F inputs.

Table 6.5 PCDD/Fs *(pg/g* dw) in Lake Ladoga sediment cores, 1990 (after Sarkka et al., 1993).

| Congener | Pitkyaranta | | Priozersk | |
|---|---|---|---|---|
| | 0-1 cm | 1-4 cm | 0-1 cm | 1-4 cm |
| 123478-HxCDD | 6.0 | <5.0 | 13.0 | 5.5 |
| 1234678-HpCDD | 20.0 | 26.5 | 16.0 | 12.5 |
| OCDD | 97.0 | 78.5 | 75.0 | 47.0 |
| 2378- TCDF | 13.0 | 10.5 | 8.0 | 11.5 |
| 12378-PeCDF | <5.0 | 6.0 | <5.0 | <5.0 |
| 123478-HxCDF | 24.0 | 15.5 | 8.0 | <5.0 |
| 1234678-HpCDF | 38.0 | 60.0 | 14.0 | 15.0 |
| 1234789-HpCDF | <10.0 | 15.5 | <10.0 | <10.0 |
| OCDF | 310.0 | 315.0 | 32.0 | 26.0 |
| *L* 9 congeners | 5.5 | 4.6 | 3.5 | 2.5 |
| I-TEa t *(pg/g)* | | | | |
| 17 PCDD/Fs: minimal estimate [a] | 10.9 | 9.1 | 7.0 | 4.9 |
| 17 PCDD/Fs: mean estimate [b] | 16.4 | 13.7 | 10.4 | 7.4 |
| 17 PCDD/Fs: upper estimate [c] | 27.3 | 22.8 | 27.9 | 19.8 |

t using *1/2* detection limit for concentrations below detection limit

a 2 X *L* 9 congeners; b 3 x *L* 9 congeners;

c 5 x *L* 9 congeners (Pitkyaranta), 8 x *L* 9 congeners (Priozersk).

Consic:!erably greater uncertainty surrounds the more crucial issue of Priozersk sediment toxicity for all 17 toxic PCDD/F species. Th~ other regional data suggest that the 9 congeners measured in Priozersk sediment should represent only about *1/3* of the potential toxicity due to all seventeen 2,3,7,8-substituted PCDD/Fs, and that the totall-TEQ could be 2-8 fold higher than that estimated for the 9 congeners. The upper uncertainty stems from the disproportionate impact that relatively minor fluctuations in concentration of the most potent congeners [2,3,7,8-TCDD and 2,3.4,7,8-PeCDF] can have on the estimated sample toxicity. Accordingly, the most recent sediments at Priozersk contain at least 7 pg/g I-TEQ, and up to 28 pg/g I-TEQ.

Sediments from near the Pitkyaranta mill producing unbleached pulp have higher PCDD/F toxicity than Priozersk sediments. Furthermore, the congener profile for Pitkyaranta sediments differs distinctly from Priozersk sediments (Figure 6.2) and the typical regional pattern. The relative amounts of OCDD and OCDF are largely reversed in the two sediments, and the concentrations of PCDFs are generally higher in the Pitkyaranta core.

Kitkunen and Salkinoja-Salonen (1990) have observed appreciable PCDD/Fs in unbleached pulps from Finnish mills. It appears that chlorination of raw water supplies to prevent slime formation and to bleach out high colour (organic matter) produces chlorophenols that serve as precursors for PCDD/F formation during the cooking stage of the unbleached pulping process. A similar process at the Pitkyaranta mill may be responsible for the PCDD/Fs seen in the nearby sediments. The process observed in Finnish unbleached pulp mills does not yield the 2,3,7,8-TCDD and 2,3,7,8-TCDF seen in bleached mill effluents, but yields elevated levels of other furans.

A search of readily available data finds a scattering of diverse samples that have profiles loosely similar to Pitkyaranta sediments, including two in the lower Yemtsa tributary of the North Dvina, a soil sample near the Novodvinsk chlorine plant, two sediment samples in Sweden's Lake Vanern (Kjeller et aI., 1990), a few in the Elbe River (Schramm et aI., 1995). However, all differ perceptibly on 1-2 congeners, and there is little contextual commonality amongst these samples to suggest obvious sources of PCDD/Fs that might explain the Pitkyaranta profile. Nevertheless, it can be said with some confidence that the potential cumulative I-TEa of all 17 toxic PCDD/F congeners in the Pitkyaranta sediment was most likely *at least* 2 fold greater than the estimate obtained from the 9 measured congeners, and that the average toxicity at diverse sites with loosely similar profiles is about 3 fold greater. The upper limit of total PCDD/F I-TEa suggested by the similar sites is 4-5 fold greater than that of the 9 congeners measured at Pitkyaranta; however, under unfavourable conditions, the total 2,3,7,8-TCDD equivalency in the Pitkyaranta sediments could be higher. More work would be required to clarify PCDD/F sources in the Pitkyaranta area.

Despite uncertainties, sediments at both sites are considerably more contaminated than river sediments in the North Dvina watershed, and marginally more contaminated than sediments in four remote northern lakes in Finland (Vartiainen et al. 1997). The Finnish sediments had a mean of 4.3 *pg/g* I-TEa, but the most contaminated lake had *10.8 pg/g* I-TEQ while the other three lakes had only 1.2-3 *pg/g* I-TEa. Thus the 2,3,7,8-TCDD equivalencies of top layer sediments obtained at Pitkyaranta and Priozersk in 1990 were likely at or near that of the remote Finnish lake with 10.8 *pg/g 1*TEQ, but could have been 2-3 times higher. These levels are similar to those in the majority of sediments reported for Scandinavia at sites somewhat removed from strong PCDD/F sources (see Chapter 7, Table 7.4).

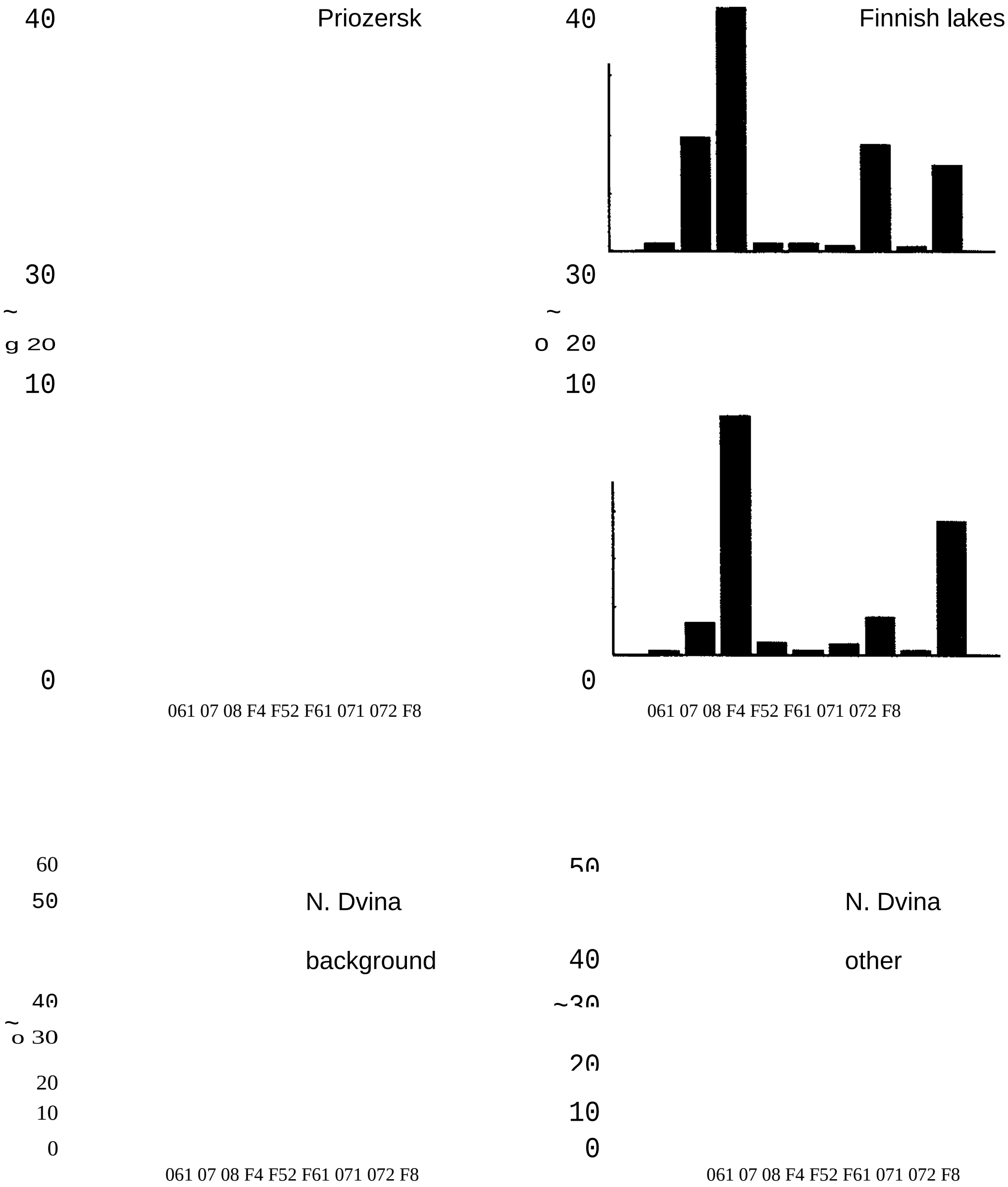
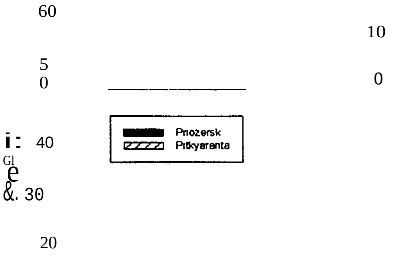


Figure 6.1 Priozersk sediment PCDD/F congener profile - regional comparisons;
. (see Appendix A; Table A.2 for congener abbreviations).



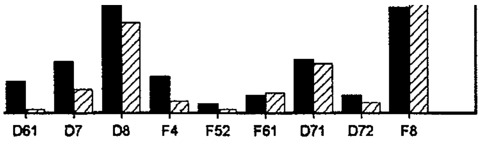


Figure 6.2 Contrast of PCDD/F congener profiles in Priozersk and Pitkyaranta sediments. (see Appendix A; Table A.2 for congener abbreviations).

## 6.4 Study 2 - 1993 Surficial Sediment Samples

In June 1993, Ristola et al. (1996a,b) collected 12 surficial sediment samples from various locations including the vicinity of Pitkyaranta on the north, and in the southeast from Volkhov Bay which is affected by the Volkhov aluminum smelter and the Syasstroi pulp mill. Samples were used for toxicity bioassays (Ristola et al., 1996a), and analyzed for suites of heavy metals, chlorobenzenes, organochlorine insecticides, 17 PCB congeners, and 14 PAHs. Although many chemicals were analyzed, the report by Ristola et al. (1996b) gave only a terse summary of results. The data for heavy metals and PAHs are not reviewed herein; however, it is worth noting that high PAHs were observed in the sediment at the Volkhov River inlet to Volkhov Bay. Aluminum smelters are known to produce high PAH emissions.

Table 6.6 1993 survey site locations and sediment textural data from Ristola et al. (1996a).

| Site no. | Location | water depth m | organic C % | tLOI % | dry matter % | :j: fraction <63 11m % |
|---|---|---|---|---|---|---|
| A. north central | | | | | | |
| 19 | Valamo Island - south coast | 103 | 0.30 | 3.10 | 54.8 | 82.2 |
| B. west side | | | | | | |
| 22 | Vuoksi R inlet | 70 | 1.60 | 4.10 | 37.0 | 48.4 |
| 23 | west side between Vuoksi inlet and Neva outlet | 24 | 0.67 | 1.90 | 63.2 | 60.2 |
| C. northeast comer | | | | | | |
| 17 | Pitkyaranta - nearshore | 53 | 3.80 | 9.90 | 16.7 | 84.0 |
| 18 | Pitkyaranta - offshore | 33 | 1.00 | 2.90 | 51.7 | 58.8 |
| 16U | south of Pitkyaranta | 43 | 1.50 | 4.90 | 64.4 | § NA |
| 16S | south of Pitkyaranta | 80 | 2.20 | 7.20 | 27.9 | 73.9 |
| D. Volkhov Bay | | | | | | |
| 4 | Volkhov Bay | 10 | 0.15 | 0.73 | 78.0 | 2.6 |
| 5 | R. Volkhov inlet - offshore | 10 | 0.39 | 1.30 | 68.4 | 10.3 |
| SA | R. Volkhov inlet - nearshore | S | 1.60 | 3.80 | 50.7 | 32.8 |
| 6 | R. Syas inlet - offshore | 11 | 0.46 | 2.20 | 69.5 | 12.3 |
| 6A | R. Syas inlet - nearshore | 7 | 1.20 | 2.90 | 61.1 | 45.4 |

t Loss-on-ignition; :j: clay size fraction;
§ Not available.

Site locations and sediment textural data are given in Table 6.7. Generally, sediment characteristics vary with the lake's bathymetry. The shallow waters of Volkhov Bay (5-11 m) have rather coarse inorganic sediments, while in the deep waters to the north, sediments have relatively high organic matter and clay size fraction.
These variables are not perfectly correlated; e:g., the sediments from the northern deeps near Valamo Island have very fine texture, but very low organic carbon content.

### 6.4.1 **Survey Results**

There were no detections anywhere of POPs insecticides above the operational quantitation limit of 1 *ng/g;* however, lindane (y-HCH) and DOT were detected at sub-quantifiable levels at sites near Pitkyaranta and in Volkhov Bay. Sarkka et al. (1993) found DOT and traces of HCH isomers near Pitkyaranta as discussed previously.

There were also sporadic detections of di-, tri- and hexachlorobenzenes at varied locations. The greatest concentration was 15 *ng/g* HCB, and only two of 12 samples had detectable HCB. Generally, chlorobenzene contamination seems to be low and intermittent. Again, sediments are not the best medium to investigate chlorobenzene contamination. HCB data for air and biota at the top of the aquatic food web would permit broader assessment of contamination.

### 6.4.2 **PCBs** - ~stimating ***Total PCBs***

Ristola et al. (1996) reported *'total PCBs'* and estimates of the 2,3,7,8-TCDD dioxin equivalents that are evidently both only for the sum 17 measured PCBs *(L17* PCBs p0. These are given in Table 6.7 along with estimates of total PCBs derived by assuming alternative parent commercial mixtures. For 1993 samples, the Aroclor 1254 estimates may be the best for general comparison with other locations. The Clophen A60 estimates should be construed as potential upper limits of *total PCBs* concentrations that might occur under unfavourable conditions.

The 17 measured PCB congeners were: PCBs 8,18, 28, 31, 52, 77, 80, 101, 105, 118, 126, 137, 138, 159, 169, 180, and 181. This short list is not the most practicable one for observing PCBs in sediments, as it is weighted heavily toward congeners that are unlikely to be detected at perceptible levels in sediments. The list omits PCB 153 that does not have dioxin-like toxicity, but is a significant component of higher chlorinated commercial mixtures such as Aroclor 1254 and Clophen A60 that is routinely found in environmental samples. Including PCB 153 generally increases the reliability of total PCB estimates derived by pro-rating.

30 *Total PCBs* extrapolated from a subset of measured congeners are expressed as *Aroclor* 1254, as *C/ophen A60,* or which ever particular commercial mixture was used as the basis for extrapolation. Ristola et al. did not indicate that an extrapolation was performed; hence, their "total PCBs· must be assumed to be LI7 PCBs, until the authors demonstrate otherwise.

Table 6.7 PCBs in 1993 Ladoga surficial sediments (Ristola et al., 1996) with estimates of total PCBs.

| | | | | *total PCBs* estimates § | | | |
|---|---|---|---|---|---|---|---|
| Site no. | Location | [a]L17 PCBs | [b]TEQ | Aroclor 1242 | [c] . mix | Aroclor 1254 | Clophen A60 |
| | | [d] *nglg* | *pg/g* | *nglg* | *nglg* | *nglg* | *nglg* |
| A. north central | | | | | | | |
| 19 | Valamo Island - south coast | 9.3 | 4.2 | 27 | 30 | 32 | 48 |
| B. west side | | | | | | | |
| 22 | Vuoksi R inlet | 9.3 | 4.2 | 27 | 30 | 32 | 48 |
| 23 | west side between Vuoksi inlet and Neva outlet | 5.9 | 4.0 | 17 | 19 | 21 | 30 |
| C. northeast comer | | | | | | | |
| 17 | Pitkyaranta - nearshore | 29.6 | 17.6 | 87 | 95 | 103 | 153 |
| 18 | Pitkyaranta - offshore | 8.0 | 5.6 | 23 | 26 | 28 | 41 |
| 16U | south of Pitkyaranta | 9.0 | 5.5 | 26 | 29 | 31 | 46 |
| 16S | south of Pitkyaranta | 18.1 | 9.7 | 53 | 58 | 63 | 94 |
| D. Volkhov Bay | | | | | | | |
| 4 | Volkhov Bay | 8.4 | 3.1 | 25 | 27 | 29 | 43 |
| 5 | R. Volkhov inlet - offshore | 7.4 | 3.7 | 22 | 24 | 26 | 38 |
| 5A | R. Volkhov inlet - nearshore | 7.5 | 5.2 | 22 | 24 | 26 | 38 |
| 6 | R. Syas inlet - offshore | 5.8 | 3.0 | 17 | 18 | 20 | 30 |
| 6A | R. Syas inlet - nearshore | 10.2 | 8.7 | 30 | 33 | 36 | 53 |
| E. Ladoga Summary | | | | | | | |
| Mean | | 10.7 | 6.2 | 31 | 34 | 37 | 55 |
| Geometric mean | | 9.5 | 5.4 | 28 | 30 | 33 | 49 |
| Min | | 5.8 | 3.0 | 17 | 18 | 20 | 30 |
| Max | | 29.6 | 17.6 | 87 | 95 | 103 | 153 |
| F. Regional background reference | | | | | | | |
| 1.H | L Hoyti~inen, Finland | 3.7 | 6.5 | 11 | 12 | 13 | 19 |

a LI7 PCBs = total PCBs given by Ristola et al. (1996); b TEFs of Safe (1990);

C equal mix of Aroclors 1242 and 1254; d dry weights.

§ pro-rating multipliers: Aroclor 1242 (2.93); Aroclor 1242/125450:50 mix (3.21); Aroclor 1254 (3.48); Clophen A60 (5.17).

### 6.4.3 Total PCBs - Assessment

Sediments nearest Pitkyaranta have the highest PCB levels seen in the 1993 survey. The total PCBs estimates for the top layer of the 1990 sediment core are within the range of the offshore (30 *ng/g)* and nearshore (103 *ng/g)* total PCB estimates obtained from 1993 data. Thus, the two surveys are approximately consistent.

The closest sites in the 1993 survey to Priozersk are Valamo Island and the River Vuoksi inlet (both having 32 *ng/g* total PCBs in 1993); however, both are far enough removed that they do not likely reflect the nearshore influences near Priozersk.

Superficially, it is reassuring that Volkhov Bay with significant urban and industrial activities in the local watershed seems not to be particularly contaminated as the five Volkhov Bay sites have modest PCB content (mean 25 *ng/g,* range 18-33 *ng/g).* However, Volkhov Bay is shallow with coarse, inorganic sediments. When PCB contents of the five samples are normalized by organic carbon or clay size fraction, total PCBs at 3-4 of 5 sites rank with the highest concentrations observed in all 12 Ladoga samples. This suggests that the circumstances of Volkhov Bay should be should be evaluated against lake water and sediment mass circulation patterns. River and point source inputs of fine suspended particles bearing PCBs and other sorptive contaminants may be swept out of Volkhov Bay into deeper waters before settling.

### 6.4.4 PCBs - TEQ

The 2,3,7,8-TCDD equivalents due to PCBs that Ristola et al. (1996) gave were calculated by Safe's 1990 TEFs (Safe, 1990; see Appendix A, Table A.4). These estimates for the 1993 survey (5.6 *pg/g* offshore, 17.6 *pg/g* nearshore) are about 2-6 fold higher than the 3 *pg/g* TEQ estimated for the 1990 survey top layer sediments, while total PCBs in the 1993 sediments are at most 1.4 times higher than in the 1990 sample. Ristola et al. (1996b) detected none of the three most toxic PCBs (nos. 77, 126, 169) anywhere in Ladoga; so that, the estimated TEQ derives identically from PCBs 105, 118 and 180 as in the 1990 survey. These three would have to be present in significantly greater proportion in the 1993 sediments for the sample TEQ to be so much greater than in the 1990 sediments.

Other sample TEQs reported by Ristola et al. are also suspiciously high vis-a-vis the two 1990 samples. Despite having half the total PCB content, the sample TEQs for Vuoksi inlet and Valamo Island sediments from the 1993 survey (both 4.2 *pg/g)* are higher than the TEQ of top layer Priozersk sediments in 1990 (3 *pg/g).* The Finnish background lake has TEQ similar to the Ladoga average, while L17 PCBs is only 35% of the Ladoga average.

Taken together these data give rise to suspicions that there may be some discrepancies in the measurements of either surveyor in the TEQ calculations by Ristola et al. (1996b).

Potential discrepancies aside, it is desirable to estimate the TEQs due to PCBs by the more conservative WHO/IPCS 1994 system. BecaUse Ristola et al. did not give the congener specific measurements, WHOIIPCS TEQs were estimated by ratios observed in the 1990 sediment core data for which the WHO/IPCS TEQs averaged about 48% (range 40-55%) of the Safe 1990 TEQs. Roughly then, the sample near Pitkyaranta with the maximum PCB content would have about 7-10 *pg/g* TEQ by the WHO/IPCS TEFs, while the Ladoga average would be about 2.5-3.5 *pg/g* TEQ due to PCBs.

### 6.4.5 PCBs - Summary

Generally, sediments seem to be only modestly contaminated with PCBs, but the lake has been systematically surveyed.

There are localized areas of contamination near Pitkyaranta and Priozersk. There may be other areas of localized pollution.

Inputs of PCBs to Volkhov Bay may be significant, but PCBs will have to be measured directly in water and suspended particulates in the influent tributary streams and major point source discharges.

The significance of the PCBs to Ladoga ecological systems cannot adequately judged until reasonably good data are obtained for fish, seal and fish-eating birds at the top of the Ladoga food web.

# Chapter 7

# Dioxins and Furans in the North Dvina Watershed

Poor health of the region's human population and a mass mortality of starfish on the White Sea coast in 1991 prompted exploratory surveys of PCDD/F and other pollution in the North (Severnaya) Dvina River basin. The North Dvina is the major tributary discharging to the White Sea. This chapter reviews the results of the surveys reported by Yufit and Khetuleva (1994) [31].

## 7.1 North Dvina Watershed Description

The North Dvina River discharges an annual average of about 100 $km^3$ water from a drainage area of about 360,000 $km^2$. The basin extends over parts of the Arkhangelsk, Vologda and Kirov Oblasts, and the Komi Republic. Arkhangelsk city sits at the head of the delta where the North Dvina debouches to the southeast corner of the Dvina Gulf of the White Sea. Generally, tidal penetration is limited to the delta channels; however, wind storms over the shallow Dvina Gulf can induce current reversals in the lower North Dvina to.up river of Novodvinsk which is about 20 km above Arkhangelsk. the North Dvina is formed about 500 km (750 river km) upstream by the confluence of the Sukhona and Yug rivers. The Sukhona rises about 500 river km to the southwest near the city of Vologda. The city of Kotlas lies about 50 km below the Sukhona-Yug junction where the Vychegda River joins from the east. The Vychegda, the North Dvina's fargest affluent in water volume, rises to the east at about 56° E. The North Dvina is navigable as far as Kotlas by river craft.

Although the North Dvina is a northern river (59°N-64°N), the regional climate is moderated by lingering maritime effects of the Gulf Stream. Hydroclimatic patterns (Figure 7.1) are relatively uniform across the watershed. Mean annual temperature in the south (Kotlas) is only about O.BoC higher than at Arkhangelsk. Annual precipitation ranges from 500-600 mm across the watershed. Ice cover may extend from November through March with break-up occurring through April in a south to north progression that may favour the formation of ice jam,s. June-September are the wettest months, but summer rainfalls are unlikely to generate large runoff and pollutant transport events.

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[31] The cover of this report identifies the sponsors as (1) N.D. Zelinsky Institute of Organic Chemistry (Moscow), (2) Centre of Independent Ecological Programs (sponsorship and location unspecified), (3) Ministry of Nature Protection and Natural Resources (Russian Federation), and the J.D. and C.T. MacArthur Foundation (USA). The agency that issued the report is not precisely identified, nor are addresses or other contact information given for the apparent authors / editors.

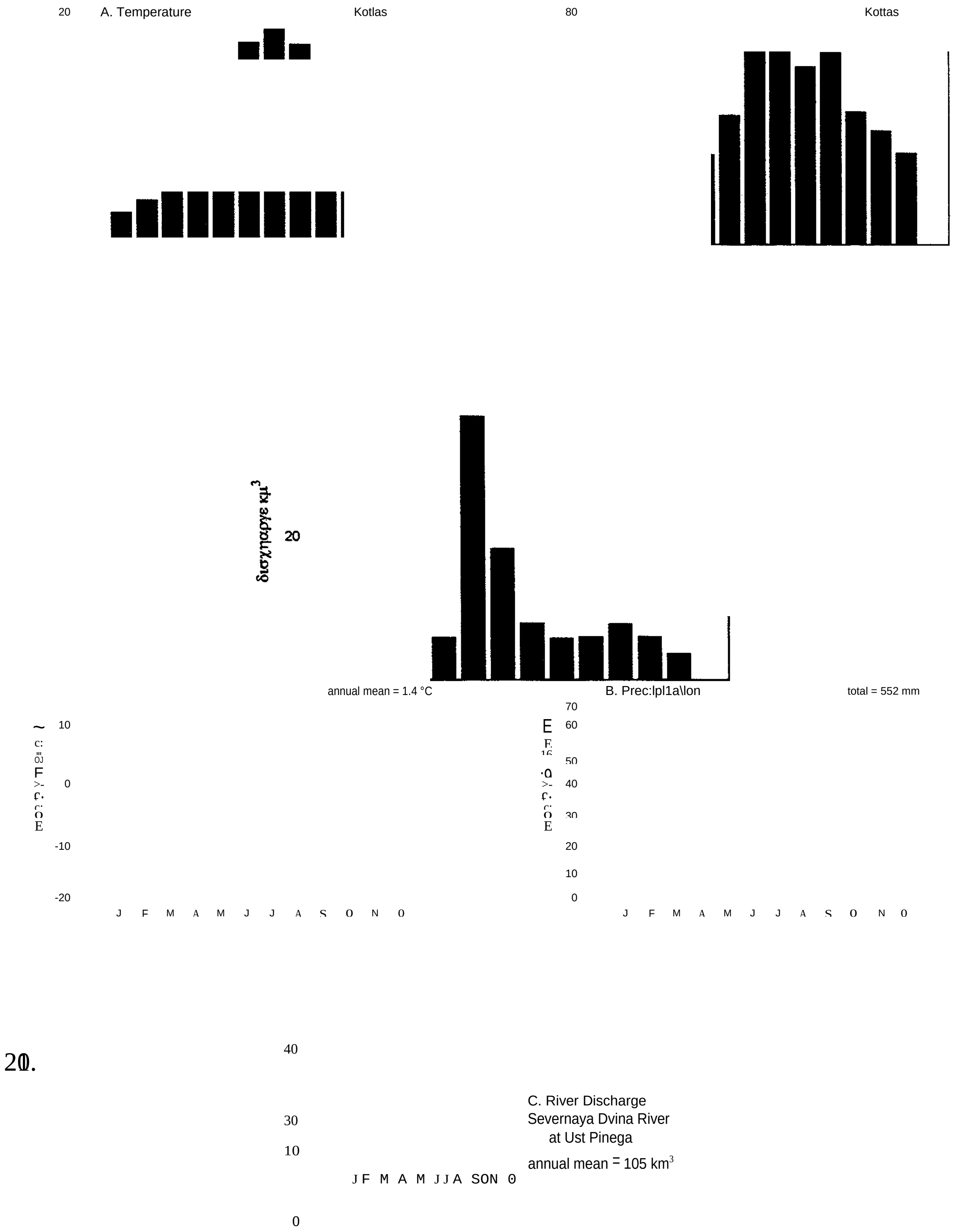


Figure 7.1 Seasonal hydroclimatic norms in the North Dvina watershed.

About half of annual surface runoff occurs as snowmelt and spring rainfall during May and June, suggesting that the North Dvina flow regime is not regulated to any appreciable extent. Significant transport of sediment bound contaminants may occur at that time. The pronounced spring discharges may also ensure that the river system might be flushed relatively quickly of POPs after inputs have been curtailed.

Human population statistics are not readily available for the North Dvina River basin. The cities of Arkhangelsk and Novodvinsk at the head of the delta have 420,000 and 48,000 inhabitants respectively. Syktyvkar, capital of the Komi Republic has 238,000 and Vologda, capital of the Vologda Oblast, has 220,000 residents. Several smaller urban centres (Sokol, Kotlas, Koryazhma, Severodvinsk, and others) may have populations similar to Novodvinsk, but otherwise the watershed has relatively sparse population.

## 7.2 PCDD/F Sources in the North Dvina Watershed

Forest product industries are the leading economic activities of the region. Numerous paper mills, woodworking plants, and supporting facilities such as thermal power stations and chlorine plants are located in the region's urban centres. According to Yufit and Khetuleva (1994), the watershed contains:

- pulp and paper mills - 5 active, 1 with an affiliated chlorine plant, 1 closed,
- numerous woodworking facilities in Arkhangelsk (and likely numerous others scattered across the basin),

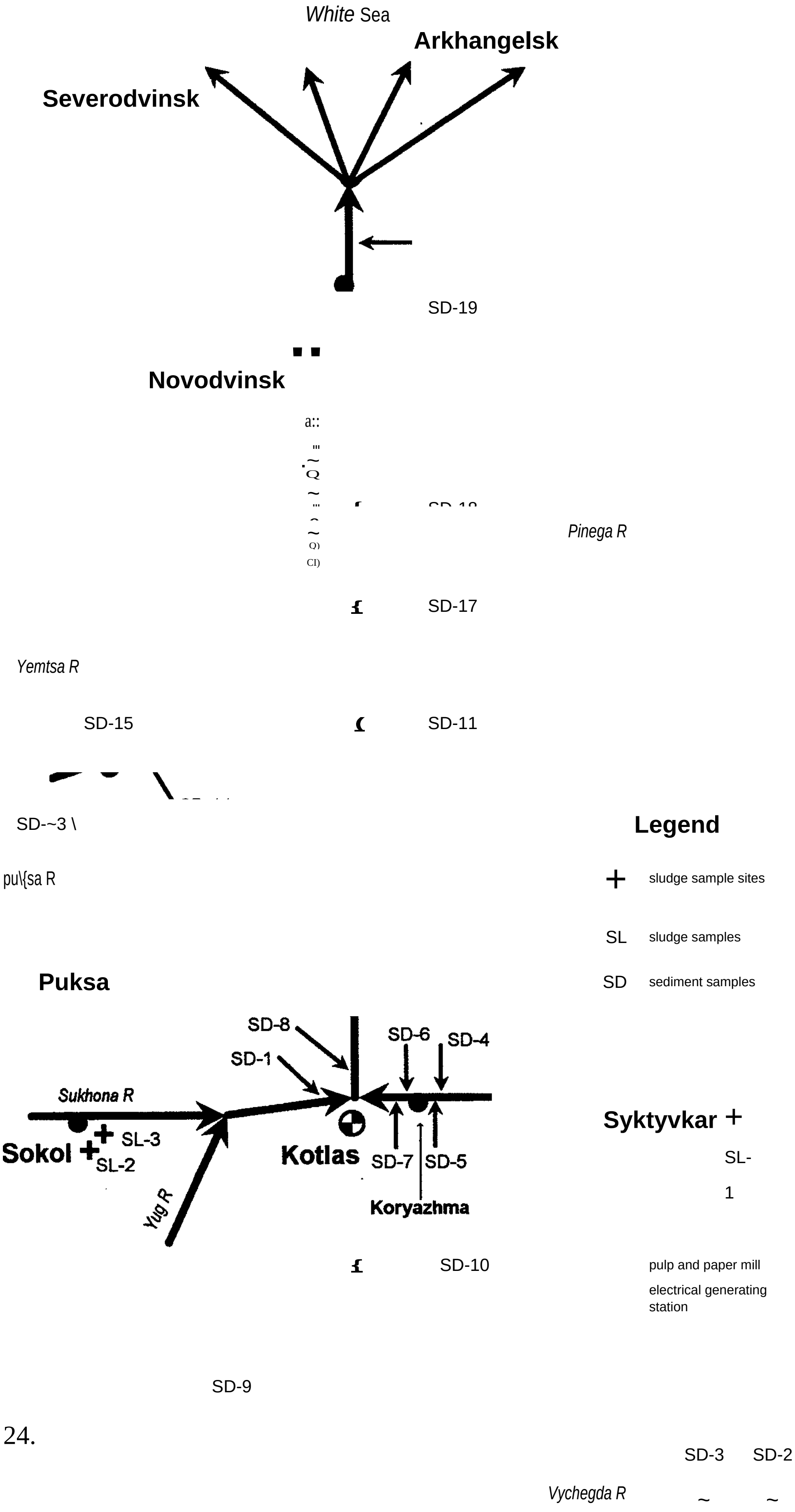
.• electrical generating stations (1 definitely coal-fired, 4 others also fossil fueled), • 1

cement plant.

All listed industries are likely past or present sources of dioxins and furans. The pulp mills that use chlorine bleaching generate PCDD/F emissions via wastewater discharges, off-gassing from chemical reactors and sludge handling facilities. Locations of the six mills in within the North Dvina watershed are shown on the schematic of Figure 7.2. Three of the pulp mills are amongst the top 10 producers in Russia: Syktyvkar LPK (Timber Industrial Complex), Kotlas (located in Koryazhma), and Arkhangelsk (located in Novodvinsk). The Solombala (evidently a precinct of Arkhangelsk city) mill has smaller capacity, but likely ranks within the top 15 Russian producers. The Syktyvkar complex produces plywood and chipboard in addition to pulp and paper, whi,le Kotlas mill produces more pulp and cardboard. The Russian mills may produce bleached and unbleached pulps, and a variety of paper products. The plant at Sokol may not be a primary pulp producer, but only a paper mill.

Information on regional mill production and waste handling are incomplete. Sewage treatment works at the Solombala mill discharge both mill wastewaters and municipal Arkhangelsk sewage to the Khataritsa channel that effectively serves as an open sewage canal. Effluent discharges from the Arkhangelsk mill in Novodvinsk were variably stated in Yufit and Khetuleva (1994) as 296 million $m^3$ in 1992 (-810,000 $m^3$/day) and 515,000-520,000 $m^3$/day. The wastewater outfall is 18 km above the drinking water intake of Arkhangelsk city, and 2 km below that of Novodvinsk. The latter can be affected by mill effluents during current reversals induced by windstorm surges. The Arkhangelsk mill also has an affiliated chlorine manufacturing plant.

The Kotlas mill in Koryazhma has three wastewater outfalls. The main one discharges directly to the Vychegda RiVer about ten fold greater effluents than the smaller two. The Puksa mill on the Puksa River, a headwater tributary of the Yemtsa system, was closed in May 1993. Wastewaters were apparently discharged untreated into the small Puksa River stream where there may be poor hydraulic conditions that favoured appreciable accumulation of contaminants in the streambed.


White Sea
Arkhangelsk
Severodvinsk
SD-19
Novodvinsk
Pinega R
SD-17
Yemtsa R
SD-15
SD-11
SD-~3 \
pu\{sa R
Legend
+ sludge sample sites
SL sludge samples
SD sediment samples
Puksa
SD-8
SD-1
SD-6
SD-4
Sukhona R
Sokol
SL-3
SL-2
Yug R
Kotlas
SD-7
SD-5
Koryazhma
Syktyvkar +
SL-
1
SD-10
pulp and paper mill
electrical generating station
SD-9
SD-3
SD-2
Vychegda R

24.

Figure 7.2 Schematic of PCDD/F sampling sites in North Dvina watershed.

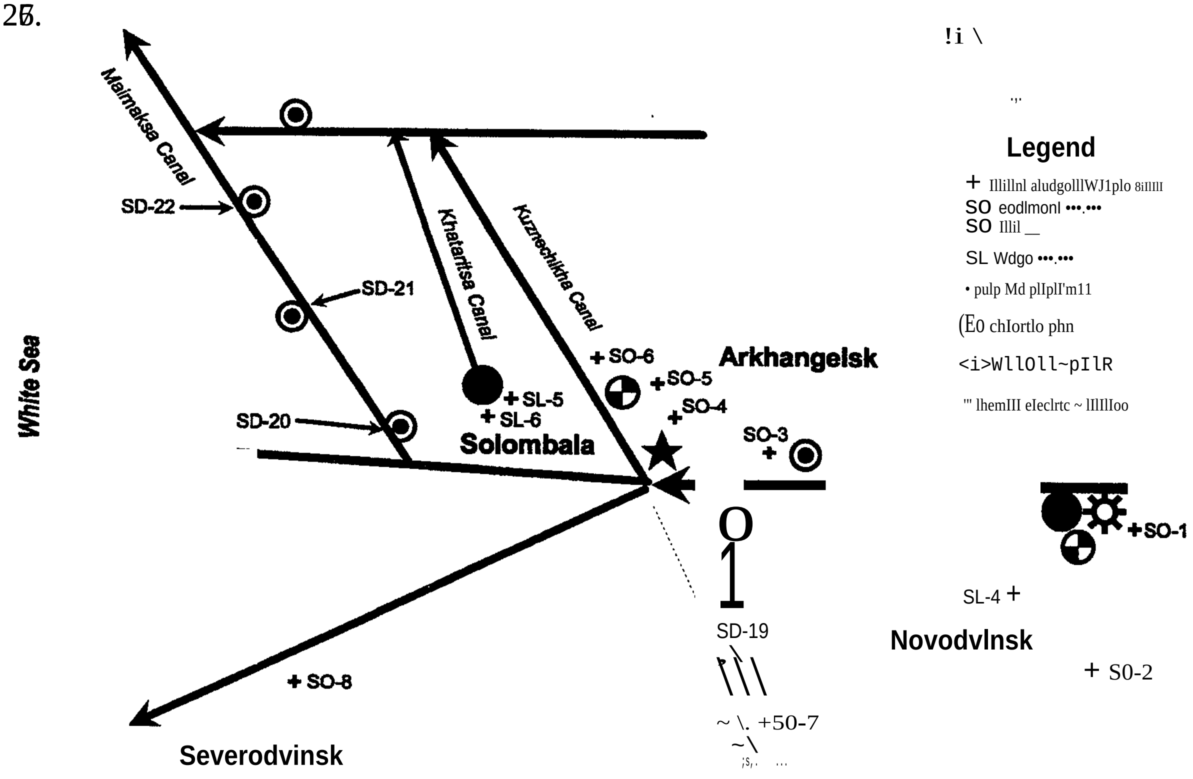


Figure 7.3 Schematic of PCDD/F sampling sites in North Dvina delta region; not to scale.

Yufit and Khetuleva (1994) variably describe these mills as having 'slime storage tanks', 'slime fields', and 'slime pits' which evidently refer to settling ponds, irrigation or sludge spreading fields, and leach pits where wastewaters and sludges from primary wastewater clarifiers are discharged prior to further disposal 32.

Woodworking facilities may contribute PCDD/Fs in various ways. The main source of contamination could derive from the usage of chlorophenolic wood preservatives that are contaminated with PCDD/Fs (e.g., Rappe et al., 1979; Koistinen et al., 1995; Vartiainen et al., 1995). Yufit and Khetuleva (1994) give no information on the extent of chlorophenolic wood preservative usage in the region, but Fedorov (1993) claimed that

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32 While Yufit and Khetuleva (1994) use the term 'slime' mainly to mean wastewater sludge, they also often apply the term to river sediments, evidently to imply high organic matter content likely reflective of organic solids derived from paper mill discharges, woodworking residues and log transport.

PCDD/F contaminated pentachlorophenol (PCP) and Na-PCP were produced at Chapayevsk for distribution as wood preservatives. Woodworking facilities may also release PCDD/Fs in emissions from bark boilers, other furnaces and scrap incineration.

Forestry product industries evidently have considerably affected the river and sediment regime of the main channels of the North Dvina system. Yufit and Khetuleva (1994) several times refer to the extensive contamination of stream beds by bark fragment residues from timber rafting and woodworking. Organic solids in the wastewater streams of paper mills would also contribute appreciable contamination. Generally, the resulting organic carbon in solution, colloids, suspended particles and bottom sediments would serve as a sorption substrate and transport medium for nonpolar POPs, including PCDD/Fs.

Waste gas emissions from thermal electric generating stations may also be sources of PCDD/Fs. There are plants in Severodvinsk, Arkhangelsk, Novodvinsk, Plesetsk (-15 km northwest of Puksa), Kotlas and Syktyvkar. Novodvinsk plant annually consumes 1-1.2 Mt of coal. About 5% is Svalbard coal known for its high chloride content and potential for PCDD/F generation. The fuels used at the other electrical generating stations in the basin have not been given, but these must be fossil fueled, as there are no nuclear generating stations in the region.

Other sources of PCDD/Fs in the region would be wood or coal combustion for general heating purposes; and incineration of municipal and woodworking wastes at numerous dumps in the vicinity of the region's urban centres. Yufit and Khetuleva (1994) also mention the cosmodrome in Plesetsk as a potential source of PCDD/Fs from solid-propellant rocket launches, but otherwise no information is given. Plesetsk also has one of watershed's the thermal generating stations, and there is a cement plant in Sevinsky about 30 km to the northwest.

## 7.3 PCDD/F Survey Description

The report by Yufit and Khetuleva (1994) comprises an overview and various small reports submitted by project participants. Field work was conducted in August 1993. Dated chromatograms presented in the report show that lab work was completed from November 1993 to January 1994.

In total, the report presents data for 63 samples of air, water, sediment, soil, and pulp and paper mill wastewater sludge; however, not all reported data are reliable. Thirty-six sediment, soil and sludge samples were sent for analysis to the Bavarian Institute of Water Problems (Bayerische Landesanstalt fur Wasserforschung, or BLW), Munich, Germany. The other 27 samples were analyzed at the Institute of Evolution and Ecology of Animals (IEMEA), Moscow. For reasons described below, sample analyses reported by IEMEA laboratory were considered unreliable.

### 7.3.1 BLW-IEMEA Lab Intercomparison

Though both BLWand IEMEA laboratories used mass spectrometers by the same manufacturer, the BL W lab used a significantly more sensitive model. A laboratory intercomparison of 8 split samples (7 sludge,' 1 soil) revealed appreciable discrepancies between BLW and IEMEA results that, in addition to differences in instruments, may also be attributable to other differences in laboratory technique. Table 7.1 presents the gross intercomparison data as expressed by the International (NATO) Toxic Equivalents (I-TEQs) calculated for each sample [33]. The BLW and IEMEA results are acceptably close for only one (no. 124) of the 8 comparison samples. This sample yielded the highest total mass and I-TEQ concentrations of toxic PCDD/F congeners in the comparison. The result may indicate that IEMEA analytical problems are confined mainly to the sub pg/g mass concentration range for most of the toxic congeners in sediments, sludge, and soil. However, more intercomparison data would be required to assess the possibility.

Table 7.1 BLW-IEMEA intercomparison data.

| | Sample data (1- TEQ fg/g) | | | Ratios | |
|---|---|---|---|---|---|
| Sample no. | BLW | IEMEA | Difference | IEMEAI BLW | BLW IIEMEA |
| 1.21 | 87 | 519 | 432 | 5.99 | 0.17 |
| 1.22 | 145 | 795 | 650 | 5.48 | 0.18 |
| C1 | 155 | 2,422 | 2,267 | 15.64 | *0.06* |
| 1.25 . | 360 | 1,457 | 1,097 | 4.05 | 0.25 |
| 1.23 | 384 | 1,269 | 885 | 3.30 | 0.30 |
| *1.20* | 413 | 2,359 | 1,946 | 5.71 | *0.18* |
| C2 | 489 | 1,515 | 1,026 | 3.10 | 0.32 |
| 1.24 | 1,824 | 1,643 | *-180* | *0.90* | 1.11 |
| Mean | 482 | 1,497 | 1,015 | 5.52 | 0.32 |
| Median | 372 | 1,486 | 955 | 4.76 | 0.21 |
| G-mean t | 316 | 1,347 | | 4.26 | 0.23 |

t G-mean = geometric mean.

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[33] TEQs in Table 7.1 were calculated directly from PCDD/F congener data tabulated in latter sections ofthe report (p. 114-116, and p. 133-136) of Yufit and Khetuleva (1994). If these data are correct, there are several discrepancies in Table 1 (p. 16) ofYufit and Khetuleva (1994).

For the remaining 7 intercomparison samples, I-TEQs estimated from the IEMEA data exceed results reported by the BLW lab. Statistical analysis suggests that discrepancies for two samples (nos. C1 and 1.20) are so great that these would be considered outliers. The remaining 5 samples suggest a weak calibration relationship 'might be developed to adjust IEMEA results to'BLW equivalents. However, until the range and validity of the IEMEA laboratory are established in a rigorous experimental design with more intercomparison samples and analysis by individual congeners, results generated by the IEMEA lab must be considered doubtful.

On the basis of the limited split sample comparison, if IEMEA data for sediments, sludges and soils, have I-TEQ s; 2.5 pg/g, there is one chance in 8 that high resolution methods will yield a similar result, and 7 chances of 8 that the IEMEA result will be 316 fold too high. Thus, the present review is confined primarily to samples analyzed at the BL W laboratory. Other than one air sample with high contamination that was likely within the reliable range of the IEMEA instrument, IEMEA sample results are not considered herein.

## 7.4 PCDD/F Contamination in North Dvina Watershed

Schematics of the North Dvina watershed and the Arkhangelsk-North Dvina delta area (Figures 7.2-7.3) show the general location of sites having sediment, soil, and paper mill sludge samples that were analyzed at the BLW lab. Table 7.2 lists the sample codes used on Figures 7.2-7.3 and the corresponding codes used by Yufit and Khetuleva (1994) in their project summary.

Comparative analysis of the 22 sediment samples processed at the BL W laboratory yields an approximate definition of nominal background PCDD/F concentrations in the main channels of the North Dvina system, and a cursory glimpse of the PCDD/F contamination wrought mainly by pulp mills and woodworking plants. Individual sample results should be interpreted cautiously as sampling was both limited and opportunistic. Also, neither organic carbon content nor physical texture was determined. Variations in PCDD/F content may be, at least partly, attributable to variations in these unmeasured or unreported variables.

### 7.4.1 PCDD/F Concentrations in River Sediments - Regional Background

Yufit and Khetuleva (1994) estimated the regional *background* of PCDD/Fs in river sediments from the 8 BLW samples having the lowest totall-TEQ concentrations. This amounts to arbitrary selection of samples with I-TEQ below 125 *fg/g.* These data are summarized in Table 7.3. All but one *background* sample were obtained in main river channels that are directly affected by paper mill emissions. The background I-TEQ observed in sediments from more remote streams and lakes may be lower.

Table 7.2 Site codes and descriptions for samples analyzed at BLW laboratory; (A) sediments.

| This report | Yufit and Khetuleva | River system | Site description | I-TEQ fg/g |
|---|---|---|---|---|
| SO-1 | 1.19d | S. Ovina | S. Ovina 5 km *u/s* Vychegda mouth; Kotlas port | 215 |
| SO-2 | Sykt1 | Vychegda | 700 m *u/s* PPM outfall t | 73 |
| SO-3 | Sykt2 | Vychegda | 1 km *d/s* PPM outfall | 609 |
| SO-4 | 1.23d | Vychegda | 1 km *u/s* Staritsa Staraya R | 384 |
| SO-5 | 1.22d | Vychegda | 200 m *d/s* Borshchovka R a | 145 |
| SO-6 | 1.21d | Vychegda | 100 m *d/s* PPM outfall | 105 |
| SO-7 | 1.20d | Vychegda | 1 .5 km *d/s* PPM outfall | 413 |
| SO-8 | 1.18d | S. Dvina | 300 m *d/s* Vychegda R | 104 |
| SD-9 | 1.17d | S. Dvina | near Verkhnaya Toima settlement | 124 |
| SO-10 | 1.16d | S. Dvina | 7 km *d/s* Vaga | 66 |
| SD-11 | 20d* | S. Dvina | Nikolo settlement 15 km *u/s* Yemtsa | 87 |
| SO-12 | 1.27d | Yemtsa | Yemtsa R 500 m *u/s* Mekhrenga | 144 |
| SO-13 | 1.24d | Yemtsa | Puksa R 20 m *d/s* Puksa cellulose plant outfall | 1.824 |
| SO-14 | 1.25d | Yemtsa | Puksa R 500 m *d/s* Puksa cellulose plant outfall | 360 |
| SO-15 | 1.28d | Yemtsa | Mekhrenga R 500-1.000 m *u/s* outlet to Yemtsa | 324 |
| SO-16 | 1.26d | Yemtsa | Yemtsa R at Yemetsk *u/s* outlet to S. Dvina | 595 |
| SO-17 | 19d* | S. Dvina | 2 km *u/s* Pinega R | 85 |
| SO-18 | 1.14d | S. Dvina | Ust-Pinega | 79 |
| SO-19 | 1.29d | S. Ovina | Lenin WWP t | 817 |
| SO-20 | 1.30d | delta | Maimaksa canal - WWP | 193 |
| SO-21 | 1.31d | delta | Maimaksa canal - WWP2 | 522 |
| SO-22 | 1.32d | delta | Maimaksa canal - WWP3 | 471 |

t Abbreviations: u/s - upstream; *d/s* - downstream; PPM - pulp and paper mill; WWP - woodworking plant.

[a] sample may reflect small wastewater discharges to Borshchovka River from the Koryazhma PPM.

Table 7.2 Cont'd; Site codes and descriptions: (B) sludge, and (C) soils.

| This report | Yufit and Khetuleva | River system | Site description | |
|---|---|---|---|---|
| B. PPM sludge samples | | | | |
| SL-1 | Sykt3 | Vychegda | Syktyvkar PPM sludge storage no. 2 | 83,990 |
| SL-2 | c-1 | Sokol | Sokol PPM sludge tank | 155 |
| SL-3 | c-2 | Sokol | Sokol PPM sewage canal | 489 |
| SL-4 | 4.5 | Novodvinsk | de-watered sludge from Arkhangelsk PPM | 3,975 |
| SL-5 | 1.5 | delta | Solombala PPM sludge tank - 1 month storage | 2,063 |
| SL-6 | 1.5* | delta | Solombala PPM sludge tank - 1 year storage | 10,868 |
| C. Soil samples | | | | |
| SO-1 | 4.6 | Novodvinsk | chlorine plant | 5,199 |
| SO-2 | 4.4 | Novodvinsk | [b]<br>suburban dump | 378 |
| SO-3 | 4.8 | Arkhangelsk | Lenin WWP | 76,714 |
| SO-4 | 4.1 | Arkhangelsk | near dump | 4,433 |
| SO-5 | 4.7 | Arkhangelsk | 1 km east of thermal electric power station | 362 |
| SO-6 | 4.3 | Arkhangelsk | dump near furniture plant C | 2,169 |
| SO-7 | 4.2 | Arkhangelsk | dump at km 20 Vologda highway [d] | 34,674 |
| SO-8 | 4.9 | delta | Rikusikha | 1,502 |

1- TEQ fg/g

[b] site is *'near'* the city, but location not precisely specified.

[c] site is som'ewhere in Arkhangelsk on S. Dvina east bank.

[d] municipal dump for Arkhangelsk community on S. Dvina west t>ank.

Oddly, sample SO-5, taken 100 m downstream of the main Kotlas pulp mill wastewater outfall, has I-TEa of only 105 *fg/g.* Near the outfall, the contaminant plume might not yet be well mixed with upstream river waters, and sample 80-5 may have been collected from a point on the streambed cross-section unaffected by the wastewater contaminant plume.

If samples 80-5 and 80-9 having the highest 2,3,7,8-TCOO concentrations are excluded from the background set, the mean *background* total I-TEa falls to 82 *fg/g.* Although OCOO and OCOF dominated the composition of the *background* samples, 1TEa composition is dominated by congeners 2,3,7,8- TCOO and 1,2,3,7,8-PentaCOO that together account for 40% of mean *background* I-TEa.

Table 7.3 Composition and toxic equivalency of PCOO/Fs in *background* river sediments t.

| | Concentration fg/g dw:j: | | | Composition % | | | I-TEa fg/g dw:j: | | | I-TEa % | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Isomer | Mean | Min | Max | Mean | Min | Max | Mean | Min | Max | Mean | Min | Max |
| 04§ | 22 | 10 | 47 | 0.4 | 0.2 | 0.5 | 22.4 | 10.0 | 47.0 | 23.6 | 12.6 | 37.9 |
| 05 | 25 | 13 | 47 | 0.4 | 0.1 | 0.6 | 12.3 | 6.5 | 23.5 | 14.4 | 5.2 | 29.7 |
| 061 | 39 | 20 | 51 | 0.7 | 0.3 | 1.2 | 3.9 | 2.0 | 5.1 | 4.4 | 2.7 | 5.5 |
| 062 | 48 | 34 | 60 | 0.8 | 0.4 | 1.3 | 4.8 | 3.4 | 6.0 | 5.5 | 3.6 | 7.0 |
| 063 | 41 | 28 | 53 | 0.7 | 0.4 | 1.1 | 4.1 | 2.8 | 5.3 | 4.6 | 3.2 | 6.1 |
| 07 | 441 | 260 | 640 | 7.8 | 5.1 | 11.9 | 4.4 | 2.6 | 6.4 | 5.0 | 3.3 | 7.5 |
| 08 | 3,538 | 1,800 | 5,900 | 60.6 | 53.5 | 70.7 | 3.5 | 1.8 | 5.9 | 4.0 | 2.3 | 5.7 |
| F4 | 54 | 22 | 93 | 0.9 | 0.4 | 1.6 | 5.4 | 2.2 | 9.3 | 6.1 | 3.3 | 12.7 |
| F51 | 20 | 8 | 31 | 0.4 | 0.1 | 0.6 | 1.0 | 0.4 | 1.6 | 1.1 | 0.5 | 2.1 |
| F52 | 17 | 6 | 30 | 0.3 | 0.1 | 0.6 | 8.4 | 3.0 | 15.0 | 9.4 | 3.5 | 20.5 |
| F61 | 48 | 25 | 71 | 0.8 | 0.4 | 1.6 | 4.8 | 2.5 | 7.1 | 5.2 | 3.4 | 7.2 |
| F62 | 29 | 16 | 51 | 0.5 | 0.3 | 1.2 | 2.9 | 1.6 | 5.1 | 3.1 | 2.3 | 4.9 |
| F63 | 68 | 41 | 120 | 1.2 | 0.7 | 2.8 | 6.8 | 4.1 | 12.0 | 7.4 | 5.9 | 11.5 |
| F64 | 6 | 3 | 15 | 0.1 | 0.0 | 0.3 | 0.6 | 0.3 | 1.5 | 0.6 | 0.3 | 1.4 |
| F71 | 369 | 130 | 950 | 6.2 | 3.4 | 9.0. | 3.7 | 1.3 | 9.5 | 4.0 | 1.6 | 7.7 |
| F72 | 41 | 21 | 67 | 0.7 | 0.3 | 1.4 | 0.4 | 0.2 | 0.7 | 0.5 | 0.2 | 0.8 |
| F8 | 1,105 | 530 | 3,100 | 17.4 | 13.0 | 28.1 | 1.1 | 0.5 | 3.1 | 1.2 | 0.5 | 2.5 |
| 2:coo | 4,154 | 2,236 | 6,642 | 71.4 | 60.3 | 79.0 | 55.4 | 34.8 | 77.2 | 61.5 | 47.6 | 72.1 |
| 2:COF | 1,755 | 933 | 4,380 | 28.6 | 21.0 | 39.7 | 35.0 | 20.6 | 51.7 | 38.5 | 27.9 | 52.4 |
| Total | ?,908 | 3,169 | 11,022 | 100.0 | | | 90.4 | 66.0 | 123.9 | 100.0 | | |

t sites SO-1, SO-5, SO-8, SO-9, SO-10, SO-11,
SO-17, SO-18'-

:j: dry weight; § abbreviations defined in Table A.2.

### 7.4.1.1 **External Comparisons**

Compared to other published data for aquatic sediments, the North Dvina River *background* PCDD/F concentrations, whether expressed as I-TEQs (Table 7.4), or as mass concentrations, are the generally'lowest reported for Europe thus far. The lowest European sediment data have I-TEO approaching 0.75-1.25 pg/g that is about 7-12 fold greater than the observed North Dvina background levels. Lake Ladoga sediments from near pulp mills in Priozersk and Pitkyaranta yield mean estimated 1- TEQs that are 90-180 fold higher than North Dvina background. The actual 1- TEQ of Ladoga sediments may vary up to ± 50% due to uncertainties in prorating from measurements on only 9 of the 17 toxic PCDD/F congeners.

Table 7.4 PCDDIFs (I-TEQ *pg/g* dw) in aquatic sediments of Europe.

| Area | Water body | Min | Max | Reference |
|---|---|---|---|---|
| Lake Ladoga | Pitkyaranta / Priozersk a | 6 | 28 | Chapter 6, Table 6.6 |
| Finland | 4 lakes t | 1 | 11 | Vartiainen et al. (1997) |
| | Kymi R. above paper mill | 34 | | Koistinen et al. (1995) |
| | Kymi R. below paper mill | 1,040 | 7,070 | ibid. |
| Sweden | Dala R. | 2 | 18 | Kjeller et al. (1990) |
| | L. Vattem | 5 | 36 | ibid. |
| | L. Vanern | 13 | 124 | ibid. |
| Baltic Sea | Gulf of Bothnia, Finland coast | 12 | 70 | Koistinen et al. (1995) |
| | Gulf of Finland, Finland coast | 20 | 26 | Koistinen et al. (1997) |
| | Baltic Proper t | 22 | | Kjeller and Rappe (1995) |
| | Baltic Proper near Gotland | 25 | 54 | Koistinen et al. (1997) |
| | German coast § | 1,170 | 19,770 | Witt et al. (1997) |
| Germany | 4 Bavarian lakes t | 22 | 231 | Bruckmeier et al. (1997);<br>JGttner et al. (1997) |
| | Elbe R. 1992 | 25 | 381 | Schramm et al. (1995) |
| | Elbe R. 1993 | 10 | 68 | ibid. |
| Rhine R. | 48, samples 1984-85 | <1 | 310 | Evers et al. (1988) |
| North Sea | North Sea | 12 | | Evers et al. (1993) |
| | Wadden Sea | 5 | 36 | ibid. |
| | Wester Scheidt | 15 | 16 | ibid. |
| | Rhine estuary | 43 | 48 | ibid. |
| | Humber estuary | 16 | 267 | ibid. |
| UK | 36 rivers and streams :t: | -1 | -125 | Rose et al. (1994) |
| Austria | R. Traun | 0.74 | 3.69 | Chovanec et al. (1994) |
| | R. Danube | 0.89 | 1.25 | ibid. |

a range of minimal and maximal estimates; t top layer of sediment cores; :t: data read from figures;

§ data are unusually high, Witt et al. (1997) may have misreported units in *nglg* rather than *pg/g*.

Congener profiles of North Dvina background samples are most similar to the recent sediment data reported for four Finnish lakes (Vartiainen et al., 1997). As shown in Figure 7.4, the compositions are dominated by the same four congeners: 1234678HpCDD, OCDD, 1234678-HpCDF, and OCDF. Three of the Finnish lakes are in remote northern Finland where the PCDD/Fs originate from atmospheric deposition. The compositions of North Dvina sediments are also somewhat similar to those in sediments of Sweden's Lake Vattern (Kjeller et al., 1990). The common congener profiles observed at these various locations may represent the broad regional signature of PCDD/Fs derived from long range atmospheric transport. In the UK, Rose et al. (1994) considered background I-TEa concentrations for England and Wales as <6 pg/g. Like the North Dvina background samples, OCDD and HpCDD were observed to dominate mass concentrations. Zook and Rappe (1994) discuss how the varying physicochemical properties of PCDD/F congeners, transformations during atmospheric transport and deposition processes that favour the higher chlorinated congeners combine to yield congener compositions in receptor media that are dominated by the higher chlorinated PCDD/Fs.

The I-TEa composition of North Dvina background sediments is dominated by 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD (Figure 7.4). In contrast, the I-TEa of the Finnish lake sediment samples is dominated by furan 2,3,4,7,8-PeCDF. This was also widely true of most other European sediments, and likely reflects the influence of other combustion and chemical sources common in industrialized countries.

### 7.4.2 **PCDD/Fs in Paper Mill Sludges and Arkhangelsk Area Soils**

Before examining contaminated river sediments, it is useful to consider the PCDD/F content of potential contaminant sources. It is not strictly guaranteed, but paper mill sludges may rc;>ughly indicate the PCDD/F composition occurring in mill effluents. Despite the primary wastewater treatments applied at these pulp mills, there are likely appreciable organic solids containing PCDD/Fs in the discharged effluents. The available soils data are more indicative of certain local *primary* PCDD/F sources in the Arkhangelsk-Novodvinsk area. Contaminated soils themselves are *secondary* sources that may ultimately affect surface water systems via wind or water erosion. The high affinity of PCDD/Fs for soil particles likely prevents their rapid movement through groundwater systems, and the low vapor pressures of PCDD/F congeners likely ensure that volatilization losses to the atmosphere are small.

The Syktyvkar sludge sample SL-1 has I-TEa of 84 pg/g, the greatest observed among available data. Figure 7.5 shows that sludge SL-1 also has toxic PCDD/F composition that seems to be a typical chlorine-bleaching pattern. Congener 2,3,7,8TCDD contributes 50% of the total mass of the 17 toxic PCDD/Fs, and 93% of sample 1_TEa. The other sludge samples from the Sokol, Novodvinsk and Solombala mills have relatively low PCDD/F content and 20-30% of sample I-TEa due to 2,3,7,8-TCDD.

The two Sokol sludges (SL-2, SL-3) have composition similar to the sediment background. The low toxicity of these sludges may indicate that the mill produces mainly paper products rather than pulp. The Novodvinsk (SL-4) and Solombala (SL-5, SL-6) samples are only moderately contaminated. Comparison of the two Solombala

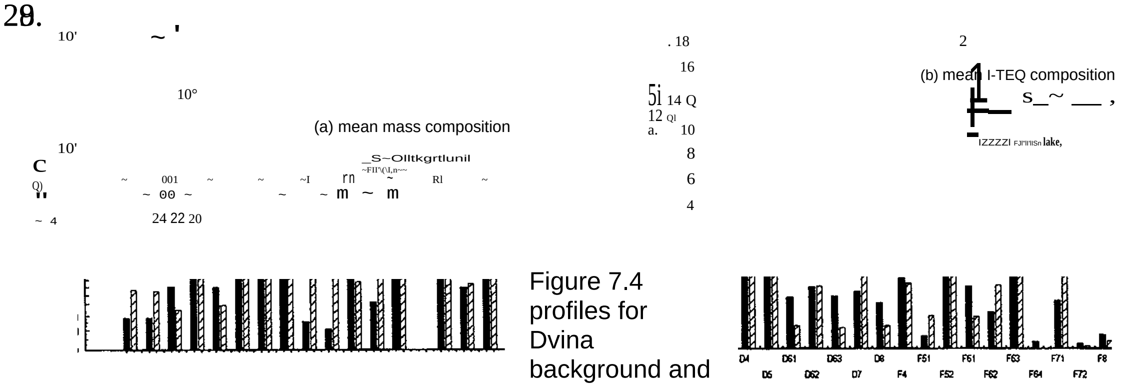

Figure 7.4 PCDD/F profiles for North Dvina background and Finnish lake sediments; mean mass (a) and I-TEQ (b) compositions as percentage of totals for 17 toxic congeners. Finnish lake sediment data from Vartiainen et al. (1997); congeners abbreviated as in Table A.2.

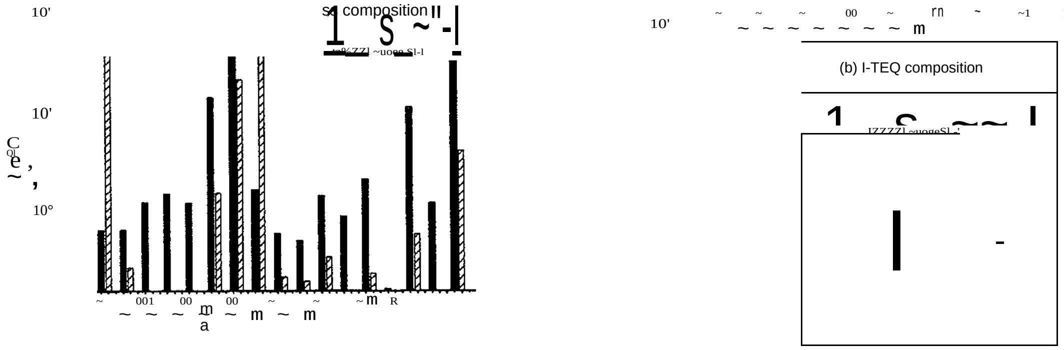

Figure 7.5 PCDD/F profile for Syktyvkar sludge SL-1 contrasted against North Dvina background; (a) mass, and (b) I-TEQ compositions as percentage of totals for 17 toxic congeners; congeners abbreviated as in Table A.2.

samples suggests that aging increases the toxicity of the sludge by 5-6 fold. The total concentration of the 17 toxic congeners increases only slightly from sample SL-5 to SL6; however, a significant decline of low toxicity congeners (1,2,3,4,6,7,8-HpCDD, OCDD and OCDF) was balanced by increases in the most toxic congeners (2,3,7,8TCDD, 2,3,7,8-TCDF, and 2,3,4,7,8-PeCDF) which increase their collective share of toxicity from 44% to 78% of the total.

The toxicities of soil samples are mostly low (SO-2, SO-5) to moderate (SO-1, SO-4, SO-6, SO-8); however, samples SO-3 and SO-7 had appreciable I-TEQs of 77 and 35 *pg/g* respectively. Sample SO-7 from the municipal dump on the west bank of Arkhangelsk is generally similar in composition to river sediment background, except that congener 1,2,3,4,6,7,8-HpCDF assumes 28% of the mass concentration and 22% of sample I-TEQ.

### 7.4.3 Lenin Woodworking Complex

The toxicity of sample 80-3 from the woodworking plant between Arkhangelsk and Novodvinsk approaches that of the 8yktyvkar sludge (8L-1). The composition of sample 80-3 is contrasted against river sediment background in Figure 7.6. Mass composition is dominated by hepta- and octa- congeners, particularly OCDD that has mass concentration 17.3 nglg and accounts for 83% of the total. PCDDs contribute about 85% to the I-TEQ of sample 80-3, but unlike 8yktyvkar sludge, I-TEQ is distributed across 5 PCDD congeners.

The congener profile of sample 80-3 indicates likely PCDD/F contamination from chlorophenolic fungicides used at the timber treatment yards. Observed congener profiles of PCDD/Fs contaminating chlorophenolic wood preservatives vary somewhat, but generally, the higher chlorinated congeners tend to dominate (Zook and Rappe, 1994). This can make it difficult to distinguish the PCDD/F signature of wood preservatives from the general background signal; however, the overwhelming dominance of a few hepta- and octa- congeners in sample 80-3, strongly suggests that wood preservatives are the source.

Long term fouling of timber yard soils by wood preservatives may have also caused significant groundwater pollution by polychlorophenols that are generally much more water soluble and mobile than PCDD/Fs. In turn, there may be significant river water pollution by chlorophenolics that has affected the Arkhangelsk drinking water supply. Vartiainen et al. (1995) discuss a case in Finland where prolonged wood preservative usage at a sawmill resulted in significant contamination of drinking water supplies by chlorophenolics. Yufit and Khetuleva (1994) did not discuss the potential pollution from chlorophenolic wood preservative usage in the region. If potential chlorophenolic contamination of Arkhangelsk and Novodvinsk drinking water supplies has not yet been investigated, it should be considered in future studies.

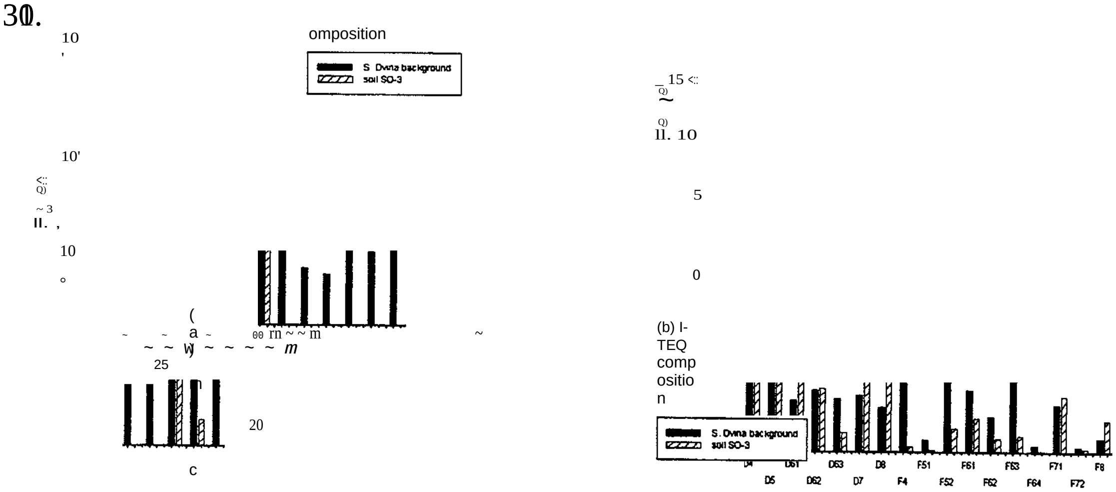

Figure 7.6 PCDD/F profile for soil 50-3 from Lenin woodworking complex compared to North Dvina background; (a) mass, and (b) 1- TEQ expressed as percentage of totals for 17 toxic congeners.

### 7.4.4 Novodvinsk Pulp Mill and Chlorine Plant

Soil sample SO-1 taken near the chlorine plant in Novodvinsk has modest burden of .5.2 *pg/g* I-TEQ, and a unique composition that likely represents, at least partly, the PCDD/Fs in emissions from electrolytic chlorine production. As Figure 7.7 reveals, the composition and toxic equivalency of sample SO-1 are dominated by furans. Sample 1TEQ is 97% attributable to PCDFs, mainly 2,3,7,8-TCDF (60%) and 2,3,4,7,8PentaCDF (19%).

A sample of Novodvinsk air processed at the IEMEA lab (number 3.4 in Yufit and Khetuleva, 1994) offers further comparison. The sample yielded 44 *pg/m*$^3$ I-TEQ with all measured congeners apparently well above detection; so that, the PCDD/F content was likely within the reliable range for the IEMEA instrument. The compositions of the air sample, sludge sample SL-4 from the Novodvinsk mill, and soil sample SO-1 are compared in Figure 7.8. While concordance is imperfect, these samples are similar in that furans dominate both the mass concentration and toxicity profiles. Over 90% of 1TEQ in air and soil samples, and 60% in sludge SL-4 are contributed by PCDFs. As these samples are unique amongst the greater set of North Dvina samples, it is reasonable to suspect that emissions from the Novodvinsk chlorine plant are largely responsible. Evidence has accumulated that significant PCDFs can be generated during electrolytic chlorine production by the graphite cathodes that historically have been made from wood pitches containing furan precursors (Zook and Rappe, 1994).

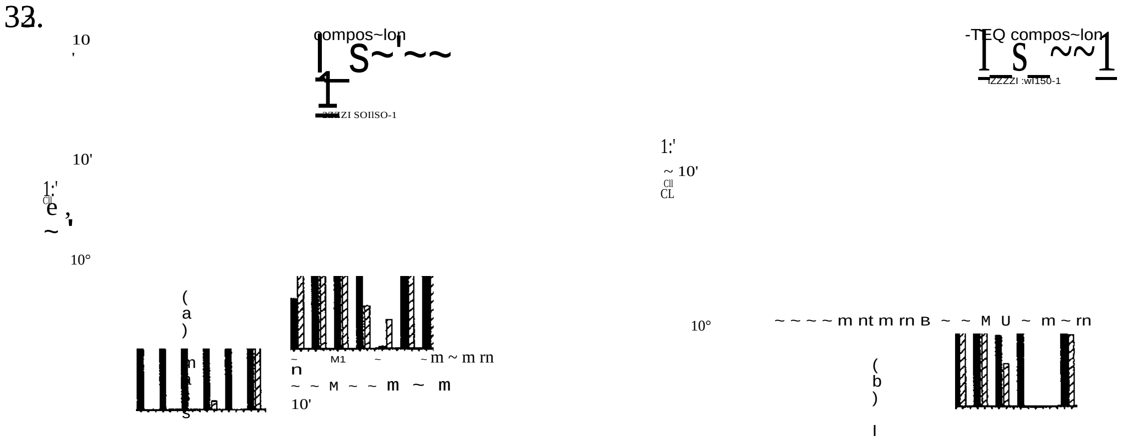

Figure 7.7 PCDD/F profile soil 50-1 from Novodvinsk chlorine plant contrasted against North Dvina background;. mass (a) and 1- TEQ (b) compositions expressed as percentage of totals for 17 toxic congeners; congeners abbreviated as in Table A.2.

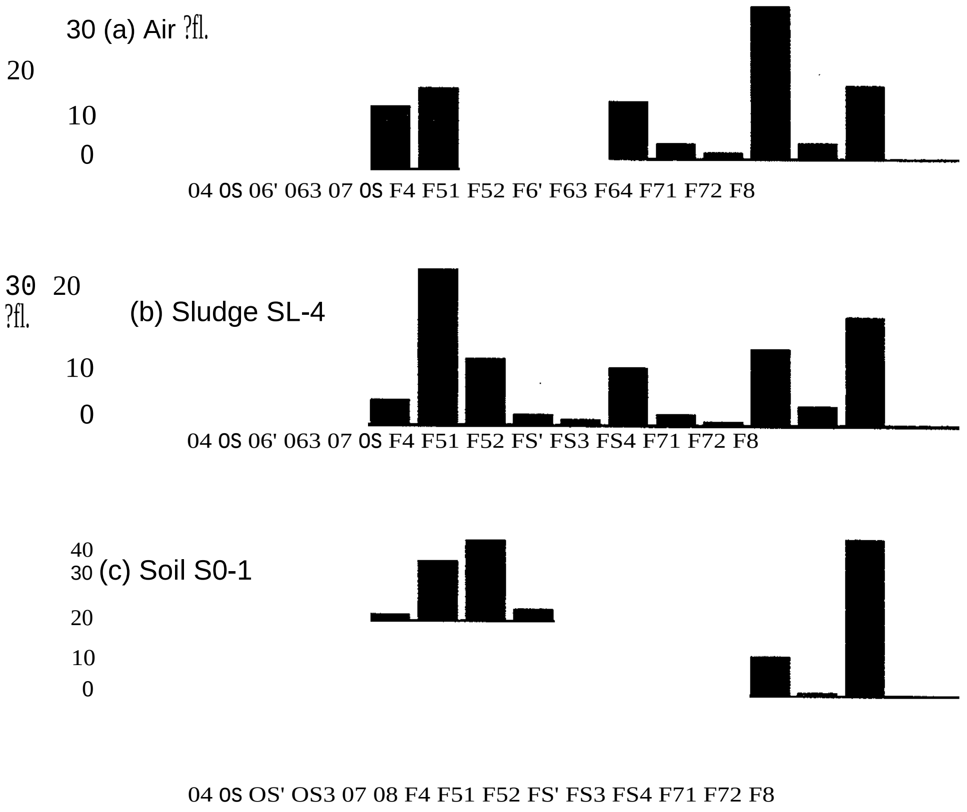

Figure 7.8 PCOO/F profiles for Novodvinsk air, paper mill sludge, and soil; congeners abbreviated as in Table A.2; 06* = 061 + 062; F6* = F61 + F62.

### 7.4.5 **Summary**

Figure 7.9 presents the 22 sediment measurements arranged in roughly longitudinal order from upstream to downstream. While pollution by forestry industries is unequivocally evident, no samples exceed the 6 pg/g I-TEQ suggested by Rose et al. (1994) as an upper limit of background contamination in England and Wales. Relative to nearly all reported data for western Europe, PCDD/F pollution in the main channels of the North Dvina system appears to be exceedingly low.

The effects of paper mill emissions are evident on the Vychegda and Yemtsa tributary systems, while the four lower North Dvina samples (5D-19, -20, -21, -22) are affected by woodworking plants, and perhaps also by paper mill and other emissions in the Arkhangelsk-Novodvinsk area. Generally, contamination is expected to be greatest near the source, and to decline downstream due to mixing and dilution. This is most evident in data for the Vychegda River below the 5yktyvkar pulp mill.

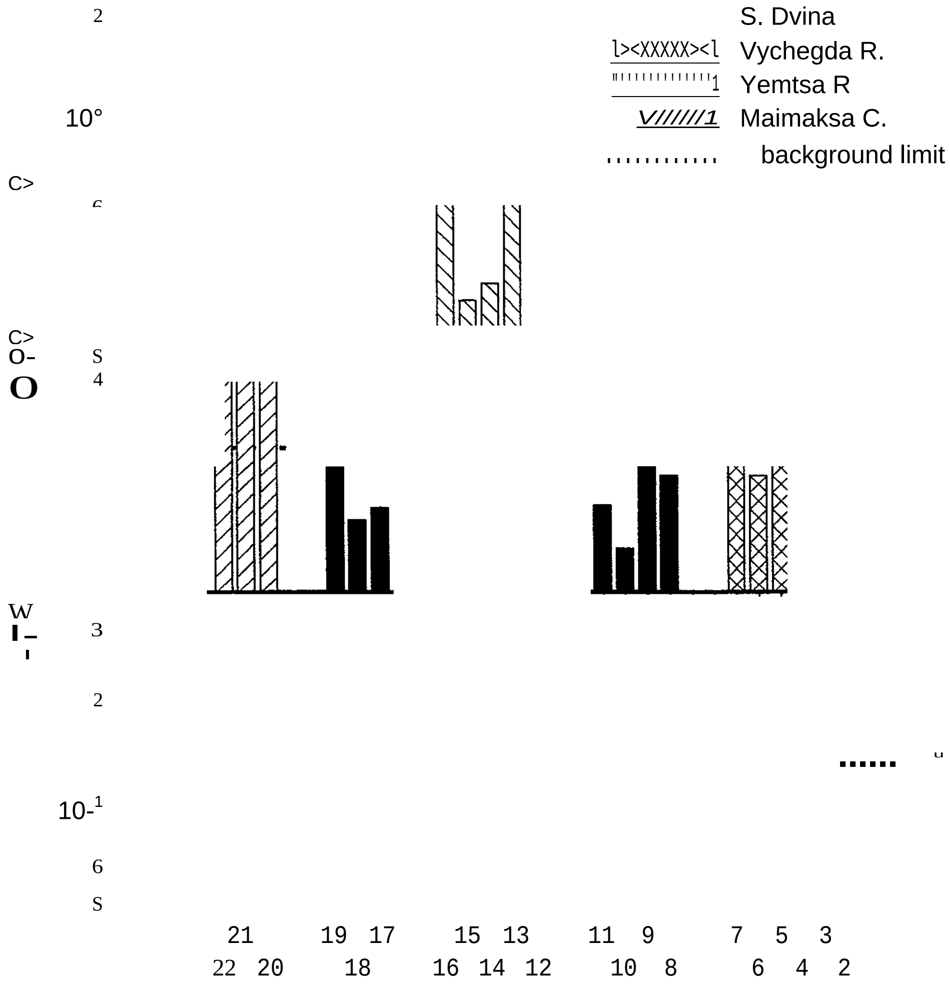

Figure 7.9 Longitudinal schematic of PCDD/F I-TEQs in North Dvina river sediments; nominal upper *background* limit = 0.125 *pg/g* dw; sample numbers correspond to the *8D-nn* labels in Table 7.2 with prefix removed; e.g., site 1 is 8D-1, etc.

Sediment sample SO-3 taken below the Syktyvkar mill outfall is the only one that shows clear similarity to a sludge sample. Syktyvkar sludge SL-1 had the highest 1TEa of 84 pg/g of which 93% was contributed by 2,3,7,8-TCDO, while the I-TEa of sediment sample SD-3 was 74% attributable to 2,3,7,8-TCDD. Sediment sample SD-4, taken near Koryazhma city upstream of local paper mill discharges, had a similar composition with 70% of I-TEa attributable to 2,3,7,8-TCDD; however, it is debatable that the Syktyvkar mill effluents would be·so influential 300 river km downstream.

Sample SD-13 ( 1,824 I-TEa *fg/g)* from the Puksa River near the outfall of the closed paper mill is the most contaminated sediment specimen. The effects of Puksa mill discharges seem to manifest downstream as far as the confluence with the North Dvina, and the Puksa-Mekhrenga-Yemtsa seems to be the most contaminated of the systems examined. Judging from the account in Yufit and Khetuleva (1994), the Puksa water course is heavily contaminated with past untreated wastewater discharges that may persist for some years if local hydraulic conditions do not favour rapid flushing of the system.

Sample SD-19, taken from the bank opposite the Lenin woodworking complex and not far downstream of the Arkhangelsk paper mill complex in Novodvinsk, is the second most contaminated sample with I-TEQ of 817 *fg/g.* Sample composition is similar to that of soil sample 80-3 from the woodworking complex insofar as 82% of I-TEQ is due to PCDDs; however, the sample congener profile more resembles background river sediment composition than soil sample SO-3 from the woodworking plant. The toxicity of sample SD-19 is concentrated in congeners 2,3,7,8-TCDD; 1,2,3,7,8-PeCDD; and 1,2,3,4,7,8-HxCDD, unlike soil sample 80-3 that also has appreciable toxicity due to 1,2,3,4,6,7,8-HpCDD and OCDF.

Along the Maimaksa distributary channel, contamination increases from 190 to 500 *fg/g* I-TEQ mainly due to 3 fold increase in 2,3,7,8-TCDD concentration. Sample compositions are not too different from river sediment background.

Attempts to cluster the sediment, sludge and soil compositional data, resulted in most sediment samples grouping with the set of nominal background samples. The most compositionally distinct samples are 8yktyvkar sludge 8L-1, and soil SO-1 from the Novodvinsk chlorine plant in Novodvinsk. The former is dominated by 2,3,7,8TCDD, while the latter is dominated by PCDFs. While a few samples bear similarities to each of the~e two extremes, the majority of samples are closer in composition to the background set of sediment samples.

# Appendix A

# Background Information on PCDD/Fs and PCBs

## A.1 Dioxins and Furans (PCDD/Fs)

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) are two closely related families of compounds comprising 75 dioxin and 135 furan *congeners* that correspond to the possible substitution patterns of chlorine atoms for carbon atoms on fused benzene rings. The general structures are shown in Figure A.1. Individual dioxins and furans may have from 1 to 8 chlorine atoms, and the subsets of congeners with identical numbers of chlorine atoms are known as *homologues* (Table A.1). Emission sources often have a distinct homologue composition profile, Le., the percentages contributed by individual homologues to the total PCDDs and PCDFs, that serves to identify the dominant sources in ambient environmental samples.

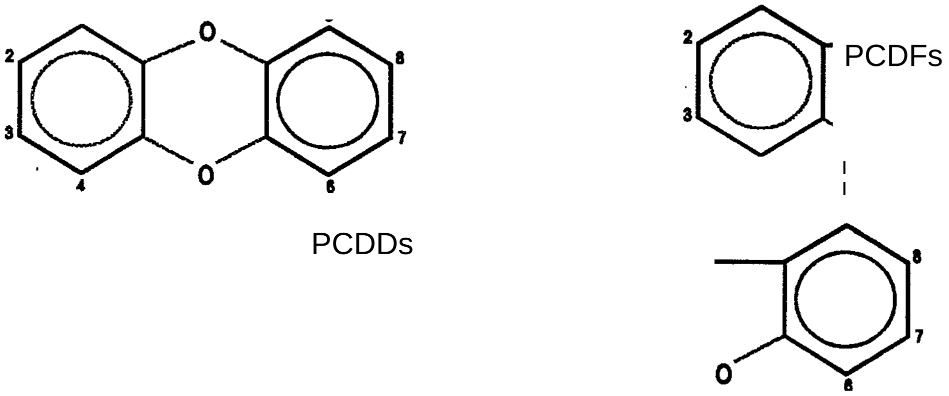

Figure A.1 Structure of PCDDs and PCDFs .

Table A.1 Number of PCDD/F congeners by homologue.

| Cl atoms | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | Total |
|---|---|---|---|---|---|---|---|---|---|
| PCDDs | 2 | 10 | 14 | 22 | 14 | 10 | 2 | 1 | 75 |
| PCDFs | 4 | 16 | 28 | 38 | 28 | 16 | 4 | 1 | 135 |

### A.1.1 PCDD/F Sources

PCDD/Fs are created by most combustion processes including forest fires and domestic wood burning if chlorine is present, and as the by-product of many chemical and industrial processes. The great variety of processes capable of producing PCDD/Fs are illustrated in the national emission assessments for the USA (Thomas and Spiro, 1995); and Belgium, Netherlands and U.K. (Chlorophiles, 1997). In these countries, municipal waste incineration is the dominant source. Zook and Rappe (1994) also give a good discussion of PCDD/F sources.

Most PCDD/Fs enter the environment via emissions to the atmosphere. Increasing evidence from sediment cores (Czuczwa and Hites, 1986; Kjeller and Rappe, 1995; JClttner et aI., 1997; Rose et aI., 1997; Vartiainen et aI., 1997) that environmental contamination increased significantly from the 1920s onward as chlorine-based industrial processes and products became widespread in developed countries.

In aquatic systems, most serious PCDD/F contamination originates from direct wastewater discharges from industrial sources. Pulp mills using chlorine bleaching processes (Kuehl et aI., 1987; Swanson et aI., 1988; Amendola et aI., 1989; Rappe et aI., 1990) and ch~mical plants producing organochlorine chemicals would be among the strongest sources. Depending on the geographic setting and atmospheric circulation patterns, atmospheric transport from heavily industrialized areas may be dominant beyond the near vicinity of local sources.

### A.1.2 Risk Assessment: Toxic Equivalency

Among'the 210 possible PCDD/Fs, only a subset of 17 with chlorine atoms substituted in the 2,3,7,8 positions have been found to elicit a range of similar toxic and biochemical responses. Toxicological effects and mechanisms are discussed in WHO (1989c), Safe (1990,1991) and van den Berg et al. (1994). Dioxin congener 2,3,7,8TetraCDD (commonly 2,3,7,8-TCDD) induces the greatest toxic response, and the other 16 toxic PCDD/Fs have been rated in relative potency by toxic equivalence factors (TEFs). TEFs are applied to the mass concentrations of the 17 toxic congeners measured in environmental samples to determine the respective individual Toxic Equivalents (TEas). Assuming that toxicities are additive, the individual TEas are summed to obtain the cumulative TEa of ,the sample.

Alternative sets of TEFs have been proposed. Table A.2 lists the main competitors. The NATO TEFs are commonly known as *International* or *I-TEFs.* As yet, there appears to be no final consensus on standardized TEFs [34]. The differences are among

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[34] In June 1997, WHO proposed new sets ofTEFs for PCDD/Fs for mammals (including humans), fish and birds. A report is in preparation. (R. van Leeuwen, *pars. comm.).*

TEFs assigned to 1,2,3,7,8-PentaCDF, 1 ,2,3,4,6,7,8-HeptaCDF and 1,2,3,4,7,8,9-HeptaCDF. While differences between cumulative Nordic and I-TEas are often minor, the Safe TEFs yield somewhat higher cumulative sample TEa if the contributions of the three aforementioned PCDFs are prominent.

Although this approach has rapidly become widely accepted for expressing the cumulative toxicity of 2, 3, 7, 8-substituted PCDD/Fs in environmental samples, and further as a basis for setting guidelines and regulations, reservations remain about the methodology. Safe et al. (1995) warn that the assumption of additive toxicity for the 17 PCDD/F congeners has yet to be extensively tested. Moreover, the cumulative sample TEa that was originally conceived as a measure of consumption risk suitable for assessing human milk, foodstuffs, drinking water, etc., has now become routinely applied to nominally inorganic media such as soil and sediments for which the meaning and interpretation are not obvious. Nevertheless, it is often convenient to reduce complex sample data to a single TEa value for comparative purposes, but excessive reporting of only the cumulative TEa renders many reports of limited value.

Table A.2 Proposed TEFs for toxic PCOOs and PCOFs.

| | Abbreviations t | Nordic a | NATO b | Safe C |
|---|---|---|---|---|
| 2,3,7,S- TCOO | 04 | 1.0 | 1.0 | 1.0 |
| 1,2,3,7,8-PeCOO | 05 | 0.5 | 0.5 | 0.5 |
| 1,2,3,4,7,8-HxCOO | 061 | 0.1 | 0.1 | 0.1 |
| 1,2,3,6,7,8-HxCOO | 062 | 0.1 | 0.1 | 0.1 |
| 1,2,3,7,S,9-HxCOO | 063 | 0.1 | 0.1 | 0.1 |
| 1,2,3,4,6,7,8-HpCOO | D7 | 0.01 | 0.01 | 0.01 |
| OCDD | DS | 0.001 | 0.001 | 0.001 |
| 2,3,7,8-TCDF | F4 | 0.1 | . 0.1 | 0.1 |
| 2,3,4,7,8-PeCOF | F51 | 0.5 | 0.5 | 0.5 |
| *1,2,3,7,8-PeCDF* | *F52* | *0.01* | *0.05* | *0.1* |
| 1,2,3,4,7,8-HxCDF | F61 | 0.1 | 0.1 | 0.1 |
| 2,3,4,6,7,8-HxCOF | F62 | 0.1 | 0.1 | 0.1 |
| 1,2,3,6,7,8-HxCOF | F63 | 0.1 | 0.1 | 0.1 |
| 1,2,3,7,8,9-HxCDF | F64 | 0.1 | 0.1 | 0.1 |
| 1,2,3,4, 6, *7,8-HpCDF* | F71 | *0.01* | *0.01* | *0.1* |
| 1,2,3,4, 7, 8, *9-HpCDF* | F72 | *0.01* | *0.01* | *0.1* |
| OCOF | FS | 0.001 | 0.001 | 0.001 |

t used in tables and figures elsewhere in report; a b c

Ahlborg, (1991); Kutz et a!. (1990); Safe (1990).

### A.1.3 Risk Assessment: Sediment Quality Guidelines

The cumulative 2,3,7,8-TCDD TEQ in a sample can be assessed against environmental quality criteria for 2,3,7,8-TCDD. In this report, only sediment criteria are considered. There does yet not appear to 'be a consensus on the most appropriate sediment criteria for 2,3,7,8-TCDD. Most readily available criteria were tentative values published before 1993. Table A.3 lists a set of interim concentrations associated with TCDD risk taken from USEPA (1993). The *Low risk* number effectively implies *no significant toxic effects,* while the *High risk* number implies *severe effects.* The methodology for determining the concentrations involved equilibrium partitioning between water and sediment, and bioaccumulation up the food web. The mammal and bird concentrations are for consumers of aquatic life, generally fish-eating species.
The limited data available at the time found mink to be the most sensitive species.

In the report on the Severnaya Dvina watershed, Yufit and Khetuleva (1994) quoted 1992 German sediment guidelines for 2,3,7,8-TCDD as 1 and 10 pg/g. The source report[35] was unavailable for inspection, but the upper and lower limits presumably correspond approximately to the notion of *Low risk* and *High risk* concentrations as given by the USEPA. The German criteria are likely also tentative, but may better indicate typical European criteria for 2,3,7,8-TCDD in sediment.

Table A.3 Interim sediment concentrations associated with 2,3,7,8-TCDD risk (USEPA, 1993).

| Organism | concentration *pg/g* dw | |
|---|---|---|
| Sediment | Low risk | High risk |
| mamrn,a | 2.5 | 0 |
| l bird | 21 | |
| fish | 6 | |
| | 0 | |
| | 2 | |
| | 5 | |
| | 21 | |
| | 0 | |
| | 10 | |

## A.2 PCBs (Polychlorinated Biphenyls)

The PCB family comprises 209 congeners of form $C_{12}H_xCl_y$ where x :::; 0-9 and y :::; 10-x. Figure A.2 shows the 10 positions labelled 2-6 and 2'-6' where chlorine atoms are substituted for hydrogen atoms on the biphenyl rings to form PCBs. Individual PCB congeners are now commonly identified by the IUPAC [International

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[35] Cited by Yufit and Khetuleva as: Manuscript fOr Entwurt. DIN 38414. Schlamm and Sedimente (Gruppes). Teil. Juni. 1992.

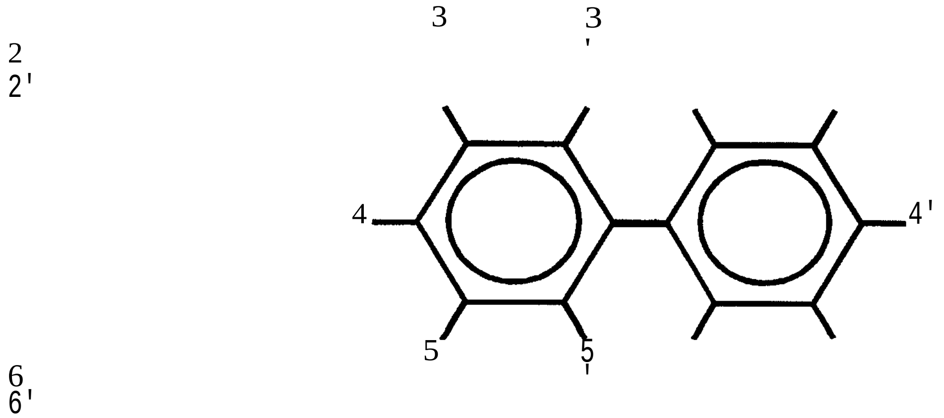

Figure A.2 Polychlorinated biphenyl.

Union of Pure and Applied Chemistry] numbering scheme. Many countries produced PCBs, usually in series of technical mixtures with increasing weight percentages of chlorine atoms. These commercial mixtures were known by national proprietary trade names such as Aroclor, Clophen, Kanechlor, and numerous others. The composition of U.S. Aroclors and German Clophens has been analyzed in detail (Schulz et al., 1989). More information on PCBs can be found in WHO (1993) and Erickson (1997).

Broadly, PCBs can be distinguished by their toxicological effects into two groups: *(1) non-ortho-* and mono-ortha-substituted PCBs, and (2) ortha-substituted PCBs with two or more chlorine atoms in *ortho* positions (Seegal and Schantz, 1994). The *ortho* positions correspond to the 2,6,2', and 6' positions on Figure A.2. The *non-ortho* congeners are also known as *coplanar* PCBs. Certain *non-ortho* and *mono-ortho* PCBs are known to exert dioxin-like toxicological effects and biochemical responses (Safe, 1990, 1991, 1994), while the ortho-substituted PCBs are linked to neurochemical and neurobehavioural effects (Seegal and Schantz, 1994). The particular toxicological risks that PCBs pose to humans remain controversial; however, there seems to be reasonable evidence that PCBs pose grave threats to certain marine mammals (small cetaceans, pinnipeds), piscivorous mammals (mink,-otter) piscivorous birds and other species (Tanabe et al., 1987; Tanabe, 1988; Tanabe, 1989; Giesy et al., 1994a,b). Small cetaceans (dolphins, porpoises), and to a lesser degree pinnipeds, appear to be most at risk as they evidently lack capacity to degrade coplanar PCBs which are highly bioaccumulative in aquatic organisms.

### A.2.1 **PCB** Risk Assessment: Dioxin-like Toxicity

The risk of dioxin-like PCBs can be assessed by estimating the cumulative 2,3,7,8-TeDD equivalents (TEQs) in an environmental sample according to several proposed systems of toxic equivalency factors (TEFs) listed in Table A.4. The cumulative TEQ determined for a sample can then be assessed against environmental criteria for 2,3,7,8-TCDD.

Table A.4 Toxic equivalency factors for dioxin-like PCBs.

| | | TEF systems t | | | |
|---|---|---|---|---|---|
| PCB congener | Structure | Safe 1990 | Safe 1994 | Ahlborg 1992 | WHO/IPCS 1994 |
| 77 | *non-ortho* | 0.01 | 0.01 | 0.0005 | 0.0005 |
| 126 | | 0.1 | 0.1 | 0.1 | 0.1 |
| 169 | | 0.05 | 0.05 | 0.01 | 0.01 |
| 105 | *mono-oltho* | 0.001 | 0.001 | 0.0001 | 0.0001 |
| 114 | | 0.001 | 0.0002 | 0.0005 | 0.0005 |
| 118 | | 0.001 | 0.0001 | 0.0001 | 0.0001 |
| 123 | | 0.001 | 0.00005 | 0.0001 | 0.0001 |
| 156 | | 0.001 | 0.0004 | 0.001 | 0.0005 |
| 157 | | 0.001 | 0.0003 | 0.001 | 0.0005 |
| 167 | | 0.001 | | | 0.00001 |
| 189 | | 0.001 | | | 0.0001 |
| 170 | di-oltho | 0.00002 | | | 0.0001 |
| 180 | | 0.00002 | | | 0.00001 |

t see Ahlborg et al. (1994) for references to all systems.

There is not yet a firm consensus on the most appropriate TEF system for dioxinlike PCBs36. Future revisions may include a TEF for non-ortho PCB 81, and the TEFs for *di-orthb* PCBs 170 and 180 may be abandoned. Of the four systems listed in Table A.4, Safe's 1990 system and the WHOIIPCS 1994 system define the limiting cases. Safe 1990 TEFs yield the highest TEQs, while WHOIIPCS 1994 TEFs assign the lowest. Depending on sample composition, differences between TEQs estimated by the two limiting systems are often small, but may occasionally be large (e.g., see Chapter 5, section 5.5 on Baikal seals).

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36 In June 1997, WHO proposed new sets of TEFs for dioxin-like PCBs for mammals (including humans), fish and birds. A report is in preparation. (R. van Leeuwen, *pers. comm.).*

## A.2.2 PCB Risk Assessment: Environmental Criteria

Selected water and sediment criteria for protection of aquatic life against *total PCBs* are given in Table A.S. These criteria are offered without endorsement to illustrate the typical range of criteria promulgated by environmental agencies. Despite growing recognition and measurement of PCBs as individual compounds, gauging the total PCB content of an environmental sample against *total PCB* criteria continues to be the simplest way to obtain a sense of the general degree of PCB contamination.

Table A.S Selected water and sediment quality criteria for total PCBs.

| Medium | Criterion | Jurisdiction | Source |
|---|---|---|---|
| water | 1 nglL | Ontario | Provincial Water Quality Guideline, OMEE (1994) |
| water | 14 nglL | USA | Chronic criterion, USEPA (1990) |
| sediment | *10 nglg* | Ontario | No Effect Level, Persaud et al. (1992) |
| sediment | *70 nglg* | Ontario | Lowest Effect Level, Persaud et al. (1992) |
| sediment | *120 nglg* | USA | Recommended threshold, Ingersoll et al. (1992) |

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