Organic compounds and heavy metals detected in wastewaters and associated sediments collected in and around Cepruss pulp and paper mill, Kaliningrad area, Russia.

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1 EXECUTIVE SUMMARY

Three samples of wastewater, and two of associated channel sediments, were collected from the Cepruss pulp and paper mill (using elemental chlorine as a bleaching agent), Kaliningrad area, Russian Federation, during January 2001:

- Two samples of wastewater discharging from the southern boundary of the mill site directly to the Pregol River
- One sample of wastewater from channel on the northern boundary of the site, discharging ultimately to the Pregol River
- One sample of sediment from the channel on the northern boundary
- One sample of sediment from a channel immediately downstream from the discharge from the bleaching plant, located in the north west part of the mill site.

Typically for wastes arising from pulp and paper plants, all samples were characterised by the presence of complex mixtures of organic chemical contaminants, a relatively small proportion of which in each case could be reliably identified. For the three wastewater samples, between 47 and 79 individual compounds were found to be present, although only 6-10 compounds could be identified with any degree of reliability in each case. Of those substances identified, hydrocarbons, organosulphur compounds, phenols and terpenoids predominated, as may be expected for discharges from a pulp mill. Heavy metal contaminants were not a substantial component of any of the three wastewaters sampled.

A number of chlorinated organic compounds, primarily chlorinated cymenes, were isolated from the sediment sample collected from the channel on the northern boundary of the site. Sediment samples may give a more integrated representation of the nature of discharges over time, and tend to accumulate the less water soluble components of the wastes discharged to water. Chlorinated cymenes are one of many groups of contaminants typically arising from pulp and paper mills using chlorine or chlorinated compounds as bleaching agents.

Similar chlorinated compounds were also found in the second sediment sample, from a channel immediately downstream from the bleach line, with chlorinated cymenes again predominating. Of a total of over 100 organic compounds resolved, only approximately 20% could be identified. Selective ion monitoring also confirmed the presence of a number of chlorinated biphenyl congeners, including PCB 138, 153 and a number of tetra- and penta-chlorinated isomers. Such compounds, including the PCBs, may arise directly as by-products of the use of chlorine to bleach the pulp. It is possible, however, that the PCBs may arise in part from the recycling of PCB-containing, carbon-free copy paper as part of the

feedstock to the mill. Further information regarding the processes and materials employed at the mill would be necessary in order to identify the source.

The results of this limited survey confirm that the Cepruss pulp and paper mill is acting as a source of organochlorine contaminants, among other compounds, to the surrounding environment. Over time, these compounds are likely to become more widely distributed in the Pregol River downstream from the mill where they may persist, accumulate through the food chain and exert adverse impacts on the physiology and ecology of riverine species. The generation of chlorinated compounds in wastes could be avoided if the plant were to convert to totally chlorine-free (TCF) pulp bleaching processes. Although this conversion would not avoid the generation of many non-chlorinated toxic compounds from the pulped material, it would, nevertheless, ultimately allow the plant to operate in a closed-loop configuration, (i.e. recycling liquid wastes back through the process) thereby avoiding the discharge of such compounds to the environment (see Johnston *et al.* 1997).

2 SAMPLING PROGRAM

During January 2001, five samples were collected in association with Cepruss pulp and paper mill, Kaliningrad area, Russia. The samples included three wastewaters and two sediments. Descriptions of the sample sites are presented in Table 1.

2.1 General Sampling Procedures

All samples were collected and stored in pre-cleaned glass bottles that had been rinsed thoroughly with nitric acid and analytical grade pentane in order to remove all heavy metals and organic residues. Sediment and solid waste samples were collected in 100ml bottles, and the water samples were collected in 1-litre bottles. All sediment, solid waste and water samples were immediately sealed and cooled upon collection. The samples were returned to the Greenpeace Research Laboratories for analysis. Detailed description of sample preparation and analytical procedures are presented in Appendix 1.

2.2 Sample Descriptions

Sample Number	Sample Description	Sample Location
Direct wastewater discharge from the mill into Pregol River (to the South from mill)		
BT01010	Wastewater	First discharge pipe from Cepruss pupl & paper mill directly into Pregol river. This discharge is located closer to the shipyard about 50 meters upstream from the second discharge BT01011.
BT01011	Wastewater	Second discharge pipe from mill directly into Pregol river.
Upper wastewater channel located on the North from the mill		
BT01008	Wastewater	Channel receiving mixed wastewater from northern section of mill through several pipes. The channel discharges to the Pregol River, downstream from the mill.
BT01009	Sediment	Collected adjacent to sample point BT01008
Stream receiving wastewater from the mill's bleaching facility		
BT01012	Sediment	Channel receiving wastewater from chlorine bleaching facility. The channel joins the waste channel which runs around the northern boundary of the plant (see BT01008).

Table 1. Description of the samples collected in and around Cepruss pulp mill, Kaliningrad area, Russia, 2001

3 RESULTS AND DISCUSSION

The results of the organic screen analysis are presented in Table 2, including a breakdown of the groups of organic compounds reliably identified in the samples. Heavy metals analysis results are presented in Table 3.

For more information on the common sources, environmental behaviour and toxicological outlines for key pollutants detected during this study, see Appendices 2 and 3.

3.1 Organic analysis

Sample Number	**BT01010**	**BT01011**	**BT01008**	**BT01009**	**BT01012**
Sample type	Waste Water	Waste water	Waste water	Sediment	Sediment
No. of organic compounds isolated	59	47	79	109	50
No. of organic compounds reliably identified	10	6	9	23	14
Groups of organic compounds reliably identified					
ORGANOHALOGENS					
Benzene, 1,4-dichloro-				*	*
Benzene, 2-chloro-1-methyl-4-(1-methylethyl)-				1	1
Benzene, 5-chloro-1-methyl-2-(1-methylethyl)-				1	1
Benzene, 2,3-dichloro-1-methyl-4-(1,1-dimethylethyl)-				1	1
Benzene, 2,5-dichloro-1-methyl-4-(1,1-dimethylethyl)-				1	1
Tetrachlorobiphenyl isomers					*(4)
Pentachlorobiphenyl isomers					*(9)
PCB-138					*
PCB-153					*
PAHs					
Naphthalene and/or its derivatives	2	1	2	2	2
Phenanthrene and/or its derivatives		2	1		
PENOLIC COMPOUNDS					
Phenol, 2-methoxy-			1		
Phenol, 2-methoxy-4-(1-propenyl)-			1		
Phenol, 2-methoxy-4-propyl-			1		
Phenol, 2-methyl-5-(1-methylethyl)-	1		1		
Phenol, 3-propyl-		1	1		
ORGANOSULPHUR COMPOUNDS					
1,2,3,5,6-Pentathiepane	1				
1,2,4,5-Tetrathiane	1				
ALIPHATIC HYDROCARBONS					
Linear				17	4
Cyclic	1				
MISCELLANEOUS COMPOUNDS					
DBP	1				
Alkyl benzenes	1	1	1	1	1
Terpenoids	2	1			

*Table 2. Organic analytical results. For groups of organic compounds, the number given is the number of compounds reliably identified; *(x) signifies the number of compounds identified at trace levels using a selective ion monitoring (SIM) method. Cepruss pulp mill, Kaliningrad area, Russia, 2001.*

Both wastewater samples BT01010 and BT01011 collected from two pipes discharging wastewater directly into the Pregol River contained a range of organic compounds including PAHs, phenolic compounds, alkyl benzene and terpenoids. Additionally, wastewater sample BT010010 had organosulphur compounds, a phthalate ester and aliphatic cyclic hydrocarbon. Organochlorine compounds have not been detected in these samples; however, it is known that pulp mills use large volumes of water through technological processes and this may result in very high dilution of contaminants in the discharging wastewater.

A further sample of the wastewater (BT01008) collected from the waste channel at the northern boundary of the site had similar composition in terms of organic compounds, but with higher number of phenolic compounds detected. Zaror *et al* (2001) reported that effluents from the kraft cellulose bleaching present a high content of phenolic compounds, generated by partial oxidation of lignin, forming soluble aromatic derivatives. Many of these aromatic compounds are toxic and poorly biodegradable, affecting the removal efficiency of conventional biological treatment systems. Again, organochlorine compounds were not found in this sample, though they may well have been present in the wastewaters at very low concentrations (i.e. below limits of detection for the techniques employed).

Nevertheless, several organochlorine compounds, commonly detected in wastes of the pulp mills using elemental chlorine as a bleaching agent (Ranito 1992, 1995, 1996; Paasivirta *et al* 1993), were found in sediment samples, BT01009 and BT01012. This may support suggestion that organochlorine compounds have been introduced into receiving waters from the Cepruss mill with effluents. Both sediments contained two isomers of monochloromethyl(1-methylethyl)benzene and two isomers of dichloromethyl(1-methylethyl)benzene, also known as monochlorocymenes and dichlorocymenes respectively. Chlorinated cymenes have been found to be the most abundant persistent chlorohydrocarbons in pulp mill sludge (Paasivirta *et al* 1993). Additionally, they have been found to bioaccumulate in fish and mussels (Rantio 1992). More recent investigations of Rantio (1995 & 1996) showed that the levels of chlorocymenes in discharges decreased sharply for the mills that replaced chlorine gas with chlorine dioxide in bleaching.

Sediment sample BT0012 contained fifteen isomers of polychlorinated biphenyls (PCBs) detected at trace levels including four tetra-, nine penta-, one hexa- and one heptachlorobiphenyl. The source of PCBs in this sample is unclear and needs to be further investigated. However, some PCBs congeners have also been detected in pulp mill effluents and particles, and in fish and mussels caught in watercourses downstream of pulp mill (Paasivirta *et al* 1993, Rantio 1992). Operation of the Cepruss pulp mill might be one of the possible sources of these highly toxic and persistent organochlorines in the stream receiving wastes from the mill's bleaching facility. The possibility that PCBs may be arising from the inclusion of old carbon-free copy paper as part of the feedstock of the mill deserves investigation.

PCBs are one of the 12 groups of chemicals targeted for global action under the developing UNEP Convention (UNEP 1995 & 1997), on the basis of their toxicity, persistence, and ability to bioaccumulate and widespread distribution in the environment. Toxic effects following exposure to PCBs include liver damage, suppression of the immune system and various adverse effects on reproduction, development and behaviour (Safe 1993, Rice 1999). Some of these effects may be mediated through interference with the endocrine system (Brouwer *et al* 1999), although the mechanisms of PCB toxicity are complex and diverse.

3.2 Heavy metals analysis

Sample Number	**BT01010**	**BT01011**	**BT01008**	**BT01009**	**BT01012**
Concentration	ug/l	ug/l	ug/l	mg/kg dry weight	mg/kg dry weight
Cadmium	<10	<10	<10	1	2
Chromium	<20	<20	<20	19	17
Cobalt	<20	<20	<20	10	7
Copper	<20	<20	<20	356	108
Lead	59	<30	<30	143	30
Manganese	298	325	476	541	154
Mercury	<1	<1	<1	0.928	0.10
Nickel	<20	<20	<20	12	13
Zinc	14	16	23	557	212

Table 3. Heavy metal analysis results. Cepruss pulp & Paper mill, Kaliningrad area, Russia, 2001.

Wastewater samples from the two pipes which discharge directly to the River Pregol (BT01010 & BT01011) did not contain any of the metals analysed for at concentrations above those generally found in uncontaminated freshwaters. Similarly, the wastewater from the channel on the northern boundary of the plant, that leads ultimately to the River Pregol (BT01008), did not contain any of the metals analysed for above these concentrations. The sediment that was collected from this channel did, however, contain a number of metals at significant concentrations.

The concentrations of copper, lead, mercury and zinc in this sediment were somewhat above those typically found in uncontaminated sediments; 45-50 mg/kg for copper (Salomons and Forstner 1984), 20-30 mg/kg for lead (USPHS 1997), 0.2-0.35 mg/kg for mercury (Salomons and Forstner 1984) and up to 100mg/kg for zinc (USPHS 1997, Salomons and Forstner 1984).

The highest elevation found was for copper, which at 356 mg/kg is approximately 7 times the concentration that can be found in uncontaminated sediments. The concentrations of lead and zinc were elevated by approximately 5 times, while that of mercury was elevated by approximately 3 times. The elevation of the concentrations of these metals in the sediment at this location suggest that wastewater discharged *via* this channel have at some time (perhaps periodically) contained higher concentrations of these metals than those found in the one wastewater sample collected for this study (BT01008). Copper and zinc are well know constituents of discharges from pulp and paper mills (Skipperud *et al.* 1998)

The sediment (BT01012) collected from the channel which receives wastewater from the chlorine bleaching facility contained only copper and zinc at significant concentrations. The concentration of copper (108 mg/kg) and zinc (212 mg/kg) are both approximately 2 times the concentration that can be found in uncontaminated sediments.

4 CONCLUSIONS

Chlorinated cymenes have been found in two sediment samples from the watercourses receiving effluents from the Cepruss pulp mill. Additionally, polychlorinated biphenyls have been detected at trace levels in one of the sediment samples. The presence of these toxic and persistent chemicals can be linked to the operation of the mill that uses chlorine gas in bleaching.

The generation of chlorinated compounds in wastes could be avoided if the plant were to convert to totally chlorine-free (TCF) pulp bleaching processes. Although this conversion would not avoid the generation of many non-chlorinated toxic compounds from the pulped material, it would, nevertheless, ultimately allow the plant to operate in a closed-loop configuration (i.e. recycling liquid wastes back through the process), thereby avoiding the discharge of such compounds to the environment (see Johnston *et al.* 1997).

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APPENDIX 1 ANALYTICAL METHODOLOGY

A1.1 Organic analysis

A1.1.1 Preparation of samples for organic screen analysis

All solvents were of High Purity Grade (PRAG or low haloform). Glassware used in extraction and clean up procedures was cleaned in detergent, rinsed with tap water and deionised water, dried in the oven overnight at 105^0C, and rinsed three times with low haloform pentane.

A1.1.1.1 Solid Samples

In preparation for analysis of extractable organic compounds, approximately 30g (wet weight) was weighed and transferred to a clean 100 ml glass bottle. Samples were spiked with deuterated naphthalene (an internal standard) at a concentration of 4.7 mg/kg. 15ml of pentane was added, followed by 5ml of acetone. All samples were then sonicated for 2 hours.

Extracts were decanted, filtered through a pre-cleaned hydrophobic phase separator filter and collected in reagent tubes. The samples were then acidified to pH 2 with 10% nitric acid. Following this, a second portion of 15ml of pentane was added, followed by 5ml of acetone and the extraction procedure repeated. Finally, both extracts obtained for each sample were combined and evaporated to a volume of approximately 3ml. 3ml of iso-propanol and 3ml of fresh prepared TBA-reagent (mixture of 3% tetrabutylammonium hydrogen sulfate and 20% sodium sulfite anhydrous in deionised water) were added to concentrated extract and the mixture shaken for 1 min. After shaking, 20ml of deionised water was added to reagent tube and the phases were allowed to separate. Finally, the organic layer was transferred with a Pasteur pipette into a pentane pre-washed Florisil column. The compounds were eluted with a 95:5 mixture of pentane: toluene, and the elluent evaporated down to a volume of 2 ml under a stream of analytical grade nitrogen. 1-Bromonaphthalene was then added at a concentration of 10mg/l to provide an indication of GC/MS performance.

A1.1.1.2 Aqueous Samples

Prior to the extraction, samples were spiked with deuterated naphthalene (an internal standard) at a concentration of 10mg/l. 20ml of pentane was added, and the sample agitated for 2 hours on a bottle roller to maximise contact between solvent and sample.

After separation of the phases, the solvent extract was filtered through a pre-cleaned hydrophobic phase separator filter and collected in a pre-cleaned reagent tube. The aqueous sample was acidified to pH 2 with 10% nitric acid, a second portion of 20ml pentane was added and the extraction procedure repeated. Both extracts were combined and cleaned up as described above for solid samples.

A1.1.2 Chromatographic Analysis

Organic compounds were identified qualitatively using Gas Chromatography Mass Spectrometry (GC-MS). Instrumentation was a Hewlett Packard (HP) 5890 Series II gas chromatograph, interfaced with a HP Chem-Station data system and linked to a HP 5972 Mass Selective Detector operated in scan mode. The identification of compounds was carried out by computer matching against a HP Wiley 275 library of 275,000 mass spectra combined with expert interpretation. Also, all extracts were analysed using selective ion monitoring (SIM) method against two standard solutions. The lists of compounds contained in Standard I and Standard II are presented below. All individual standards were obtained from Sigma Aldrich Co. Ltd., Supelco, UK. Additionally, samples were analysed using SIM method against PCBs standard mixture Aroclor 1254, obtained from Chem Service Inc., UK.

Compound	**Ions to monitor**
Benzene, 1,3-dichloro-	146, 148, 111, 75
Benzene, 1,4-dichloro-	146, 148, 111, 75
Benzene, 1,2-dichloro-	146, 148, 111, 75
Benzene, 1,3,5-trichloro-	180, 182, 145, 74
Phenol, 2,4-dichloro-	162, 164, 63, 98
Benzene, 1,2,4-trichloro-	180, 182, 145, 109
Benzene, 1,2,3-trichloro-	180, 182, 145, 109
Dichlorvos	109, 185, 79, 47
Benzene, 1,2,3,5-tetrachloro-	216, 214, 218, 179
Benzene, 1,2,4,5-tetrachloro-	216, 214, 218, 179
Benzene, 1,2,3,4-tetrachloro-	216, 214, 218, 179
Benzene, pentachloro-	250, 252, 248, 215
alpha-HCH	181, 183, 219, 217
Benzene, hexachloro-	284, 286, 282, 249
Simazine	200, 215, 202, 173
beta-HCH	181, 183, 219, 217
gamma-HCH	181, 183, 219, 217
delta-HCH	181, 183, 219, 217
o,p'-DDE	246, 248, 318, 176
p,p'-DDE	246, 318, 246, 316
o,p'-DDD	235, 237, 165, 199
p,p'-DDD	235, 237, 165, 199
o,p'-DDT	235, 237, 165, 199
p,p'-DDT	235, 237, 165, 199

Table A.1.1 List of compounds in the Standard I used for SIM analysis

Results are reported as either reliably or tentatively identified. Match qualities of 90% or greater against HP Wiley 275 library or identification confirmed against standard compounds (using retention times and mass-spectra obtained during calibration) are assumed to give reliable identifications. Tentative identification refers to qualities between 51% and 90% against HP Wiley 275 library only. Analytes yielding match qualities of 50% or less are assumed to be unidentified.

Compound	Ions to monitor
Phenol, 2-chloro-	128, 64, 92, 39
Phenol, 2-methyl-	108, 79, 90, 51
Phenol, 3-methyl- and 4-methyl-	108, 107, 79, 77
Phenol, 2,5-dichloro-	162, 164, 63, 99
Phenol, 2,3-dichloro-	162, 126, 63, 99
Phenol, 4-chloro-	128, 65, 130, 100
Phenol, 2,6-dichloro-	162, 164, 63, 98
Butadiene, hexachloro-	225, 190, 260, 118
Phenol, 2,3,5-trichloro-	196, 198, 160, 97
Phenol, 2,4,5-trichloro-	196, 198, 97, 132
Phenol, 3,5-dichloro-	162, 164, 99, 63
Phenol, 2,3,6-trichloro-	196, 198, 97, 132
Phenol, 3,4-dichloro-	162, 164, 99, 63
Atrazine	200, 215, 202, 173
Phenol, pentachloro-	266, 268, 264, 165
Chlordane I	373, 375, 272, 237
Chlordane II	373, 375, 272, 237
PCB-153	360, 362, 290, 218
PCB-138	360, 362, 290, 292
PCB-180	394, 396, 324, 252

Table A.1.2 List of compounds in the Standard II used for SIM analysis

A1.2. Heavy Metal Analysis

A1.2.1. Preparation of samples for heavy metal analysis

All chemicals were of High Purity Aristar Grade. All glassware was cleaned in detergent, rinsed with tap water and deionised water, soaked in 10% nitric acid overnight, rinsed with deionised water and dried in an oven.

A1.2.1.1. Solid Samples

Samples were air dried until weighing readings became constant (approx. 5 days). They were then crushed using a pestle and mortar until homogenous and sieved through a 2-mm mesh.

0.5 g of sample was weighed into a glass 100 ml boiling tube and to this 10 ml of deionised water was added, followed by 7.5 ml of concentrated hydrochloric acid and 2.5 ml of concentrated nitric acid. The samples were digested at room temperature overnight prior to being placed onto a Gerhardt Kjeldatherm digestion block (40 space) connected to a Gerhardt Turbosog scrubber unit (filled with 10% w/v sodium hydroxide). The samples were then refluxed at 130°C for four hours.

After cooling to ambient temperature, the digests were filtered into volumetric flasks, diluted with deionised water, made up to a volume of 50 ml and mixed. A Standard Reference Material, BCR-143 (trace elements in a sewage sludge amended soil), certified by the Commission of the European Communities, Brussels, and a blank sample, were prepared with the batch of samples. All were prepared in 15% v/v hydrochloric acid and 5% v/v nitric acid.

A1.2.1.2. Aqueous samples

On arrival, 100ml of sample was transferred to a clean glass bottle and acidified with nitric acid (10% v/v). 50 ml of this solution was subsequently transferred to a 100ml boiling tube, placed onto the Gerhardt Kjeldatherm digestion block, and refluxed at 130°C for four hours. After cooling to ambient temperature, the digests were filtered into volumetric flasks, diluted with deionised water, made up to a volume of 50 ml and mixed.

A1.2.2. Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

Following preparation, samples were analysed by ICP-AES, using a Varian Liberty-100 Sequential Spectrometer. The following metals were quantified directly: manganese, chromium, zinc, copper, lead, nickel, cobalt and cadmium. A multi-element instrument calibration standard was prepared at a concentration of 10 mg/l, matrix matched to the samples (i.e. in 15% v/v hydrochloric acid and 5% v/v nitric acid). The calibration was validated using a quality control standard (8 mg/l), prepared internally from different reagent stocks. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed.

Mercury (Hg) was determined using Cold Vapour Generation ICP-AES. Hg (II) was reduced to Hg (0) i.e. a vapour, following reduction of the samples with sodium borohydride (0.6% w/v), sodium hydroxide (0.5% w/v) and hydrochloric acid (10 molar). The vapour was carried in a stream of argon into the spectrometer. Two calibration standards were prepared, at 10 ug/l and 100 ug/l, matrix matched to the samples (i.e. in 15% v/v hydrochloric acid and 5% v/v nitric acid). The calibration was validated using a quality control standard (80 ug/l), prepared internally from different reagent stock. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed.

APPENDIX 2 TOXICOLOGICAL OUTLINES FOR KEY COMPOUNDS

A.2.1 Polychlorinated biphenyls (PCBs)

Polychlorinated biphenyls are a group of synthetic organic chemicals that contain 209 individual compounds (known as congeners) with varying harmful effects. There are no known natural sources of polychlorinated biphenyls in the environment. PCBs are either oily liquids or solids, and are colourless to light yellow in colour. PCBs enter the environment as mixtures containing a variety of individual components and impurities.

The polychlorinated biphenyls have been used in a wide variety of applications, including transformer oils, hydraulic fluids, plasticisers, 'kiss-proof' lipsticks and carbonless copy papers. They have also been used in capacitor dielectrics, heat transfer fluids, lubricating and cutting oils, and in paints and printing inks (ATSDR 1997).

PCBs have always been sold as technical mixes rather than individual chemicals. de Voogt & Brinkman (1989) list some 46 trade names used for PCBs and PCB-containing products. Of these, the Aroclor range manufactured by the American company Monsanto was probably the most widely used. The most important PCB applications in tonnage terms were transformer oils and capacitors (de Voogt & Brinkman 1989). In transformer oils, the PCBs were mixed with chlorobenzenes (mainly trichlorobenzenes and tetrachlorobenzenes) as solvents (Swami *et al*. 1992, de Voogt & Brinkman 1989). PCBs are also synthesised as by-products in processes ranging from incinerators (USEPA 1998, Ballschmiter *et al.* 1989, Alcock *et al.* 1998) to metallurgical processing (Knutzen & Oehme 1989, Alcock *et al.* 1998, Thiesen *et al.* 1993) to dye manufacturing (USEPA 1998).

PCBs can be absorbed through the skin as well as through ingestion and inhalation. For the general population today, food is the primary source, though dermal exposure may be dominant amongst those directly handling PCBs or PCB-contaminated materials (Lees *et al*. 1987).

Kidney cancer has been reported in workers with known exposure to PCBs although insufficient data are available for statistical analysis and more research is called for (Shalat *et al*. 1989). In a review of epidemiological PCB research, cancer of the kidney and skin were marginally significant but the reviewers regarded the overall picture as inconclusive (Longnecker *et al*. 1997). Exposure of “clean” PCBs in an occupational setting exerts effects on the human CNS, with symptoms such as headaches, lassitude and slowed nerve signals (Rogan & Gladen 1992).

In a review of PCB toxicity, Safe (1984) lists the following symptoms of PCB toxicity: enzyme induction, decreased vitamin A levels, lymphoid involution, thymic and splenic atrophy, immunosuppression, chloracne, alopecia, oedema, hyperkeratosis, blepharitis, hyperplasia of the epithelial lining of the extrahepatic bile duct, the gall bladder and urinary tract, hepatomegaly and liver damage including necrosis, haemorrhage, hepatotoxicity (altered porphyrin metabolism), tumour promotion, altered levels of steroid and thyroid hormones, reproductive toxicity including menstrual irregularities, reduced conception, early abortion, excessive menstrual and postconceptual haemorrhage, anovulation, testicular atrophy, decreased spermatogenesis, teratogenesis and developmental toxicity. In addition, low levels of PCBs have caused behavioural impairment in monkeys (Rice 1999).

Aroclors 1221, 1254 and 1268 all reduced in vitro fertilisation rates in mice, with PCB 1254 being the most potent mixture (Kholkute *et al.* 1994). Aroclor 1254 also compromised the immune response of earthworms (Roch & Cooper 1991).

Although much of the toxicological research relates to technical mixtures of PCBs, individual congeners have different effects and act through several different mechanisms. Certain of the PCBs are called coplanar since the molecules can take of a flattened shape and these can act in the same was as the dioxins.

Some congeners, or their metabolites, exhibit endocrine disruption, including both oestrogenicity and anti-oestrogenicity. In general, ortho-substituted PCBs are oestrogenic whereas coplanar PCBs are anti-oestrogenic, as is 2,3,7,8-TCDD (Li *et al*. 1994). According to a recent review (Brouwer *et al.* 1999), PCBs may affect not only the oestrogen system, but also the androgen system, the thyroid hormone system, the retinoid system, the corticosteroid system and several other endocrine pathways. In addition, effects on the thyroid system on wild populations of fish-eating birds and captive seals have been correlated with PCB exposure (Brouwer *et al*. 1999).

Ortho-substituted (non-dioxin-like) PCBs have been found to have the greatest effects on neurochemical function. They were found to reduce dopamine synthesis and it was further established that the effects were caused by the congeners rather than their metabolites. 2,2'-dichlorobiphenyl (PCB 4) was the most potent congener (Seegal & Shain 1992).

The dioxin-like PCB 77 (3,3',4,4'-TeCB) also caused long-term changes in behavioural and neurochemical changes in laboratory animals, including alterations in dopamine function. This congener, however, did not accumulate in brain tissue in the same way as some ortho-substituted congeners, indicating that it operates via a second mechanism, or that it is a metabolite which is the active agent (Seegal & Shain 1992).

The extensive body of information concerning the global cycling of PCBs has been accumulated in response to concerns about the environmental impact of these chemicals. PCBs are highly persistent. Although there is evidence of biodegradation in contaminated sediments (see: Brown & Wagner 1989) and some marine mammals appear to be able to selectively degrade some of the lower chlorinated congeners (Boon *et al.* 1987), the detoxification potential of these processes would appear to be rather limited. Indeed, Cummins (1988) has suggested that unless further escape of PCBs is prevented then the eventual extinction of marine mammals is a very real possibility.

Levels of PCBs in biological material may be several orders of magnitude higher than ambient. PCBs are bioconcentrated to a factor of 6 000 for fish and 47 000 for invertebrates (Jones *et al.* 1988). Train (1979) reports bioconcentration factors of between 2 500 and 100 000.

The effects of chronic exposure to PCBs in marine mammals has been found to include physical deformity and impairment of reproductive success (Reijnders 1986). More recently, they have been implicated in the outbreaks of disease amongst populations of seals and dolphins (see review by Gilbertson 1989) suggesting that they may have a disruptive influence on immune capability.

The PCBs are controlled under most of the international legal instruments relating to organochlorines, *inter alia*, the Barcelona, Helsinki, Basel, Bamako, Rotterdam OSPAR and LRTAP Conventions and the International Joint Commission on the Great Lakes. In addition, PCBs are targeted for global production ban under the UNEP POPs Convention which will be signed in Stockholm in May 2001. Within the EC, applications for the PCBs were first restricted by directive 76/769/EEC, which deals with the marketing and use of dangerous substances and preparations (EC 1976). This directive, and its amendment (EC 1991), restricted the applications of PCBs and their replacements, the polychlorinated terphenyls (PCTs).

EC regulations on disposal of PCBs, as set out in a 1996 Directive, dictate that the PCB phaseout should be completed by 2010. Further, national enabling legislation should have been emplaced by March 1998. Several countries have missed this deadline and in mid 1999, the EC initiated action through the European Court of Justice against Germany, Greece, Spain, Portugal and UK for failing to implement the directive (ENDS 1999).

The US Toxics Substances Control Act (TOSCA) designates wastes containing greater than 50ppm PCBs are designated as hazardous (Rogan 1995).

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