Identification of organic pollutants in samples collected from Celulosa Argentina Capitan Bermudez and Petroquimica Capitan Bermudez, Parana River, Santa Fe Province, Argentina, 1998.

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Sample description

In May and September 1998, seven samples of materials associated with the pulp and paper plant Celulosa Argentina Capitan Bermudez, and the chlorine plant Petroquimica Capitan Bermudez, were collected. Both plants are located in the district of Capitan Bermudez, in the province of Santa Fe.

Two samples of wastewater (LA8076 and LA8078) were collected from two pipes discharging into the Parana River. Both pipes belonging to the Celulosa Argentina Capitan Bermudez plant. In addition, one sample of solid waste (LA8007) was collected from under one of the pipes (see LA8076). Sample LA8040 was collected from the Parana River, at a location where unidentified discharge was observed.

Two samples of wastewater (LA8039 and LA8074) were collected from a pipe belonging to the chlorine company Petroquimica Capitan Bermudez. LA8039 was collected in May 1998, with LA74 collected in September. In addition, one sample of sediment was collected (LA8075) immediately below the discharge pipe.

Sampling methodology

All samples were collected and stored in glass bottles, previously rinsed with pentane, to remove all organic residues. Solid samples were collected with wooden spoons, previously rinsed with deionised water, nitric acid and pentane, and stored in 100ml glass Duran bottles. Aqueous samples were collected in 1-litre bottles, rinsed three times with the sample before the final collection. Bottles were filled completely, ensuring no air bubbles were present. They were then transported to the Greenpeace Research Laboratory, kept cold during transit, and refrigerated immediately on arrival. Organic compounds were identified qualitatively using Gas Chromatography Mass Spectrometry (GC-MS).

Organic Screen Analysis

All solvents were of High Purity Grade (PRAG or low haloform). Glassware used in extraction and cleaning 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.

Solid Samples

For each sample, approximately 30 g (wet weight) was weighed and transferred to a clean 100 ml glass bottle. Samples were spiked with deuterated (d8) naphthalene (an internal standard) at a concentration of 4.7 mg/kg. 15 ml of pentane was added, followed by 5 ml 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. They were then acidified to pH 2 with 10% nitric acid. Following this, a second portion of 20 ml pentane was added and the extraction procedure repeated. Finally, both extracts obtained for each sample were combined and evaporated to a volume of approximately 3 ml. The concentrated extract was cleaned through Florisil column, eluted with a 95:5 mixture of pentane:toluene, and evaporated down to a volume 2 ml under a stream of clean nitrogen. 1-bromonaphthalene was then added as a marker.

In addition, approximately 2g of sample were transferred to a 20ml Headspace vial for Volatile Organic Compound (VOC) analysis.

Aqueous Samples

Prior to the extraction, samples were spiked with deuterated (d8) naphthalene (an internal standard) at a concentration of 150 ug/l. 20 ml of pentane were 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 hydrophobic phase separator filter and collected in pre-cleaned reagent tube. The aqueous sample was acidified to pH 2 with 10% nitric acid, a second portion of 20 ml pentane was added and the extraction procedure repeated. The same clean up procedure, as described above, was employed.

Chromatographic Analysis

Samples were analysed using a Hewlett Packard (HP) 5890 Series II gas chromatograph, interfaced with a HP ChemStation 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 270,000 mass spectra. Results are reported as a list of those compounds reliably and tentatively identified. Match qualities of 90% or greater are assumed to give reliable identifications; tentative identification refers to qualities between 51% and 90%. Analytes yielding match qualities of 50% or less are assumed to be unidentified.

Volatile organic compounds (VOC) were analysed using a Hewlett Packard (HP) 5890 Series II gas chromatograph with HP 19395A Head-Space Sampler, interfaced with a HP Chem-Station data system, and linked to a HP 5970 Mass Selective Detector operated in scan mode.

Results

Results are given in Table 1 and 2.

Table 1 shows the groups of organic compounds reliably identified in each of the samples collected. By far the most abundantly identified group were the organohalogens, reliably identified in five of the samples (LA7074, LA8075, LA8077, LA8078 and LA8039). These included chlorinated butadienes, chlorinated benzenes, chlorinated phenols and guaiacols, and the more volatile chlorinated alkenes and alkanes. In addition, the phenol derivative, methoxyphenol was reliably identified in sample LA8078, along with two organo-sulphur compounds, dimethylsulphide and 2-formyl-5-methyl-thiophene.

Groups of compounds identified to better than 90%	**Number of samples**	**Sample codes**
Trichlorobutadienes	1	LA8075
Tetrachlorobutadienes	1	LA8075
Pentachlorobutadienes	1	LA8075
Hexachlorobutadienes	1	LA8075
Monochlorobenzenes	1	LA8075
Dichlorobenzenes	1	LA8075
Trichlorobenzenes	1	LA8075
Hexachlorobenzene	1	LA8075
Dichlorophenols	1	LA8078
Trichlorophenols	1	LA8078
Dichloroguaiacols	1	LA8078
Trichloroguaiacols	1	LA8078
Tetrachloroguaiacols	1	LA8078
Trichloroethene	2	LA8074, LA8075
Tetrachloroethene	2	LA8074, LA8075
Carbon tetrachloride	1	LA8074
Chloroform	2	LA8077, LA8078
Bromoform	2	LA8074, LA8039
PHENOL DERIVATIVES		
Methoxyphenol	1	LA8078
METHOXYBENZENES	1	LA8078
TERPENOIDS	1	LA8078
ORGANO-SULPHUR COMPOUNDS		
Thiophene derivatives	1	LA8078
Alkylsulphides	1	LA8078
ALIPHATIC HYDROCARBONS	4	LA8074, LA8075, LA8077, LA8078

Table 1 Groups of organic compounds reliably identified in samples collected from Petroquimica Capitan Bermudez and Celulosa Capitan Bermudex, Argentina 1998.

Table 2 shows the number and types of organic compounds reliably identified in each of the samples. With the numbers of reliably identified compounds ranging from zero (LA8040 and LA8076) to 38% (LA8074).

Sample Code	Sample Type	Compounds isolated	Reliably identified	Halogenated compounds
LA8039	Effluent	16	1 (6%)	1
LA8040	River water	2	0	0
LA8074	Effluent	13	5 (38%)	4
LA8075	Sediment	45	15 (33%)	12
LA8076	Effluent	11	0	0
LA8077	Solid waste	18	5 (28%)	1
LA8078	Effluent	138	23 (17%)	9

Table 2 Results of organic screening analysis, Petroquimica Capitan Bermudez and Celulosa Capitan Bermudez, Argentina 1998

Discussion

1. Celulosa Capitan Bermudez

Three samples were collected from the Celulosa Capitan Bermudez plant. Two samples of effluent collected from different pipes (LA8076 and LA8078), and one sample of solid waste, LA8077.

Sample LA8076 did not contain any reliably identified organic compounds, however sample LA8078 contained a large number of chlorinated methoxyphenols (also known as chlorinated guaiacols), dichloro- and trichlorophenols, methyoxyphenol, alkylbenzenes, dimethylsulphide, 2-formyl-5-methyl-thiophene, and a number of long chain hydrocarbons. With sample LA8077 containing a number of long chain hydrocarbons along with the volatile organic compound, chloroform (trichloromethane).

The compounds identified in sample LA8078 are typical of those found in effluents from pulp and paper plants using elemental chlorine, or chlorine-containing reagents, e.g. hypochlorite, chlorine dioxide (Smith et al. 1994).

Chlorinated Guaiacols

Six individual chlorinated guaiacols were reliably identified in sample LA8078, along with one unchlorinated guaiacol. Due to their resistance to degradation, the chlorinated guaiacols are among the most persistent organic chemicals. They are commonly formed during the chlorine bleaching of pulp (Palm et al. 1995). In addition, the guaiacols have been shown to bioaccumulate up to 100-1000 times in animal tissues, and have been shown to inhibit kidney function in rats (Oikari et al. 1995).

Chlorinated Phenols

2,4-Dichlorophenol and 2,4,6-trichlorophenol, were reliably identified in sample LA8078. Industrial wastes containing phenolic compounds are highly toxic and pose a direct threat to human (Veningerova et al. 1994) and aquatic life. They are compounds with a wide spectrum

of toxic effects including teratogenic (Zhao et al. 1995) and carcinogenic actions (Mehmood et al. 1997, Nagyova & Ginter 1995). They are also relatively persistent in the environment (Narasimhan et al. 1992, Zhao et al. 1995), and known precursors of the polychlorinated dibenzo-p-dioxins and dibenzofurans (Ghorishi and Altwicker 1996)..

2,4-Dichlorophenol is rapidly absorbed through the skin, either as a pure chemical or dissolved in water, where it can then enter the blood stream (USPHS 1991). Although a single dose may have a relatively short biological half-life in humans (2-3 days), long term or repeated exposure to significant doses may lead to permanent damage to the skin, eyes, liver and kidney. In addition, this compound is a suspected animal carcinogen, and a probable or possible human carcinogen (USPHS 1991). 2,4,6-Trichlorophenol may reasonable be anticipated to be a carcinogen.

Alkylbenzenes

Alkylbenzenes occur in the environment due to their presence in crude oil and petroleum products. They are also produced following the degradation of linear alkylbenzene sulphonate (LAS) detergents. The alkylbenzenes are highly resistant to degradation and may accumulate and reside in sediments for long periods of time (Preston and Raymundo 1993).

In terms of toxicity, acute exposure can cause central nervous system (CNS) depression. With impaired reaction times and impaired speech the two most commonly noted CNS effects (Casarett & Doull, 1996). All alkylbenzenes can be irritating to the eyes and mucous membranes and can cause irritation and burning of the skin. All are narcotics at high concentrations (Merck 1989).

Chloroform

This compound was reliably identified in sample LA8077. When intentionally used it is most commonly employed as a solvent. However it is often found as an unintentional by-product of many chlorine chemistry processes, including pulp bleaching and PVC manufacture (Johnston et al. 1994). In humans exposed to highly contaminated air or water, chloroform can affect the central nervous system, the liver and the kidneys. If smaller amounts are consumed over a long period of time, liver and kidney damage may still result (USPHS 1997). Furthermore, studies in which humans were exposed to chloroform-contaminated drinking water showed a possible link between the chloroform in chlorinated drinking water and the occurrence of cancer of the colon and bladder. Based on these studies, the U.S. Department of Health and Human Services has determined that chloroform may reasonably be anticipated to be a carcinogen. The International Agency for Research on Cancer (IARC) has determined that chloroform is possibly carcinogenic to humans. Whilst the EPA has determined that chloroform is a probable human carcinogen.

Thus our results have highlighted the presence of a wide number and variety of organochlorine compounds. However the elimination of organochlorine discharges can be achieved, by the use of Totally Chlorine Free (TCF) bleaching agents, such as hydrogen peroxide and ozone (Johnston *et al.* 1996). The only necessary prerequisite of TCF bleaching

is a pulp with low residual lignin, and this can be produced through extended cooking and oxygen delignification. Further more, conversion of existing mills favours this technology over chlorine dioxide (elemental chlorine free, ECF) based processes in economic terms. In addition the cost of new TCF plants is cheaper than ECF plants (Johnston *et al.* 1996).

2. Petroquimica Capitan Bermudez

Three samples were collected from the chlorine plant Petroquimica Capitan Bermudez. Two samples of effluent (LA8039 and LA8074), and sample of sediment (LA8075). Only tribromomethane (bromoform) was reliably identified in sample LA8039. However VOC analysis of sample LA8074 revealed the presence of a number of other organohalogens including tetrachloroethene, trichloroethene and tetrachloromethane (cabon tetrachloride).

Sediment sample LA8075 also contained a large number of organochlorines including trichloro-, tetrachloro-, pentachlor- and hexachlorobutadiene; chloro-, 1,3-dichloro-, 1,4-dichloro, 1,2,3- trichloro- and 1,2-4-trichlorobenzene; hexachlorobenzene, tetrachloroethene and trichloroethene.

Chlorinated Butadienes

Little information is available regarding the toxicity of pentachlorobutadiene, tetrachlorobenzene and trichlorobutadiene, however hexachlorobutadiene (HCDB) has been fairly well characterised. It is likely that, as with the chlorinated phenols and benzenes, toxicity may decline with increasing degree of chlorination, HCBD being the most toxic. Increased chlorination is also likely to mean increased environmental persistence (USPHS 1997).

HCBD is a fairly common contaminant produced as a by-product in a number of industrial processes involving chlorine chemistry (Johnston et al. 1994). It is also reported as a contaminant in technical formulations of pentachlorophenol, used widely as a wood preservative (Goodrichmahoney et al. 1993). It is often considered to be useful indicator for the presence of chlorinated dioxins and furans (Costner et al. 1995).

In terms of toxicity, HCBD is a potent kidney toxin in laboratory animals (Werner et al. 1995), often showing greater toxicity in males than females for equivalent doses (Birner et al. 1995). It is a known animal carcinogen and a suspected carcinogen in humans (listed by the USEPA). If ingested, HCBD concentrates in the kidney, interferes with fundamental processes of cell respiration and can, as a result of conjugation with other compounds in the body, react with DNA, resulting in cell death or the development of tumours (USPHS 1997). Short and long term exposure to very low doses via food, induced kidney and liver damage in laboratory animals, with juveniles more at risk than adults.

Hexachlorobenzene (HCB)

HCB has been used as a fungicide and as an intermediate in organic synthesis, especially of chlorinated chemicals, including PVC and pulp bleaching processes, where it is often formed

as a by-product or present as a contaminant (Johnston et al. 1994, Merck 1989). It is highly toxic, persistent and bioaccumulative. Animal studies show that oral exposure can damage the liver, the immune system, the kidneys and the skin. With exposure to very high concentrations resulting in cancers of the liver and thyroid (USPHS 1997). The International Agency for Research on Cancer (IARC) has listed HCB as a confirmed carcinogen. In terms of environmental persistence, half-lives for HCB in soils and aerobic aquatic systems have been estimated as between 2.7 and 5.7 years. In anaerobic sediments this could be as long as 10-23 years (Howard et al. 1991). On account of its acute and chronic toxicity, and its persistence in the environment, HCB is one of the twelve priority POPs (persistent organic pollutants), intended for global action by the UN Environment Programme (UNEP) Governing Council. It is intended that HCB will be phased out worldwide under a convention currently being drawn up (UNEP 1995, 1997).

Other Chlorinated Benzenes

Dichlorobenzenes (DCBs) are potent liver and, to a lesser extent, kidney toxins (Valentovic et al. 1993). Their toxicity depends on their precise isomeric structure (i.e. the positioning of the chlorine atoms around the benzene ring), with 1,2-dichlorobenzene (o-DCB) generally reported as more toxic to laboratory rats than 1,3- (m-DCB) and 1,4- (p-DCB) substituted isomers (Valentovic et al. 1993, Umemura et al. 1996). These compounds are not naturally occurring, but are produced by chemical companies to make products for home use, e.g. moth repellent products, fumigants and toilet deodoriser blocks (Merck 1989). However it is probable that they are present at this site as byproducts of production of pulp bleaching chemicals rather than through dedicated manufacturing processes.

The fate of released DCBs in the environment is dictated by the low solubility of these compounds in water (USPHS 1997). Therefore, once discharged to surface waters or to land, DCBs are expected to adsorb to soils and sediments. However sorption can be reversible, Considering p-DCB specifically, it has been observed that this compound may leach from discharged raw sewage, land applied sewage sludge and hazardous waste sites. It may be transported through groundwater and migrate from surface water to groundwater through soil. It is expected to bioconcentrate in aquatic organisms, with examples of measured mean bioconcentration factors (which express the concentration in tissues compared to the concentration in the media) of 370-720 observed for rainbow trout and 1800 for guppies. There is also evidence to suggest that p-DCB has a high potential for bioaccumulation (USPHS 1997).

In terms of human and animal health, p-DCB is reported to cause headaches and dizziness, toxic effects in the liver and kidney, and increases in the rates of cancer among experimental animals (USPHS 1997, Bornatowicz et al. 1994). There is no direct evidence that p-DCB can cause cancer, birth defects, or affect reproduction in humans. However the Department of Health and Human Services (DHHS) in the United States has determined that p-DCB may reasonably be anticipated to be a carcinogen. The International Agency for Research on Cancer (IARC) has determined that p-DCB is possibly carcinogenic to humans. The EPA has also determined that p-DCB is a possible human carcinogen. p-DCB is a listed animal carcinogen (Umemura et al. 1992).

Trichlorobenzenes (TCBs) induce similar toxic effects in aquatic and terrestrial organisms, to those seen in organisms exposed to DCBs. As with DCBs, they are extremely persistent in the environment, and have a high tendency to bioaccumulate, with bioconcentration factors for invertebrates, fish and mammals in the range of 100 to 10000 frequently quoted (IUCLID 1996).

Chlorobenzene is most frequently used as a solvent, but is also employed as an intermediate in the synthesis of other halogenated organics (USPHS 1997). Animal studies have shown that exposure to high concentrations can cause damage to the brain, liver and kidney. Unconsciousness, tremors and restlessness have been observed, as well severe injury to the liver and kidneys. Studies in animals have also shown that chlorobenzene can produce liver nodules, providing some, but not clear, evidence of cancer risk (USPHS 1997).

Tetrachloroethene

Tetrachloroethene is used extensively as a solvent, most commonly in dry-cleaning and metal-degreasing operations. It is also used as a starting material in the production of other synthetic chemicals. Furthermore it is frequently found in PVC and pulp bleaching wastes (Johnston et al. 1994). Due to its volatility, the most common exposure comes from inhalation. Human exposure to high concentrations can cause dizziness, headaches, sleepiness, confusion, nausea, and possibly unconsciousness and death if exposed to high concentrations in a closed, poorly ventilated area. As expected, these symptoms occur almost entirely in the working environment. However the long-term effects to humans exposed to lower level have not yet been fully identified (USPHS 1997). Based on animal data, the U.S. Department of Health and Human services has determined that tetrachloroethene may reasonably be anticipated to be a carcinogen. In addition, the International Agency for Research on Cancer (IARC) has determined that tetrachloroethene is possibly carcinogenic to humans (USPHS 1997).

Trichloroethene

Trichloroethene is a widely produced by-product of the chlorine chemical industry (Johnston et al. 1994), as well as being used intentionally as a degreasing solvent. In the past it was used as an anesthetic for surgery. Hence, as expected, people exposed to large amounts of trichloroethene can become dizzy or sleepy and may become unconscious. Death may occur from inhalation of large amounts. Animals that were exposed to moderate levels of trichloroethene had enlarged livers, and high-level exposure caused liver and kidney damage. However, it is not known whether these changes would occur in humans although research continues (USPHS 1997).

Tetrachloromethane (carbon tetrachloride)

Tetrachloromethane is also produced as a by-product of chlorine chemistry (Johnston et al. 1994), whilst intentionally used as a solvent for oils, fats, varnishes, rubber, waxes and resins. It is also the starting product in the manufacture of many organic compounds. It is highly toxic, and acute exposure, via inhalation, ingestion or skin absorption can cause nausea, vomiting, diarrhoea, headaches, renal damage and liver failure. Chronic exposure to lower

concentrations over a longer period of time can result in permanent liver damage, along with kidney failure and visual impairments. Repeated skin contact can cause dermatitis (Merck 1989). The U.S. Department of Health and Human Services (DHHS) has determined that carbon tetrachloride may reasonably be anticipated to be a carcinogen. The International Agency for Research on Cancer (IARC) has determined that carbon tetrachloride is possibly carcinogenic to humans, and the EPA has determined that carbon tetrachloride is a probable human carcinogen (USPHS 1997).

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