Identification of organic pollutants and heavy metal contaminants in samples collected from a petrochemical complex located in the district of La Plata, Argentina 1998.

Prepared by Angela Stephenson and Iryna Labunska Greenpeace Research Laboratories, University of Exeter, UK December 1998

Sample description

In May 1998, six samples were collected downstream of a large petrochemical complex, located in the district of La Plata (see Table 1). Companies including YPF (oil distillery), PETROKEN (polypropylene) and IPAKO (polyethylene) are on site, and wastewaters from these companies are discharged through two large channels (East and West) into the Rio Santiago, which itself discharges into the Rio de la Plata.

Sample	Sample	Sample Description
Number	Туре	
LA8046	Sediment	Collected from the WEST channel, 100 metres upstream of the Rio
		Santiago
LA8047	River water/	Collected from the WEST channel, 100 metres upstream of the Rio
	Industrial	Santiago
	waste	
LA8048	River water/	Collected from the EAST channel, within the petrochemical complex
	Industrial	
	waste	
LA8049	Sediment	Collected from the EAST channel, within the petrochemical complex
LA8050	River water/	Collected from the WEST channel, within the petrochemical complex
	Industrial	downstream of PETROKEN and IPAKO, opposite YPF.
	waste	
LA8051	Sediment	Collected from the WEST channel, within the petrochemical complex
		downstream of PETROKEN and IPAKO, opposite YPF.

Sampling methodology

All samples were collected and stored in glass bottles, previously rinsed with pentane and nitric acid, to remove all organic and heavy metal residues. Solid samples were collected with wooden spoons, previously rinsed with deionised water, nitric acid and pentane. 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), heavy metals were determined quantitatively using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

1. 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^{0} C, 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 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 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.

2. Heavy Metals Analysis

Solid Samples

Solid samples were dried in an oven for 48 hours, until dry weight readings became constant. They were then crushed using a pestle and mortar until homogenous and sieved through a 2 mm mesh. 0.5 g of sample was then weighed into a 120 ml Teflon microwave vessel. 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 vessels were then sealed, placed on a rotating table in a microwave oven (model MDS-2000, CEM Corp.), and allowed to digest for one hour at full power (630 W).

Aqueous Samples

Aqueous samples were preserved in 5% v/v nitric acid on arrival. After 24 hours, 50 ml was transferred to a 120 ml Teflon microwave vessel microwave vessel fitted with a screw cap and pressure relief valve. The vessel was then sealed, placed on a rotating table in a microwave oven (model MDS-2000, CEM Corp.), and allowed to digest for one hour at full power (630 W).

After cooling to ambient temperature, all digests were filtered into volumetric flasks, diluted with deionised water, made up to a volume of 50 ml and mixed. A blank sample, and two internally prepared quality controls (8mg/l, 0.8 mg/l for mercury) were also prepared, matrix matched to the samples.

ICP-AES Analysis

Following preparation, the samples were analysed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), using a Varian Liberty-100 Sequential Spectrometer. The following metals were quantified directly: manganese (Mn), chromium (Cr), zinc (Zn), copper (Cu), lead (Pb), nickel (Ni), cobalt (Co) and cadmium (Cd). A multi-element instrument calibration standard was prepared at a concentration of 10 mg/l (matrix matched to the samples). The calibration was validated using a quality control standard, prepared from different reagent stocks, at 8 mg/l. Samples exceeding the calibration range were diluted appropriately, in duplicate, and reanalysed.

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). Samples exceeding this range were diluted and re-analysed. The quality control standard was again prepared from a different reagent stock at 80% of the calibration range (i.e. 80 ug/l).

Reporting limits of 0.01 mg/l were used for all metals with the exception of lead (0.03 mg/l) and mercury (0.002 mg/l). These were calculated using statistical methods supplied by the UK Water Research Centre (1989).

Results

Are given in Tables 2-4.

Groups of compounds identified to better than	Number of	Sample codes		
90%	samples			
PAHs				
9H-fluorene and derivatives	1	LA8051		
Naphthalene and derivatives	2	LA8046, LA8051		
Phenanthrene and derivatives	2	LA8050, LA8051		
Pyrene and derivatives	2	LA8050, LA8051		
Azulene and derivatives	1	LA8051		
ALKYLBENZENES	2	LA8046, LA8050		
(both straight and chain)				
OTHER AROMATICS				
Biphenyls and alkyl derivatives	1	LA8051		
ALIPHATIC HYDROCARBONS AND	4	LA8046, LA8048, LA8050, LA8051		
DERIVATIVES				
(both straight and chain)				
STEROIDS AND DERIVATIVES				
Pregnane and derivatives	1	LA8046		

Table 2 Groups of organic compounds reliably identified in samples collected from the YPF, PETROKEN, IPAKO petrochemical complex, Argentina 1998

Sample	Compounds	Reliably	PAHs	Alkylbenzenes	Aliphatic	
Number	Isolated	Identified			hydrocarbons	
LA8046	100	8 (8%)	3	1	3	
LA8047	23	0	0	0	0	
LA8048	14	5 (7%)	0	0	5	
LA8049	2	0	0	0	0	
LA8050	27	7 (26%)	2	2	3	
LA8051	154	28 (18%)	17	0	10	

Table 3 Results of organic screening, YPF, PETROKEN, IPAKO petrochemical complex, Argentina 1998

Sample	Mn	Cr	Zn	Cu	Pb	Ni	Со	Cd	Hg
Number	(ppm)								
LA8046	275.8	108.3	340.7	119.1	56.7	67.5	59.3	n/d	5.4
LA8047	0.07	< 0.01	< 0.01	< 0.01	< 0.03	< 0.01	< 0.01	< 0.01	< 0.002
LA8048	0.30	< 0.01	< 0.01	< 0.01	< 0.03	< 0.01	< 0.01	< 0.01	< 0.002
LA8049	1109.8	32.5	296.9	40.7	144.3	18.6	10.8	n/d	1.0
LA8050	0.21	< 0.01	0.10	< 0.01	< 0.03	< 0.01	0.01	< 0.01	< 0.002
LA8051	641.4	31.0	367.1	131.4	36.7	92.4	207.1	n/d	5.1

Table 4 Results of heavy metals analysis, YPF, PETROKEN, IPAKO petrochemical complex, Argentina 1998

Discussion

Organic Pollutants

What is evident from the results shown in Tables 2 and 3, is that the samples collected from the west channel are far more contaminated than those collected from the east channel. 14 compounds were isolated from sample LA8048, a mixture of river water and industrial effluent collected from the east channel, with 2 compounds isolated in sediment sample LA8049 collected from the same

site. In contrast, sediment samples LA8046 and LA8051, collected from the west channel, contained 100 and 154 organic compounds respectively, with the two water samples collected from this channel also containing relatively large numbers of compounds. 23 compounds were isolated in sample LA8074, 27 in sample LA8050.

The compounds reliably identified in these West channel samples, fall into three broad chemical groups: alkylbenzenes, polycyclic aromatic hydrocarbons, and long chain aliphatic hydrocarbons; and when these groups of compounds are found together, their presence is often indicative of petroleum contamination (Overton 1994).

Petroleum hydrocarbons

Petroleum is a complex mixture of hydrocarbons that is formed from the partial decomposition of biogenic material, over geological time-scales. Petroleum hydrocarbons are released into the environment through natural seeps, non-point source urban runoffs, and by large quantities of accidentally released oil. Petroleum substances can also be found, albeit at low concentrations, in sewage (Connell, 1974), however the total amount discharged is relatively high due to the large volumes involved. Refined petroleum products principally contain the alkanes. It is often difficult to distinguish the origin of the hydrocarbons found in environmental samples. In cases of anthropogenic pollution, i.e. crude oil or petrol spills, alkanes are present together with monoaromatic hydrocarbons (benzenes) and polyaromatic hydrocarbons (naphthalene and others) (Overton 1994).

Alkylbenzenes

The occurrence of these compounds in the environment is largely due to their presence in crude oil and petroleum products, although they are also produced following the degradation of the linear alkylbenzene sulphonate (LAS) detergents. The alkylbenzenes themselves are highly resistant to degradation and may accumulate in sediments (Preston & Raymundo 1993). Alkylbenzenes are useful sewage markers (Chalaux *et al.* 1995) and due to their stability in sediments, they are very useful in tracing the transport of contaminants from their point sources.

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 (Klaassen *et al.* 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 (Budavari *et al.* 1989).

Polycyclic aromatic hydrocarbons (PAHs)

PAHs are a group of compounds found in coal and oil. They are also formed during the combustion of coal, oil and gas. More than 100 different PAHs are known, however only a few have industrial / domestic applications.

Monoaromatic and polyaromatic hydrocarbons are considered to be the most toxic, and are known to be present at the highest concentrations during the initial phase of a crude oil spill (Overton 1994). The PAHs which were found in these samples were mainly naphthalene and its alkyl derivatives, along with phenanthrene.

Once PAHs are released into the aquatic environment, degradation by micro-organisms is often slow, leading to their accumulation in exposed sediments, soils, aquatic and terrestrial plants, fish and invertebrates. PAHs can have a deleterious effect on human health, and individuals exposed to

mixtures of PAHs, through inhalation or skin contact, for long periods of time, have been shown to develop cancer (ATSDR 1997).

Many of the carcinogenic polycyclic aromatic hydrocarbons are derived from an angular benz[a]anthracene skeleton. Anthracene itself is not carcinogenic, but benz[a]anthracene appears to have weak carcinogenicity. Addition of another benzene ring in select positions result in agents with powerful carcinogenicity such as dibenz[a,h]anthracene or benzo[a]pyrene. In addition, substitution of methyl groups on specific carbons of the ring also enhances carcinogenicity. Thus, 7,12-dimethylbenz[a]anthracene (DMBA) is one of the most powerful synthetic, polycyclic aromatic hydrocarbon carcinogens known (Klaassen *et al.* 1996).

Heavy Metals

Heavy metal results are shown in Table 3. Levels determined in the water samples are low, with only manganese, zinc and cobalt present at detectable levels. However sediment levels are more significant, with elevated levels of chromium, zinc, copper, cobalt and mercury found in the west channel samples (LA8046 and LA8051), and elevated levels of zinc and lead found in the east channel sample (LA8049).

Uncontaminated riverine sediments will usually contain less than 0.5 mg/kg of Hg; less than 50 mg/kg of Pb, Cr, Cu, and Co; and less than 100 mg/kg of Zn (Goncalves 1990, Salomons and Forstner 1984). Thus in sample LA8046, levels of chromium, zinc and copper are 2-3 times greater than those usually found in clean sediments, with levels of mercury, 10 times greater. In sample LA8049, levels of zinc and lead are 3 times greater than those usually associated with clean sediment; and in sample LA8051, zinc levels are 3 times greater, copper twice as great, cobalt four times greater and mercury ten times greater than levels usually found in clean sediment.

As is evident from these results, heavy metals discharged into the environment will bind predominantly to suspended material, and finally accumulate in the sediment, thus providing a reliable history of pollution. As concentrations in sediment can exceed those of the overlying water by between three and five orders of magnitude (Schuhmacher et al. 1995, Bryan and Langston 1992), the bioavailability of even a minute fraction of the total sediment metal assumes considerable importance.

Many of these metals are toxic at very low concentrations; they are also persistent in the environment and have the potential to bioaccumulate through the food chain. Therefore continued discharge can only lead to further increases in sediment concentrations.

Clearly the two most direct potential routes of exposure to humans following such discharges to the river would be consumption of the water or of fish or other food derived from the river. It is not, however, possible to estimate the magnitude of the hazard, which may be presented by the discharges in question in this study. The toxicological properties of these metals can however be summarised as follows:

Lead

Unlike some heavy metals, lead is not required by animals (including humans) or plants for normal growth and development. It has no known nutritional or biochemical function and if present in sufficient quantities will inhibit animal and plant growth, development and health (Nriagu 1988).

It is not considered to be one of the most environmentally mobile metals, often heavily bound to suspended particulate and sediment material (Berg *et al.* 1995, Hapke 1991), however there is appreciable evidence to show that sediment-bound lead is available to deposit-feeding species (Bryan and Langston 1992). With high bioconcentration factors (BCFs) being determined in studies using oysters (6,600 for *Crassostrea virginica*), freshwater algae (92,000 for *Senenastrum capricornutum*) and rainbow trout (726 for *Salmon gairdneri*) (Eisler 1988). It is toxic to all aquatic biota, and organisms higher up the food chain may experience lead poisoning as a result of eating lead-contaminated food.

In terms of human health the effects of lead are the same irrespective of whether it is inhaled or ingested (ATSDR 1997). Lead can cause irreversible central nervous system damage and decreased intelligence at extremely low doses (Needleman *et al.* 1990, ATSDR 1997). At higher levels of exposure anaemia may result, along with severe kidney damage (ATSDR 1997). Children are especially susceptible to lead poisoning because they absorb and retain more lead in proportion to their weight than adults (ATSDR 1997).

Cadmium

Cadmium has no biological function, and is highly toxic to both animals and plants. The low concentrations of cadmium usually encountered in the environment do not cause acute toxicity, however elevations above background concentrations can have deleterious effects on plant and animal health (Bryan and Langston 1992, Alloway 1990).

Toxic effects on exposure biota include observed correlations between increased levels of cadmium found in limpets and a reduced ability to utilise glucose (Shore *et al.* 1975, Bryan and Langston 1992). Reductions in reproduction rates and thus population numbers in copepods and isopods (Giudici and Guarino 1989) have also been observed. The toxicity of low sediment-cadmium concentrations was also suggested by observations showing that in San Francisco Bay, the condition of certain species of clam declined as cadmium concentrations rose from 0.1 to 0.4 mg/kg (Luoma *et al.* 1990).

Regarding potential human exposure, food, water and cigarette smoke will be the largest sources of cadmium for members of the general population. Eating food or drinking water with very high cadmium levels can severely irritate the stomach, leading to vomiting and diarrhoea (ATSDR 1997). Eating lower levels of cadmium over a long period of time can lead to a build up in the kidneys. This cadmium build-up causes kidney damage, and also leads to the weakening of bone (Nriagu 1988). Studies concerned with the effects of eating and drinking high levels of cadmium are not strong enough to show that such exposure can lead to an increased rate of cancer. However the U.S. Department of Health and Human Services and the U.S. Environment Protection Agency have both determined that cadmium and cadmium compounds may reasonably be anticipated to be carcinogens (ATSDR 1997).

<u>Zinc</u>

Although zinc is not regarded as being especially toxic, it is sometimes released into the environment in appreciable quantities, and can thus have deleterious effects on certain species at specific concentrations. For example, effects on fertilisation and embryonic development have been observed in species of fish and harpacticoid copepods (Ojaveer *et al.* 1980, Verriopoulos and Hardouvelis 1988).

In terms of human health, most of the studies relating to the effects of zinc concentrate on exposure via inhalation (which can cause a specific short-term disease called metal fume fever). Less is known about the long-term effects of ingesting too much zinc, through food, water or dietary supplements. It is an essential trace element, but ingestion of higher than recommended levels can have adverse effects on health. The recommended Dietary Allowances for zinc are 15 mg/day for men and 12 mg/day for women. If doses 10 –15 times higher than these recommendations are taken by mouth, even for a short time, stomach cramps, nausea and vomiting may occur (ATSDR 1997). Ingesting high levels for several months may cause anaemia, damage to the pancreas, and decreased levels of high-density lipoprotein (HDL) cholesterol (ATSDR 1997).

Copper

Copper is highly toxic to aquatic species, even at very low (part per billion) levels. A very significant relationship between copper levels in aquatic biota and the levels found in sediments has been demonstrated, with clear relationships found between animal and sediment concentrations from as little as 10 mg/kg to more than 2000 mg/kg (Bryan and Langston 1991). The bioconcentration factor (BCF) of copper in fish obtained in field studies is 10-100. The BCF is higher in molluscs, especially oysters, where it may reach 30,000 (Perwack *et al.* 1980). This may be due to the fact that they are filter feeders, and copper concentrations are higher in particulates than in water.

Like zinc, copper is necessary for good health in trace amounts. However very large single or daily intakes of copper, or prolonged exposure to lower levels can have adverse effects on human health. Consumption of food or drinking water containing elevated levels of copper can result in vomiting, diarrhoea, stomach cramps and nausea (ATSDR 1997).

Mercury

Mercury is a non-essential trace metal, having no biochemical or nutritional function. Biological mechanisms for its removal are poor, and mercury is the only metal known to biomagnify i.e. progressively accumulate through the food chain (WHO 1989, ICME 1995). It is extremely toxic to both animals and plants at low concentrations. Therefore any elevation above baseline levels could have a deleterious effect on any exposed biota (ATSDR 1997).

Since the poisoning incident that devastated the Japanese town of Minamata, the implementation of widespread regulations on mercury disposal has greatly reduced the threat of similar incidents. However the retention of mercury by sediments may delay the elimination of contamination for many years. Thus for example concentrations as high as 100 mg/kg were still present in sediments at certain sites in Minamata Bay, ten years after discharges ceased (Bryan and Langston 1992, Tsubaki and Irukayama 1977). The importance of this is the fact that mercury accumulation from sediments may be a dominant pathway for uptake in aquatic organisms and accounts for relatively high concentrations in deposit-feeders both in freshwater and estuarine systems (Bryan and Langston 1992, Kiorboe *et al.* 1983). Also it known that inorganic mercury can be methylated by microorganisms within the sediment, and it is widely accepted that organic forms of mercury are even more toxic than the inorganic forms (ATSDR 1997).

The most common form of mercury is methylmercury (MeHg), and although there is evidence which links levels of total mercury in the environment with those in higher predators such as fish, concern centers on MeHg accumulation. MeHg exhibits high lipid solubility. It is able to cross cell membranes easily, and therefore quickly enters the aquatic food chain. It also has a long biological half-life, and due to increased longevity of top predators in association with these other properties, it provides one of the rare examples of metal biomagnification in food chains. For example, MeHg concentrations in carnivorous fish at the top of freshwater and salt-water food chains (e.g., pike, tuna and swordfish) are biomagnified in the order of 10,000-1000,000 times the concentrations found in ambient waters (Callahan *et al.* 1979, EPA 1980, 1984, ATSDR 1997).

The significance of this is that biomagnification of MeHg in aquatic food chains is considered the most important source of non-occupational human exposure to the element (EPA 1984, ATSDR 1997), and as mercury is highly toxic and persistent, anomalous environmental levels warrant concern. Mercury has no beneficial effects in humans, and there is no known homeostasis for it (i.e. no maintained equilibrium between mercury entering the body and leaving). Any long-term exposure may therefore be expected to progressively cause severe disruptions in the normal functioning of any accumulating organ (Nriagu 1988). Accumulating organs include the kidneys, liver and central nervous system, and exposure to high levels of metallic, inorganic or organic mercury can permanently damage these organs (ATSDR 1997).

<u>Chromium</u>

Elevations above the background range are nearly always due to anthropogenic discharges. Information on the effects of elevated environmental levels on aquatic biota, fish, deposit feeding and wading birds is limited; and how sediment-bound chromium reaches animal and plant tissues is uncertain, although it is recognised that the speciation of chromium determines its bioavailability. Chromium (VI) will be accumulated more readily than chromium (III), as it has been shown to cross biological membranes more readily (Bryan and Langston 1992). Whereas chromium (III) is a trace nutrient at low concentrations, chromium (VI) is non-essential and toxic. Its compounds have been classified as carcinogenic by the International Agency of Research on Cancer (ATSDR 1997).

For freshwater fish and shellfish, the uptake of metals through their food may be quite substantial (Heath 1987, Dallinger *et al.* 1987), and metals taken up by plants can be an important route to make metals in the sediments bioavailable to herbivore species (Berg *et al.* 1995).

An average daily intake of 50-200 ug/day of chromium (III) is recommended for adults (ATSDR 1997), chromium (III) being an essential nutrient, required for normal energy metabolism. However the consumption of contaminated fish, other foodstuffs and drinking water could increase the daily intake levels far beyond those recommended. Ingesting small amounts of chromium (both III and VI forms) has not been reported to cause harm, however ingesting higher than recommended levels over long periods of time can result in adverse health effects including gastro-intestinal irritation, stomach ulcers, kidney and liver damage (ATSDR 1997).

Dermal exposure to both chromium (III) and chromium (VI) can result in severe redness and swelling of the skin (ATSDR 1997). Whereas breathing in high levels of chromium (far less likely in this case) can cause irritation of the nasal and respiratory membranes. These effects have primarily occurred in factory workers who make or use chromium (VI) for several months to many years. Long term occupational exposure to chromium (VI) is believed to be primarily responsible for the increased lung cancer rates (ATSDR 1997).

Cobalt

In terms of environmental exposure, cobalt has both beneficial and harmful effects on human health. It is beneficial as it is incorporated in the vitamin B12 molecule, essential for growth and its anti-anaemic properties. Cobalt is also essential for the growth and development of certain animals, such as cows and sheep. However when too much cobalt is taken into the body, harmful health

effects can occur.

Animal studies have shown that short-term exposure of high levels of cobalt in the air can result in lung damage and possibly death, with longer-term exposure to lower concentrations causing the same effects. Short-term exposure to high levels in food and drinking water caused damage and changes to the blood, liver, kidneys and heart, with longer-term exposure to lower levels causing the same damage and changes, as well as affecting reproduction and behaviour (ATSDR 1997).

Human exposure to high airborne levels can have serious effects on the lungs, including wheezing, asthma and pneumonia. Allergies resulting in asthma and skin rashes can also occur. Ingestion of high levels of cobalt can cause vomiting and nausea.

Cobalt has not been found to cause cancer in humans or in animals, following exposure in the air or in the food or water. However cobalt has been shown to cause cancer when placed directly into the muscle or under the skin. Based on the animal data available, the International Agency for Research on Cancer (IARC) has determined that cobalt is possibly carcinogenic to humans (ATSDR 1997).

References

Alloway, B.J. (1990). Heavy metals in soils. Blackie and Son Ltd, Glasgow/London, UK. . ISBN 0-470-21598-4

ATSDR (1997). Toxicological Profile for Cadmium. Agency for Toxic Substances and Disease Registry, U.S. Public Health Service (CD-ROM)

ATSDR (1997). Toxicological Profile for Chromium. Agency for Toxic Substances and Disease Registry, U.S. Public Health Service (CD-ROM)

ATSDR (1997). Toxicological Profile for Cobalt. Agency for Toxic Substances and Disease Registry, U.S. Public Health Service (CD-ROM).

ATSDR (1997). Toxicological Profile for Copper. Agency for Toxic Substances and Disease Registry, U.S. Public Health Service (CD-ROM)

ATSDR (1997). Toxicological Profile for Lead. Agency for Toxic Substances and Disease Registry, U.S. Public Health Service (CD-ROM)

ATSDR (1997). Toxicological Profile for Mercury. Agency for Toxic Substances and Disease Registry, U.S. Public Health Service (CD-ROM)

ATSDR (1997). Toxicological profile for polycyclic aromatic hydrocarbons. Agency for Toxic Substances and Disease Registry, U.S. Public Health Service (CD-ROM)

ATSDR (1997). Toxicological Profile for Zinc. Agency for Toxic Substances and Disease Registry, U.S. Public Health Service (CD-ROM)

Berg, H., Kiibus, M., and Kautsky, N. (1995). Heavy metals in tropical Lake Kariba, Zimbabwe. Water, Air and Soil Pollution 83: 237-252

Bryan, G.W. and Langston, W.J. (1992). Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom Estuaries: a review. Environmental Pollution 76: 89-131

Budavari, S.M., O'Neil, J., Smith A., and Heckleman P.E. [Eds] (1989) The Merck index: an encyclopaedia of chemicals, drugs and biologicals. 11th Edn Merck and Co, Inc., New Jersey, USA

Callahan, M.A., Slimak, M.W. and Gabel, N.W. (1979). Water related environmental fate of 129 priority Pollutants, introduction and technical background, metals and inorganics, pesticides and PCBs. Washington, D.C: U.S. Environmental Protection Agency, Office of Water Waste and Management. Document no. EPA 440/4-79-029a, 14-1 - 14-15

Chalaux N., Takada H., Bayona J.M. (1995). Molecular markers in Tokyo Bay sediments – sources and distribution. Marine Environmental Research 40 (1) : 77-92

Connell D.W. (1974). A kerosene-like taint in the sea mullet, *Mugil cephalus* (Linnaeus). I. Composition and environmental occurrence of the tainting substance. Australian Journal of Marine and Freshwater Research 25: 7-24

Dallinger, R., Prosi, F., Segner, Back, H. (1987). Contaminated food and uptake of heavy metals by fish. A review and proposal for further research. Oecologia 73: 91-98

Eisler, R. (1988). Lead hazards to fish, wildlife, and invertebrates: A synoptic review. Laurel, MD: U.S. Department of the Interior, Fish and Wildlife Service. Biological Report 85 (1.14)

EPA, 1980. Ambient water quality criteria for mercury. Washington, DC: U.S. Environmental Protection Agency, Office of Water Regulations and Standards. Document no. EPA 440/5-80-058

EPA, 1984. Mercury health effects update: Health issue assessment. Final report. Washington, DC: U.S. Environmental Protection Agency, Office of Health and Environmental Assessment. Document no. EPA 600/8-84-019F

Goncalves, E.P.R., Boaventura, R.A.R., and Mouvet, C. (1990). Sediments and aquatic mosses as pollution indicators for heavy metals in the Ave river basin, Portugal. The Science of the Total Environment 114: 7-24

Guidici, M.N. and Guarino, S.M. (1989). Effects of chronic exposure to cadmium or copper on Idotea balthica sp. (Crustacea Isopoda). Marine Pollution Bulletin 20: 69-73

Hapke, H.J. (1991). Metal accumulation in the food chain and load of feed and food. Metals and Their Compounds in the Environment, Merian, VCH, Weinheim, p1438

Heath, A.G. (1987). The effects of waterborne copper or zinc on the osmoregularity response of bluegill to a hypertonic NaCl challenge. Comparative Biochemistry and Physiology 88: 307-311

I.C.M.E. (International Council on Metals and the Environment), 1995. Persistence, bioaccumulation and toxicity of metals and metal compounds. Paramex Inc., Washington, USA. ISBN 1-895720-07-9

Kiorboe, T., Mohlenberg, F. and Riisgard, H.V. (1983). Mercury levels in fish, invertebrates and

sediment in a recently recorded polluted area. Marine Pollution Bulletin 14: 21-24

Klaassen, C.D, Amur, M.O. and Doull, J. [Eds](1996). Casarett and Doull's Toxicology: The basic science of poisons. 5th Edition, McGraw-Hill Companies Inc. IBSN 0-07-105476-6

Luoma, S.N., Dagovitz, R. and Axtmann, E. (1990). Temporally intensive study of trace metals in sediments and bivalves from a large river-estuarine system: Suisun Bay / Delta in San Francisco Bay. The Science of the Total Environment 97/98: 685-712

Needleman, H.L., Schell, A. and Bellinger, D. (1990). The long-term effects of exposure to low doses of lead in childhood. An 11 -year follow-up report. New England Journal of Medicine 322: 83-88

Nriagu, J.O. (1988). A silent epidemic of environmental metal poisoning? Environmental Pollution 50: 139-161

Ojaveer, E., Annist, J., Jankowski, H., Palm, T. and Raid, T. (1980). Effects of copper, cadmium and zinc on the embryonic development of Baltic spring spawning herring. Marine Research 247: 135-140

Overton, E.B. (1994). Toxicity of petroleum. In: Basic Environmental Toxicology. Cockerham & Shane [Eds], Chapter 5: 133-156

Perwak, J., Bysshe, S. and Goyer, M. (1980) Exposure and Risk Assessment for Copper. Cincinnati, OH: U. S. Environmental Protection Association. EPA 440/4-81-015. NTIS PB85-211985

Preston, M.R. & Raymundo, C.C. (1993) The associations of linear alkyl benzenes with the bulk properties of sediments from the River Mersey estuary. Environmental Pollution 81: 7-13

Salomons, W. and Forstner, U. (1984). Metals in the Hydrocycle. ISBN 3-540-12755-0, Springer-Verlag, Berlin, Heidelberg, New York, Tokyo

Schuhmacher, M., Domingo, J.L., Llobet, J.M., and Corbella, J. (1995). Variations of heavy metals in water, sediments and biota from the delta of the Ebro River, Spain. Journal of Environmental Science and Health, A30 (6): 1361-1372

Shore, R., Carney, G. and Stygall, T. (1975). Cadmium levels and carbohydrate metabolism in limpets. Marine Pollution Bulletin 6: 187-189

Tsubaki, T. and Irukayama, K. (1977). Minimata Disease. Kodansha, Tokyo and Elsevier, Amsterdam

Verriopoulos, G. and Hardouvelis, D. (1988). Effects of sub-lethal concentrations of zinc on survival and fertility in four successive generations of Tisbe. Marine Pollution Bulletin 19: 162-166

Water Research Centre (1989). A Manual on Analytical Quality Control for the Water Industry. Cheeseman R.V., Wilson, A.L. and Gardner M.J. [Eds] Water Research Cente plc. ISBN 0-902156-85-3

World Health Organisation (1989). Environmental Health Criteria 86. Mercury: Environmental Aspects. ISBN 92-4-154286-1