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Identification of organic pollutants and heavy metal contaminants in samples collected from the vicinity of the Oxiquim plant, the Sector el Salto, Viña del Mar, Chile, 2000

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EXECUTIVE SUMMARY

Oxiquim is one of the largest chemical producers in Chile, being the sole producers of phenol and urea formaldehyde resins in the country. The plant located in the Sector el Salto of Viña del Mar has manufacturing facilities for formaldehyde and its derivatives including urea formaldehyde resins as well as phenol based resins. In March 1999 Oxiquim was awarded the "Best work in Clean Production" award by the Chilean Minister of Economy.

Greenpeace visited the Oxiquim plant in Viña del Mar in August 2000 and collected two samples of industrial wastewaters from the discharge pipe of Oxiquim and from a communal drain to which these wastewaters are discharged. The combined effluents from this communal drain are believed to be discharged to the Pacific Ocean. The analysis of these samples for organic contaminants and heavy metals demonstrated the following:

- The wastewater discharge from the Oxiquim plant contained at least 25 organic compounds, including a number of organochlorine compounds. The most noteworthy of the compounds identified were two tris(monochloroisopropyl) phosphates (TMCPPs). These toxic chlorinated organophosphates are widely used as flame retardants.

- A number of compounds detected in the waste stream from the Oxiquim plant were not detected in the communal drain on the preceding day, which suggests a variability in the waste stream from the Oxiquim plant.

- Inputs to the communal drain from sources other than the Oxiquim plant contain a number of pollutants of concern, including the persistent organochlorine alpha-hexachlorocyclohexane (HCH) and a number of potentially toxic metals.

In summary, this report demonstrates that the discharge of chemical wastes from the Oxiquim plant clearly needs to be addressed. In light of the apparent variability in the Oxiquim waste stream, further investigation to fully characterise the wastes currently being discharged from this plant need to be carried out. In addition, more information on the raw materials, processes and wastes from the Oxiquim plant needs to be made available.

Further information on the inputs to the communal drain from sources other than the Oxiquim plant need to be made available and procedures need to be put in place to prevent the discharge of pollutants to the environment.

1. INTRODUCTION

Oxiquim is one of the largest chemical producers in Chile, being the sole producers of phenol and urea formaldehyde resins in the country. Oxiquim is also one of the largest manufacturers of formaldehyde in Latin America, producing over 200 000 mt/yr at sites in Viña del Mar and Concepción in Chile, and in Puerto Ordaz, in Venezuela. (Oxiquim 2000). In March 1999 Oxiquim was awarded the "Best work in Clean Production" award by the Chilean Minister of Economy.

The main Oxiquim production plant in Chile is located in the Sector el Salto of Viña del Mar. A distribution center is located in an industrial complex in the Quilicura district of the city of Santiago. The site in Viña del Mar has manufacturing facilities for formaldehyde and its derivatives. These include special resins, the majority of which are phenol and urea formaldehyde resins. The main products from this plant include pentaerythritol, sodium formate, and urea formaldehyde moulding compounds (Oxiquim 2000).

2. SAMPLING PROGRAM

In August 2000, two samples of industrial wastewaters were collected from the vicinity of the Oxiquim plant in Viña del Mar as part of an investigation into industrial pollution in Chile.

All samples were collected and stored in pre-cleaned 1 litre bottles glass bottles that had been rinsed thoroughly with nitric acid and analytical grade pentane in order to remove all heavy metals and organic residues. Both samples were immediately sealed and cooled upon collection. The samples were returned to the Greenpeace Research Laboratories for analysis.

A detailed description of sample preparation and analytical procedures is presented in appendix 1.

2.1. Sample descriptions

One sample of wastewater (AM0168) was collected from a discharge pipe of the Oxiquim plant prior to discharge into a communal drain. On the preceding day, a sample of combined wastewater (AM0167) was collected from this communal drain, downstream of the Oxiquim discharge point. The combined wastewaters from the communal drain are believed to be discharged to the Pacific Ocean via an underground pipe. The Oxiquim discharge pipe is located close to the Marga-Marga River, but wastewaters are not believed to be discharged into this river.

Sample Number	Sample Description	Sample Location
AM0167	Industrial wastewater	Collected from a communal drain, into which Oxiquim wastewaters are discharged. 27th August 2000.
AM0168	Industrial wastewater	Collected from a discharge pipe of the Oxiquim plant prior to discharge into a communal drain. 28th August 2000.

Table 2.1: Description of samples collected from the vicinity of the Oxiquim plant in the Sector el Salto of Viña del Mar, Chile, 2000.

3. RESULTS AND DISCUSSION

The results of organic screen analysis and heavy metals analysis are presented in table 3.1, including a breakdown of the groups of organic compounds reliably identified in the samples. For a full list of organic compounds both reliably and tentatively identified in the samples, see appendix 2. For more information on the common sources, environmental behaviour and toxicological outlines for key pollutants detected during this study see appendices 3 & 4.

The sample of combined effluents from the communal drain (AM0167) contained a range of organic pollutants including two organochlorines, as well as a number of toxic and potentially toxic metals.

Of the total number of organic contaminants identified, aliphatic hydrocarbons, both linear and cyclic, were predominant. These compounds probably derive from crude oils and petroleum, which are extremely widespread pollutants. The level of contamination, from these types of compounds, was not particularly high in this location.

Another very common pollutant detected in the wastewaters from the communal drain was 1,4-dichlorobenzene. The chlorinated benzenes are highly volatile and may be found as ubiquitous contaminants in many urban and industrial areas. In particular, 1,4-dichlorobenzene is especially widespread, as a result of its use in sanitary disinfectant products.

One phenolic compound was identified in this sample, 2,6-bis(1,1-dimethylethyl)-4-methylphenol, also called butylated hydroxytoluene (BHT). This compound is used as an antioxidant in food products, rubbers, soaps, and in the production of plastics and other petrochemical products (Jobling *et al* 1995).

The alpha isomer of hexachlorocyclohexane (alpha-HCH) was detected at trace levels. alpha-HCH is a major isomer of technical grade hexachlorocyclohexane (Safe 1993). Technical grade HCH can be purified to extract the gamma isomer, which has insecticidal properties and is best known under the trade name "lindane". The technical mix has also been used unpurified as an insecticide, under which circumstances it is more usually called technical HCH or BHC. Among eight possible isomers of hexachlorocyclohexane alpha-, beta-, and gamma-HCH are the most important isomers in terms of environmental impact.

The presence of alpha-HCH could either be due to releases from the manufacturing of technical HCH or lindane, or to the use of technical HCH as an insecticide.

Chemical identified	Sample codes	
	AM0167	AM0168
Total number of organic compounds isolated	18	26
Total number of organic compounds reliably identified	13 (72%)	12(46%)
Groups of organic compounds reliably identified		
ORGANOHALOGEN COMPOUNDS		
1,4-Dichlorobenzene	✓	*
alpha-Hexachlorocyclohexane	*	
Tris(chloroisopropyl) phosphate		✓ (2 isomers)
PHENOLIC COMPOUNDS		
Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-	✓	
OTHER AROMATICS		
Benzaldehyde, 2,4-dimethyl-		✓
Diphenyl ether	✓	✓
1,1'-Biphenyl		✓
ALIPHATIC HYDROCARBONS		
Linear	✓ (8 compounds)	✓ (5 compounds)
Cyclic	✓ 1 compound)	✓ (1 compound)
Metal (with concentrations in ug/l)		
Cadmium	<10	<10
Chromium	47	<20
Cobalt	<20	<20
Copper	1479	<20
Lead	<30	<30
Manganese	54	24
Mercury	<1	<1
Nickel	312	<20
Zinc	259	<10

Table 3.1: Organic chemicals and heavy metals (concentrations in ug/l) identified in effluent samples from the Oxiquim plant and a communal drain, Viña del Mar, Chile, 2000.
For groups of organic compounds reliably identified:
✓ - compounds identified using general GC/MS screening method;
* * - compounds identified only at trace levels using GC/MS selective ion monitoring (SIM) method;*

The aromatic hydrocarbon diphenyl ether identified in the communal drain wastewaters is often used in organic synthetic processes. Possible sources of this compound are discussed below.

In addition to the organic contaminants, the combined effluent sample collected from the communal drain (AM0167) contained certain metals at significant levels, most noticeably copper, nickel, and zinc at 1479, 312 and 259 ug/l, respectively.

The levels of copper, nickel and zinc in unpolluted rivers generally range from 20-50 ug/l (ATSDR 1997). The levels of these metals in the combined effluents exceed these background levels by 30 times for copper, 6 times for nickel and 5 times for zinc. The background levels of these metals in coastal and estuarine waters are in the range 0.35-4.0 ug/l for copper (Law *et al.* 1994), 0.2-4.9 for nickel (Law *et al.* 1994), and 0.3-70 ug/l for zinc (UNEP 1993). Upon discharge to the ocean, there will be a very large dilution of these metals in the effluent. There is, however, the potential for an impact on the immediate aquatic environment at the point of discharge. Aquatic toxicity of copper is well studied, and there is experimental evidence that a considerable number of species are sensitive to dissolved concentrations as low as 1-10 ug/l (Bryan & Langston 1992). The total quantities of these metals discharged to the local environment cannot be calculated without further information on the total volume of discharge from the communal drain.

The sample of combined effluent from the communal drain also contained chromium at 47 ug/l. The average background level of chromium is 0.4-8.0 ug/l in drinking water (USPHS 1997). Legislation for levels of chromium in drinking water include U.S. Public Health Service guidelines and World Health Organisation recommends limits of 50 ug/l (WHO 1993, USPHS 1997). While the level of chromium in the combined effluent is not excessively high, the total discharge of this toxic metal may place a further burden on the local environment.

As the communal drain receives discharges from a number of sources, it is not possible to identify the source or sources of these metals.

The effluent sample AM0168 was collected from the discharge pipe of the Oxiquim facility before it joins the communal drain. The analysis results presented in table 3.1 indicate some similarities between this waste stream and the combined effluent in the communal drain, although differences are also clear.

The hydrocarbons and the 1,4-dichlorobenzene discussed above were both detected in sample AM0168 from the Oxiquim discharge as well as in sample AM0167 from the communal drain. These are both very common pollutants. 1,4-dichlorobenzene was slightly more abundant in the sample of Oxiquim effluent (AM0168) than in the sample from the communal drain (AM0167), which may be as a result of a dilution due to other discharges into communal drain. However, due to its regular occurrence in domestic sewage, it is difficult to draw any firm conclusions about the source or sources of this persistent organochlorine pollutant in this area. Therefore, although 1,4-dichlorbenzene and the hydrocarbons are evidently being released to the environment from Oxiquim it is highly likely that there are other additional sources of these pollutants to this drainage system.

Diphenyl ether was identified in the Oxiquim effluent (AM0168) as well as in the sample collected from the communal drain (AM0167). The presence of this compound in both samples suggests that Oxiquim is likely to be the primary source of this chemical, although the possibility of contributions from other industrial inputs to the communal

drain cannot be ruled out. This compound is a fairly common industrial contaminant, being used in a range of organic synthetic processes.

The sample of effluent collected from the discharge pipe of Oxiquim (AM0168) did not contain any of the metals listed in table 3.1 at concentrations of concern. The only metal found above detection levels was manganese at 24 ug/l. The average background level of manganese in fresh water is 12 ug/l, but this value can vary with local geology (Bowen 1966).

Some of the organic contaminants present in the Oxiquim effluent were not detected in the wastewater from the communal drain. Of these, 1,1'-biphenyl is used in a variety of organic syntheses, or it may be a component of commonly used oil based products.

Of more concern, is the presence of two isomers of tris(monochloropropyl) phosphate (TMCPP). These compounds are representatives of the class of chlorinated alkyl phosphate esters and they are used as a flame retardant in rigid and flexible polyurethane foams (NRC 2000). TMCPP mixtures are sold under various trade names, including Fyrol PCF, Antiblaze 80, Amgard TMCP, and Hostaflam OP 820 (NRC 2000). It is not known whether TMCPPs have been used or formulated at the Oxiquim plant, although flame retardants (without specification) are mentioned in the list of products of this company (Oxiquim 2000).

Studies have shown that TMCPPs show acute toxicity to a number of organisms in the environment, with LD_{50} values ranging from 3.6 to 180 mg/litre. In addition, aquatic toxicity information shows that changes occur in algae, daphnids and fish at concentrations of 6, 32, and 9.8 mg/litre, respectively. No studies of the effects of this flame retardant on humans are available (IPCS 1998).

The reproductive toxicity, immunotoxicity and carcinogenic potential of tris(1-chloro-2-propyl) phosphate have not been investigated. However, studies on a very similar compound, tris(2-chloroethyl) phosphate, showed carcinogenic properties when tested on mice and rats (IPCS 1998).

Tris(1-chloro-2-propyl) phosphate is relatively stable and is not readily biodegraded in sewage sludge inocula. There is little further information on the degradation products of these TMCPPs other than under combustion conditions, which leads to the production of hydrochloric acid and chlorinated hydrocarbons (Akzo Nobel 1999).

The absence of the 1,1-biphenyl and the chlorinated flame retardants in the combined effluent from the communal drain may be partly due to the fact that the samples were collected on different days since industrial effluents can vary significantly from day to day (Johnston *et al.* 1991). This can mean that not all pollutants being discharged are detectable at any one time.

4. CONCLUSIONS

The results of this investigation clearly show that wastewaters discharged from the Oxiquim plant via the communal drain contain compounds that can have a detrimental

impact on the environment to which they are released. Of these pollutants, the presence of the toxic chlorinated organophosphates (TMCPPs) is of greatest concern.

Despite being awarded the "Best work in Clean Production" award by the Chilean Minister of Economy in March 1999, the discharge of chemical wastes from the Oxiquim plant clearly need to be addressed. Clean production implies the elimination of all toxic compounds from the processes employed at this plant.

In light of the apparent variability in the Oxiquim waste stream, further investigation to fully characterise the wastes currently being discharged from this plant need to be carried out. In addition, more information on the raw materials, processes and wastes from the Oxiquim plant needs to be made available. While this study addressed only the discharges of wastes to water, discharges to air and their control also need to be addressed.

Inputs to the communal drain from sources other than the Oxiquim plant have been demonstrated to contain pollutants of concern, including the persistent organochlorine alpha-hexachlorocyclohexane (HCH) and a number of potentially toxic metals. Information on the source of these chemicals need to be made available, and procedures put in place to prevent the discharge of pollutants that have a potential environmental impact.

5. REFERENCES

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A.1. Organic analysis

A.1.1. Preparation of samples for organic screen analysis

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

A.1.2. 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 pentane (15ml) and acetone (5ml) were added and the extraction procedure repeated. Finally, both extracts obtained for each sample were combined and evaporated to a volume of approximately 3ml. The concentrated extract was cleaned through a Florisil column, eluted with a 95:5 mixture of pentane: toluene, and evaporated down to a volume of 2 ml under a stream of analytical grade nitrogen. 1-Bromonaphthalene was then added at a concentration of 10 mg/l to provide an indication of GC/MS performance.

A.1.3   Aqueous samples

Prior to the extraction, samples were spiked with deuterated naphthalene (an internal standard) at a concentration of 10 mg/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 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 pentane (20ml) was added and the extraction procedure repeated. Both extracts were combined and cleaned up as described above for solid samples.

A.1.4. Chromatographic analysis

Organic compounds were identified qualitatively and quantitatively using Gas Chromatography Mass Spectrometry (GC-MS).

The instrumentation used 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. In addition, 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. Identification of tris(2-chloroisopropyl) phosphate isomers was additionally checked against technical Fyrol PCF kindly provided by Akzo Nobel, UK.

Compound	Ions monitored
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-BHC	181, 183, 219, 217
Benzene, hexachloro-	284, 286, 282, 249
Simazine	200, 215, 202, 173
beta-BHC	181, 183, 219, 217
gamma-BHC	181, 183, 219, 217
delta-BHC	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

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

Compound	Ions monitored
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

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

Results are reported as a list of those compounds reliably and 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 quality matches of between 51% and 90% against the HP Wiley 275 library only. Analytes yielding match qualities of 50% or less are assumed to be unidentified.

A.1.2   Heavy Metal Analysis

A.1.2.1   Preparation of samples for heavy metal analysis

On arrival, 100ml of the sample was transferred to a clean glass bottle and acidified with nitric acid (10% v/v). Of this solution, 50 ml was transferred to a 100ml boiling tube, placed onto the Gerhardt Kjeldatherm digestion block 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, made up to a volume of 50 ml with deionised water, and mixed.

A.1.2.2   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 10% 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 10% 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.

* - COMPOUNDS IDENTIFIED ONLY AT TRACE LEVELS USING SELECTIVE ION MONITORING
(SIM) METHOD

Sample Number: AM0167	Sample Number: AM0168
Number of Compounds isolated:18	Number of compounds isolated:26
COMPOUNDS RELIABLY IDENTIFIED: Benzene, 1,4-dichloro- Cyclohexane, .alpha.-hexachloro- * Diphenyl ether Eicosane Heneicosane Heptadecane Hexadecane Limonene Octadecane Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl- Tetradecane Tricosane Tetracosahexaene, 2,6,10,15,19,23-hexamethyl- COMPOUNDS TENTATIVELY IDENTIFIED: Benzene, (1-butyloctyl)- Tricosane	COMPOUNDS RELIABLY IDENTIFIED: 1,1'-Biphenyl 2,4,6-Cycloheptatrien-1-one Benzaldehyde, 2,4-dimethyl- Benzene, 1,4-dichloro- * Diphenyl ether Docosane Eicosane Octadecane Pentacosane Tetratetracontane Tris(2-chloroisopropyl) phosphate (2 isomers) COMPOUNDS TENTATIVELY IDENTIFIED : 3-Heptyne, 5,5-dimethyl- Decane, 2,4,6-trimethyl- Pentadecane Tridecane, 5-propyl-

APPENDIX 3   **TOXICOLOGICAL OUTLINES FOR KEY ORGANIC COMPOUNDS**

A.3.1 Tris(monochloroisopropyl) phosphates (TMCPPs)

Tris(monochloropropyl) phosphates (TMCPPs) are four isomers having the molecular formula $C_9H_{18}Cl_3O_4P$ which belong to the class of chlorinated alkyl phosphate esters. The most abundant isomer in commercial products is the completely branched isomer, tris(1-chloro-2-propyl) phosphate and the least abundant form is the completely liner isomer, tris(2-chloropropyl) phosphate. Variations in manufacturing methods result in commercial formulations that contain different proportions of four isomers. Although tris(1-chloro-2-propyl) phosphate is the most abundant isomer, companies have tended to refer to their product by the name tris(2-chloropropyl) phosphate.

TMCPPs are not known to occur naturally but are manufactured from propylene oxide and phosphorous oxychloride (IPCS 1998). TMCPPs are used as a flame retardants in rigid and flexible polyurethane foams, although they may also be used for textile (non-apparel) finishes (NRC 2000). According to the International Programme on Chemical Safety, (IPCS 1998), the annual worldwide demand for TMCPPs exceeded 40,000 metric tonnes in 1997. TMCPP mixtures are sold under various trade names including Antiblaze 80, Amgard TMCP, Fyrol PCF, and Hostaflam PO 820.

Tris(1-chloro-2-propyl) phosphate is not readily biodegraded in sewage sludge inocula though it is rapidly metabolised by fish (IPCS 1998). These compounds are relatively stable and undergo only slow hydrolysis under weak alkaline or acid conditions. There is little or no further information on the degradation products of TMCPPs other than under combustion conditions, which leads to the production of hydrochloric acid and chlorinated hydrocarbons (Akzo Nobel 1999).

Traces of tris(1-chloro-2-propyl) phosphate have been detected in industrial and domestic effluents, but not in surface waters and sediments (IPCS 1998). Also three isomers of TMCPP have been detected in air samples from some common indoor work environment, i.e., an office building, a day care center, and a school building (Carlsson *et al* 1997).

Tris(1-chloro-2-propyl) phosphate is of low to moderate acute toxicity by oral (LD_{50} in rats is 101-4200 mg/kg body weight), dermal (LD_{50} in rats and rabbits is > 5000 mg/kg body weight) and inhalation routes (LD_{50} in rats is > 4.6 mg/litre) (IPCS 1998). Rabbit eye and skin irritant studies have indicated that tris(1-chloro-2-propyl) phosphate is either non-irritant or mildly irritant.

The reproductive toxicity, immunotoxicity and carcinogenic potential of tris(1-chloro-2-propyl) phosphate have not been investigated. There are no data on the subchronic or chronic toxicity of TMCPPs for dermal, inhalation, or oral routes of exposure (NRC 2000). The National Research Council (NRC) recommends that further studies need to be carried out into the effects of the release of TMCPPs vapours into air and into saline from treated fabric. (NRC 2000). In addition, no studies of the effects of this flame retardant on humans are available. However, acute toxicity values for other organisms in the environment are available, with LD_{50} values ranging from 3.6 to 180 mg/litre. Aquatic toxicity information shows that changes occur in algae, daphnids and fish at concentrations of 6, 32, and 9.8 mg/litre, respectively (IPCS 1998).

Despite the lack of information on the carcinogenic potential of the TMCPPs identified, studies on a very similar compound, tris(2-chloroethyl) phosphate, showed that is possesses carcinogenic properties when tested on mice and rats (IPCS 1998).

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A.3.2 Dichlorobenzenes

1,2-dichlorobenzene and 1,3-dichlorobenzene are colourless liquids; 1,4-dichlorobenzene forms colourless crystals at room temperature (Ware 1988a & b).

Ware (1988b) reports human symptoms after exposure to dichlorobenzenes, but does not distinguish between isomers. Effects reported are anaemia, skin lesions, vomiting, headaches, eye and respiratory tract irritation, anorexia, weight loss, yellow atrophy of the liver, blood dyscrasias, porphyria, and chromosomal breaks in blood samples. Animal experiments recorded liver and kidney damage to be the most frequent effects, though high doses caused CNS perturbation and death through respiratory depression. The dichlorobenzenes are bioaccumulative in algae, aquatic invertebrates and fish (Ware 1988b). All three have also been reportedly found in blood (Ware 1988b).

1,4-Dichlorobenzene (p-dichlorobenzene) is used largely in the production of deodorant blocks and room deodorants. It is also used as a moth control agent, as an insecticide and an intermediate for production of insecticides and dyes. An emerging market is in the manufacture of poly(phenylene sulphide) resin (PPS), and minor uses are as a germicide, fungicide and extreme pressure lubricant (Bryant 1993, CEC 1986). 1,4-dichlorobenzene is not spontaneously combustible and does not assist fire, but it is flammable nevertheless. It may be absorbed both through the inhalation of vapours, through the skin and though consumption of contaminated food. Human symptoms include damage to the liver, kidneys and lungs. Accidental poisoning of children, presumably who has eaten moth repellent was widespread in the 1970s (CEC 1986). Once absorbed, 1,4-dichlorobenzene is stored in the adipose tissue, and has been detected in human samples (CEC 1986, Ware 1988b). The metabolism of 1,4-dichlorobenzene by mammals varies from that of the other two isomers in that mercapturic acids are not formed. 1,4-dichlorobenzene causes abnormal mitosis in higher plants. The presence of 1,4-Dichlorobenzene has been reported in human adipose tissue, as well as in blood (Ware 1988b).

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A.3.3 Hexachlorocyclohexane

Hexachlorocyclohexanes are produced by the photochemical reaction between chlorine and benzene (Safe 1993). Technical grade hexachlorocyclohexane (HCH) comprises of different isomeric forms. The approximate isomer content is alpha-HCH (60-70%), beta-HCH (7-10%), gamma-HCH (14-15%), delta-HCH (7%), and epsilon-HCH (1-2%). Lindane is the gamma isomer of hexachlorocyclohexane and it is commercially produced by purification of the technical HCH (Safe 1993). This compound has been produced worldwide for use as an insecticide to control grasshoppers, cotton and rice pests, wireworms, and other soil pests. Lindane has been used for protection of seeds, for treatment of poultry and livestock, and for control of household insects. It is also still used as a scabicide and pediculocide, usually in lotions, creams, and shampoos.

Alpha-, beta-, and gamma-HCH are the most important isomers in terms of environmental impact. The relatively high stability and lipophilicity of HCH and its global use pattern has resulted in significant environmental contamination by this chlorinated hydrocarbon. Once introduced into environment HCH may persist for many years (Martijn & Schreuder 1993). The beta-isomer is more persistent than others (ATSDR 1997).

Human intake of HCH compounds is largely through food consumption (Toppari *et al.* 1995). Alpha-, beta- and gamma-HCH have been recorded in human breast milk with the beta-isomer being the most ubiquitous (Waliszewski *et al.* 1996; Safe 1993).   The generally less widespread nature of the alpha- and gamma-isomers in comparison to beta-HCH is due to the more rapid clearance of these isomers from the body. Like many persistent organochlorines, HCH levels in the body have been found to increase with age (ASTDR 1997).

Hexachlorocyclohexane isomers have been detected in air, surface and ground water, soil and sediments (El-Gendy *et al.* 1991; Safe 1993; Xu 1994; Tan & Vijayaletchumy 1994; Skark & Zullei-Seibert 1995; Ramesh *et al.* 1991), plants (Xu 1994), birds, fish and mammals (Smith 1991; Xu 1994; Abd-Allah 1994; Norstrom & Muir 1994). In humans lindane mostly concentrates in adipose tissue (Safe 1993). It has been reported that lindane and other organochlorine compounds can be transferred through the pathway soil→earthworm→bird/mammal (Hernandez, *et al.* 1992; Romijn *et al.* 1994) thereby causing secondary poisoning.

Lindane, the gamma-isomer of hexachlorocyclohexane, is toxic to animals, humans, and aquatic species. Acute animal poisoning by lindane causes increased respiratory rate,

restlessness accompanied by increased frequency of urination, intermittent muscular spasms of the whole body, salivation, grinding of teeth and consequent bleeding from the mouth, backward movement with loss of balance and somersaulting, retraction of the head, convulsions, gasping and biting, and collapse and death usually within a day (Smith 1991).

Chronic health effects can occur at some time after exposure to lindane and can last for months or years. Lindane has been shown to cause liver, lung, endocrine gland and certain other types of cancer in animals (Smith 1991). Repeated overexposure may damage the liver. Chronic toxic effects may also include shortened lifespan, reproductive problems, lower fertility, and changes in appearance or behaviour. The differential actions of hexachlorocyclohexane isomers may produce variable effects on different regions of the nervous systems and in different species of animals (Nagata *et al.* 1996).

Hexachlorocyclohexane may be introduced to the environment from industrial discharges, insecticide applications or spills, and may cause significant damage. Acute toxic effects may include the death of animals, birds, or fish, and death or low growth rate in plants (Bunton 1996, Smith 1991). The insecticide load in surface waters does not ordinarily reach concentrations acutely toxic to aquatic fauna. However, lindane has high chronic toxicity to aquatic life. The effects of the low insecticide concentrations often appear only after relatively long exposure times. Chronic exposure to insecticides, such as lindane, can be hazardous to freshwater macroinvertebrates even at unexpectedly low concentrations (Schulz *et al.* 1995). The low-concentration effects may depend on both species and substance and therefore cannot be predicted from toxicity data at higher concentrations.

Hexachlorocyclohexane, as a toxic, persistent and bioaccumulative chemical, is a subject to the European Community legislation. The limit values and quality objectives for discharges of hexachlorocyclohexane are set by the Council Directive 84/491/EEC (EEC 1984) as amended. The uses of hexachlorocyclohexane (including lindane) were severely restricted under the Persistent Organic Pollutants (POPs) Protocol, which was adopted in 1998 and has 36 contracting parties encompassing not only Europe but also Canada and the United States of America (UNECE 1998). The POPs Protocol is part of the 1979 Convention on Long-Range Transboundary Air Pollution (LRTAP), which is under the auspices of the United Nations Economic Council for Europe. Lindane is also included in the Annex III of the 1998 Rotterdam Convention on the Prior Informed Consent procedure (PIC procedure) among 27 other chemicals (FAO/UNEP 1998). Under the PIC procedure countries should not export any chemical to any other country without first receiving explicit permission. In order to avoid unfair trade barriers arising through the implementation of the Convention, any country that has denied import of any chemical must also stop producing it domestically and may not import it from any country that is not a party to the Convention.

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A.3.4 1,1'-Biphenyl

The main users of 1,1'-biphenyl, also called diphenyl, are thought to be textile mills that use biphenyl in mixtures that dissolve dyes (US EPA, 1994). This aromatic hydrocarbon is also used specifically as fungicides (e.g. oranges, applied to the sides of shipping containers) and more generally, in organic synthesis (Budavari *et al* 1989). In the past, companies have used biphenyl as a heat transfer agent, and as a starting material to make polychlorinated biphenyls (Edwards *et al,* 1991; Budavari *et al* 1989). Biphenyl has been found toxic to the experimental animals causing CNS depression, paralysis and convulsions (Budavari *et al* 1989). Biphenyl has high acute toxicity and low chronic toxicity to aquatic life (US EPA 1994).

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A.4.1 Chromium (Cr)

A.4.1.1 Environmental levels

Chromium is found in varying concentrations in nearly all uncontaminated aquatic and terrestrial ecosystems (see Table A.4.1.1). However, in areas associated with anthropogenic emissions, ecosystem levels can far exceed natural, background concentrations (see Table A.4.1.2).

Environmental Matrix	Concentration	Reference
Seawater (open ocean)	0.057-0.234 ug/l	Bryan and Langston 1992
Freshwater	1.30 ug/l	USPHS 1997
Drinking water	0.4-8.0 ug/l	USPHS 1997
Marine sediment	30-200 mg/kg	Bryan and Langston 1992
Freshwater sediment / suspended particulates	1-500 mg/kg	USPHS 1997
Soil	<1-100 mg/kg 4-80 mg/kg	Alloway 1990 Dudka and Adriano 1997

Table A.4.1.1: Background concentrations of chromium found in water, sediment and soil

Environmental Matrix	Concentration	Reference
Marine sediment, Loughor Estuary (tin plate production) in South Wales	800 mg/kg	Bryan and Langston 1992
Marine sediment, Sawyer's Bay, New Zealand (tannery waste)	3700 mg/kg	Bryan and Langston 1992
Soil, chromium smelting, Japan	30-4560 mg/kg	Dudka and Adriano 1997
Soil, of sewage sludge amended farms, UK	138-2020 mg/kg	Alloway 1990
MSW incinerator ash, UK	44-1328 mg/kg	Mitchell et al. 1992

Table A.4.1.2: Chromium concentrations (mg/kg) associated with anthropogenic contamination and waste

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A.4.2. Copper (Cu)

A.4.2.1 Natural occurrence

Abundance of copper in the Earth's crust is reported as ranging from 24-55 mg/kg (Alloway 1990), although higher levels are associated with some shales and clays (Thornton 1995).   The largest deposits of copper are found in the USA, Chile, Canada, the Commonwealth of Independent States, Zambia and Peru (Dudka and Adriano 1997, Alloway 1990).

Volcanic activity is the major source of copper released to the atmosphere, followed by emissions from wind-borne soil particles, forest fires, sea salt spray and biogenic processes. It is estimated that the total amount of copper released to the atmosphere from natural sources is 28,000 tonnes / year, compared with an estimated anthropogenic load of 35,000 tonnes / year (Nriagu 1990).

A.4.2.2 Use and anthropogenic sources

Copper is a highly malleable and ductile metal, as well as being an excellent conductor of heat and electricity. Its principal use is as an electrical conductor (copper cables and wires), however it is also widely employed in coinage alloys, in traditional alloys such as bronze (copper and tin), brass (copper and zinc) and Monel (copper and nickel), in corrosive-resistant and decorative plating, in munitions and in dental alloys. Its compounds are used as chemical catalysts, wood preservatives, algicides, fungicides, anti-fouling paints, disinfectants, nutritional supplements in fertilisers and feeds, in petroleum refining and as printing inks and dyes, (USPHS 1997, UNEP 1993).

Estimates of anthropogenic emissions of copper are given in Tables 1-3 (Nriagu 1990, Nriagu and Pacyna 1988):

SOURCE	Emission (thousand tonnes / year)
Non-ferrous metal production (Cu, Pb, Zn, Cd, Ni)	23.2
Energy production (coal and oil combustion)	8.04
Steel and iron manufacturing	2.01
Waste incineration (municipal refuse and sewage sludge)	1.58
Mining	0.42
TOTAL	35.25

Table A.4.2.1: Worldwide atmospheric emissions (thousand tonnes / year) of copper from anthropogenic sources

SOURCE	Emission (thousand tonnes / year)
Manufacturing processes (metal, chemicals, paper, petroleum products)	34
Domestic wastewaters	28
Base metal mining and smelting	14
Electric power plants	13
Sewage discharges	12
Atmospheric fallout	11
TOTAL	112

Table A.4.2.2: Worldwide inputs of copper (thousand tonnes / year) into aquatic ecosystems

SOURCE	Emission (thousand tonnes / year)
Discarded manufactured products	592
Coal ashes	214
Agricultural and animal wastes	67
Logging and wood wastes	28
Urban refuse	26
Atmospheric fallout	25
Municipal sewage and organic waste	13
Solid wastes from metal fabrication	4.3
Fertilisers and peat	1.4
TOTAL	970.7

Table A.4.2.3: Worldwide inputs of copper (thousand tonnes / year) to soils

A.4.2.3 Environmental levels, contamination and behaviour

Copper is a relatively abundant "trace" metal, found at varying concentrations in nearly all uncontaminated aquatic and terrestrial ecosystems (see Table 4). However, as anthropogenic emissions of copper exceed those from natural sources, elevations above these natural, background concentrations are often found (see Table 5).

Environmental Matrix	Concentration	Reference
Seawater (English Channel, Irish Sea, North Sea)	0.35-4.0 ug/l (coastal) 0.14-0.9 ug/l (open ocean)	Law et al. 1994
Seawater (background)	0.1 ug/l	Sadiq 1992, Bryan and Langston 1992
Freshwater, UK	<20 ug/l	Mance et al. 1984
Soil	20 –30 mg/kg	Alloway 1990
Marine sediment	10-30 mg/kg	UNEP 1993, Bryan and Langston 1992
Freshwater sediment	45-50 mg/kg	Salomons and Forstner 1984,

Table A.4.2.4: Background concentrations of copper found in water, sediment and soil

Copper may exist in natural waters either in the dissolved form as the cupric (+2) ion or complexed with inorganic anions or organic ligands (e.g. carbonates, chlorides, humic and fulvic acids). It may also be present as an insoluble precipitate (e.g. a hydroxide, phosphate, or sulphide) or adsorbed onto particulate matter. Alternatively it can be adsorbed to bottom sediments or exist as settled particulates. The relative concentrations of each of these forms is dependant upon a number of chemical parameters, including pH, salinity, alkalinity, and the presence of organic ligands, inorganic anions and other metal ions. However studies have frequently shown that the free +2 ion concentration is low, compared to the levels of copper associated with suspended and bottom sediments (USPHS 1997, Mance et al. 1984).

Site Description	Concentration	Reference
Seawater, Restronguet Creek, UK (receives acidic drainage from past and present mining activities)	>2000 ug/l	Bryan and Langston 1992
Sediment, Restronguet Creek	3000 mg/kg	Bryan and Langston 1992
Sediment, Izmir Bay (receives large quantities of industrial and domestic wastes)	33-866 mg/kg	UNEP 1993
Soil (nickel-copper mining and smelting, Sudbury, Ontario)	11-1890 mg/kg	Dudka et al 1995
Soil treated with copper fungicidal sprays	110-1500 mg/kg	Alloway 1990
MSW incinerator ash (UK)	296-1307 mg/kg	Mitchell et al. 1992

Table A.4.2.5: Copper concentrations associated with sites of anthropogenic contamination and waste

Copper in a soluble form is far more bioavailable and far more likely to migrate through the environment, than if it is bound to organic matter or present as an insoluble precipitate. It is one of the most important, essential elements for plants and animals. However if plants and animals are exposed to elevated concentrations of bioavailable copper, bioaccumulation can result, with possible toxic effects (USPHS 1997).

A.4.2.4 Toxicity and essentiality

Copper is an essential nutrient that is incorporated into numerous plant and animal enzyme systems, e.g. in humans, those involved in haemoglobin formation, carbohydrate metabolism, melanin formation, and cross-linking of collagen, elastin and hair keratin (USPHS 1997). Human deficiency is characterised by anaemia, resulting from defective haemoglobin synthesis (Goyer 1996). At the other extreme, however, vomiting, hypotension, jaundice, coma and even death, can result from acute poisoning (USPHS 1997).

Therefore, even though copper is essential for good health, a very large single dose, or long term elevated exposure can be harmful. Oral exposure to high levels can cause vomiting, diarrhoea, stomach cramps and nausea (USPHS 1997). Copper homeostasis plays an important role in the prevention of copper toxicity, in humans, terrestrial animals, and aquatic organisms. Copper is readily absorbed from the stomach and small intestine; and after requirements are met, there are several mechanisms that prevent copper overload

e.g. bile excretion, increased storage in the liver or bone marrow (USPHS 1997). However, failure of this homeostatic mechanism can occur in humans and animals following exposure to high levels of copper. This rare disease, known as Wilson's disease, is characterised by the excessive retention of copper in the liver and impaired copper excretion in the bile. Resulting in liver and kidney damage and haemolytic anaemia (USPHS 1997).

In addition to these effects, developmental and reproductive damage, following exposure to high levels of copper, has been seen in animals. However no such effects have been reported in humans (USPHS 1997).

Aquatic toxicity to copper is well studied, and there is experimental evidence that a considerable number of species are sensitive to dissolved concentrations as low as 1-10 ug/l (Bryan and Langston 1992). For example, studies have shown that at levels of 2 ug/l, the survival rate of young bay scallops was significantly affected; and in the embryos of oysters and mussels concentrations of 5 ug/l were seen to induce abnormalities. A similar concentration resulted in increased mortalities in populations of the isopod crustacean *Idothea baltica* (UNEP 1993, Bryan and Langston 1992, Giudici et al. 1989). Other studies have reported reductions in the survival, growth and fertility of amphipods and copepods (Conradi and DePledge 1998, UNEP 1993), and embryonic sensitivity in fish exposed to levels of 25 ug/l (UNEP 1993, Mance et al. 1984). Furthermore, a study of species diversity in benthic communities from Norwegian fjords, led to the conclusion that the most sensitive animals were missing from sites where sediment-copper levels exceeded 200 mg/kg. In the UK, such concentrations are exceeded in a number of estuaries, including the Fal and the Tamar. Here, many species of bivalves, including some mussels, clams and cockles are absent, and at best distribution is severely limited. The toxicity of the surface sediment containing over 2000 mg/kg of copper, towards juvenile bivalves appears to be the reason (Bryan and Langston 1992).

A.4.2.5 Legislation

Unlike mercury, cadmium and lead, copper and its compounds are not included on National and International lists of priority pollutants. However, whilst the reduction of anthropogenic emissions does not require priority action, pollution of terrestrial and aquatic environments by copper still needs to cease. Copper is therefore included on the majority of subsidiary and secondary pollutant lists. Examples of guidelines and permissible environmental levels include the following:

European Council Directive 75/440/EEC concerning the quality required of surface water intended for the abstraction of drinking water in the Member States. Water containing more that 50 ug/l must be subjected to physical and chemical treatment prior to use.

European Council Directive 76/464/EEC on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community. Copper is included in List II, and as such, water pollution caused by its presence must be reduced in keeping with National Environmental Quality Standards.

European Council Directive 78/659/EEC on the quality of fresh waters needing protection or improvement in order to support fish life. An Environmental Quality Standard of 40 ug/l is set.

The Water Research Centre in the UK recommends the following Environmental Quality Standards for copper: protection of freshwater fish, other freshwater life and associated non-aquatic organisms 1-28 ug/l; protection of saltwater fish, shellfish, other saltwater life and associated non-aquatic organisms 5 ug/l (Mance et al. 1984).

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A.4.3. Nickel (Ni)

A.4.3.1. Natural occurrence

Nickel is the 24th most abundant element in the Earth's crust, with an average concentration of 75 mg/kg. However in some igneous rocks, clays and shales, higher concentrations can be found (Alloway 1990). The largest deposits of nickel are found in Canada, Cuba, Australia, CIS, and South Africa, with the most important single deposit (supplying over a quarter of the world's nickel), found in Canada, at Sudbury Basin (Greenwood and Earnshaw 1984).

Volcanic activity is the largest natural source of atmospheric nickel, followed by emissions from wind-borne soil particles, forest fires, sea salt spray and biogenic processes. It is estimated that the total amount of nickel released to the atmosphere from natural sources is 29,000 tonnes / year, compared with an estimated anthropogenic load of 52,000 tonnes / year (Nriagu 1990).

A.4.3.2. Use and anthropogenic sources

Nickel extensively used in electroplating, in the petroleum industry, in ceramics, in nickel-cadmium batteries and as an industrial catalyst, used for the hydrogenation of fats and methanation of fuel gases (USPHS 1997, Alloway 1990, Greenwood and Earnshaw 1984).

Estimates of anthropogenic emissions of nickel are given in tables 4.3.1-4.3.3 (Nriagu 1990, Nriagu and Pacyna 1988):

SOURCE	Emission (thousand tonnes/year)
Energy production (coal and oil combustion)	42.0
Steel and iron manufacture	4.47
Non-ferrous metal production (Ni, Cu, Pb)	3.99
Mining	0.80
Waste incineration (municipal refuse & sewage sludge)	0.35
TOTAL	51.61

Table A.4.3.1: Worldwide atmospheric emissions of nickel (thousand tonnes/year) from anthropogenic sources

SOURCE	Emission (thousand tonnes/year)
Domestic wastewaters	62
Base metal mining and smelting	13
Electrical power plants	11
Sewage discharges	11
Atmospheric fallout	10
Manufacturing processes (metal, chemicals, paper, petroleum products)	7.4
TOTAL	114.4

Table A.4.3.2: Worldwide inputs of nickel (thousand tonnes/year) into aquatic ecosystems

SOURCE	Emission (thousand tonnes/year)
Coal ashes	168
Agricultural and animal wastes	45
Atmospheric fallout	24
Discarded manufactured products	19
Municipal sewage and organic waste	15
Logging and wood wastes	13
Urban refuse	6.1
Fertilisers and peat	2.2
Solid wastes from metal fabrication	1.7
TOTAL	294

Table 4.3.3: Worldwide inputs of nickel to soils

A.4.3.2. Environmental levels, contamination and behaviour

Nickel is found in varying concentrations in nearly all uncontaminated aquatic and terrestrial ecosystems (see table 4.3.4). However, as anthropogenic emissions of nickel far exceed those from natural sources, elevations above these natural, background concentrations, are often found (see table 4.3.5).

Environmental Matrix	Concentration	Reference
Seawater	0.1-0.5 ug/l	USPHS 1997, Law et al. 1994
Freshwater	<10-20 ug/l	USPHS 1997, Mance and Yates 1984
Freshwater sediment	45-65 mg/kg	Salomons and Forstner 1984
Soil	5-500 mg/kg (average 50 mg/kg) 40 mg/kg	USPHS 1997 Alloway 1990

Table 4.3.4: Background concentrations of nickel found in water, sediment and soil

Nickel persists in water with an estimated residence time of 23,000 years in deep oceans and 19 years in near shore waters (Nriagu 1980). Its behaviour in the aquatic environment is governed by reactions with both soluble species and particulate matter. Complexes may be formed, with a variety of soluble organic and inorganic species. In addition, interactions with solid phases may occur. For example, direct adsorption onto particles such as clays; adsorption to or co-precipitation with hydroxides of iron and manganese, complexation with natural organic particles or direct precipitation. Studies have shown that nickel is a fairly mobile metal in natural waters, especially soluble at higher pH values. However generally speaking, concentrations of soluble nickel are low compared with that associated with suspended and bottom sediments (USPHS 1997, Mance and Yates 1984).

Nickel is significantly bioaccumulated in some, but not all, aquatic organisms. Typical bioconcentration factors for significant bioaccumulators include marine phytoplankton <20-2000, seaweeds 550-2000 and algae 2000-40,000 (USPHS 1997).

Site Description	Concentration	Reference
Drinking water, near a large, open-pit mine, USA	200 ug/l	USPHS 1997
Seawater, coastal and estuarine sites of industrial and domestic discharges, UK	0.23-4.9 ug/l	Law et al. 1994
Sediment, Elsburgspruit-Natalspruit Rivers, South Africa (mining discharges and sewage)	54.5-890 mg/kg	Steenkamp et al. 1995
Soil, Sudbury Basin/Coniston, Canada (nickel mining and smelting)	100-3000 mg/kg 160-12300 mg/kg	Freedman & Hutchinson 1980 Hazlett et al. 1983
Soil, Upper Silesia, Poland (mining and smelting)	5-2150 mg/kg	Dudka et al. 1995
MSW incinerator ash, UK	45-2204 mg/kg	Mitchell et al. 1992

Table 4.3.5: Nickel concentrations associated with anthropogenic contamination and waste

In soils, the average residence time of nickel is estimated to be 2400-3500 years (Nriagu 1980), and although it is extremely persistent in soil, it is reasonably mobile and has the potential to leach through soil and subsequently enter groundwater (USPHS 1997, Alloway 1990).

A.4.3.3. Toxicity and essentiality

Very small amounts of nickel have been shown to be essential for normal growth and reproduction in some species of animals, plants and micro-organisms. It is therefore assumed that small amounts may also be essential to humans, although the precise function of nickel is unclear (USPHS 1997, Alloway 1990). However, at the other extreme, there is sufficient evidence for the carcinogenicity of nickel and certain nickel compounds e.g. oxide, subsulphide, carbonate, acetate, carbonyl and hydroxide. The US Department of Health and Human Services, in its 8th Report on Carcinogens, lists nickel and these compounds as Reasonably Anticipated to be Human Carcinogens (USPHS 1998). Metallic nickel and its alloys are listed as possible human carcinogens (Group 2B) by the International Agency for Research on Cancer (1998).

Few studies on the aquatic toxicity of nickel are available. However one toxicity study, carried out using temperate marine diatoms (Nitzschia closterium), juvenile banana prawns (Penaeus merguiensis), leader prawns (Penaeus monodon) and gastropods (Nerita chamaeleon), did find that survival and growth rates were effected by increased concentrations of nickel (Florence et al 1994).

A.4.3.4. Legislation

Unlike mercury, cadmium and lead, nickel and its compounds are not included on National and International lists of priority pollutants. However, whilst the reduction of anthropogenic emissions does not require priority action, pollution of terrestrial and aquatic environments by nickel still needs to cease. Nickel is therefore included on the majority of subsidiary and secondary pollutant lists. Examples of guidelines and permissible environmental levels include the following:

European Council Directive 76/464/EEC on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community. Nickel is included in List II, and as such, water pollution caused by its presence must be reduced in keeping with National Environmental Quality Standards.

European Community Council Directive 80/778/EEC relating to the quality of water intended for human consumption. A Maximum Permissible Limit of 50 ug/l is set.

The Water Research Centre in the UK recommends the following Environmental Quality Standards for nickel: protection of freshwater fish 50-200 ug/l; protection of other freshwater life and associated non-aquatic organisms 8-100 ug/l; protection of saltwater fish, shellfish, other saltwater life and associated non-aquatic organisms 30 ug/l (Mance and Yates 1984).

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A.4.4. Zinc (Zn)

A.4.4.1 Natural occurrence

Zinc is a relatively common metal, being 23rd in order of chemical abundance. It is found in the Earth's crust at an average concentration of 80 mg/kg, although some clay sediments and shales may contain higher concentrations (Alloway 1990, Salomons and Forstner 1984). It is not found naturally in its pure form (as a lustrous, blue-white metal) but as a mineral (most commonly sphalerite, zinc sulphide), often associated with the ores of other metals (e.g. copper, lead and cadmium) (Kroschwitz and Howe-Grant 1995).

Natural sources of atmospheric zinc include wind-borne soil particles, emissions from forest fires and volcanoes, biogenic emissions and sea-salt sprays. The total amount of Zinc released to the atmosphere from natural sources is estimated at 45,000 tonnes / year, compared with an estimated anthropogenic load of 132,000 tonnes / year (Nriagu 1990).

A.4.4.2. Use and anthropogenic sources

Zinc is one of the most extensively utilised "trace" metals (Nriagu 1990). It is most commonly employed as a protective coating for other metals e.g. galvanised steel, or as a component of bronze, brass and die-casting alloys. In addition, zinc salts are widely employed as wood preservatives, herbicides, catalysts, analytical reagents, vulcanisation accelerators for rubber, and stabilisers in PVC. They can also be found in ceramics, textiles, fertilisers, paints, pigments, batteries and dental, medical, and household products (USPHS 1997, Annema and Ros 1994, UNEP 1993, Budavari *et al.* 1989).

Estimates of anthropogenic emissions of Zinc are given in tables A.4.4.1-A.4.4.3 (Nriagu 1990, Nriagu and Pacyna 1988):

SOURCE	Emission (thousand tonnes/year)
Non-ferrous metal production (Zn, Cu, Pb, Cd, Ni)	72.0
Steel and iron manufacturing	33.4
Energy production (coal and oil combustion)	16.8
Waste incineration (municipal refuse and sewage sludge)	5.90
Commercial uses (e.g. phosphate fertilisers, cement, paper, chemicals)	3.25
Mining	0.46
TOTAL	131.81

Table A.4.4.1: Worldwide atmospheric emissions of zinc (thousand tonnes/year) from anthropogenic sources

SOURCE	Emission (thousand tonnes/year)
Manufacturing processes (metal, chemicals, paper, petroleum products)	85
Domestic wastewaters	48
Atmospheric fallout	40
Base metal mining and smelting	29
Electric power plants	18
Sewage discharges	17
TOTAL	237

Table A.4.4.2: Worldwide inputs of zinc (thousand tonnes/year) into aquatic ecosystems

SOURCE	Emission (thousand tonnes/year)
Discarded manufactured products	465
Agricultural, animal wastes, food wastes	316
Coal ashes	298
Atmospheric fallout	92
Urban refuse	60
Logging and wood wastes	39
Municipal sewage and organic waste	39
Solid wastes from metal fabrication	11
Fertilisers and peat	2.5
TOTAL	1322.5

Table A.4.4.3: Worldwide inputs of zinc (thousand tonnes/year) to soils

A.4.4.3. Environmental levels, contamination and behaviour

Zinc is a relatively abundant "trace" metal, found at varying concentrations in nearly all uncontaminated aquatic and terrestrial ecosystems (see Table 4). However, as anthropogenic emissions of zinc far exceed those from natural sources, elevations above these natural, background concentrations are often found (see Table 5).

Environmental Matrix	Concentration	Reference
Seawater	<1 ug/l (open ocean) 0.3-70 ug/l (coastal and estuarine)	Bryan and Langston 1992. UNEP 1993
Freshwater	<50 ug/l	USPHS 1997
Drinking water	0.02-1.2 mg/l	USPHS 1997
Soil	10-300 mg/kg (50 mg/kg average)	Alloway 1990
Freshwater sediment	<100 mg/kg	USPHS 1997, Salomons and Forstner 1984
Marine Sediment	<100 mg/kg	Bryan and Langston 1992, UNEP 1993

Table A.4.4.4: Background concentrations of zinc found in water, sediments and soil

Site Description	Concentration	Reference
Restronguet Creek sediment, branch of the Fal estuary, UK. Receiving acidic drainage from past and present mining activities.	3000 mg/kg	Bryan and Langston 1992
Seawater, Restronguet Creek Seawater, polluted harbours in the Mediterranean	20-20460 ug/l 450 ug/l	Bryan and Langston 1992 UNEP 1993
River water, from sites receiving urban and industrial waste, USA	0.01-2.4 mg/l	USPHS 1997
Donana National Park, Spain. Contaminated river sediments close to mining sites	879-12200 mg/kg	Pain et al. 1998

Table A.4.4.5: Zinc concentrations associated with sites of anthropogenic contamination

Zinc occurs in the environment primarily in the +2 oxidation state, either as the free (hydrated) zinc ion, or as dissolved and insoluble complexes and compounds (USPHS 1997). In soils, it often remains strongly sorbed, and in the aquatic environment it will predominantly bind to suspended material before finally accumulating in the sediment (USPHS 1997, Bryan and Langston 1992, Alloway 1990). However re-solubilisation back into an aqueous and therefore more bioavailable phase is possible under certain physical-chemical conditions, e.g. the presence of soluble anions, the absence of organic matter, clay minerals and hydrous oxides of iron and manganese, low pH and increased salinity (USPHS 1997). Zinc in a soluble form (e.g. sulphate or chloride, present in incinerator ash, or mine tailings) is far more likely to migrate through the environment than if it is bound to organic matter or present as an insoluble precipitate (e.g. as in sewage sludge) (USPHS 1997).

Zinc is an essential element, present in the tissues of animals and plants even at normal, ambient concentrations. However if plants and animals are exposed to high concentrations of bioavailable zinc, significant bioaccumulation can results, with possible toxic effects (USPHS 1997).

A.4.4.4. Toxicity and essentiality

Zinc is a nutritionally essential metal, having enzymatic, structural and regulatory roles in many biological systems (Goyer 1996, Aggett and Comerford 1995). Deficiency in humans can result in severe health consequences including growth retardation, anorexia, dermatitis, depression and neuropsychiatric symptoms (Aggett and Comerford 1995). At the other extreme, excessive dietary exposure, in both humans and animals, can cause gastrointestinal distress and diarrhoea, pancreatic damage and anaemia (USPHS 1997, Goyer 1996).

Due to the essentiality of zinc, dietary allowances of 15 mg/day for men, and 12 mg/day for women are recommended (USPHS 1997). Seafood provides a major source, and several species such as oysters, mussels, shrimps and crabs have bioconcentration factors ranging from several hundreds to several thousands (UNEP 1993). However, eating food containing very large amounts of zinc can induce the symptoms listed above. For

example, animal studies involving doses 1,000 times higher than the RDA, taken over a period of a month, resulted in anaemia and injury to the pancreas and kidney; and rats that ate very large amounts of zinc became infertile (USPHS 1997). Humans taking supplements at higher than recommended doses (400-500 mg/day) suffered severe gastro-enteritis (Abernathy and Poirier 1997); and humans who drank water from galvanised pipes, over a prolonged period, suffered irritability, muscular stiffness and pain, loss of appetite and nausea (UNEP 1993).

With regard to industrial exposure, metal fume fever resulting from the inhalation of zinc oxide fumes presents the most significant effect. Attacks usually begin after 4-8 hours of exposure, and last between 24-48 hours. Symptoms include chills and fever, profuse sweating and weakness (USPHS 1997, Goyer 1996).

Aquatic studies have shown that whilst zinc is not considered as being especially toxic to organisms, it is sometimes released into the aquatic environment in appreciable quantities. Zinc can have a direct disrupting effect on the external cell membranes or cell walls of organisms when present in appreciable quantities, resulting in rapid mortality (UNEP 1993). However, many studies now report that zinc is not only harmful at high concentrations, but also at lower sub-lethal concentrations, especially after prolonged exposure. For example, studies have shown that at concentrations as low as 15 ug/l, carbon fixation rates in natural phytoplankton populations were depressed. Others observed that the growth of cultured diatoms was inhibited at 20 ug/l (Bryan and Langston 1992). Effects on fertilisation and embryonic development in Baltic spring-spawning herring at low salinity were detected at only 5 ug/l (UNEP 1993); and the fertility of successive generations of harpacticoid copepod *Tisbe holothuria* was reduced by continuous exposure to only 10 ug/l (Verriopoulos and Hardouvelis 1988).

At slightly higher concentrations, studies investigating the effects of zinc on the hatching of brine shrimp (*Artemia salina*), noted that although increased concentrations of zinc did not affect development before emergence, the hatching stage of development was highly sensitive to, and heavily disrupted by, zinc (Bagshaw *et al* 1986). In addition, the inhibition of larval development was observed in the echinoderm (e.g. sea urchins and starfish) *Paracentrotus lividus* at a zinc concentration of only 30 ug/l (UNEP 1993). Shell growth in the mussel *Mytillus edulis* was effected at a concentration of 200 ug/l. With oxygen uptake, feeding and filtration rates were reduced at concentrations ranging between 750-2000 ug/l. Harmful effects on mollusc larva were seen to occur at levels as low as 40 ug/l (UNEP 1993).

Plant studies have shown that although an essential element for higher plants, in elevated concentrations zinc is considered phytotoxic, directly affecting crop yield and soil fertility. Soil concentrations ranging from 70-400 mg/kg are classified as critical, above which toxicity is considered likely (Alloway 1990).

A.4.4.5. Legislation

Unlike mercury, cadmium and lead, zinc and its compounds are not found on National and International Lists of priority pollutants. However, whilst the reduction of anthropogenic sources of zinc does not require priority action, pollution of terrestrial and aquatic environments by zinc still needs to cease. Zinc is therefore included on the majority of

subsidiary and secondary pollutant lists. Examples of guidelines and permissible environmental levels include the following:

European Council Directive 76/464/EEC on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community. Zinc is included in List II, and as such water pollution caused by its presence must be reduced in keeping with National Environmental Quality Standards.

European Council Directive 78/659/EEC on the quality of fresh waters needing protection or improvement in order to support fish life. An Environmental Quality Standard of 0.3 mg/l is set.

The Water Research Centre in the UK recommends the following Environmental Quality Standards for zinc: protection of freshwater salmonid fish 8-125 ug/l; protection of freshwater coarse fish 75-500 ug/l; protection of other freshwater life and associated non-aquatic organisms 100 ug/l; protection of saltwater fish, shell fish and associated non-aquatic organisms 40 ug/l (Mance and Yates 1984).

For the protection of fresh and saltwater life, environmental quality standards of 570 and 170 ug/l respectively, are set. Furthermore, any release of more than 1,000 pounds (or in some cases 5,000 pounds) of zinc or its compounds into the environment (i.e., water, soil, or air) must be reported to EPA (USPHS 1997).

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