

**Heavy metals and organic contaminants in the vicinity of the Teshima Island
illegal dumpsite, Kagawa Prefecture, Japan**

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1. Summary

Samples taken in the vicinity of the Teshima illegal waste dumpsite in the Kagawa Prefecture, Japan, were analysed for toxic heavy metals and for organic chemical contaminants. Analyses of samples obtained revealed elevated concentrations of lead, copper, nickel, manganese, cadmium and cobalt. These suggest that, while the distribution of metals and hence of metal containing wastes in the site is not homogenous, that nonetheless the site is acting as a source of heavy metals to the leachate ditch immediately adjacent to the sea and directly onto the shore on the western boundary of the site.

On the basis of a sample obtained from an excavation on the Teshima site, it is clear that the landfill contains PCBs together with other organochlorine chemicals, principally chlorobenzenes. Although, at 8.9 ppm, the PCB concentrations found were not extreme, it nevertheless indicates the possibility of a serious environmental threat. The potential for organic contaminants to escape from the site is suggested by the presence of chlorobenzenes in sediment from the leachate ditch to the northern side of the site.

The results from the Teshima site clearly indicate that materials are poorly contained and are entering the wider environment. In both cases a full characterisation of the dump contents and the integrity of the sites is warranted in order to evaluate the scope of the problem and to identify suitable remediation options.

2. Introduction

During November 1999, seven samples were collected within or on the boundaries of the illegal dump site located on Teshima Island in the prefecture of Kagawa. Three samples were collected from the north boundary of the site; one sediment adjacent to an old leachate discharge pipe, and one sediment and one liquid sample from a ditch running alongside the northern boundary. Three sediment samples were collected along the west boundary of the site, associated with two leachate seep channels which were discharging water to the sea at the time of sampling. One additional sample was taken from the waste contained within the site itself, collected approximately 5-10 cm below the surface at a point at which a 4-5 metre deep hole had been dug into the waste.

The samples were analysed in order to determine the quantities of heavy metals and the nature of organic contaminants in material contained within the site, in leachates and in sediments adjacent to the site.

3. Materials and Methods

All samples were collected in pre-cleaned glass bottles and returned immediately to the Greenpeace Research Laboratories, University of Exeter, UK, for analysis. Brief descriptions of the samples collected, along with laboratory codes assigned at the Greenpeace Research Laboratories, are summarised in Table 1. Heavy metal concentrations were determined by ICP atomic emission spectrophotometry, following acid digestion and using appropriate certified reference materials in addition to intralaboratory standards. Organic compounds were isolated and identified as far as possible using gas chromatography and mass spectrometry, following

liquid:liquid extraction into pentane (for aqueous samples) or liquid:solid extraction into a mixture of pentane and acetone (for solid samples). Full details of the methods for sample preparation and for metals and GC-MS screening analysis are given in Appendix 1. In addition, quantitative PCB analysis was conducted on sample JP9009 by EUS Laboratories, Southampton, UK, according to UKAS standards.

Sample Code	Sample description
<i>Teshima Island illegal dumpsite, north side, leachate pond and discharge point</i>	
JP9004	Sediment from directly in front of old, partially blocked leachate drain
JP9005	Sediment from leachate collection ditch running along north boundary of site
JP9011	Liquid from leachate collection ditch running along north boundary of site
<i>Teshima Island illegal dumpsite, west side, leachate seeps</i>	
JP9006	Sediment from seep on west side of landfill (ongoing discharge to sea)
JP9007	As JP9006, but black material also seen to be coating rocks
JP9008	Sediment from second seep on west side of landfill (approx. 5-10 m from JP9006)
<i>Teshima Island illegal dumpsite, solid waste</i>	
JP9009	Waste collected 5-10cm beneath surface at location of 4-5m deep excavation

Table 1: samples collected from Teshima Island landfill site, November 1999

3. Results and Discussion

3.1 Heavy metals

Concentrations of nine heavy metals in sediments and the single solid waste sample collected are presented in Table 2, and concentrations in the liquid sample in Table 3, below.

Elevated levels of lead, along with copper and nickel, were detected in the sediment collected from the leachate ditch running along the northern boundary of the Teshima Island dumpsite (JP9005). At 2.7 g/kg dry weight, copper was particularly abundant in this material, although levels of lead (0.65 g/kg) and nickel (0.27 g/kg) were also substantial. Elevated levels of copper and nickel were also detectable in the liquid/leachate overlying this sediment in the ditch (JP9011), despite heavy rain preceding the sampling which might have diluted the leachate, and in the single solid waste sample collected from a nearby location within the landfill site itself (JP9009, 2.6 g/kg copper and 0.28 g/kg nickel). Levels of lead in this waste sample were extremely high, over 3.5 g/kg dry weight, indicating the hazardous nature of the waste contained on the site.

Lead, copper and nickel all exert toxic effects at elevated exposure concentrations. The toxicity of lead is particularly well studied, with a wide range of reported adverse effects including nervous system and blood disorders and changes in bone metabolism and kidney function (Goyer 1996, USPHS 1997). Of particular concern for humans are the reported impacts of

relatively low level lead exposure on cognitive and behavioural development in children (Pirckle *et al.* 1998). Both lead and copper have long been known to be toxic to a wide range of aquatic organisms, in some cases at low ug/l (ppb) concentrations (Bryan and Langston 1992). Nickel and nickel compounds have also been shown to be toxic to marine diatoms and invertebrates (Florence *et al.* 1994).

Sample code	Mn (mg/kg)	Cr (mg/kg)	Zn (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	Co (mg/kg)	Cd (mg/kg)	Hg (mg/kg)
<i>Teshima Island illegal dumpsite, north side, leachate pond and discharge point</i>									
JP9004	1168.6	17.7	137.3	195.1	28.4	8.8	2.0	n/d	n/d
JP9005	941.4	55.8	2435.6	2719.2	647.1	266.4	15.4	5.8	0.6
<i>Teshima Island illegal dumpsite, west side, leachate seeps</i>									
JP9006	18480.4	7.8	275.5	123.5	22.6	10.8	23.5	90.2	1.0
JP9007	6359.3	1.9	164.8	121.3	66.7	8.3	4.6	6.5	0.7
JP9008	3387.8	n/d	82.7	45.9	27.6	4.1	4.1	6.1	n/d
<i>Teshima Island illegal dumpsite, solid waste</i>									
JP9009	1021.0	207.0	7746.0	2628.0	3553.0	280.0	22.0	11.0	1.8

Table 2: summary of heavy metal concentrations in solid (sediment and waste) samples (expressed in mg/kg dry weight) collected from within or in the vicinity of Teshima Island landfill site, November 1999.

Sample code	Mn (ug/l)	Cr (ug/l)	Zn (ug/l)	Cu (ug/l)	Pb (ug/l)	Ni (ug/l)	Co (ug/l)	Cd (ug/l)	Hg (ug/l)
<i>Teshima Island illegal dumpsite, north side, leachate pond</i>									
JP9011	30	<10	190	710	60	130	10	<10	<2

Table 3: Summary of heavy metal concentrations in liquid (possibly leachate) samples (expressed in ug/l) collected adjacent to Teshima landfill site, November 1999.

Sample JP9006, collected from one of the two seeps identified on the western boundary of the Teshima Island site, also contained elevated concentrations of heavy metals, although in this case the predominant metals were manganese (18.4 g/kg, or 1.8% by dry weight), cadmium (0.09 g/kg) and, to a lesser degree, cobalt (0.02 g/kg). There was some evidence for elevation of manganese concentrations in the other two sediment samples collected on the western boundary of the landfill.

Further background information on sources and toxicities of the heavy metals lead, copper, nickel and cadmium are provided in Appendix 3.

The differences between heavy metal profiles of samples collected in the north and west sides of the site may indicate variations in the nature of the wastes dumped in different areas of the landfill itself. It is not possible, however, to deduce anything further about possible sources of these metals within the site. It is clear, nonetheless, that the site appears to be acting as a source of heavy metals to the leachate ditch immediately adjacent to the sea and directly to the shore on the western boundary of the site.

3.2 Organic contaminants

Table 4 provides a summary of the numbers and classes of organic chemicals isolated and identified in each of the samples from the landfill. Details of the organic compounds identified in each sample are given in Appendix 2. Typically for organic chemicals in wastes and environmental samples, a relatively small proportion (percentages in column 3) of the organic compounds isolated could be identified with any reliability. This renders detailed discussion of the content of the samples, and their toxicological significance, extremely difficult from the outset (see, e.g. Johnston *et al.* 1996).

Sample Code	Sample type	Compounds Isolated	Reliably Identified	Halogenated Compounds	PAHs	Phenolic compounds	Other Aromatics	Aliphatics
<i>Teshima Island illegal dumpsite, north side, leachate pond and discharge point</i>								
JP9004	sediment	54	2	0	1	0	0	0
JP9005	sediment	100	8	4	1	1	0	1
JP9011	leachate	2	0	0	0	0	0	0
<i>Teshima Island illegal dumpsite, west side, leachate seeps</i>								
JP9006	sediment	75	5	0	1	0	3	1
JP9007	sediment	42	3	0	0	0	1	2
JP9008	Sediment	61	2	0	1	0	0	1
<i>Teshima Island illegal dumpsite, solid waste</i>								
JP9009	waste	228	77	24	5	1	26	11

Table 4: summary of qualitative results from GC/MS analysis of samples for organic contaminants Teshima Island landfill sites, November 1999.

Organochlorine contaminants were present in two of the samples collected from the Teshima Island landfill. Di- and tri-chlorinated benzenes were identified in the sediment collected from the leachate ditch to the north side of the site (JP9005), and di-, tri-, tetra- and pentachlorobenzenes from the samples of waste collected from the site itself (JP9009).

Analyte	Concentration (ug/g)
Total PCBs	8.9
PCB 28	0.65
PCB 52	0.03
PCB 101	0.04
PCB 77	0.01
PCB 118	0.03
PCB 153	0.01
PCB 138	0.01
PCB 126	<0.005
PCB 156	<0.005
PCB 180	<0.005
PCB 169	<0.005

Table 5: Results of quantitative analysis for PCBs in sample JP9009 collected at Teshima landfill site, November 1999. Results are reported on a total (formulation) and congener specific basis.

Chlorinated benzenes are toxic and persistent contaminants, some of which are known to accumulate in the tissues of fish and other organisms (Ware 1988). Primary target organs for chlorobenzene toxicity in animals include the liver and kidney (Bryant 1993, Meek *et al.* 1994a,b), although the higher chlorinated benzenes (tetra- and penta-) have also been implicated in damage to the thyroid and in certain types of foetal and developmental toxicity (Giddings *et al.* 1994a,b,c). Trichlorobenzenes have been demonstrated to be toxic to phytoplankton (Sicko-Goad and Andersen 1993).

Di- through to penta-chlorinated benzenes have been manufactured as chemical intermediates for the preparation of other chlorinated chemicals, and in some cases as pesticides and deodorising chemicals in their own right, although current production and use now concentrates principally on mono- and dichloro-benzenes. As a result of their use in open applications, dichlorobenzenes are now widespread environmental contaminants. The presence of di-through to penta- chlorinated benzenes in the waste sample analysed in this study, however, is more suggestive of a particular industrial source than more general environmental contamination. It is also worth noting that chlorinated benzenes (particularly tri- and tetra-chlorinated) were commonly used as solvents in PCB formulations (Swami *et al.* 1992). This may account for the co-presence of these two chemical groups in the landfilled wastes.

The waste sample also yielded a range of other organochlorine chemicals (24 of the 77 compounds identified to a high degree of reliability), including a number of compounds identified by spectral matching as polychlorinated biphenyls (PCBs, tri-, tetra-, penta- and hexachloro). PCBs are one of the 12 groups of chemicals targeted for global action under the developing UNEP POPs Convention, on the basis of their toxicity, persistence, ability to bioaccumulate and widespread distribution in the environment. Toxic effects following exposure to PCBs include liver damage, suppression of the immune system and various adverse effects on reproduction, development and behaviour (Safe 1993, Rice 1999). Some of these effects may be mediated through interference with the endocrine system (Brouwer *et al.* 1999), although the mechanisms of PCB toxicity are complex and diverse.

Following the qualitative matching of PCBs, a subsample of the waste from the landfill was forwarded to a separate laboratory for quantitative analysis of PCBs on a congener specific basis. The predominant congener identified in the mixture was PCB-28 (2,4,4'-trichlorobiphenyl). This would be indicative of the presence of one of the less heavily chlorinated technical mixes, such as Kanechlor 300 or Aroclor 1242. These would typically contain a greater proportion of trichlorinated PCBs than of other homologue groups (de Voogt & Brinkman 1989). On a formulation basis, analysis of this sample revealed PCBs to be present at 8.9 ppm by weight. The disposal of PCBs in a landfill of this type poses a potentially very serious environment problem and should be investigated further. Some further information on the production, distribution and toxicity of chlorinated benzenes and PCBs is provided in Annex 3.

The organic screen results provide a further indication of the highly hazardous nature of the wastes contained within the illegal landfill site on Teshima Island, and of the fact that some of the more mobile chlorinated compounds (the chlorinated benzenes) are detectable in the sediments of the leachate ditch on the north boundary. Given the close proximity of this ditch to the sea, and the apparent absence of any effective physical barrier to the further movement of such contaminants, it is reasonable to deduce that the landfill could, over time, act as a source of chlorinated organic compounds to the surrounding environment through direct run-off of leachate and sediments or by migration through the solid wastes, soils and sediments. Note also that, though not evaluated in this study, the site could act as a source of such chlorinated compounds as a result of their revolatilisation to, and distribution through, the atmosphere.

That chlorinated benzenes were not detectable in the water/leachate overlying the contaminated sediments in the ditch is of little surprise given the relatively low water solubility of these compounds. Trace levels of these and other chlorinated chemicals in the water may well have been present below limits of detection of the qualitative GC/MS screening technique employed. Furthermore, the heavy rain immediately prior to sampling may well have diluted levels of any organic contaminants present.

The appearance of chlorinated benzenes in both the waste and the sediment from the ditch reaffirms the apparent relationship between contaminants at these sampling locations which was suggested by the heavy metal profile and by the apparent dissimilarity between materials at these locations and sediments collected from the seeps on the western side of the site (JP9006-9008). Numerous organic compounds were isolated from the sediments from the west side of the landfill. This is suggestive of contamination from the site. However, no chlorinated chemicals were found.

Sediments JP9006 and 9007, sampled in close proximity to each other, yielded a similar range of organic compounds, with a predominance of branched alkyl benzenes (e.g. 1-pentylheptyl benzene, 1-propylnonyl benzene). While it is not possible to determine specific sources for such compounds, alkyl benzenes are common components of many petrochemical products and wastes and probably indicate runoff of such contaminants from the site itself. Alkylbenzenes are also produced following the degradation of the linear alkylbenzene sulphonate (LAS) detergents. The alkylbenzenes are highly resistant to degradation and may accumulate in sediments (Preston & Raymundo 1993). The absence of related compounds in the second seep sampled, only 5-10 m from the first, again suggests that the wastes contained in the site are highly heterogenous in nature.

4. References

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Appendix 1: Materials and Methods

All samples were collected and stored in clean glass bottles that had been thoroughly washed with detergent, and rinsed with deionised water, analytical grade pentane and nitric acid to remove all organic and heavy metal residues. Soil samples for heavy metal determinations and organic screen analysis were collected in 100ml clear glass bottles. All samples were stored cold, kept cold during transit, and refrigerated at 4°C immediately on arrival at the Greenpeace Research Laboratories.

A1. Preparation of samples for Organic Screen analysis

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

A1.1 Solid Samples

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

Extracts were decanted, filtered through a pre-cleaned hydrophobic phase separator filter and collected in reagent tubes. They were then acidified to pH 2 with 10% nitric acid. Following this, a second portion of 20ml pentane was 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 concentration 10mg/l to provide an indication of GC/MS performance.

A1.2 Aqueous Samples

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

A1.3 Chromatographic Analysis

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

Instrumentation was a Hewlett Packard (HP) 5890 Series II gas chromatograph, interfaced with a HP Chem-Station data system and linked to a HP 5972 Mass Selective Detector operated in

scan mode. The identification of compounds was carried out by computer matching against a HP Wiley 275 library of 275,000 mass spectra combined with expert interpretation.

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 qualities between 51% and 90% against HP Wiley 275 library only. Analytes yielding match qualities of 50% or less are assumed to be unidentified.

A2. Heavy Metal Analysis

A2.1 Preparation of solid samples for heavy metals analysis

Samples were air dried until weighing readings became constant (approx. 5 days). They were then crushed using a pestle and mortar until homogenous and sieved through a 2-mm mesh. 0.5 g of sample was weighed into a glass 100 ml boiling tube and to this 10 ml of deionised water was added, followed by 7.5 ml of concentrated hydrochloric acid and 2.5 ml of concentrated nitric acid. Boiling tubes were then placed onto a Gerhardt Kjeldatherm digestion block (40 space) connected to a Gerhardt Turbosog scrubber unit (filled with 10% w/v sodium hydroxide). The samples were then refluxed at 130 °C for five hours.

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

A2.2 Preparation of liquid samples for heavy metals analysis

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

A2.3 Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

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

Mercury (Hg) was determined using Cold Vapour Generation ICP-AES. Hg (II) was reduced to Hg (0) i.e. a vapour, following reduction of the samples with sodium borohydride (0.6% w/v), sodium hydroxide (0.5% w/v) and hydrochloric acid (10 molar). The vapour was carried in a

stream of argon into the spectrometer. Two calibration standards were prepared, at 10 ug/l and 100 ug/l, matrix matched to the samples (i.e. in 15% v/v hydrochloric acid and 5% v/v nitric acid). The calibration was validated using a quality control standard (80 ug/l), prepared internally from different reagent stock. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed.

Appendix 2: Organic Analytical Results

ANALYTICAL RESULTS

Sample Number: JP9004

Reference Number: JPSED04

Sample Type: Sediment

Location: Teshima, Tonosho-cho, Shozu-gun, Kagawa pref., Japan

Sampling Date: 15.11.99

Sample Information: Sample collected in front of pipe from leachate drain of the Teshima Island illegal waste dump.

ORGANIC ANALYTICAL RESULTS

Analysis method: GC/MS screen

PREPARED BY IRYNA LABUNSKA

Number of compounds isolated: 54

Compounds identified to better than 90%:

Naphthalene
Sulfur, mol. (S8)

Compounds tentatively identified:

3-Tetradecene, (E)-
Cyclotetradecane
Docosane
Dodecane
Eicosane
Heneicosane
Hentriacontane
Hexadecane
Hexadecane, 2,6,10,14-tetramethyl-
Hexane, 3,3-dimethyl-
Hexatriacontane

Nonane, 3-methyl-5-propyl-
Octadecane
Tetradecane
Tetratetracontane
Tricosane
Tridecane, 5-methyl-
Tritriacontane
Undecane, 2,10-dimethyl-
Undecane, 2-methyl-

ANALYTICAL RESULTS

Sample Number: JP9005

Reference Number: JPSED05

Sample Type: Sediment

Location: Teshima, Tonosho-cho, Shozu-gun, Kagawa pref., Japan

Sampling Date: 15.11.99

Sample Information: Sample collected in the middle of the leachate pond/drain on the north side of the Teshima Island illegal waste dump.

ORGANIC ANALYTICAL RESULTS

Analysis method: GC/MS screen

PREPARED BY IRYNA LABUNSKA

Number of compounds isolated: 100

Compounds identified to better than 90%:

Benzene, 1,2,4-trichloro-
Benzene, 1,3,5-trichloro-
Benzene, 1,3-dichloro-
Benzene, 1,4-dichloro-
Naphthalene
Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-
Sulfur, mol. (S8)
Tricosane

Compounds tentatively identified:

.alpha.-Gurjunene
11-Tricosene
17-Pentatriacontene
1-Hexadecanol
2,10-Undecanedione, 6,6-dimethyl-
4-Hexenoic acid, 3-methyl-2,6-dioxo-

Benzene, 1,1'-(1,3-propanediyl)bis-
Clovene
Cyclododecane
Cyclohexanol, dodecyl-
Docosane
Docosane, 7-hexyl-
Dodecane
Dotriacontane
Eicosane
Heptane, 2,4-dimethyl-
Hexadecane
Naphthalene
Naphthalene, 1,2,3-trimethyl-4-propenyl-, (E)-
Nonadecane
Nonadecane, 3-methyl-
Nonahexacontanoic acid
Octadecane
Octadecane, 2-methyl-
Octadecane, 3-ethyl-5-(2-ethylbutyl)-
Octadecane, 4-methyl-
Octane, 6-ethyl-2-methyl-
Pentacosane
Pentadecane, 2,6,10,14-tetramethyl-
Phenanthrene
Tetradecane
Tetratetracontane
Tetratriacontane
Triacontane
Tridecane
Tridecane, 2-methyl-
Undecane
Undecane, 2,7-dimethyl-
Undecane, 2-methyl-

ANALYTICAL RESULTS

Sample Number: JP9006

Reference Number: JPSED06

Sample Type: Sediment

Location: Teshima, Tonosho-cho, Shozu-gun, Kagawa pref., Japan

Sampling Date: 15.11.99

Sample Information: Sample collected from a leachate stream on the west side of the Teshima Island illegal waste dump.

ORGANIC ANALYTICAL RESULTS

Analysis method: GC/MS screen

PREPARED BY IRYNA LABUNSKA

Number of compounds isolated: 75

Compounds identified to better than 90%:

Benzene, (1-pentylheptyl)-
Benzene, (1-propylnonyl)-
Benzene, (1-propyloctyl)-
Cyclotetradecane
Naphthalene

Compounds tentatively identified:

1-Dodecene
1-Hexadecene
3-Methylheneicosane
9-Octadecen-1-ol, (Z)-
Benzene, (1-butylheptyl)-
Benzene, (1-butylhexyl)-
Benzene, (1-butylnonyl)-
Benzene, (1-butylloctyl)-
Benzene, (1-ethyldecyl)-

Benzene, (1-ethylnonyl)-
Benzene, (1-ethylundecyl)-
Benzene, (1-methyldecyl)-
Benzene, (1-methyldodecyl)-
Benzene, (1-methylnonyl)-
Benzene, (1-methylundecyl)-
Benzene, (1-pentylloctyl)-
Benzene, (1-propyldecyl)-
Decane, 2,9-dimethyl-
Docosane, 11-butyl-
Hexadecane, 2,6,10,14-tetramethyl-
Octadecane
Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-
Tricosane
Undecane, 2,9-dimethyl-

ANALYTICAL RESULTS

Sample Number: JP9007

Reference Number: JPSED07

Sample Type: Sediment

Location: Teshima, Tonosho-cho, Shozu-gun, Kagawa pref., Japan

Sampling Date: 15.11.99

Sample Information: Sample collected from a leachate stream (Nr.1) on the west side of the Teshima Island illegal waste dump.

ORGANIC ANALYTICAL RESULTS

Analysis method: GC/MS screen

PREPARED BY IRYNA LABUNSKA

Number of compounds isolated: 42

Compounds identified to better than 90%:

5-Octadecene, (E)-

Benzene, (1-ethyldecyl)-

Eicosane

Compounds tentatively identified:

1H-Indene, 1-methylene-

1-Pentadecene

5-Octadecene, (E)-

Benzene, (1-butylheptyl)-

Benzene, (1-butylnonyl)-

Benzene, (1-butylloctyl)-

Benzene, (1-ethylnonyl)-

Benzene, (1-methyldecyl)-

Benzene, (1-methyldodecyl)-

Benzene, (1-methylundecyl)-

Benzene, (1-pentylheptyl)-

Benzene, (1-propylnonyl)-

Cyclododecane

Docosane

Heneicosane

Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-, methylcarbamate

ANALYTICAL RESULTS

Sample Number: JP9008

Reference Number: JPSED08

Sample Type: Sediment

Location: Teshima, Tonosho-cho, Shozu-gun, Kagawa pref., Japan

Sampling Date: 15.11.99

Sample Information: Sample collected from a leachate stream (Nr.2) on the west side of the Teshima Island illegal waste dump. Leachate stream Nr.2 is located about 5-10m further along shore from the stream Nr.1.

ORGANIC ANALYTICAL RESULTS

Analysis method: GC/MS screen

PREPARED BY IRYNA LABUNSKA

Number of compounds isolated: 61

Compounds identified to better than 90%:

9-Octadecene, (E)-
Naphthalene

Compounds tentatively identified:

1-Octanol, 2-butyl-
3-Hexadecene, (Z)-
3-Octadecenal
Cyclododecane
Decane, 2,3,8-trimethyl-
Decane, 2,9-dimethyl-
Dodecane
Eicosane
Ether, hexyl pentyl
Heneicosane

Heptacosane
Heptane, 2,4-dimethyl-
Hexadecane
Hexadecane, 2,6,10,14-tetramethyl-
Nonane, 4,5-dimethyl-
Octacosane
Octadecane, 3-ethyl-5-(2-ethylbutyl)-
Octane
Octane, 4-methyl-
Pentacosane
Tetracosane, 3-ethyl-
Triacontane
Undecane
Undecane, 2,10-dimethyl-
Undecane, 2-methyl-

ANALYTICAL RESULTS

Sample Number: JP9009

Reference Number: JPSED09

Sample Type: Solid waste

Location: Teshima, Tonosho-cho, Shozu-gun, Kagawa pref., Japan

Sampling Date: 15.11.99

Sample Information: Sample collected 5-10cm below the surface of the solid waste pile inside of 4-5m hole dug at Teshima Island illegal waste dump.

ORGANIC ANALYTICAL RESULTS

Analysis method: GC/MS screen

PREPARED BY IRYNA LABUNSKA

Number of compounds isolated: 228

Compounds identified to better than 90%:

.alpha.-Amorphene
.alpha.-Longipinene
.alpha.-Terpinolene
.beta.-Serratan-3.alpha.-ol
1,1':3',1''-Tercyclopentane, 2'-dodecyl-
1,1'-Biphenyl, 2,2',3,4,4',5'-hexachloro-
1,1'-Biphenyl, 2,2',3,4,5'-pentachloro-
1,1'-Biphenyl, 2,2',3,4',5'-pentachloro-
1,1'-Biphenyl, 2,2',4,4', 5,5'-hexachloro-
1,1'-Biphenyl, 2,2',4,5,5'-pentachloro-
1,1'-Biphenyl, 2,2',4,5'-tetrachloro-
1,1'-Biphenyl, 2,2',5,5'-tetrachloro-
1,1'-Biphenyl, 2,3,3',4,4'-pentachloro-
1,1'-Biphenyl, 2,3',4,4', 5,5'-hexachloro-
1,1'-Biphenyl, 2,3',4,4',5'-pentachloro-
1,1'-Biphenyl, 2',3,4,5,5'-pentachloro-
1,1'-Biphenyl, 2,4,4'-trichloro-
1,1'-Biphenyl, 2,4,5-trichloro-
1,1'-Biphenyl, 3,3',4,4'-tetrachloro-

1,1'-Biphenyl, 3,4'-dimethyl-
1,1-Bis(p-tolyl)ethane
2,6,10,14,18,22-Tetracosahexaene, 2,6,10,15,19,23-hexamethyl-
28-nor-17alpha(h)-Hopane
9,19-Cyclocholestan-3-ol, 14-methyl-, (3.beta.,5.alpha.)-
9H-Fluorene
Benzene, (1-methylethyl)-
Benzene, 1,1'-(1,3-propanediyl)bis-
Benzene, 1,2,3,4-tetrachloro-
Benzene, 1,2,3,4-tetramethyl-
Benzene, 1,2,3,5-tetrachloro-
Benzene, 1,2,3-trichloro-
Benzene, 1,2,3-trimethyl-
Benzene, 1,2,4,5-tetrachloro-
Benzene, 1,2,4,5-tetramethyl-
Benzene, 1,2,4-trichloro-
Benzene, 1,2,4-trimethyl-
Benzene, 1,2-dichloro-
Benzene, 1,3,5-trichloro-
Benzene, 1,3-dichloro-
Benzene, 1,4-dichloro-
Benzene, 1-methyl-2-(1-methylethyl)-
Benzene, 1-methyl-4-(1-methylethyl)-
Benzene, 2-ethyl-1,4-dimethyl-
Benzene, pentachloro-
Cholest-5-en-3-ol (3.beta.)-
Cholestan-3-ol, 2-methylene-, (3.beta.,5.alpha.)-
Cholestan-3-one, 4,4-dimethyl-, (5.alpha.)-
Cyclotetradecane
D-Homoandrostane, (5.alpha.,13.alpha.)-
Dibenzothiophene
Ergost-22-en-3-ol, (3.alpha.,5.beta.,22E)-
Ergosta-5,7-dien-3-ol, (3.beta.)-
Fluoranthene
Hexadecane, 2,6,10,14-tetramethyl-
Junipene
Naphthalene
Naphthalene, 1,2,3,4-tetrahydro-1,6-dimethyl-4-(1-methylethyl)-, (1S-cis)-
Naphthalene, 1,2,3,4-tetrahydro-1-phenyl-
Naphthalene, 1,4,5-trimethyl-
Naphthalene, 1,4,6-trimethyl-
Naphthalene, 1,6,7-trimethyl-
Naphthalene, 1-methyl-
Naphthalene, 2,6-dimethyl-
Naphthalene, 2-ethenyl-
Naphthalene, 2-methyl-
Pentadecane, 2,6,10,14-tetramethyl-
Phenanthrene
Phenanthrene, 2-dodecyltetradecahydro-
Phenanthrene, trans-4a,4b,8,8,2-pentamethyl-1-butylpenhydro-

Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-
p-Mentha-1,5,8-triene
Pyrene
Tetradecane
Tricosane
Tridecane
Valencene
Widdrene

Compounds tentatively identified:

(+)-Aromadendrene
.alpha.-Cedrol
.alpha.-Thujone
[2,2]Paracyclophan
1,1':4',1'-Terphenyl, 2',4,4''-trinitro-
1,1'-Biphenyl, 2, 3',5-trichloro-
1,1'-Biphenyl, 2,2',6,6'-tetrachloro-
1,1'-Biphenyl, 2,3',4,4'-tetrachloro-
1,1'-Biphenyl, 2,3,4,5-tetrachloro-
1,1'-Biphenyl, 2,3,5,6-tetrachloro-
1,1'-Biphenyl, 2,4,4',5-tetrachloro-
1,1'-Biphenyl, 4-methyl-
11-Hexacosyne
1-Acetonaphthone, 6-methoxy-
1H-Indene, 2-butyl-4-hexyloctahydro-
2-Heptyn-1-ol
3-Octyne, 5-methyl-
5.alpha.-Androstan-3.beta.-ol, 4,4-dimethyl-
5.alpha.-Ergost-8(14)-ene
5.beta.-Cholest-23-ene, (Z)-
7-Tetradecene
7-Thiabicyclo[4.1.0]heptane, 2-methyl-
9,9'-Biphenanthrene, octacosahydro-
Acenaphthylene, 1,2-dihydro-
Anthracene, 9,10-dimethyl-
Benzene, (1,2,2-trimethylpropyl)-
Benzene, (1-methylpropyl)-
Benzene, (2-methyl-1-butenyl)-
Benzene, 1,1'-oxybis-
Benzene, 1,2-diethyl-
Benzene, 1-ethyl-3,5-dimethyl-
Benzene, 1-ethyl-3-methyl-
Benzene, 1-methyl-3-propyl-
Benzene, cyclopropyl-
Benzene, propyl-
Bicyclo[3.1.0]hexan-2-one, 4-methyl-1-(1-methylethyl)-
Cholest-23-ene, (5.beta.)-
Cholest-2-ene-2-methanol, (5.alpha.)-

Cholestane
Cholestane, 4,5-epoxy-, (4.alpha.,5.alpha.)-
Cycloprop[7,8]ergost-22-en-3-ol, 3',7-dihydro-
Cycloprop[a]inden-6-ol, 1,1a,6,6a-tetrahydro-
Cyperene
Dibenzothiophene, 3-methyl-
dl-Limonene
Ergost-22-en-3-ol, (3.beta.,5.alpha.,22E,24R)-
Ergost-5-en-3-ol, 22,23-dimethyl-, (3.beta.)-
Ethanone, 1-(3-methylphenyl)-
Furan, 2-acetyl-5-(2,5-dichlorophenyl)-
Gorgostane, (5.alpha.)-
Hexadecane
Isolongifolene
Lupanol
Naphthalene, 1,2,3,4-tetrahydro-2,7-dimethyl-
Naphthalene, 1,2,3,4-tetrahydro-6-methyl-
Naphthalene, 1,6-dimethyl-4-(1-methylethyl)-
Octane, 2,3,6,7-tetramethyl-
Pentadecane
Phenanthrene, 2-methyl-
Pregnane, (5.alpha.)-
Stigmast-5-en-3-ol, (3.beta.)-
Tricyclo[6.2.1.0(2,6)]undec-2(6)-ene
Tridecane, 2-methyl-
Undecane, 2,4-dimethyl-
Verrucarol

ANALYTICAL RESULTS

Sample Number: JP9011

Reference Number: JPLEA02

Sample Type: Leachate/Effluent

Location: Teshima, Tonosho-cho, Shozu District, Kagawa pref., Japan

Sampling Date: 15.11.99

Sample Information: Sample collected from pool of leachate of the Teshima Island illegal waste dump. It rained for 12-16 hours before sampling.

ORGANIC ANALYTICAL RESULTS

Analysis method: GC/MS screen

PREPARED BY IRYNA LABUNSKA

Number of compounds isolated: 2

Compounds identified to better than 90%:

None

Compounds tentatively identified:

None

Appendix 3: Toxicological Profiles

A3.1 Polychlorinated biphenyls (PCBs)

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

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

PCBs were always sold as technical mixes rather than individual chemicals. de Voogt and Brinkman (1989) list some 46 trade names used for PCBs and PCB containing products. The Aroclor range manufactured by Monsanto was probably the most widely used. The most important PCB applications in tonnage terms were transformer oils and capacitors (de Voogt & Brinkman 1989). In transformer oils, the PCBs were mixed with chlorobenzenes (mainly trichlorobenzenes and tetrachlorobenzenes) as solvents (Swami *et al.* 1992, de Voogt and Brinkman 1989). PCBs may also be generated as a by-product in the chlorine chemical industry. Such industries include the PVC industry, where waste EDC tars are contaminated, together with aqueous effluents, by dichlorobiphenyls.

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

Levels of PCBs in biological material may be several orders of magnitude higher than ambient. PCBs are bioconcentrated to a factor of 6000 for fish and 47000 for invertebrates (Jones *et al.* 1988). Train (1979) reports bioconcentration factors of between 2500 and 100,000.

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

Safe (1993) lists the following symptoms of PCB toxicity:

- enzyme induction
- decreased vitamin A levels
- lymphoid involution
- thymic and splenic atrophy

immunosuppression
chloracne
alopecia
oedema
hyperkeratosis
blepharitis
hyperplasia of the epithelial lining of the extrahepatic bile duct
the gall bladder and urinary tract
hepatomegaly and liver damage including necrosis
haemorrhage
altered porphyrin metabolism
tumour promotion
altered levels of steroid and thyroid hormones
reproductive toxicity including menstrual irregularities, reduced conception, early abortion, excessive menstrual and postconceptual haemorrhage, anovulation, testicular atrophy, decreased spermatogenesis, teratogenesis and developmental toxicity.

In addition, low levels of PCBs caused behavioural impairment in monkeys (Rice 1999). Aroclor 1254 compromised the immune response of earthworms (Roch & Cooper 1991). Aroclors 1221, 1254 and 1268 all reduced in vitro fertilisation rates in mice. PCB 1254 was the most potent mix (Kholkute *et al.* 1994).

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

Invertebrates display a differential response to individual PCB congeners. In the aquatic snail, *Lymnaea stagnalis*, 2,2'-dichlorobiphenyl was substantially more toxic than the other congener under test, 4,4-dichlorobiphenyl (Wilbrink *et al.* 1987), being rapidly fatal to over 60% of the test animals (Wilbrink *et al.* 1990) and inhibiting production of egg masses more rapidly.

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

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

The dioxin-like PCB 77 (3,3',4,4'-TeCB) also caused long-term changes in behavioural and neurochemical changes in laboratory animals, including alterations in dopamine function. This

congener, however, did not accumulate in brain tissue in the same way as some ortho-substituted congeners, indicating that it operates via a second mechanism, or that it is a metabolite which is the active agent (Seegal & Shain 1992).

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

The control of PCBs is addressed under most of the international legal instruments relating to organochlorines, *inter alia* the Barcelona, Helsinki, Basel, Bamako, Rotterdam OSPAR and LRTAP Conventions and the International Joint Commission on the Great Lakes. In addition, PCBs are targeted for global production ban under the UNEP POPs Convention currently being drafted. Within the EC, applications for the PCBs were first restricted by Directive 76/769/EEC, which deals with the marketing and use of dangerous substances and preparations (EC 1976). It, and its amendment (EC 1991), restricted the applications of PCBs and their replacements, the PCTs.

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

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

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A3.2 Chlorinated benzenes

The production of chlorinated benzenes is a multiple product operation achieved by direct chlorination of benzene in the liquid phase using a ferric chloride catalyst. Only limited control can be exerted over the final product mix. The distillation train used for separating the mixture has a limited resolving power and the distillates are always mixtures of close boiling isomers which can be further separated by crystallisation (see eg Bryant 1993). Distillation also gives rise to chlorinated tars.

12 chlorinated benzenes are possible, with substitution patterns as follows:

- | | |
|-------------|---|
| 1 chlorine | monochlorobenzene, |
| 2 chlorines | 1,2-di-, 1,3-di- and 1,4-dichlorobenzenes |
| 3 chlorines | 1,2,3-tri-, 1,2,4-tri- and 1,3,5-trichlorobenzenes |
| 4 chlorines | 1,2,3,4-tetra-, 1,2,3,5,-tetra- and 1,2,4,5-tetrachlorobenzenes |
| 5 chlorines | pentachlorobenzene |
| 6 chlorines | hexachlorobenzene. |

Both technological changes and environmental concerns have severely affected the production of chlorobenzenes; today only monochlorobenzene and 1,2- and 1,4-dichlorobenzenes are manufactured in large quantities. These are often produced together, with the economically optimised reaction yielding approximately 85% monochlorobenzene, 10% 1,4-dichlorobenzene and 5% 1,2-dichlorobenzene. Monochlorobenzene yield can be increased to 90% by careful monitoring of the reaction mix density and recycling of unreacted benzene, but total elimination of dichlorobenzene formation is not economical. Should the primary interest be in the para-isomer, yield may be increased by use of a selective catalyst, or the mix can be further chlorinated to produce a mixture of 1,4-dichlorobenzene and 1,2,4-trichlorobenzene. These two products can easily be separated by distillation (Bryant 1993, CEC 1986).

A3.2.1 Mono- and di-chlorobenzenes.

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

One of the earliest uses of chlorobenzene was as an intermediate for the explosive picric acid during the First World War (CEC 1986). It is used as a solvent and as an intermediate in chemical synthesis. In the US in the 1980s, the predominant use was for the production of ortho- and para-chlorobenzenes. These are used as intermediates for rubber chemicals, antioxidants, dyes and pigments, pharmaceuticals and agricultural chemicals. The fungicide benomyl, and carbofuran and the parathion group of insecticides are all derived from chlorobenzene. One previously important use was in the manufacture of DDT. Chlorobenzene production has fallen due to the development of other routes to aniline and phenol and the restriction of DDT use. Chlorobenzene is also used for the manufacture of specialty silicones, Grignard reagents and catalysts (Bryant 1993). Release to the environment is expected to derive from its use as a solvent, either through fugitive emissions or volatilisation from pesticides for which it used as a carrier. Thus, inhalation is thought to be a major route of exposure for humans since it is rarely if ever found in food. It bioaccumulates in algae, fish and aquatic invertebrates. Mammalian metabolites are reported to be p-chlorophenol, p-chlorocatechol and p-chlorophenyl mercapturic acid. Human exposure causes CNS depression and respiratory tract irritation and animal studies have reported liver necrosis, renal toxicity and effects on the pancreas, blood and lymph and adrenal glands (Ware 1988a, Meek *et al.* 1994a). Canada has derived a TDI of 8.1ug/kg body weight/day; estimated exposures (0.05-0.14ug/kg/day) are considerably lower than this (Meek *et al.* 1994a).

Ware (1988b) reports human symptoms after exposure to DCBs, 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).

1,2-Dichlorobenzene is produced unavoidably in the production of monochlorobenzene, but it is also possible to maximise dichlorobenzene production to 98% of the reaction mixture using suitable catalysts or alternative production methods leading to specific isomers. It is used mainly in the production of dyes and pesticides after conversion to 1,2-dichloro- 4-nitrobenzene

or dichloroaniline. Other uses include the solvent phase in the production of toluene diisocyanates, production of deodorants and disinfectants and on a small scale as a heat transfer fluid. According to Meek *et al.* (1994b), the largest use is in degreasing for the metal and automotive industries.

Exposed laboratory animals exhibited hepatic, renal and haematological effects as well as lymphoid depletion of the thymus and spleen and multifocal mineralisation of both muscular and heart muscles (Ware 1988b, Meek *et al.* 1994b). Developmental toxicity was only observed at concentrations that were overtly toxic to the mother. Human toxicity data are sparse, but chromosomal aberrations, anaemia and leukemia have been reported (Meek *et al.* 1994b). Mammals metabolise 1,2-dichlorobenzene to phenols and/or catechols, most of which are excreted after conjugation with glucuronic or sulphuric acids. Mercapturic acids may also be produced. The primary metabolites in humans are conjugated phenols (Ware 1988b). 1,2-dichlorobenzene is found in air, food, breast milk and drinking water (Meek *et al.* 1994b). It is also toxic to higher plants, inducing abnormal mitosis (cell division) in onions (Ware 1988b).

1,3-Dichlorobenzene is growing in importance as a starting product in the manufacture of dyes, pesticides and pharmaceuticals. However, this has not yet reached commercial importance. There are some other small, specialised uses, but larger markets have not been developed, mainly because 1,3-dichlorobenzene only occurs as a minor constituent (approx 1%) of the technical dichlorobenzene reaction mix, and to produce it by other routes is expensive (Bryant 1993). Mammalian (and human) metabolism is as for 1,2-dichlorobenzene above, but generally little is known about this 1,3-dichlorobenzene in comparison to the more commercially important dichlorobenzenes.

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 through consumption of contaminated food. Human symptoms include damage to the liver, kidneys and lungs. Accidental poisoning of children with 1,4-dichlorobenzene was widespread in the 1970s and was presumed to be caused by their having eaten moth repellent (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. 1,4-Dichlorobenzene has been reported in human adipose tissue, as well as in blood (Ware 1988b).

A3.2.2 Trichlorobenzenes

1,2,3- and 1,2,4-trichlorobenzene have been produced from the dehydrohalogenation of the unwanted isomers of the production of the pesticide 1,2,3,4,5,6-hexachlorocyclohexane. Environmental regulations have curbed the use and discharge of trichlorobenzenes to the environment, at least in Europe and the USA (Harper *et al.* 1992, Bryant 1993). Not surprisingly, therefore, little research appears to have been carried out in comparison with some other chlorobenzenes.

The general human population would probably receive their greatest exposure to trichlorobenzenes through inhalation. The toxicity of all three appear similar; they damage the liver, kidney and thyroid. There is some indication of slight fetotoxicity at high doses. There is little evidence of mutagenicity and too few data are available for the trichlorobenzenes to give a carcinogenicity classification (Giddings *et al.* 1994a). All three isomers are toxic to phytoplankton (Sicko-Goad *et al.* 1989a-d, Sicko-Goad & Andresen 1993a & b).

1,2,3-trichlorobenzene has been detected in air, drinking water, food and breast milk (Giddings *et al.* 1994a) as well as industrially polluted surface waters (Harper *et al.* 1992) and sediment (Labunska *et al.* 1998), though it was not found in human adipose tissue from Canada (Hermanson *et al.* 1997). Little is known about its toxicity other than its ability to damage the liver, kidney and thyroid (Giddings *et al.* 1994a).

More information is available about 1,2,4-trichlorobenzene. According to Giddings *et al.* (1994a), only 1,2,4-trichlorobenzene has industrial application in Canada. It is imported for solvent and intermediate use. Environmental releases come from industrial discharges and from spillage of dielectric fluids. As mentioned above, it is toxic to the liver, thyroid and kidney. Liver and kidney weights and porphyrin excretion increase. In some studies, more severe liver damage has occurred, including necrotic and non-necrotic degeneration. 1,2,4-trichlorobenzene may be found in all environmental media, though there is insufficient analytical data to tell how widespread contamination is and it was not found in human adipose tissue from Canada (Hermanson *et al.* 1997).

Giddings *et al.* (1994a) report 1,3,5-trichlorobenzene air, drinking water, food, breast milk, though it was not found in human adipose tissue from Canada (Hermanson *et al.* 1997). It can be found in association with industrial operations (Harper *et al.* 1992).

A3.2.3 Tetrachlorobenzenes

Giddings *et al.* (1994b) reviewed toxicity and exposure data for the tetrachlorobenzenes. They are no longer used or produced in Canada and releases come only from dielectric fluid spills and long-range transport. 1,2,4,5-Tetrachlorobenzene used to be used in the production of 2,4,5-trichlorophenol on a large scale, but this use has now been mostly discontinued. There are not expected to be large differences between the behaviour of the isomers. Uptake of 1,2,4,5-tetrachlorobenzene was studied in rainbow trout. It is not volatile enough to evaporate from water easily, and is accumulated by the fish, through its gills. Bioaccumulation depended upon the rate of activity and oxygen uptake of the fish, and only the low water solubility prevented significant toxicity occurring (Brauner *et al.* 1994).

The greatest exposure of the general population is probably through food. All isomers were found to affect the liver, kidney, thyroid and lungs, with 1,2,4,5-tetrachlorobenzene being the most toxic. Not enough information was available to classify tetrachlorobenzenes as to carcinogenicity.

In addition to the effects noted above, 1,2,4,5-tetrachlorobenzene has also caused changes in spleen, thymus, lymph nodes and haematological parameters in animals (Giddings *et al.* 1994b). An increase in chromosomal aberrations was seen in workers exposed to 1,2,4,5-tetrachlorophenol at a pesticide manufacturing complex (Giddings *et al.* 1994b).

In rats, 1,2,3,4- and 1,2,3,5-tetrachlorobenzene caused reduction in the number of live offspring at concentrations too low to adversely affect the mother (Giddings *et al.* 1994b).

All isomers have been detected in ambient air, drinking water and food and 1,2,3,4- and 1,2,3,5-tetrachlorobenzene have been identified in breast milk (Giddings *et al.* 1994b), though none of the isomers were detected in Canadian human adipose tissue (Hermanson *et al.* 1997).

A3.2.4 Pentachlorobenzene

Giddings *et al.* (1994c) found that, although it is no longer manufactured or used in Canada, pentachlorobenzene could still enter the Canadian environment through spillage of dielectric fluids or atmospheric transport. Animal studies demonstrate weight loss and effects on the liver, thymus, kidney, adrenal glands and digestive tract. Anaemia and malformation of sperm also occurred. There is some indication of fetotoxicity and developmental toxicity. The thyroid was impacted, with and thyroid hormone (free and total thyroxin) concentrations reduced. Pentachlorobenzene cannot be assigned a carcinogenicity classification because of lack of data. Pentachlorobenzene accumulates in, and is toxic to algae (Sicko-Goad *et al.* 1989d).

Pentachlorobenzene has been detected in air, drinking water, food and breast milk (Giddings *et al.* 1994b), though according to Hermanson *et al.* (1997) it was found in less than 15% of human adipose samples collected in Ontario, Canada.

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A3.3 Alkylbenzenes

Alkylbenzenes are single-ring aromatic compounds containing one or more aliphatic side chains. While there are theoretically thousands of alkylbenzenes, the major products of commerce and, therefore, those to which humans are most likely to be exposed included

toluene (methylbenzene), ethylbenzene, cumene (isopropylbenzene), and three xylenes (1,2-, 1,3-, and 1,4-dimethylbenzene).

The occurrence of these compounds in the environment is due to their presence in crude oil and petroleum products. Alkylbenzenes are also produced following the degradation of the linear alkylbenzene sulphonate (LAS) detergents. The alkylbenzenes are highly resistant to degradation and may accumulate in sediments (Preston & Raymundo 1993). Alkylbenzenes are useful sewage markers (Chaloux *et al.* 1995) and due to their stability in sediments, they are very useful in tracing the transport of contaminants from their point sources. Monoaromatic (benzene derivatives) and polyaromatic hydrocarbons (PAHs) 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 acute toxicity of inhaled alkylbenzenes is best described as central nervous system (CNS) depression (Andrews & Snyder, 1986). Acute toxicity does not vary very much within the group. In animal models, relatively similar concentrations of inhaled alkylbenzene vapours were found to be lethal. Impaired reaction times and impaired speech are the two most commonly noted CNS effects (Klaassen *et al.* 1996). All alkylbenzenes mentioned above are irritating to the eyes and mucous membranes, can cause irritation and burning of the skin, and all are narcotics at high concentrations. Benzene itself is a known carcinogen. Chronic exposure can lead to bone marrow depression, which in a few cases, can progress to leukemia (Budavari *et al.* 1989).

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A3.4 Lead (Pb)

A3.4.1 Occurrence, Production and Use

There is a general agreement that the abundance of lead in the average crustal rock is approximately 16 mg/kg; although black shales, rich in organic matter and sulphide minerals, can have far higher concentrations (Alloway 1990). Lead is chiefly obtained from the sulphide ore galena, by a roasting process; and is currently mined in 47 countries, making it one of the most widespread metals in terms of primary production. In addition to this, secondary smelters, processing lead metal products, are located in 43 countries, reflecting widespread recycling of lead in electric storage batteries (Dudka and Adriano 1997).

Natural sources of atmospheric lead include wind-borne soil particles and volcanic emissions, forest fires, biogenic processes and sea salt sprays. The total amount of lead released to the atmosphere from natural sources is estimated at 12,000 tonnes / year, compared with an estimated anthropogenic load of 332,000 tonnes /year (Nriagu 1990). Estimates of anthropogenic emissions of lead are given in Tables 1-3 (Nriagu 1990, Nriagu and Pacyna 1988):

SOURCE	Emission (thousand tonnes / year)
Transportation (anti-knock petrol additives)	248
Non ferrous metal production (Pb, Zn, Cu, Ni, Cd)	46.5
Steel and iron manufacturing	15.7
Energy production	12.7
Commercial uses (cement, chemicals, paint, ceramics)	4.5
Mining	2.55
Waste incineration (municipal refuse and sewage sludge)	2.37
TOTAL	332.32

Table 1 World-wide atmospheric emissions of lead from anthropogenic sources

SOURCE	Emission (thousand tonnes / year)
Atmospheric fallout	100
Manufacturing processes (metal, chemicals, paper, petroleum products)	14
Sewage discharges	9.4
Base metal mining and smelting	7.0
Domestic wastewaters	6.8
Electric power plants	0.72
TOTAL	137.92

Table 2 World-wide inputs of lead into aquatic ecosystems

SOURCE	Emission (thousand tonnes / year)
Discarded manufactured products	292
Atmospheric fallout	232
Coal ashes	144
Urban refuse	40
Agricultural and animal wastes	26
Solid wastes from metal fabrication	7.6
Logging and wood wastes	7.4
Municipal sewage and organic waste	7.1
Fertilisers and peat	2.9
TOTAL	759

Table 3 World-wide inputs of lead into soils

Uses of lead and its compounds are extensive. As a metal, it is often used as pipe-work for water distribution, or as containers for storing for corrosive liquids (e.g. sulphuric acid). Its alloys are used in welding, printing and as anti-friction metals; and great quantities, both of the metal and its dioxide, are used in electric storage batteries. Other uses include cable coverings, ammunition, and in the manufacture of lead tetraethyl, used as an anti-knock compound in petrol. Compounds of lead are used as paint pigments, PVC stabilisers, pesticides, varnishes, lubricants, as glazes for pottery and porcelain, and in leaded glass crystal (Budavari *et al.* 1989, USPHS 1997).

A3.4.2 Environmental Levels, Contamination and Behaviour

Lead is present in uncontaminated aquatic and terrestrial ecosystems at relatively low levels (see Table 4).

Environmental Matrix	Concentration	Reference
Seawater (estuarine waters around England and Wales)	24-880 ng/l	Law <i>et al.</i> 1994
Seawater (open ocean)	5 ng/l 1-14 ng/l 20-71 ng/l	UPHS 1997 Bryan and Langston 1992 Law <i>et al.</i> 1994
Freshwater (mean value from 39,490 measurements)	3.9 ug/l	USPHS 1997
Drinking water	<5-30 ug/l	USPHS 1997
Soil	10-30 mg/kg	Alloway 1990
Freshwater / marine sediment	20-30 mg/kg	USPHS 1997

Table 4 Background concentrations of lead found in water, sediments and soil

However, as anthropogenic emissions far exceed those from natural sources, elevations above these natural, background concentrations are often found (Table 5).

When lead is released into the environment it has a long residence time compared with most pollutants. As a result, it tends to accumulate in soils and sediments. Where, due to low solubility, it can remain accessible to the food chain and to human metabolism far into the future (Sauve *et al.* 1997, USPHS 1997, Alloway 1990). However, as with all metals, speciation is critical when assessing bioavailability and the potential threat to the environment.

Two oxidation states of lead, +2 and +4, are stable, but the environmental chemistry is dominated by the Pb^{+2} ion, its compounds, and complexes. In general the free +2 ion is more toxic than inorganic complexes, and therefore any factor which increases complexation and decreases the concentration of the free ion is bound to affect lead toxicity adversely. Toxic organic forms of lead are also present in the environment. From direct inputs (manufacture, transport and storage of leaded petrol and consequent car exhaust emissions) and the possible chemical / biological methylation of inorganic lead in anaerobic sediments (Sadiq 1992, Forsyth *et al.* 1991).

As mentioned, lead has a tendency to form compounds with anions having low solubility, such as hydroxides, carbonates, and phosphates. Thus the amount of lead remaining in solution in

surface waters (also dependent upon pH and salinity) is often low. In addition to this, a significant fraction of insoluble lead may be incorporated in surface particulate matter from runoff, or as sorbed ions or surface coatings on sediment, or may be carried as a part of suspended living or nonliving organic matter (USPHS 1997).

Site Description	Concentration	Reference
River water, Donana National Park, Spain (close to mining site)	<5-2500 ug/l	Pain <i>et al.</i> 1998
Drinking water, USA (contaminated from lead pipes / lead solder).	500 ug/l	USPHS 1997
Soil, Socorro, New Mexico (USA). Close to an abandoned lead smelter	25-10,000 mg/kg	Brandvoid <i>et al.</i> 1996
Paddy soil, Taiwan. Close to plastic stabiliser manufacturing plant	6.3-12,740 mg/kg	Chen 1991
Soil close to lead smelting sites, Montreal, Canada	40-14,860 mg/kg	Sauve <i>et al.</i> 1997
Gannel estuary sediments, UK. Received waste from old lead mines	2700 mg/kg	Bryan and Langston 1992
Oiartzun river sediments, Spain. Close to lead-zinc mining sites	68-5540 mg/kg	Sanchez <i>et al.</i> 1994

Table 5 lead concentrations associated with anthropogenic contamination

In soils and sediments, the fate of lead is affected by similar processes, which often lead to the formation of relatively stable organic-metal complexes. Most of the lead is retained strongly, and very little is transported into surface water or groundwater. However re-entry to surface waters as a result of erosion of lead-containing soil particulates; or through the conversion to the relatively soluble lead sulphate at the soil / sediment surface, can occur (USPHS 1997, Sadiq 1992, Alloway 1990). As can the downward movement of lead from soil to groundwater by leaching (USPHS 1997).

Plants and animals can accumulate lead from water, soil and sediment, with organic forms being more easily absorbed than inorganic. In general, the highest lead concentrations are found in aquatic and terrestrial organisms that live near to lead mining, smelting, and refining facilities; storage battery recycling plants; areas affected by high automobile and truck traffic; sewage sludge and spoil disposal areas; sites where dredging has occurred; areas of heavy hunting (spent lead shot); and in urban and industrialised areas (USPHS 1997).

A3.4.3 Toxicity

Lead is one of the most ubiquitous toxic metals. It has no known, nutrition, biochemical or physiological function, and because there is no demonstrated biological need, and because it is toxic to most living things, the major concern of the moment is at what dose does lead become toxic (Goyer 1996)? The toxic effects of lead are the same, irrespective of whether it is ingested or inhaled, and blood levels as low as <10-100 ug/dl in children, and 10-100 ug/dl in adults have been associated with a wide range of adverse effects. Including nervous system disorders, anaemia and decreased haemoglobin synthesis, cardiovascular disease, and disorders in bone metabolism, renal function and reproduction. Of particular concern, is the effect of relatively

low exposure on cognitive and behavioural development in children (Pirkle *et al.* 1998, USPHS 1997, Bernard *et al.* 1995, Goyer 1993, Nriagu 1988).

In 1975 the Centre for Disease control (CDC) in Atlanta recommended that the maximum permissible level of blood-lead be 30 ug/dl (for both adults and children). This levels was revised downward in 1985 to 25 ug/dl, and again in 1991, defining a blood-lead of 10 ug/l as an action or intervention level (USPHS 1997). Perhaps even more importantly is the now suggested recommendation that there may be no level of blood-lead that does not produce a toxic effect, particularly in the developing central nervous system (USPHS 1997, Goyer 1993).

Animals studies have reproduced many of the toxic effects listed above, and animals feeding close to smelting, mining and recycling facilities, have often ingested levels of lead that have resulted in poisoning and death (Henny *et al.* 1991, Blus *et al.* 1991, USPHS 1997, WHO 1989, Collivignarelli *et al.* 1986). In addition, birds feeding on contaminated prey or ingesting lead shot into their gizzards, can be exposed to severe levels of lead. Resulting in high kidney, liver and bone concentrations, reduced growth and development, behavioral abnormalities, and sometimes death (Mateo *et al.* 1997, WHO 1989).

Lead is also toxic to all aquatic biota, and even though it is not considered one of the most environmentally mobile of metals, there is still appreciable evidence showing the bioavailability of sediment-bound lead to deposit feeding species (Bryan and Langston 1992). In addition, lead can be accumulated directly from sea and fresh waters, especially in organisms that utilise gill tissue as the major nutrient uptake route (Sadiq 1992). Toxicological studies have reported sub-lethal effects in fish including changes in morphology, metabolism and enzymatic activity. Avoidance behaviour has also been observed in adult fish exposed to levels ranging from 10-100 mg/l (WHO 1989). Studies involving invertebrates (oysters, sea urchins, snails, copepods and water fleas) often report a reduction in growth, fertility and reproduction suppression, and mortality, at ug/l (parts per billion) concentrations (WHO 1989).

A3.4.4 Legislation

European legislation concerned with water quality and permissible environmental levels, does not generally treat lead as a priority pollutant. However, anthropogenic discharges of lead into the aquatic environment still need to cease, and therefore lead is included on the majority of subsidiary and secondary lists. Examples include:

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 than 50 ug/l must be subjected to intensive physical and chemical treatment prior to use.

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

Council Directive 80/778/EEC relating to the quality of water intended for human consumption. A maximum permissible concentration of 50 ug/l is set.

Other drinking water legislation includes that set by the Bureau of Indian Standards, which currently set a maximum permissible concentration for lead of 50 ug/l (1995); the USEPA,

which limits the concentration of lead to 15 ug/l (USPHS 1997); and the WHO, which currently recommends a limit of 50 ug/l, however there is much current discussion and desire to reduce this to 10 ug/l (WHO 1993).

The Water Research Centre in the UK recommends the following Environmental Quality Standards for lead: protection of freshwater salmonid fish 4-20 ug/l; protection of freshwater coarse fish 50-250 ug/l; protection of other freshwater life and associated non-aquatic organisms 5-60 ug/l; protection of saltwater fish, shellfish, other salt water life and associated non-aquatic organisms 25 ug/l (Brown *et al.* 1984).

Regarding soil contamination, the UK Department of the Environment (ICRCL) regards a level of 0-500 mg/kg as being typical of uncontamination. Anything above this is regarded as being contaminated, and as such, restrictions on recreational and agricultural uses apply (Alloway 1990). In terms of permissible sewage sludge levels, acceptable concentrations for lead range from 300-1200 mg/kg. However resulting soil concentrations should not exceed 50-100 mg/kg (recommended EC, UK, France, Germany) (Alloway 1990).

Finally, lead is included in the list of priority hazardous substances agreed by the Third North Sea Conference (MINDEC 1990), Annex 1A to the Hague Declaration, and confirmed at the Fourth Conference in Esbjerg, Denmark, in 1995 (MINDEC 1995). Here it was agreed that environmental concentrations of hazardous substances should be reduced to near background level within the next 25 years. An objective further reinforced in the Sintra Statement at the 1998 Ministerial Meeting of the OSPAR Commission (OSPAR 1998a). Lead and organic lead compounds were selected for priority action, and as such as included in Annex 2 of the OSPAR Strategy with regard to Hazardous Substances (OSPAR 1998b).

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A3.5 Nickel (Ni)

A3.5.1 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). Its commercially important ores are of two types, laterites, which are oxide and silicate ores, and sulphides (e.g. pentlandite) often associated with precious metals, copper and cobalt. 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).

A3.5.2 Production, Use and Anthropogenic Sources

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 and sewage sludge)	0.35
TOTAL	51.61

Table 1 World-wide atmospheric emissions of nickel 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 2 World-wide inputs of nickel into aquatic ecosystems

Primary nickel is recovered from mined ore, which is first crushed, enriched and concentrated, prior to roasting and smelting operations; secondary nickel can also be recovered, from scrap metal. Alternatively, reduced nickel oxide ores can be electrolysed in the presence of nickel sulphate or chloride, to yield metal of 99% purity (Greenwood and Earnshaw 1984).

Nickel is a white-silver metal, hard but brittle, polishable, and a good conductor of both heat and electricity. It is most commonly used to form stainless and heat resistant steels, high nickel heat- and corrosion resistant alloys, alloy steels, super-alloys and cast irons. It is 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 1-3 (Nriagu 1990, Nriagu and Pacyna 1988):

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 3 World-wide inputs of nickel to soils

A3.5.3 Environmental Levels, Contamination and Behaviour

Nickel is found in varying concentrations in nearly all uncontaminated aquatic and terrestrial ecosystems (see Table 4). However, as anthropogenic emissions of nickel far exceed those from natural sources, elevations above these natural, background concentrations, are often found (see Table 5).

Environmental Matrix	Concentration	Reference
Seawater	0.1-0.5 ug/l	USPHS 1997, Law <i>et al.</i> 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 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 <i>et al.</i> 1994
Sediment, Elsburgspruit-Natalspruit Rivers, South Africa (mining discharges and sewage)	54.5-890 mg/kg	Steenkamp <i>et al.</i> 1995
Soil, Sudbury Basin / Coniston, Canada (nickel mining and smelting)	100-3000 mg/kg 160-12300 mg/kg	Freedman and Hutchinson 1980 Hazlett <i>et al.</i> 1983
Soil, Upper Silesia, Poland (mining and smelting)	5-2150 mg/kg	Dudka <i>et al.</i> 1995
MSW incinerator ash, UK	45-2204 mg/kg	Mitchell <i>et al.</i> 1992

Table 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).

A3.5.4 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, therefore lists nickel and these compounds as Reasonably Anticipated to be Human Carcinogens (USPHS 1998). Whereas metallic nickel and its alloys are listed as possible human carcinogens (Group 2B), by the International Agency for Research on Cancer (1998).

Nickel is a respiratory tract carcinogen in workers in the nickel refining and processing industries. Here, individuals are frequently exposed to atmospheric levels in excess of 1 mg of nickel per cubic meter of air (USPHS 1997, Goyer 1996). Other serious consequences of long term exposure to nickel may include chronic bronchitis and reduced lung function (USPHS 1997). Whilst other studies have reported pregnancy complications in nickel-exposed workers, i.e. an increased rate of spontaneous abortion, and a higher incidence of birth malformations, including cardiovascular and musculoskeletal defects (Chashschin *et al.* 1994).

Allergic contact dermatitis is the most prevalent adverse effect of nickel in the general population (2-5% may be nickel sensitive). Here, people become sensitive to nickel when jewellery or other nickel-containing objects are in direct contact with the skin. Once a person is sensitised to nickel, any further contact will produce a reaction. A rash at the site of contact is visible, and in some cases eczema may develop. Therefore, although non-sensitised individuals would have to ingest or inhale a large amount of nickel to suffer adverse health effects, sensitised individuals react adversely to far lower concentrations (USPHS 1997).

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 merguensis*), leather 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).

A3.5.5 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).

Regarding soil contamination, the UK Department of the Environment (ICRCL) classifies a level of 0-20 mg/kg as being typical of uncontamination. Anything above this is classified as contaminated, and as such, restrictions on recreational and agricultural uses apply (Alloway 1990). In terms of permissible sewage sludge levels, acceptable concentrations for nickel range from 30-500 mg/kg. However soil concentrations should not exceed 30-50 mg/kg (EC, France, Germany) (Alloway 1990).

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A3.6 Copper (Cu)

A3.6.1 Natural Occurrence

Copper was almost certainly one of the first three metals discovered (the others being gold and silver), and although opinion on the earliest use varies, 5000 BC is not an unreasonable estimate (Hong *et al.* 1996, Greenwood and Earnshaw 1984). Abundance 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). Copper can occur in the elemental state, however it is found more commonly as a sulphide (copper pyrite), oxide (cuprite) or carbonate (malachite). 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).

A3.6.2 Production, Use and Anthropogenic Sources

After the copper ore has been mined, crushed, enriched and concentrated, it is roasted at temperatures in excess of 1200 ° C, sintered and smelted. Alternatively copper can be recovered from secondary sources (i.e. scrap). This process is far less energy intensive, and therefore is playing an increasingly important role in terms of global copper production (UNEP 1993).

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 1 World-wide atmospheric emissions 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 2 World-wide inputs of copper 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 3 World-wide inputs of copper to soils

A3.6.3 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 <i>et al.</i> 1994
Seawater (background)	0.1 ug/l	Sadiq 1992, Bryan and Langston 1992
Freshwater, UK	<20 ug/l	Mance <i>et al.</i> 1984
Soil	20 –30mg/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 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 <i>et al.</i> 1995
Soil treated with copper fungicidal sprays	110-1500 mg/kg	Alloway 1990
MSW incinerator ash (UK)	296-1307 mg/kg	Mitchell <i>et al.</i> 1992

Table 5 copper concentrations associated with sites of anthropogenic contamination and waste

In soils, copper has a high affinity for sorption by organic and inorganic ligands (e.g. humic and fulvic acids, hydroxides of iron, aluminium and manganese). However it can also exist as soluble ions and complexes. 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. Therefore, copper sulphate, or chloride, present in MSW incinerator ash or mine tailings, is far more bioavailable and migratory than the organically bound copper found in sewage sludge (USPHS 1997, Alloway 1990, Mance *et al.* 1984).

Copper 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).

A3.6.4 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). However at the other extreme, 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. Inhalation of dust and vapours can irritate the nose, mouth and eyes, and cause headaches, dizziness, nausea and diarrhoea. 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).

A3.6.5 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 than 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.

European Council Directive 80/778/EEC relating to the quality of water intended for human consumption. Guide levels of 100 ug/l (for outlets of pumping and / or treatment works) and 3000 ug/l (after water has been standing for 12 hours in the piping / made available to the customer) are set.

Other drinking water standards include those set by the Bureau of Indian Standards (1995) (50ug/l), the USEPA (1300 ug/l) (USPHS 1997) and the WHO (1000 ug/l)(1993)

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).

Regarding soil contamination, the UK Department of the Environment (ICRCL) classifies a level of 1-100 mg/kg as being typical of uncontamination. Anything above this is classified as contaminated, and as such, restrictions on recreational and agricultural uses apply (Alloway 1990). In terms of permissible sewage sludge levels, acceptable concentrations for copper range from 500-3000 mg/kg. However soil concentrations should not exceed 50-100 mg/kg (EC, France, Germany) (Alloway 1990).

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A3.7 Cadmium (Cd)

A3.7.1 Natural Occurrence

Cadmium is a relatively rare metal, being 67th in order of chemical abundance. It is found in the Earth's crust at an average concentration of 0.1 mg/kg (WHO 1992), although some sedimentary rocks, black shales and marine phosphates can accumulate higher levels (WHO 1992, Alloway 1990). It is usually found in association with the sulphide ores of zinc, copper and lead, and is obtained as a by-product during the processing of these ores. Volcanic activity is the major natural source of cadmium 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 cadmium released to the atmosphere from natural sources is 1400 tonnes / year, compared with an estimated anthropogenic load of 7600 tonnes / year (Nriagu 1990).

A3.7.2 Production, Use and Anthropogenic Sources

Cadmium is a by-product of zinc and lead mining and smelting, and is currently used primarily for the production of nickel-cadmium batteries (37%) and for metal plating (25%). It is also used in pigments for glasses and plastics (22%), as a stabiliser in polyvinyl chloride (12%), and as a component of various alloys (4%) (USPHS 1997, WHO 1992). Estimates of anthropogenic emissions of cadmium are given in Tables 1-3 (WHO 1992, Nriagu 1990).

SOURCE	Emission (thousand tonnes / year)
Non-ferrous metal production (Zn, Cd, Cu, Pb, Ni)	5.43
<i>Energy production (coal and oil combustion)</i>	0.79
<i>Waste incineration (municipal refuse and sewage sludge)</i>	0.75
<i>Manufacturing processes (steel, iron, phosphate fertilisers, cement)</i>	0.60
<i>TOTAL</i>	<i>7.57</i>

Table 1 World-wide atmospheric emissions of cadmium from anthropogenic sources

SOURCE	Emission (thousand tonnes / year)
Manufacturing (metal, batteries, pigments, plastics)	2.4
Atmospheric fallout	2.2
Base metal mining and smelting	2.0
Domestic wastewaters	1.7
Sewage discharges	0.69
Electric power plants	0.12
<i>TOTAL</i>	<i>9.11</i>

Table 2 World-wide inputs of cadmium into aquatic ecosystems

SOURCE	Emission (thousand tonnes / year)
Coal ashes	7.2
Atmospheric fallout	5.3
Urban refuse	4.2
Agriculture and animal wastes	2.2
Discarded manufactured products	1.2
Logging and wood wastes	1.1
Fertilisers and peat	0.2
Municipal sewage / organic waste	0.18
Solid waste from metal fabrication	0.04
<i>TOTAL</i>	<i>21.62</i>

Table 3 World-wide inputs of cadmium to soils

A3.7.3 Environmental Levels, Contamination and Behaviour

Cadmium is a rare metal, found naturally as very low concentrations (see Table 4). However, as anthropogenic emissions far exceed those from natural sources, elevations above these natural, background levels, are often found (see Table 5).

Environmental matrix	Concentration	Reference
Freshwater, groundwater, drinking water	<1 ug/l	USPHS 1997, WHO 1992
Seawater (open ocean)	0.02-0.12 ug/l	Sadiq 1992, Bryan and Langston 1992
Seawater (coastal)	0.01-0.17 ug/l	Bryan and Langston 1992
Marine sediment	<1 mg/kg	Sadiq 1992, Salomons and Forstner 1984
Estuarine sediment	0.2 mg/kg	Bryan and Langston 1992
River sediment	1 mg/kg	Salomons and Forstner 1984
Soil	0.01-2.0 mg/kg	USPHS 1997, Alloway 1990

Table 4 Background concentrations of cadmium found in water, sediment and soil

Site description	Concentration	Reference
Seawater, Restronguet Creek, UK (receives acid mine drainage from past and present mining activities)	50 ug/l	Bryan and Langston 1992
Sediment, Donana National Park, Spain (sites contaminated by mining waste)	2.4-38.6 mg/kg	Pain <i>et al.</i> 1998
Soils and sediments, Taiwan, close to a plastic stabiliser factory	0.22-1,486 mg/kg(soil) 134-4,700 mg/kg (sed.)	Chen 1991
Soil, Zn-Pb smelting, Upper Silesia, Poland	0.3-102 mg/kg	Dudka <i>et al.</i> 1995a
Soil, Cu-Ni mining site, Sudbury, Ontario	0.1-10 mg/kg	Dudka <i>et al.</i> 1995b
Garden soil, Shipham, UK (site of past Zn-Pb mining)	360 mg/kg (max.)	Alloway 1996
MSW fly ash (UK incinerators)	21-646 mg/kg	Mitchell <i>et al.</i> 1992

Table 5 cadmium concentrations associated with sites of anthropogenic contamination and waste

Cadmium is more mobile in aquatic environments than most other metals. It is also bioaccumulative and persistent in the environment ($t^{1/2}$ of 10-30 years) (USPHS 1997). It is found in surface and groundwater as either the +2 hydrated ion, or as an ionic complex with other inorganic or organic substances. While soluble forms may migrate in water, cadmium in insoluble complexes or adsorbed to sediments is relatively immobile. Similarly, cadmium in soil may exist in soluble form in soil water, or in insoluble complexes with inorganic and organic soil constituents (USPHS 1997, WHO 1992). In soils, the agricultural use of phosphate

fertilisers or cadmium-containing sewage sludge, can dramatically increase cadmium concentrations. Furthermore, cadmium is readily available for uptake in grain, rice and vegetables, and there is a clear association between the cadmium concentration in soil and the plants grown on that soil (Elinder and Jarup 1996, Cabrera *et al.* 1994, WHO 1992).

When present in a bioavailable form, both aquatic and terrestrial organisms are known to bioaccumulate cadmium. Studies have shown accumulation in aquatic animals at concentrations hundreds to thousands of times higher than in the water (USPHS 1997). With reported bioconcentration factors ranging from 113 to 18,000 for invertebrates and from 3 to 2,213 for fish. Cadmium accumulation has also been reported in grasses and food crops, and in earthworms, poultry, cattle, horses, and wildlife (USPHS 1997, WHO 1992). Evidence for biomagnification is inconclusive. However, uptake of cadmium from soil by feed crops may result in high levels of cadmium in beef and poultry (especially in the liver and kidneys). And this accumulation of cadmium in the food chain has important implications for human exposure, whether or not significant biomagnification occurs (USPHS 1997).

A3.7.4 Toxicity

Cadmium has no biochemical or nutritional function, and it is highly toxic to both plants and animals (USPHS 1997, WHO 1992, Alloway 1990). In humans and animals, there is strong evidence that the kidney is the main target organ of cadmium toxicity, following extended exposure (USPHS 1997, Elinder and Jarup 1996, Goyer 1996, Roels *et al.* 1993, Iwata *et al.* 1993, WHO 1992, Mueller *et al.* 1992). Renal damage includes tubular proteinuria (the excretion of low molecular weight proteins) and a decrease in the glomerular filtration rate. The latter results in a depressed re-sorption of enzymes, amino acids, glucose, calcium, copper, and inorganic phosphate. Furthermore, studies have shown that even when cadmium exposure ceases, proteinuria does not decrease, and renal tubular dysfunction and reduced glomerular filtration increase in severity (USPHS 1997, Jarup *et al.* 1997, Elinder and Jarup 1996, Goyer 1996, Iwata *et al.* 1993, WHO 1992, Nriagu 1988).

Other toxic effects of cadmium, based on findings from occupation, animal, and epidemiological studies, can be summarised as follows:

Case studies indicate that calcium deficiency, osteoporosis, or osteomalacia (softening of the bones) can develop in some workers after long-term occupational exposure to high levels of cadmium. A progressive disturbance in the renal metabolism of vitamin D and an increased urinary excretion of calcium is often seen, suggesting that bone changes may be secondary to disruption in kidney vitamin D and calcium metabolism (USPHS 1997, Goyer *et al.* 1994, WHO 1992). In the Jinzu River Basin, a cadmium-contaminated area in Japan, a cadmium induced skeletal disorder known as Itai-Itai disease disabled many children born to women of middle age and poor nutrition (Alloway 1996).

The inhalation of high levels of cadmium oxide fumes or dust is intensely irritating to respiratory tissue, and acute high-level exposures can be fatal. Typical non-fatal symptoms can include severe tracheobronchitis, pneumonitis, and pulmonary oedema, which can develop within hours of exposure (USPHS 1997, Goyer 1996, WHO 1992). At lower levels, lung inflammation have been known to cause emphysema (swelling of the lung air sacs resulting in breathlessness) and dyspnoea (difficult and laboured breathing) (USPHS 1997, Goyer 1996, WHO 1992). Animal studies have confirmed that inhalation exposure to cadmium leads to respiratory injury (USPHS 1997, WHO 1992).

There have been a number of epidemiological studies intended to determine a relationship between occupational (respiratory) exposure to cadmium and lung and prostatic cancer, and these along with animal studies have provided considerable support for the carcinogenic potential of cadmium (IARC 1998, Goyer 1996). Cadmium and certain cadmium compounds are therefore listed by the International Agency for Research on Cancer (IARC) as carcinogenic (IARC 1998). The US Department of Health and Human Services in its 8th Report on Carcinogens, lists cadmium and certain cadmium compounds as Reasonably Anticipated to be Human Carcinogens (USPHS 1998).

In addition to these toxic effects, it has also been suggested that cadmium may play a role in the development of hypertension (high blood pressure) and heart disease (USPHS 1997, Goyer 1996, Elinder and Jarup 1996). It is also known that severe oral exposure can result in severe irritation to the gastrointestinal epithelium, nausea, vomiting, salivation, abdominal pain, cramps and diarrhoea (USPHS 1997).

Regarding plant toxicity, adverse effects on plant growth and yield have been reported. Alloway (1990) reported stunted growth and toxic signs on leaves of lettuce, cabbage, carrot and radish plants, (which resulted from a cadmium content of around 20 mg/kg in the upper parts of the plants). Other studies have shown reductions in the rates of photosynthesis and transpiration (WHO 1992).

Regarding the toxicity of cadmium to aquatic organisms, numerous findings have been reported. For example, some species of phytoplankton are very sensitive to cadmium, with inhibition of growth observed at concentrations as low as 1 ug/l (Bryan and Langston 1992). Deleterious effects have also been reported in limpets, where correlations between increased levels of cadmium and reduced ability to utilise glucose were found. Reductions in reproduction rates and population numbers in copepods and isopods have been shown at concentrations as low as 5 ug/l, and exposure to similar levels has resulted in changes in immune function in some fish, and depressed growth seen in juvenile fish and invertebrates (Bryan and Langston 1992, Thuvander 1989). Furthermore the toxicity of low sediment-cadmium concentrations has also been suggested following observations in San Francisco Bay. Here the condition of certain species of clam declined as cadmium concentrations rose from 0.1 to 0.4 mg/kg (Bryan and Langston 1992).

A3.7.5 Legislation

European Directives and Decisions on water quality and permissible discharges treat cadmium as a priority pollutant. Therefore legislation is concerned with the elimination of pollution caused by cadmium, and not just the reduction. Examples include:

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 than 1 ug/l of cadmium must be subjected to intensive physical and chemical treatment prior to use.

Council Directive 76/464/EEC on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community. Cadmium is included in List I, and as such water pollution caused by its presence should be eliminated.

Council Directive 80/778/EEC relating to the quality of water intended for human consumption. A maximum permissible concentration of 1 ug/l is set.

Other drinking legislation includes that devised by the Bureau of Indian Standards (1995) and the USEPA (USPHS 1997), which both set a maximum permissible concentration for cadmium of 10 ug/l, although the USEPA does have plans to reduce this limit to 5 ug/l. The WHO currently recommends a guideline level of 5 ug/l (WHO 1993).

Regarding soil contamination, the UK Department of the Environment (ICRCL) classifies a level of 0-1 mg/kg as being typical of uncontamination. Anything above this is classified as contaminated, and as such, restrictions on recreational and agricultural uses apply (Alloway 1990). In terms of permissible sewage sludge levels, acceptable concentrations for cadmium range from 8-30 mg/kg. However resulting soil concentrations must not exceed 3 mg/kg (EC, UK, France, Germany) (Alloway 1990).

Finally, cadmium is included in the list of priority hazardous substances agreed by the Third North Sea Conference (MINDEC 1990), Annex 1A to the Hague Declaration, and confirmed at the Fourth Conference in Esbjerg, Denmark, in 1995 (MINDEC 1995). Here it was agreed that environmental concentrations of hazardous substances should be reduced to near background levels within the next 25 years. An objective further reinforced in the Sintra Statement at the 1998 Ministerial Meeting of the OSPAR Commission (OSPAR 1998a). Cadmium has been selected for priority action, and as such as included in Annex 2 of the OSPAR Strategy with regard to Hazardous Substances (OSPAR 1998b).

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