

# **Heavy metals and other contaminants in bottom ash and fly ash generated by incinerators at Phuket and Samui Island, Thailand**

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## Summary

Greenpeace International visited the municipal and medical waste incinerator complex near Phuket, Thailand, both in June and October 1999 in order to collect samples of incinerator ashes stored on site for chemical analysis. A single sample was also collected from the waste incinerator located on Samui Island.

Analyses, conducted at the Greenpeace Research Laboratories, revealed that:-

1. bottom ash and fly ash residues arising from the Phuket municipal solid waste incinerator contained high levels of the toxic heavy metals lead and cadmium (with lead present at over 0.1% by weight of the ash). Similar levels were recorded in ashes dumped from test burns conducted early in 1998 as were found in ashes arising from the operation of the plant between June and October 1999.
2. levels of metals in bottom ash from the medical waste incinerator on the same site were lower than in the other materials sampled, although a much wider range of organic contaminants (typical products of incomplete combustion) were isolated and identified in this sample. These contaminants included some chlorinated residues and phthalate esters which could have arisen from the incomplete combustion of PVC components in the medical waste.
3. the single fly ash sample from the Samui Island incinerator contained heavy metal concentrations as high as for the MSW residues from Phuket (with particularly high levels of cadmium) and a similar range of products of incomplete combustion.
4. the very limited study of sediment samples collected adjacent to the Phuket complex in October 1999 did not reveal contaminant signatures which could be traced directly to the incinerator operations at this stage. However, neither incinerator had been operating for an extended period prior to the time of sampling. Whether continued operation of the Phuket plant will ultimately lead to systematic contamination of the surrounding environment remains to be seen, although given the hazardous nature of the incinerator ash residues stored on site, in particular their high heavy metal content, localised contamination resulting from leaching or run-off would seem very likely in the medium to longer term. Incinerator stack emissions were not evaluated in this study, although such emissions are also likely to contribute significantly to more widespread heavy metal and persistent organic pollution over time.

The results of this preliminary study demonstrate the hazardous nature of the solid wastes generated by incineration of medical and even municipal solid waste. Toxic heavy metals are present in MSW ash residues as a result of their continued use in a wide range of commercial and consumer products. Incineration does not destroy these metals, but simply disperses them via the incinerator stack and, as demonstrated in the current study, concentrates them into bottom and fly ash residues. Far from solving a waste problem, therefore, incineration is simply creating a new and more toxic one.

It was not possible to conduct specific analyses for chlorinated dioxins and furans in this study, although these compounds would undoubtedly have been present. Given the high toxicity of dioxins, such analyses should be commissioned as a matter of urgency by the Thai authorities

## **Introduction**

The Phuket landfill/incinerator complex, located along side the BangYai canal downstream from the city and close to its confluence with the sea, comprises separate facilities for the incineration of municipal and medical wastes. The municipal waste incinerator underwent test burns between April and June 1998. Bottom ash/clinker and fly ash from these operations had been dumped or stored in ash pits constructed within the boundaries of the complex. The storage area containing bottom ash residues was partly filled with water, giving it the appearance of a waste lagoon. The visible presence of glass medical waste containers within one area of this lagoon suggested that bottom ash from the incineration of medical waste had also been dumped there; this was confirmed by the manager of the medical waste incinerator.

Greenpeace International visited the complex on two occasions in 1999 in order to collect samples of ash wastes from the incinerators for analysis of heavy metal and organic contaminants. During the first visit in June 1999 the municipal waste incinerator was not operational and had not been for approximately 1 year. Routine operations of the incinerator began subsequent to this visit. Greenpeace International therefore visited the complex for a second time in October 1999 in order to collect samples of freshly generated bottom and fly ash for analysis.

In June 1999, a visit was also made to the solid waste incinerator plant located near Lamai Beach on the island of Samui. At this time the incinerator was not fully operational, working only to approximately 20% full capacity. Again both bottom and fly ash appeared to be dumped in pits on site. A single sample of fly ash was collected for analysis.

This brief report summarises the results of those analyses and discusses them in relation to levels of contamination found.

### **1. Phuket incinerator complex**

#### **1.1 Materials and Methods**

##### **1.1.1 Sample collection**

During the first visit (10<sup>th</sup> June 1999), 3 samples were collected, 2 from the main pit/lagoon containing bottom ash from the two incinerators (TH9001/2) and 1 from the main "ash pit" containing fly ash from the municipal incinerator (TH9003).

During the second visit (14<sup>th</sup> October 1999), both the lagoon (TH9010) and fly ash pit (TH9009) were re-sampled, in order to collect recently dumped material. In addition, single sediment samples were collected from a mud flat below mangroves on a tidal river immediately adjacent to the south-west boundary of the landfill/incinerator complex (IT9007) and from the shores of the Bang Yai Canal, approximately 50m downstream from the bottom ash lagoon (TH9008). Both the river and the canal drain areas of the city of Phuket.

Details of the samples collected are summarised in Table 1.

Sample number	Sample date	Sample description
TH9001	10-6-99	bottom ash/clinker from ash pit/lagoon adjacent to municipal waste incinerator
TH9002	10-6-99	bottom ash/clinker from area of lagoon receiving waste from medical waste incinerator
TH9003	10-6-99	fly ash collected 10-20 cm below surface in pit receiving ash from municipal incinerator
TH9007	14-10-99	sediment from mud-flat on tidal river to south-west of landfill/incinerator complex
TH9008	14-10-99	sediment from BangYai Canal, north-west boundary of landfill/incinerator complex
TH9009	14-10-99	freshly dumped fly ash collected from pit receiving ash from municipal incinerator
TH9010	14-10-99	freshly dumped bottom ash/clinker from lagoon adjacent to municipal waste incinerator

**Table 1: Descriptions of samples collected from the Phuket landfill/incinerator complex.**

### 1.1.2 Analysis

All samples were returned to the Greenpeace Research Laboratories, University of Exeter, UK, for quantitative analysis of heavy metals (using ICP-AES) and for qualitative analysis of organic contaminants (using gas chromatography/mass spectrometry). For full details of analytical methodology employed, refer to Appendix I. Samples were not analysed for chlorinated dioxins and furans or related compounds in this study.

## 1.2 Results

Results of the heavy metal analyses are summarised in Table 2 below. Compounds identified in the organic screen analysis are listed by sample in Appendix II.

### 1.2.1 Incinerator bottom and fly ashes

Sample TH9001, collected from the bottom ash lagoon at a location receiving waste from the municipal incinerator, contained notably high levels of lead, copper and cadmium (Table 1). Although the materials are not directly comparable, some idea of the levels of contamination can nevertheless be gained through comparison with levels which might be expected in uncontaminated soils and sediments. For example, the residues contained over 1 g/kg of lead (or >0.1% by mass), compared to the 10-30 mg/kg which might be expected in uncontaminated soils/sediments (Alloway 1990). Similarly, 21.6 mg/kg cadmium indicates substantial elevation above the 1-2 mg/kg maximum which might normally be found in uncontaminated soils (USPHS 1997). Copper was also present at levels (407 mg/kg) in excess of those expected for

Sample number	Sample type	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)
TH9001	btm ash	703.9	50.0	3361.1	407.2	1051.4	23.1	6.7	21.6	0.5
TH9002	btm ash	101.9	59.6	5384.6	322.1	165.7	24.0	9.6	7.8	1.2
TH9003	fly ash	193.2	37.7	2108.6	205.5	615.9	11.4	0.5	46.8	1.0
TH9009	fly ash	276.5	65.3	2530.6	333.7	855.1	18.4	9.2	60.2	1.8
TH9010	btm ash	870.4	72.5	1461.2	378.6	399.0	51.0	11.2	8.2	0.2
TH9007	sediment	198.1	30.2	51.9	25.5	46.2	10.4	5.7	n/d	0.4
TH9008	sediment	276.0	34.0	11.0	44.0	49.0	13.0	6.0	n/d	0.2

**Table 2: Concentrations of heavy metals in ash wastes and in sediments collected adjacent to the Phuket landfill/incinerator complex. All values are in mg/kg dry weight.**

uncontaminated materials (10-50 mg/kg). Organic contaminants were dominated by non-chlorinated hydrocarbons. Note, however, that the analytical techniques employed in this study would not have the sensitivity nor specificity to detect chlorinated dioxins, furans and related compounds although these compounds would undoubtedly be present in the ashes.

TH9002 was collected from the same lagoon, but at a location confirmed to contain waste from the adjacent medical waste incinerator. Concentrations of heavy metals (particularly lead at 166 mg/kg) were again elevated above background, although not as high as in sample TH9001. There was some evidence for the presence of trace quantities of chlorinated benzenes (chlorobenzene and 1,2-dichlorobenzene) and of phthalate esters, albeit at concentrations close to limits of detection. It is possible that the presence of the phthalates and chlorinated chemicals in the bottom ash could result from the incomplete combustion of plasticised PVC contained in the medical waste, although it is clearly not possible to confirm this on the basis of available data. Chlorinated benzenes are, for example, highly volatile and may be found as ubiquitous contaminants in many urban and industrial areas (particularly 1,4-dichlorobenzene, as a result of its use in sanitary disinfectant products).

A number of branched alkylbenzenes, typical non-chlorinated compounds formed through incomplete combustion, were also recovered. The organic analysis also revealed the presence of a substantial proportion of unresolvable organic material, i.e. a complex mixture of organic compounds which could not be resolved as discrete peaks and nor, therefore, identified.

The sample of fly ash collected in June 1999 (TH9003) was also found to contain elevated levels of lead (616 mg/kg) and cadmium (46.8 mg/kg) and trace quantities of phthalate esters and a dichlorinated benzene.

Analyses of the freshly dumped fly ash (TH9009) and bottom ash (TH9010) collected from the site on 14th October 1999 yielded results of a similar nature (lead concentrations of 855 and 399 mg/kg respectively). Cadmium contamination was particularly high in sample TH9009 (60.2 mg/kg). The organic screen analysis revealed a wide range of non-chlorinated organic compounds of a similar nature to those identified in the previous samples. Trace levels of 1,4-dichlorobenzene were recovered in each case. The chromatogram for sample TH9009 (fly ash) was dominated by a large broad peak of complex unresolved organic material.

### **1.2.2 Sediments from river and Bang Yai Canal**

Samples of sediment collected from beyond the site boundaries (TH9007 and TH9008) contained levels of heavy metals which were within, or only slightly elevated above, the range which might be expected in uncontaminated sediments (e.g. 46 and 49 mg/kg lead respectively, compared to a "background" range of 10-30 mg/kg). Slight elevation in the lead levels could theoretically result from run off from the contaminated ashes, landfill or even localised deposition of lead emitted from the incinerator stacks, but might also reflect run-off from storm-drains in the Phuket area or even natural variation in lead levels. Analysis of further samples collected at a greater distance from the incinerator complex would be necessary to resolve this.

Organic compounds identified were dominated by hydrocarbons and organic acids, many of which may be of natural origin. Although 1,4-dichlorobenzene was again detectable in both samples, levels were barely distinguishable above the baseline of the chromatogram.

Given the rather widespread distribution of this contaminant (see above), it is not possible to link the presence of 1,4-dichlorobenzene in the sediments with its presence in the ashes on site. Its presence in the sediments might relate to localised deposition of this volatile chemical following emission from the incinerator stacks but could equally be explained by its discharge from nearby urban sewer outfalls, for example. Again, further sampling and analysis would be necessary to address this issue in more detail.

The chromatograms obtained for the two sediments were qualitatively very similar, suggesting a similar sediment composition at both sites. Other than the presence of a complex mixture of hydrocarbons (which could be naturally occurring in the sediments or may arise in part from discharges or run-off from Phuket) and of trace residues of dichlorobenzene, neither sediment yielded chromatograms which were qualitatively comparable to the fly ash or bottom ash contained within the site boundaries.

## 2. Samui Island municipal solid waste incinerator

### 2.1 Sample collection and analysis

A single sample of fly ash was collected on 11th June 1999 and returned to the Greenpeace Research Laboratories for analysis as outlined above and detailed in Appendix I.

### 2.2 Results

The relative and absolute levels of heavy metals determined in this fly ash sample (Table 3) were of a similar order to those reported above for the Phuket ashes (see Table 1). Lead and cadmium were again present at particularly elevated levels (1.02 g/kg and 86.5 mg/kg respectively), reflecting significant lead and cadmium content of the material being incinerated. Organic analyses revealed similar complex mixtures of non-chlorinated hydrocarbons and other organics as were reported for the Phuket ashes, plus a significant component of unresolvable material. 1,4-dichlorobenzene was again identified at relatively low levels.

Sample number	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)
TH9004	404.7	82.3	2984.4	626.0	1020.8	24.5	8.3	86.5	0.4

**Table 3: Concentrations of heavy metals in fly ash collected from the Samui Island landfill/incinerator complex. All values are in mg/kg dry weight.**

### General Discussion

Taken together, these results are indicative of the hazardous nature of the ash residues generated by the incineration process, resulting from the presence of large quantities of heavy metals in the ash which are carried over from the material incinerated at the municipal plant. Lead, cadmium and copper are used in a wide range of consumer products. For example, lead and lead compounds are used extensively as additives in paints, plastics (particularly as stabilisers in PVC), glazes and solder preparations. Cadmium is also used as a PVC stabiliser and as a pigment in other plastics, as well as in nickel cadmium batteries and in some metal plating applications (USPHS 1997).

Heavy metals are not destroyed in the incineration process but are simply concentrated up to high levels in the ash residues or dispersed over the surrounding environment from the incinerator stack. Emissions of metals from the stack were not covered in the current study, but may be highly significant nevertheless. Both lead and cadmium are highly toxic metals. For example, exposure to elevated levels of lead have been associated with numerous adverse effects on renal function, development and reproduction in animals and humans (Pirkle *et al.* 1998, Bernard *et al.* 1995). For further information on the uses, environmental levels and toxicity of lead and cadmium, see Appendix III.

No locally relevant legislative limits or standards can be found concerning levels of heavy metals in incinerator bottom or fly ash. Again, some indication of relative levels of contamination may be gained by comparison with indicator levels for the classification of contaminated land in the UK. According to indices for clean-up of contaminated gas works sites formulated by the UK Interdepartmental Committee on Reclamation of Contaminated Land (ICRCL), for example, soils containing levels of heavy metals reported for the incinerator ashes above would be classified as "contaminated" with respect to lead and "heavily" or "unusually heavily contaminated" with respect to cadmium (Alloway 1990). Although the ashes are clearly quite different in nature from soils, the comparison nevertheless serves to indicate the problematic nature of the wastes and some of the potential problems associated with their onward management or disposal. Over time, run-off or leachate from the ashes stored on site might result in the release of substantial quantities of heavy metals to the surrounding environment. Leaching of metals from incinerator ashes might be expected to be even more rapid than from contaminated soils and sediments, given the relatively low organic content of these wastes.

Close comparison between current heavy metal concentrations and presence of organic compounds in the two sediment samples collected adjacent to the Phuket incinerator complex, one of which was collected downstream from the bottom ash storage lagoon, does not provide any evidence that sediment downstream has yet been systematically contaminated by activities or waste storage on this site. It must be noted, however, that this conclusion is based on the semi-qualitative analysis of single sediment samples from each location only. More extensive sampling and analysis would be required to investigate this issue further, focussing in particular on the location of any discharge points carrying effluent, leachate or run-off from the complex.

Moreover, these sediment samples were collected only a relatively short time after operations on the Phuket incinerator site began (and following only a very limited period of active operation). The possibility cannot be ruled out that continued operation of the incinerators and open storage of contaminated ashes and other residues on site might ultimately lead to localised or more widespread contamination of the surrounding environment. Similarly, any planned removal of the ashes for final disposal at another location might simply transfer the potential for surface and groundwater contamination to that site.

Note that it is not possible from the results of this study to draw conclusions relating to the levels of dioxins and furans in the ash wastes or in the stack emissions, although these and related products of incomplete combustion would undoubtedly be present. Quantification of these highly persistent and toxic organic pollutants would require additional study. Indeed, the Government of Thailand should ensure that determination of dioxin and furan emissions from the incinerator stacks, and their concentrations in ash residues, is undertaken and reported as a matter of urgency.

## References

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## **Appendix I: Details of sample preparation and analysis**

### **Materials and Methods**

All samples were collected and stored in clean 100 ml 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. All samples were stored cold, kept cold during transit, and refrigerated at 4°C immediately on arrival at the Greenpeace Research Laboratories.

### **1. Organic Analysis**

#### **1.1 Preparation of samples for Organic Screen analysis**

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

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.

#### **1.2 Chromatographic Analysis**

Organic compounds were identified qualitatively and quantitatively 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.

### **2. Heavy Metal Analysis**

#### **2.1 Preparation of 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.

## **2.2 Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)**

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

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

## Appendix II: Results of organic screen analysis for ash and sediment samples

**Sample Number:** TH9001

**Reference Number:** TH001

**Sample Type:** Solid waste

**Location:** Phuket Municipal Waste Plant, THAILAND

**Sampling Date:** 10.6.99

**Sample Information:** Bottom ash collected from ash pit/lagoon within the Phuket municipal waste incinerator site.

**Analysis method:** GC/MS screen

**Number of compounds isolated:** 19

### Compounds identified to better than 90%:

Benzene, 1,4-dimethyl-

Benzene, ethyl-

Cyclododecane

Heptadecane

Triacontane

### Compounds tentatively identified:

Benzene, (1-methyldecyl)-

Benzene, (1-methylundecyl)-

Cyclopropane, cis-1-butyl-2-methyl

Docosane

Eicosane

Heneicosane

Heptacosane

Nonadecane

Octacosane

Octane

Tricosane

**Sample Number:** TH9002

**Reference Number:** TH002

**Sample Type:** Solid waste

**Location:** Phuket Municipal Waste Plant, THAILAND

**Sampling Date:** 10.6.99

**Sample Information:** Bottom ash collected from a small dump close to the Phuket medical waste incinerator (from different location within same pit/lagoon as sample TH9001).

**Analysis method:** GC/MS screen

**Number of compounds isolated:** 100

**Compounds identified to better than 90%:**

1,1':2',1"':3",1""-Quaterphenyl  
1,1':3',1"':4",1""-Quaterphenyl  
1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester  
1-Dodecene  
3-Octadecene, (E)-  
Benzaldehyde  
Benzene, (1-ethyldecyl)-  
Benzene, 1,1'-(1,3-propanediyl)bis-  
Benzene, 1,2-dichloro-  
Benzene, 1,2-dimethyl-  
Benzene, 1,3,5-trimethyl-  
Benzene, 1-methyl-2-(1-methylethyl)-  
Benzene, 1-methyl-2-(2-propenyl)-  
Benzene, chloro-  
Benzene, ethyl-  
dl-Limonene  
Docosane  
Eicosane  
Heneicosane  
Heptadecane  
Hexadecane  
Naphthalene  
Naphthalene, 1,6,7-trimethyl-  
Nonadecane  
Octadecane  
Pentadecane  
Phenol, 3-methyl- or 4-methyl-  
Styrene  
Tetradecane

**Compounds tentatively identified:**

1,1':2',1"-Terphenyl  
1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester  
1-Heptadecene  
1-Hexadecanol  
1H-Indene, 1-(phenylmethylene)-  
1H-Indole, 5-methyl-2-phenyl-

1-Tetradecanol  
5-Decene, (E)-  
5-Octadecene, (E)-  
Benzene, (1-butylheptyl)-  
Benzene, (1-ethyloctyl)-  
Benzene, (1-methyldecyl)-  
Benzene, (1-methylethenyl)-  
Benzene, (1-methylundecyl)-  
Benzene, (1-propylnonyl)-  
Benzene, methyl(1-methylethyl)-  
Benzonitrile  
Cyclohexane, 1,4-didecyl-  
Decane, 2-methyl-  
Docosane, 11-decyl-  
Dodecane  
Ethanone, 1-(4-methylphenyl)-  
Ethanone, 1-phenyl-  
Heptacosane  
Hexadecane  
Naphthalene, 2-ethenyl-  
Naphthalene, 2-phenyl-  
Pentacosane  
Phenanthrene  
Tricosane  
Tridecane  
Tridecane, 3-methyl-

**Sample Number:** TH9003

**Reference Number:** TH003

**Sample Type:** Solid waste

**Location:** Phuket Municipal Waste Plant, THAILAND

**Sampling Date:** 10.6.99

**Sample Information:** Fly ash collected from ash pit within Phuket municipal waste incinerator site.

**Analysis method:** GC/MS screen

**Number of compounds isolated:** 55

**Compounds identified to better than 90%:**

1,1':3',1":4",1'''-Quaterphenyl  
1-Dodecene  
1-Octadecene  
1-Tetradecene  
9,10-Anthracenedione  
Benzene, 1,4-dichloro-  
Docosane  
Eicosane  
Heptadecane  
Methanone, diphenyl-  
Octadecane  
Tetracosane

**Compounds tentatively identified:**

1,1':4',1''-Terphenyl  
1,2-Benzenedicarboxylic acid, diisobutyl ester  
1,2-Benzenedicarboxylic acid, di-n-butyl ester  
17-Pentatriacontene  
1-Hexadecanol  
1-Hexanol, 2-ethyl-  
2-Pentanone, 4-hydroxy-4-methyl-  
5-Decene, (E)-  
Benzene, (1-ethyldecyl)-  
Benzene, (1-ethylnonyl)-  
Benzene, (1-methylundecyl)-  
Benzene, (1-pentylheptyl)-  
Benzene, 1,4-dimethoxy-  
Cyclohexane, 1,2,4-trimethyl-  
Decane, 2,3,5-trimethyl-  
Dimethyl-2,3-heptene-3  
Dodecane  
Dodecane, 2,6,11-trimethyl-  
Ethanone, 1-cyclopentyl-  
Furan, 2-methyl-5-isopropyl-  
Hexadecane  
Naphthalene  
Nonadecane

Octadecanal  
Pentacosane  
Tetradecane  
Tricosane

**Sample Number:** TH9009  
**Reference Number:** ASH01  
**Sample Type:** Fly ash  
**Location:** Phuket, THAILAND

**Sampling Date:** 14.10.99

**Sample Information:** Fly ash collected from ash pit within Phuket municipal waste incinerator site.

**Analysis method:** GC/MS screen

**Number of compounds isolated:** 161

**Compounds identified to better than 90%:**

2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-  
Benzene, 1,4-dichloro-  
Cyclododecane  
Cyclotetradecane  
Docosane  
Eicosane  
Hexacosane  
Hexacosane  
Nonadecane  
Nonadecane, 2-methyl-  
Octadecane  
Pentacosane  
Tricosane

**Compounds tentatively identified:**

1-Docosanethiol  
1-Heptacosanol  
1-Nonadecene  
Anthracene, 9-butyltetradecahydro-  
Benzaldehyde  
Benzophenone, 3'-methyl-  
Benzothiazole  
Cyclodocosane, ethyl-  
Cycloeicosane  
Cyclohexane, (1-octylonyl)-  
Cyclooctadecane, ethyl-  
Cyclopentane, (2-hexyloctyl)-  
Cyclopropane, 1-ethyl-2-heptyl-  
Cyclotetradecane, 1,7,11-trimethyl-4-(1-methylethyl)-  
Decane, 1,1'-oxybis-  
Docosane, 2,21-dimethyl-  
Dodecane, 6-cyclohexyl-  
Eicosane, 2-methyl-  
Heptacosane  
Heptadecane, 2-methyl-  
Hexadecane  
Hexadecane, 1-(ethenyloxy)-

Hexadecane, 2,6,10,14-tetramethyl-  
Methanone, diphenyl-  
Octacosane  
Octadecanal  
Octadecane, 3-methyl-  
Tetracosane  
Tridecane, 6-cyclohexyl-  
Tritetracontane

## ***ANALYTICAL RESULTS***

**Sample Number:** TH9010  
**Reference Number:** ASH02  
**Sample Type:** Bottom ash  
**Location:** Phuket, THAILAND  
**Sampling Date:** 14.10.99

**Sample Information:** Bottom ash collected from ash pit/lagoon within the Phuket municipal waste incinerator site.

**Analysis method:** GC/MS screen

**Number of compounds isolated:** 76

### **Compounds identified to better than 90%:**

5-Tetradecene, (E)-  
Benzene, 1,4-dichloro-  
Eicosane  
Heptadecane  
Naphthalene, 1,2,3-trimethyl-4-propenyl-  
Nonadecane  
Octadecane

### **Compounds tentatively identified:**

1-Hexadecene  
1-Octanol, 2-butyl-  
2-Heptenal, (E)-  
3-Ethylthiophene  
4-Undecene, 6-methyl-, cis/trans  
5-Eicosene, (E)-  
9-Octadecen-1-ol, (Z)-  
9-Undecen-2-one, 6,10-dimethyl-  
Benzene, (1-butylheptyl)-  
Benzene, (1-butylpentyl)-  
Benzene, (1-ethyldecyl)-  
Benzene, (1-ethylnonyl)-  
Benzene, (1-methyldecyl)-  
Benzene, (1-methylundecyl)-  
Benzene, (1-pentylheptyl)-  
Benzene, (1-pentylhexyl)-  
Benzene, (1-pentylloctyl)-  
Benzene, (1-propylnonyl)-  
Benzene, (1-propyloctyl)-  
Benzene, 1-methyl-3-[(4-methylphenyl)methyl]-  
Cyclopentadecanone, 2-hydroxy-  
dl-Limonene  
Hexadecane

Hexadecane, 2,6,10,14-tetramethyl-

Hexane, 2,3,5-trimethyl-

Nonacosanol

Pentadecane, 2,6,10,14-tetramethyl-

Tetracosane, 2,6,10,15,19,23-hexamethyl-

**Sample Number:** TH9007

**Reference Number:** SED01

**Sample Type:** Sediment

**Location:** Phuket, THAILAND

**Sampling Date:** 14.10.99

**Sample Information:** Sediment from mud-flat on tidal river to south-west of landfill/incinerator complex.

**Analysis method:** GC/MS screen

**Number of compounds isolated:** 53

**Compounds identified to better than 90%:**

Benzene, 1,4-dichloro-

**Compounds tentatively identified:**

9-Eicosene, (E)-

Docosane

Dodecane, 2-methyl-

Heptadecane

Heptadecane, 4-methyl-

Heptane

Hexadecane

Hexane, 2,3,4-trimethyl-

Nonacosane

Octadecane

Octadecane, 3-ethyl-5-(2-ethylbutyl)-

Pentadecane, 2,6,10-trimethyl-

Tetracosane, 2,6,10,15,19,23-hexamethyl-

Tetradecane

Tetratetracontane

Undecane, 2-methyl-

Undecane, 4,7-dimethyl-

**Sample Number:** TH9008  
**Reference Number:** SED02  
**Sample Type:** Sediment  
**Location:** Phuket, THAILAND

**Sampling Date:** 14.10.99

**Sample Information:** Sediment from BangYai Canal, north-west boundary of landfill/incinerator complex

**Analysis method:** GC/MS screen

**Number of compounds isolated:** 76

**Compounds identified to better than 90%:**

Benzene, 1,4-dichloro-  
Docosane  
Docosane, 11-decyl-  
Hentriacontane  
Octadecane  
Tetratetracontane  
Tetratriacontane

**Compounds tentatively identified:**

1-Dodecene  
1-Hexadecene  
2-Heptenal, (E)-  
3-Methylheneicosane  
9-Octadecene, (E)-  
Cycloheptane, methyl-  
Decane  
Decane, 2,3,8-trimethyl-  
Decane, 2,4-dimethyl-  
Decane, 2-methyl-  
Dodecane  
Dodecane, 2,6,11-trimethyl-  
Dodecane, 2,7,10-trimethyl-  
Dotriacontane  
Eicosane  
Heneicosane  
Heptacosane  
Heptadecane  
Hexadecane  
Hexadecane, 2,6,10,14-tetramethyl-  
Hexane, 3,3-dimethyl-  
Naphthalene, 2,6-diisopropyl-  
Nonadecane, 3-methyl-  
Nonahexacontanoic acid  
Nonane, 4,5-dimethyl-  
Nonane, 5-butyl-

Octacosane  
Octadecane, 3-ethyl-5-(2-ethylbutyl)-  
Octane  
Octane, 2,4,6-trimethyl-  
Octane, 5-ethyl-2-methyl-  
Pentacosane  
Pentadecane  
Pentadecane, 2,6,10,14-tetramethyl-  
Tetradecane  
Triacontane  
Tricosane  
Undecane, 3,8-dimethyl-  
Undecane, 4,7-dimethyl-  
Undecane, 4-methyl-

## ***ANALYTICAL RESULTS***

**Sample Number:** TH9004

**Reference Number:** TH004

**Sample Type:** Solid waste

**Location:** Samui Solid Waste Incineration Plant, Samui Island, THAILAND

**Sampling Date:** 11.6.99

**Sample Information:** Incinerator ash collected from an ash pit within the Samui Solid Waste Incineration Plant.

**Analysis method:** GC/MS screen

**Number of compounds isolated:** 49

### **Compounds identified to better than 90%:**

1,1':3',1"':3",1""-Quaterphenyl  
1-Decene  
1-Tetradecene  
Benzene, (1-ethyldecyl)-  
Benzene, (1-ethylnonyl)-  
Benzene, (1-propylnonyl)-  
Benzene, 1,2-dimethyl-  
Benzene, 1,4-dichloro-  
Benzene, chloro-  
Benzene, ethyl-  
Cyclododecane  
Eicosane  
Naphthalene  
Octadecane  
Tricosane

### **Compounds tentatively identified:**

1-Hexadecene  
Benzene, (1-butylheptyl)-  
Benzene, (1-butynonyl)-  
Benzene, (1-butyloctyl)-  
Benzene, (1-ethyl-1-methylpropyl)-  
Benzene, (1-methyldecyl)-  
Benzene, (1-methyldodecyl)-  
Benzene, (1-methylundecyl)-  
Benzene, (1-propyloctyl)-  
Docosane  
Dodecane  
Fluoranthene  
Heptacosane  
Heptadecane  
Hexane, 3,3-dimethyl-

Hexatriacontane  
Octadecane  
Octane, 4-methyl-  
Octane, 6-ethyl-2-methyl-  
Pentacosane  
Pentadecane, 3-methyl-  
Pyrene  
Tetracosane  
Tetradecane  
Tetratriacontane  
Tridecane  
Tridecane, 3-methyl-  
Undecane

## Appendix III: Brief toxicological profiles for lead and cadmium

### Lead (Pb)

#### 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).

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).

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**

## 2. Environmental Levels, Contamination and Behaviour

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

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

Environmental Matrix	Concentration	Reference
Seawater (estuarine waters around England and Wales)	24-880 ng/l	Law et al. 1994
Seawater (open ocean)	5 ng/l 1-14 ng/l 20-71 ng/l	UPHS 1997 Bryan and Langston 1992 Law et al. 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**

Site Description	Concentration	Reference
River water, Donana National Park, Spain (close to mining site)	<5-2500 ug/l	Pain et al. 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 et al. 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 et al. 1997
Gannel estuary sediments, UK. Received waste from old lead mines	2700 mg/kg	Bryan and Langston 1992
Oartzun river sediments, Spain. Close to lead-zinc mining sites	68-5540 mg/kg	Sanchez et al. 1994

**Table 5 lead concentrations associated with anthropogenic contamination**

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).

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).

### 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).

#### 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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## ***Cadmium (Cd)***

### **1. Natural Occurrence**

Cadmium is a relatively rare metal, being 67<sup>th</sup> 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).

## 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
Energy production (coal and oil combustion)	0.79
Waste incineration (municipal refuse and sewage sludge)	0.75
Manufacturing processes (steel, iron, phosphate fertilisers, cement)	0.60
TOTAL	7.57

*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
TOTAL	9.11

*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
TOTAL	21.62

*Table 3 World-wide inputs of cadmium to soils*

### 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).

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).

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 et al. 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 et al. 1995a
Soil, Cu-Ni mining site, Sudbury, Ontario	0.1-10 mg/kg	Dudka et al. 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 et al. 1992

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

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).

#### 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 8<sup>th</sup> 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).

## 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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