Hazardous emissions from Thai coal-fired power plants:

Toxic and potentially toxic elements in fly ashes collected from the Mae Moh and Thai Petrochemical Industry coal-fired power plants in Thailand, 2002

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EXECUTIVE SUMMARY

Coal contains trace amounts of a wide range of elements including toxic metals and metalloids. These elements are not destroyed during the combustion of coal, but are released in various wastestreams, which include fly ash, bottom ash, wastes from gas scrubber units and gaseous emissions to the atmosphere.

This study was carried out to determine the content of a range of elements in fly ashes produced by two coal fired power plants located in Thailand;

- Mae Moh coal fired power plant, Lampang.
- Thai Petrochemical Industry (TPI) coal fired power plant, Rayong.

Greenpeace visited the facilities in April and May 2002 and collected samples of fly ash. The analysis of these samples demonstrated that all samples were contaminated with a range of toxic and potentially toxic elements including arsenic, chromium, lead and mercury.

Of the three fly ash samples, that from the Mae Moh plant contained the highest concentrations of many of the most toxic elements, including arsenic, lead and mercury. The two samples from the TPI plant contained higher concentrations of other elements including chromium, cobalt, nickel and zinc.

Estimates of the total annual quantities of each element contained in the fly ashes produced by the Mae Moh and TPI plants have been calculated from the annual quantities of fly ash produced and the elemental composition of the fly ash samples collected from each plant. The larger Mae Moh plant is estimated to produce ashes containing many hundreds of tonnes of toxic elements annually. The considerably smaller TPI facility is estimated to have production quantities of many tonnes annually, as detailed in Table 5.

The fly ash sample from the Mae Moh plant contained arsenic and mercury at concentrations above concentrations typically found in uncontaminated soils by three and fourteen times respectively. The fly ash samples from the TPI plant contained mercury at approximately twice the background soil concentration. The concentrations of the additional elements detected in the fly ash samples are not significantly higher than typical uncontaminated soil concentrations.

The presence of toxic and potentially toxic elements in the fly ash samples at less elevated concentrations than those of arsenic and mercury does contribute further to the potential environmental hazards from the ashes as a result of the very large quantities of ashes produced, and the tendency for a significant fraction of these elements to leach from the ashes into the immediate environment.

In addition to their toxic element content, fly ashes produced by these facilities pose a threat due to the very fine particles contained within them. These particles are small enough to be inhaled into the extremities of the lung airways, and as a result can lead to adverse human health effects. Pollution control devices are significantly less efficient at capturing such small ‘respirable’ particles, which can contain higher concentrations of toxic elements than the bulk fly ash.

Fly ash is only one of the wastestreams from coal combustion. Considerable quantities of elements including arsenic and mercury are often released in gaseous form with the flue gases. In addition to fly ash and gaseous emissions from coal burning, a smaller but significant quantity of bottom ash is also produced. Certain elements are preferentially retained in the bottom ashes over the fly ashes.

Any production, storage and disposal/use of fly ashes from the Mae Moh and TPI facilities must take into account the concentrations of the toxic elements contained within them, especially arsenic and mercury. Treatment processes to reduce the quantities of these elements in the fly ashes would simply result in the production of additional contaminated wastestreams.

Ongoing use of coal combustion for power production will result in future releases of toxic and potentially toxic elements to the environment. This can only be avoided through the cessation of coal combustion and the implementation of sustainable technologies such as solar- and wind-power generation.

1 INTRODUCTION

Coal contains trace amounts of a wide range of elements including toxic metals and metalloids (Querol *et al.* 1995). These elements are not destroyed during the combustion of coal, but are released in various wastestreams, which include fly ash, bottom ash, wastes from gas scrubber units and gaseous emissions to the atmosphere.

This study was carried out to determine the content of a range of elements in fly ashes produced by two coal fired power plants located in Thailand. The facilities studied were;

- Mae Moh coal fired power plant, Lampang, Thailand.
- Thai Petrochemical Industry (TPI) coal fired power plant, Rayong, Thailand

Mae Moh coal power plant

The Mae Moh coal power plant is a 2500+ megawatt (MW) lignite coal fired thermal power plant, consisting of ten 300 MW units. The facility is equipped with ionizing wet scrubbers for the collection of fly ash. Lime (calcium oxide) desulphurisation is also carried out on the flue gases for the removal of sulphur oxides.

Of the ten units, the fly ashes from six units are supplied to cement manufacturing companies. The fly ashes from the remaining four units are dumped in a disused mine, approximately five kilometres from the Mae Moh plant. These ashes are not processed in any way prior to dumping.

Thai Petrochemical Industry (TPI) coal power plant

The Thai Petrochemical Industry (TPI) coal power plant is a 108 MW bitumous coal fired thermal power plant. The facility is equipped with electrostatic precipitators (ESPs) for fly ash collection. Lime desulphurisation of the flue gases is also carried out. This power plant supplies electricity to its own cement manufacturing facility.

The fly ashes from this plant are temporarily stored on site prior to being supplied as a raw material to the TPI cement industry.

Facility		Mae Moh	TPI
Energy production	(MW)	2 500+	108
Coal consumption	(tonnes/unit/day)	4 100	500
	(thousand tonnes/year)	15 000	183
Fly ash production	(tonnes/day/unit)	1 200	40-50
	(thousand tonnes/year)	4 380	15 - 18

Table 1. Summary of consumption and production figures for the two coal power plants. Data was obtained through personal communications with the Mae Moh and TPI plants.

2 SAMPLING PROGRAM

In April and May 2002, one sample of fly ash was collected from the Mae Moh coal fired power station in Lampang and two samples of fly ash were collected from the Thai Petrochemical Industry coal fired power station in Rayong, Thailand. The samples were returned to the Greenpeace Research Laboratories in the UK for analysis. Detailed description of sample preparation and analytical procedures are presented in Appendix 1.

2.1 Sample descriptions

All three samples of fly ash were fine powders. The sample from the Mae Moh plant (MI02011) was collected from a hopper used to store and transport the ash, located adjacent to the coal plant unit 4-13. The two samples from the TPI plant (MI02015-16) were collected from different locations within an ash storage area located adjacent to the outside coal storage area. The ashes in this area were not contained in any way. A description summary of the samples is given in Table 2.

Sample number	Sample description	Facility	Location
MI02011	fly ash	Mae Moh power plant	Ash storage hopper adjacent to coal plant unit 4-13
MI02015	fly ash	Thai Petrochemical Industry power plant	Unconfined ash storage pile adjacent to the outside coal storage area
MI02016	fly ash	Thai Petrochemical Industry power plant	Unconfined ash storage pile adjacent to the outside coal storage area

Table 2. Description of samples collected from two coal-fired power plants in Thailand.

3 RESULTS AND DISCUSSION

The results of the heavy metal and metalloid analyses of the fly ash samples are presented in Table 3. All three samples of fly ash contained detectable concentrations of all elements analysed for other than cadmium. The sample from the Mae Moh plant (MI02011) contained the highest concentrations of many of the most toxic elements analysed for, including arsenic, lead and mercury. The two samples from the TPI plant (MI02015, MI02016) contained higher concentrations of other elements including chromium, cobalt, nickel and zinc.

Sample number		MI02011	MI02015	MI02016
Description		fly ash	fly ash	fly ash
Power facility		Mae Moh	TPI	TPI
Element		mg/kg dry weight	mg/kg dry weight	mg/kg dry weight
Arsenic	(As)	172	22.0	13.5
Cadmium	(Cd)	<1	<1	<1
Calcium	(Ca)	108604	7925	17532
Chromium	(Cr)	39	72	31
Cobalt	(Co)	16	17	57
Copper	(Cu)	52	27	24
Lead	(Pb)	22	9	19
Manganese	(Mn)	566	182	431
Mercury	(Hg)	8.8	1.1	1.3
Nickel	(Ni)	36	78	242
Zinc	(Zn)	156	185	249

Table 3. Concentrations of elements identified in samples of fly ash from the Mae Moh and Thai Petrochemical Industry (TPI) coal power plants, Thailand.

A significant variation was found in the concentrations of a number of elements between the two ash samples from the TPI plant (MI02015 and MI02016). These variations may be due to the fly ash resulting from the combustion of different types of coal. The composition of trace elements in fly ash from a single coal fired power plant has, however, been reported to vary measurably on a daily basis (Egeman & Yurteri 1996).

The concentrations of elements detected in the three fly ash samples are within a similar range to concentrations reported for fly ashes from similar facilities in other countries (see Table 4).

Fly ash producer	4 coal power plants, Greece	1050 MW coal power plant, Spain	11 coal power plants, UK	Coal fly ash, China
Data sources	Fytianos & Tsaniklidi 1998	Llorens *et al.* 2001	Wadge *et al.* 1986	Liao & Jiang 1999
Element	concentration (mg/kg dry weight)	concentration (mg/kg dry weight)	concentration (mg/kg dry weight)	concentration (mg/kg dry weight)
Arsenic (As)	n/r	60	40-205 (104)	n/r
Cadmium (Cd)	11.6-14.4	1.3	0.13-0.82 (0.30)	312-315
Calcium (Ca)	n/r	39700	n/r	n/r
Chromium (Cr)	110-160	134.2	n/r	n/r
Cobalt (Co)	n/r	29.2	n/r	n/r
Copper (Cu)	31.8-62.8	71.8	n/r	n/r
Lead (Pb)	123-143	52.0	17-176 (59)	843-847
Manganese (Mn)	213-330	324.6	n/r	n/r
Mercury (Hg)	n/r	0.01	n/r	8.1-8.3
Nickel (Ni)	n/r	87.9	n/r	n/r
Zinc (Zn)	59.6-86.9	221.3	n/r	n/r

Table 4. Summary of reported element composition of fly ashes from similar coal fired power facilities. Data in parentheses are average figures; n/r indicates that no data were reported.

Very large quantities of fly ash are produced by these two facilities. The total quantities of toxic and potentially toxic elements contained in the fly ashes produced by these two plants can be estimated from the total quantities of fly ashes produced and the elemental composition of the fly ashes (see Table 5). The figures in Table 5 are only approximate as they are based upon the composition of a very small fraction of the total fly ashes produced. The differences in composition between samples MI02015 and MI02016 from the TPI plant demonstrate the variability that can occur in the elemental composition of fly ashes from one facility. These data, however, give an indication of the large quantities of elements produced in one of the wastestreams as a result of coal burning at the Mae Moh and TPI plants.

Element	Quantity contained in the fly ash produced (tonnes/year)	
	Mae Moh	TPI[a]
Arsenic (As)	753	0.20-0.40
Chromium (Cr)	170	0.45-1.31
Cobalt (Co)	70	0.25-1.04
Copper (Cu)	230	0.35-0.49
Lead (Pb)	96	0.13-0.35
Manganese (Mn)	2480	2.66-7.87
Mercury (Hg)	39	0.016-0.024
Nickel (Ni)	160	1.14-4.42
Zinc (Zn)	683	2.70-4.54

Table 5. Total element quantities produced in fly ashes by the Mae Moh and TPI coal fired power plants. Data calculated from the composition of the fly samples (Table 3) and ash production data (Table 1). a; Range derived from composition data on both fly ash samples, MI02015 and MI02016.

Of the elements detected in the fly ash samples, calcium was present at significantly higher concentrations in all samples compared to all other elements analysed for, most noticably for sample MI02011 from the Mae Moh plant. Calcium, however, does not pose a toxic threat to animals or humans.

Fly ashes from coal combustion typically contain significant quantities of calcium (Senior *et al.* 2000). Levels may be elevated by the use of lime (calcium oxide) as a flue gas scrubbing agent. This type of pollution control is used at both the Mae Moh and TPI plants. The higher concentration of calcium in the fly ash sample from the Mae Moh plant (MI02011) may be due to the type of flue gassing scrubbing technology employed, or as a result of the type of coal burned at this facility.

Lime is used as a gas scrubbing agent due, in part, to its high sorption capacity for some elements vapourised during coal combustion, including arsenic, cadmium, nickel, lead and zinc (Querol *et al.* 1995, Sandelin & Backman 2001).

Of the remaining elements detected in the samples, many are highly toxic to plants, terrestrial and aquatic life and humans. These include arsenic, cobalt, lead and mercury and certain forms of chromium. Other elements detected in the fly ashes are can be toxic to plants, animals and humans when present in higher concentrations, including copper, manganese, nickel and zinc. A number of the elements detected also have the potential to bioaccumulate (build up in plants or animals), such as arsenic, chromium, lead, mercury and zinc (Kimbrough *et al.* 1999, USPHS 2000). Consequences of the presence of these elements in the fly ashes are discussed below, for additional information on key elements see Appendix 2.

Other than for arsenic and mercury, the concentrations of those elements detected in the fly ash samples are not significantly higher than those typical found in uncontaminated soils (Alloway 1990).

Arsenic and mercury are typically found in uncontaminated soils at concentrations up to 50 mg/kg and 0.625 mg/kg respectively (Alloway 1990, WHO 1989). The concentration of arsenic in the fly ash sample from the Mae Moh plant (MI02011) was over three times this background soil level. The concentration of mercury in this sample was fourteen times the background soil level. The samples from the TPI plant (MI02015-16) contained mercury at concentrations approximately twice the background soil level. The higher concentrations of arsenic and mercury in the fly ash from the Mae Moh plant may result from the use of ionizing wet scrubbers at this facility, which can increase the removal of these elements from gaseous emissions into solid wastestreams.

Arsenic

Arsenic is toxic to many plants, animals and humans, though lethal doses in animals are somewhat higher than the estimated lethal dose in humans (Kaise *et al.* 1985, USPHS 2000). In addition, bioconcentration of arsenic can occur in aquatic organisms, primarily in algae and lower invertebrates (USEPA 1980).

Most cases of human toxicity from arsenic have been associated with exposure to inorganic arsenic. Long-term low-level human exposures may lead to damage to the vascular system and can cause injury to the nervous system (USPHS 2000). Of greater concern is the increased risk of carcinogenicity through prolonged ingestion of inorganic arsenic.

Arsenic and certain arsenic compounds are known to be carcinogenic to humans by both the oral and inhalation routes. The US Department of Health and Human Services in its 9th Report on Carcinogens lists arsenic compounds as "known to be human carcinogens". Skin cancer is the prevalent form resulting from exposure, though there is also evidence for an increased risk of internal cancers, including liver cancer (USPHS 2001). Primarily as a result of its carcinogenicity, in 2002 the USEPA set a limit of 10 μg/l (0.01 mg/l) for arsenic in drinking water (USEPA 2002b).

Most arsenic compounds can readily dissolve in water, and so upon release to the environment arsenic can readily enter groundwater and waterways such as rivers and lakes (USPHS 2000).

Mercury

The concentrations of mercury in the three fly ash samples MI02011, MI02015 and MI02016 were significantly lower than those of the other elements analysed for. The presence of mercury at these concentrations is of concern, however, as it is extremely toxic and is usually found in very low levels in the environment. The majority of reported toxic effects that can result from exposure to mercury affect the central nervous system (CNS) (USPHS 2000).

Inorganic mercury, as present in the fly ashes, can be converted into organic forms, including methylmercury, by micro organisms indigenous to soils and fresh water and marine sediments. Methylmercury is more toxic to both humans and animals than any of the inorganic forms. Effects of exposure to methylmercury can include permanent damage to the CNS, kidneys, and the developing foetus. It is quick to enter the food chain and provides one of the rare examples of metal biomagnification (i.e. concentrations increase up the food chain). This process results in one of the most important sources of human, non-occupational, mercury exposure (USPHS 2000, WHO 1989).

The presence of the additional elements detected in the fly ash samples, albeit at lower concentrations relative to background levels, pose an environmental threat due to their toxicity and their ability to leach into the environment.

Chromium

Chromium can exist in many different forms, though only the trivalent (III) and hexavalent (VI) forms are of biological importance. In general, chromium (VI) is the predominantly soluble form in aquatic environments (USPHS 2000).

Both chromium (III) and chromium (VI) can accumulate in many aquatic species (Kimbrough *et al.* 1999). Whilst chromium (III) is an essential trace element in animals, chromium (VI) is non-essential and toxic at low concentrations (USPHS 2000, Goyer 1996). Chromium (VI) compounds are corrosive, and allergic skin reactions readily occur following exposure. Damage to the kidney and liver has also been reported (USPHS 2000).

Hexavalent chromium (VI) has been classified by The International Agency for Research on Cancer as a known carcinogen (IARC 1998). Also, the US Department of Health and Human Services in its 9th Report on Carcinogens, lists classifies chromium (VI) compounds as "known to be human carcinogens" (USPHS 2001).

The methods employed to analyse the fly ash samples from Mae Moh and TPI plants are not able to quantify individual chromium species, giving data only on the total chromium concentrations. Studies on fly ash from similar coal power plants, however, have shown a significant fraction of chromium in leachate from coal fly ash to be present in the hexavalent form (Lecuyer *et al.* 1996).

Lead

Lead is highly toxic to most living things, with no known nutritional biochemical or physiological function (Goyer 1996). In humans the toxic effects of lead include damage to the kidneys, cardiovascular and nervous systems. Of particular concern is the effect of relatively low exposure on cognitive and behavioural development in children (Pirkle *et al.* 1998, USPHS 2000, Goyer 1993, Nriagu 1988). When released to the environment, lead has a long residence time compared with most pollutants, remaining accessible to the food chain and to human metabolism far into the future (Sauve *et al.* 1997, USPHS 2000, Alloway 1990).

Nickel

Nickel can be reasonably mobile when released to the environment, and can bioaccumulate in some organisms in the aquatic environment (USPHS 2000). Very small amounts of nickel have been shown to be essential for normal growth and reproduction in many species of animals, plants and micro organisms (USPHS 2000, Alloway 1990). Human toxicity generally only results through intake of high levels of nickel (USPHS 2000).

There is, however, evidence for the carcinogenicity of nickel and certain nickel compounds. The US Department of Health and Human Services, in its 9th Report on Carcinogens, lists nickel and its compounds as “reasonably anticipated to be human carcinogens” (USPHS 2001).

Zinc

Zinc is an essential element, present in the tissues of animals and plants even at normal, ambient concentrations. However, if plants and animals are exposed to high concentrations of bioavailable zinc, significant bioaccumulation can results with possible toxic effects (USPHS 2000).

The production, storage and disposal/use of fly ashes from the Mae Moh and TPI facilities must take into account the presence of toxic pollutants contained within them, especially arsenic and mercury. The fly ashes stored at these facilities are not contained in a way to prevent their dispersion. These ashes contain very fine particles that can be inhaled by workers at these facilities and those living in the vicinity.

3.1 Respirable particles

Minute particles of matter suspended in the air, often called particulates, are present as a result of both natural and human activities. As a broad generalisation, natural particulates are generally larger in size (>2.5μm) than the finer particulates formed from combustion processes (<2.5 μm) (QUARG 1996, COMEAP 1995, EPAQS 1995).

These finer particulates, known as "respirable particles" are of concern in relation to human health. Particulate pollution is implicated in the worsening of respiratory illnesses such as asthma, and increasing premature mortality from respiratory and heart diseases. This is because the respirable particulates are small enough to be inhaled into the extremities of the lung airways, whereas larger particles are prevented from reaching the deep airways by the respiratory system's protective mechanisms. In particular, those particulates sized <0.1µm, termed ultrafine particles, are of greatest concern in regard to adverse effects on human health. The smallness of ultrafine particles and their high surface area for the release of metals are believed to contribute to the observed adverse health effects (Allsopp *et al.* 2001).

Most naturally produced particles are generally greater than 20 µm in size (QUARG 1996, EPAQS 1995). Fine particles of less than 10 µm do occur naturally, mainly in the form of re-suspended sea salts. In this form, the fine particulates pose no threat to health and, if inhaled, are simply absorbed into the body (Howard 2000).

During coal combustion, certain elements contained within the coal are vapourised to varying degrees. Upon cooling of the combustion gases these vapourised elements are fully or partially sorbed onto fly ash particles. Due to the relatively large surface area of the smaller fly ash particles, this process leads to these elements being present in higher concentrations in the smaller sized particles. This is especially the case for those particles less than 10µm (0.01mm) in diameter. Elements for which this enrichment has been observed include arsenic, cadmium, chromium, cobalt, lead, mercury and zinc (Coles *et al.* 1979, Querol *et al.* 1995, Wadge *et al.* 1986).

The higher concentrations of these elements in the very fine particles of the fly ash have implications relating to the failure of pollution control devices to capture ultrafine particles, and on the threat posed by such particles upon inhalation.

Electrostatic precipitators (ESPs) and fabric filters typically retain more than 99% of fly ash produced, with ESP efficiencies of 99.95% reported for some plants (Querol *et al.* 1993). The use of ionizing wet scrubbers results in similar particulate collection efficiencies to the use of ESPs (USEPA 1999). Due to the considerable quantities of fly ash produced, however, particulate emissions to the atmosphere can still be considerable where pollution control devices are employed. Emitted fly ash particles can be deposited at distances up to hundreds of kilometres from the emission point, depending on factors including chimney height (Mason 1992).

The collection efficiencies of pollution control devices are, however, significantly lower for those particles less than 10µm in diameter, with the greatest penetration for ultra-fine particles of 0.1-1µm diameter (Senior *et al.* 2000, Swaine 2000). Partly as a result of the elemental enrichment in the smaller particle fraction, as discussed above, emission plumes can contain particles that are enriched with certain elements, including arsenic, compared with particles in the stack gases (Ondov *et al.* 1989). Estimates of the quantities of toxic elements emitted to the atmosphere that are based on the percentage of fly ash retained may underestimate the total quantities as a result of these elemental enrichments in the finest particles (Llorens *et al.* 2001, Senior *et al.* 2000).

The combination of the poor capture efficiencies by pollution control devices for these fine "respirable" particles produced through coal combustion, and their elevated element concentrations has clear implications for human health.

3.2 Gaseous emissions

In addition to the production of ashes containing toxic elements as a result of coal burning, some toxic elements are also emitted to the atmosphere in gaseous form. Considerable quantities of arsenic and mercury are usually released in gaseous form with the flue gases. Estimates of the fraction of elements emitted in flue gases compared to the amounts in all wastestreams include; mercury (up to 95%) and arsenic (up to 30%) (Llorens *et al.* 2001). The quantities of gaseous arsenic released to the atmosphere can be significantly reduced by the use of flue gas scrubbing with lime (calcium oxide) through sorption to lime particles (Senior *et al.* 2000).

The use of ionizing wet scrubbers, as installed at the Mae Moh plant, can reduce the quantities of water soluble pollutants in the gas streams, including certain forms of arsenic and mercury (Senior *et al.* 2000). These pollutants, however, cannot be destroyed by such end-of-pipe technologies, but are simply moved into the solid and liquid wastestreams from the plant.

Coal burning plants equipped with electrostatic precipitators (ESPs) have been estimated to emit up to and above 95% of the mercury liberated upon coal burning to the atmosphere, in either gaseous or particulate form (Kotnik *et al.* 2000, Llorens *et al.* 2001). The use of ionizing wet scrubbers can reduce the emission to gaseous mercury through the absorption of a substantial fraction of water-soluble divalent mercury (Senior *et al.* 2000). This process removes more, but not all, mercury from the gaseous emissions into the solid and liquid wastestreams from the plant, as reflected in the higher mercury concentration in the fly ash sample from the Mae Moh plant (MI02011) compared to those in the samples from the TPI plant (MI02015-16).

Atmospherically emitted mercury can be present in a number of chemical forms. Elemental mercury comprises about 20-50% of the total mercury emitted. The remainder is in the form of divalent mercury, which may be predominantly mercury chloride ($HgCl_2$). After emission to the atmosphere, divalent mercury, which is water soluble, may be deposited close to the incinerator. On the other hand, elemental mercury may be transported for very long distances by atmospheric currents before it is eventually converted to the divalent form. This can then become deposited on the ground (Carpi 1997).

Approximately three-quarters of global mercury emissions (estimated to be about 1900 tonnes) has been calculated to results from the combustion of fuels, particularly coal combustion. Asian countries contribute about 50% to the total emissions of all forms of mercury, including about 56% of global atmosphere mercury emissions (Pacyna & Pacyna 2002).

Recent studies have demonstrated that newly deposited mercury is more readily converted into highly toxic methylmercury than mercury that is already in the ecosystem (Renner 2002). This implies that a reduction in such deposition would result in significant near-term reductions in the production of methylmercury. Such deposition reductions could easily be achieved through a reduction in atmospheric mercury emissions that would result from the cessation of power production through coal burning (Carpi 1997, Pacyna & Pacyna 2002).

While the bioaccumulation of methylmercury in the food chain is a complex process, a reduction in the levels of this neurotoxic compound in the food chain would be expected from a lower rate of methylmercury production.

3.3 Leaching from fly ash

Very large quantities of contaminated fly ash are produced by these facilities. Although the majority of elements present are not significantly elevated compared to background soil levels they are generally not fully bound to the fly ash particles. As a result, a significant fraction of the toxic and potentially toxic elements contained within the ashes are able to leach into the immediate environment. All the elements quantified in this study are able to leach from fly ash to varying degrees (Querol *et al.* 2001, Llorens *et al.* 2001).

The storage and disposal of coal fly ash can result in releases of leached metals into soils, surface and ground waters. The majority of these elements are able to accumulate in soils and sediment. The elements detected in this study are persistent and many are high toxic to animals, humans and plants.

The rate and quantity of such leaching is dependent on a number of factors, which include the fly ash source and leaching time (Egeman & Coskun 1996, Hansen & Fisher 1980). Acidity also has a major influence. In general, higher rates and quantities of leaching occurs under more acidic conditions (low pH). While most fly ashes and their leachates are alkaline (higher pH), fly ash leachates can vary from acidic (pH=4.2) to alkaline (pH=12.4) (Page *et al.* 1979).

Various data is available on the amount of different elements that are able to leach from fly ash, with values varying between the different study methods employed. Studies using sequential extraction methods have demonstrated that, for most elements present in fly ash, a significant fraction is able to leach from the ash; arsenic (57%), chromium (17%), cobalt (8%), copper (7%), nickel (8%), lead (13%) and zinc (12%) (Fytianos & Tsaniklidi 1998, Querol *et al.* 1996).

Studies designed to approximate field conditions have shown that those metals generally found to leach to the greatest extent were cadmium, chromium and lead (Fytianos & Tsaniklidi 1998). The use of pure water has been shown to result in the leaching of appreciable fractions of the arsenic, chromium, cobalt, copper, nickel, lead and zinc present in coal fly ash (Llorens *et al.* 2001). Certain trace elements present in fly ash, including chromium, lead and zinc, can also be leached by seawater (Kress 1993).

A study designed to simulate the leaching of elements from coal fly ash by rainwater produced concentrations of arsenic in the leachate of up to 260 µg/l (Praharaj *et al.* 2002). This concentration is 26 times the US Environmental Protection Agency (USEPA) limit and the World Health Organization (WHO) recommended value for drinking water (USEPA 2002b, WHO 1998). The quantity of arsenic present in fly ash leachates can be reduced through the use of lime flue gas scrubbing (Lecuyer *et al.* 1996).

Of the total amounts of chromium present in fly ash leachate, one form is of particular concern, hexavalent chromium (VI). This form of chromium is highly toxic and a known carcinogen. While the analytical methods employed in this study were not able to determine the presence of hexavalent chromium (VI) in the samples from the Mae Moh and TPI facilities, previous studies have shown this form of chromium to be present in leachate from coal fly ashes.

Hexavalent chromium (VI) has been found to constitute up to 88% of the total chromium present in fly ash leachate (Lecuyer *et al.* 1996). An earlier study, however, indicated that all soluble chromium leached from fly ash under acidic conditions (pH<4.8) was present solely as chromium (III) (Rai & Szelmecka 1990).

Impacts on animals inhabiting locations contaminated with coal fly ash have been demonstrated in many studies. For example, adult southern toads (*Bufo terrestris*), freshwater grass shrimp (*Palaemonetes paludosus*) and fish (*Erimyzon sucetta*) have been shown to accumulate trace elements from coal ash polluted areas, including arsenic and cadmium (Hopkins *et al.* 1999, Rowe 1998, Hopkins *et al.* 2002). Larval southern toads (*Bufo terrestris*) and larval bullfrogs (*Rana catesbeiana*) inhabiting similar sites have been shown to suffer elevated incidences of survival-threatening physiological impacts (Hopkins *et al.* 2000, Rowe *et al.* 2001). Such effects are believed to result from the complex mixtures of pollutants in coal ashes. Amongst these are elements such as selenium, chromium, cadmium and copper, known to have the potential to be teratogenic to such species (cause malformations of the embryos) (Hopkins *et al.* 2000).

The ability of toxic elements to leach from coal fly ashes has serious implications where such ashes are added to agricultural land as soil stabilisers. Plants grown on soils amended with coal fly ashes have been demonstrated to absorb a range of potentially toxic elements (El-Mogazi *et al.* 1988).

Furthermore, grasses and legumes grown on soil capped coal fly ash landfill sites can become enriched with potentially toxic elements (Weinstein *et al.* 1989).

3.4 Other ash wastes

In addition to fly ash and gaseous emissions from coal burning, a significant quantity of bottom ash is also produced. Of all ashes produced through coal combustion, fly ash is generally the major ash waste, constituting up to 88% of total ash production from coal burning power plants (Sandelin & Backman 2001, Swaine 2000).

Certain elements are preferentially retained in either the fly or bottom ashes. The relative enrichment of these elements in either of these wastestreams is to some degree dependant on the technologies employed at the facility.

Elements that are reported to be selectively retained in the bottom ashes to a small degree include copper and manganese. Those reported to be selectively retained in the fly ashes include arsenic, cadmium, chromium, lead, mercury and zinc. The degree of enrichment is particularly large for mercury, with over 90% of that retained in all ashes being found in the fly ash. Some elements show little or no selectivity between the fly and bottom ashes (Querol *et al.* 1995, Sandelin & Backman 2001). The enrichment of elements in one or other of the ashes does not take into account the large fraction of elements such as mercury that are released to the atmosphere in gaseous form.

3.5 Fly ash disposal

In many countries, fly ashes produced from coal combustion are utilised rather than disposed of, in part as cement raw material (Hall & Livingston 2002). Although this method can reduce the immediate leaching of heavy metals and other toxic elements from the ashes, weathering and erosion over time will ultimately cause their release back to the environment.

The demolition of structures constructed from cement that has been produced with the use of coal fly ash, or mechanical operations (such as drilling) on such materials will result in the release of fragments and dusts, including respirable particles, containing the toxic and potentially toxic elements present in the fly ash raw material. In addition to the production of potentially harmful dusts, such physical fragmentation will hasten the releases of leachable elements into the environment as well as pose a human and animal health threat through the inhalation of contaminated dust particles.

Methods have been developed to reduce the content of toxic elements in the fly ashes through conventional water based leaching and, more recently, using supercritical carbon dioxide (Kersch *et al.* 2002, Querol *et al.* 2001). These methods, however, do not eliminate the toxic elements but simply create an additional contaminated wastestream to be dealt with.

4 CONCLUSIONS

The production of power through the combustion of coal at the Mae Moh and TPI coal power plants in Thailand produces fly ash contaminated with a range of toxic and potentially toxic elements. Due to the very large quantities of coal burned and fly ash produced, each plant liberates many tonnes of these elements each year (see Table 5).

Particles emitted to the environment either directly with the flue gases, or as a result of inadequate fly ash storage, pose a threat to human and animal health. For the finest particles, the health impacts due to their very small size are combined with the tendency for these particles to contain the highest concentrations of toxic and potentially toxic elements.

Despite the use of efficient end-of-pipe pollution control devices such as electrostatic precipitators (ESPs) and ionizing wet scrubbers, appreciable quantities of potentially toxic elements bound to fly ash particles and in gaseous form will be released to the atmosphere along with flue gases. The release of certain gaseous forms of arsenic and mercury tends to be lower where ionizing wet scrubbers are employed. These reductions in atmospheric emissions are, however, reflected in higher concentrations in other wastestreams, including fly ash and scrubber wastes.

The elements contained in the fly ashes have the ability to leach from them, and thus enter the environment where they can accumulate in sediments and soils. In addition, many of these elements have the potential to bioaccumulate.

The use of fly ash in cement production will not prevent the release of significant quantities of heavy metals and other toxic elements into the environment due to weathering and erosion over time. Mechanical operations on cement that has been produced using coal fly ash as a raw material may produce dusts containing respirable contaminated particles, as well as hastening elemental leaching through weathering processes.

Treatment processes to reduce the quantities of hazardous elements in the fly ashes will simply result in the production of additional contaminated wastestreams.

Ongoing use of coal combustion for power production will result in future releases of toxic and potentially toxic elements to the environment. This can only be avoided through the cessation of coal combustion and the implementation of sustainable production technologies such as solar- and wind-power generation.

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APPENDIX 1. ANALYTICAL METHODOLOGY

All chemicals were of High Purity Aristar Grade. All glassware was cleaned in detergent, rinsed with tap water and deionised water, soaked in 10% nitric acid overnight, rinsed with deionised water and dried in an oven.

A1.1 Preparation of samples for analysis

A1.1.1 Heavy metals

Samples were air dried until weighing readings became constant. Approximately 0.5 g of sample was accurately weighed into a glass 100 ml boiling tube. To this 10 ml of deionised water was added, followed by 7.5 ml of concentrated hydrochloric acid and 2.5 ml of concentrated nitric acid. The samples were digested at room temperature overnight prior to being 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 three hours.

After cooling to ambient temperature, the digests were filtered into volumetric flasks, diluted with deionised water, made up to a volume of 50ml and mixed. The Standard Reference Material, BCR-038 (fly ash from pulverised coal), 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. Digest recoveries of 52-72% for the Standard Reference Material were obtained for those metals quantified directly. For arsenic and mercury, digest recoveries of 93% and 72% were obtained respectively.

A1.1.2 Metalloids; arsenic and mercury

The samples were prepared in an identical manner to that described in Section A1.1.1, other than a digestion temperature of 80°C for three hours was used.

A1.2 Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

A1.2.1 Heavy metals

Following preparation, samples were analysed by ICP-AES, using a Varian Liberty-100 Sequential Spectrometer. The following metals were quantified directly: cadmium (Cd), calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), manganese (Mn), nickel (Ni), zinc (Zn). 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.

A1.2.2 Metalloids; Mercury and arsenic

Mercury (Hg) and arsenic (As) were 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 µg/l and 100 µg/l, matrix matched to the samples (i.e. in 15% v/v hydrochloric acid and 5% v/v nitric). The calibration was validated using a quality control standard (80 µg/l), prepared internally from different reagent stock. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed.

Prior to Cold Vapour Generation ICP-AES analysis, 10 ml of the digest from each sample, the certified reference material, and digest blank was transferred to a 40 ml boiling tube. An arsenic quality control solution (400 µg/l) and blank, matrix matched to the samples (i.e. in 15% v/v hydrochloric acid and 5% v/v nitric), were prepared in an identical manner. The tubes were 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 100 °C until evapourated to dryness.

After cooling, the dried residues were dissolved in 5% v/v hydrochloric acid (7 ml), transferred to 10 ml volumetric flasks. To convert any arsenate (As V) species to arsenite (As III), potassium iodide (KI) (0.5 ml, 0.4 molar) in 5% v/v hydrochloric acid was added to give an ultimate concentration of 0.02 molar potassium iodide, the solutions were made up to a volume of 10 ml and mixed.

Ionic arsenite (As III) was converted to gaseous arsine (AsH_3), following reaction 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. Three calibration standards were prepared, at 50 µg/l, 100 µg/l and 500 µg/l, matrix matched to the samples (i.e. in 5% v/v hydrochloric acid and potassium iodide 0.02 molar). The calibration was validated using a quality control standard (400 µg/l), prepared internally from different reagent stock. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed.

APPENDIX 2. TOXICOLOGICAL OUTLINES FOR KEY ELEMENTS

1 Arsenic

Arsenic is a metalloid elements that can exist in several different valence states and as many different inorganic and organic compounds.

When released to land, arsenic is relatively immobile through binding to soil particles. However, most arsenic compounds can readily dissolve in water, and soluble forms may be leached by rainwater or snowmelt into surface waters or groundwater. In the aquatic environment, the transport and partitioning of arsenic is dependent on the forms of arsenic present. It may be adsorbed from water onto sediments or soils, especially onto clays or compounds of iron, aluminum, manganese and calcium. Soluble forms may be carried long distances through rivers (Alloway 1990, USPHS 2000, Welch *et al.* 1988).

Arsenic in the atmosphere exists primarily bound to particulate matter, less than 2 μm in diameter (Coles *et al.* 1979). These particles can be transported considerable distances by wind and air currents until they are redeposited to earth (USPHS 2000).

For the majority of the human population, diet is the largest source of exposure, with an estimated average daily intake of about 50 μg. Intake from air, soil, and water are usually considerably less, but exposure from these sources can become significant in arsenic contaminated areas (USPHS 2000).

Bioconcentration of arsenic can occurs in aquatic organisms, primarily in algae and lower invertebrates. Certain plants may also accumulate substantial levels of arsenic by root uptake from the soil or by absorption of airborne arsenic deposited on the leaves (USPHS 2000).

Arsenic is toxic to many plants, animals and humans. Most cases of human toxicity have been associated with the intake of inorganic forms of arsenic (Levin-Scherz *et al.* 1987, USPHS 2000). The lethal dose for humans has been estimated to be 70-180 mg, or 1-3 mg per kg body weight (USPHS 2000). Lethal doses in animals are somewhat higher than the estimated lethal dose in humans (Kaise *et al.* 1985).

Low level ingestion of arsenic can cause a range of human health effects including pain, nausea and vomiting. Long-term low-level human exposures may lead to damage to the vascular and cardiovascular systems, and can cause injury to the nervous system (USPHS 2000). A dramatic example of the effects on the vascular system is "Blackfoot disease", which is characterised by a progressive loss of circulation in the hands and feet, ultimately leading to necrosis and gangrene (Hall 2002).

Of greater concern is the increased risk of carcinogenicity through prolonged ingestion of inorganic arsenic. Arsenic and certain arsenic compounds are known to be carcinogenic to humans by both the oral and inhalation routes. The US Department of Health and Human Services in its 9th Report on Carcinogens lists arsenic compounds as “known to be human a carcinogen” (USPHS 2001).

Skin cancer is the prevalent form resulting from exposure, though there is also evidence for an increased risk of internal cancers, including bladder, liver and lung cancers (USPHS

2001). An increase in human cancer risk for 1 in 100 people, dependant on gender, has been estimated for those drinking water containing arsenic at a concentration of 50 ug/l (Smith *et al.* 1992).

While there is substantial evidence that arsenic intake by either oral or inhalation routes is carcinogenic to humans, there is very little evidence that arsenic induces cancers in animals (USPHS 2000, USPHS 2001).

Primarily as a result of its human carcinogenicity, the World Health Organization (WHO) recommended value for arsenic in drinking water is 10 μg/l (0.01 mg/l) (WHO 1998). In 2002, the US Environmental Protection Agency (EPA) similarly set a limit of 10 μg/l arsenic in drinking water (USEPA 2002).

2 Chromium

Chromium may exist in many different forms, though only the trivalent (III) and hexavalent (VI) forms are considered to be of biological importance

In aquatic environments, chromium (VI) is present predominantly in soluble forms that may be stable enough to undergo intra-media transport, however chromium (VI) will eventually be converted to chromium (III) by reducing species such as organic substances (Kimbrough *et al.* 1999, USPHS 2000). This trivalent form does not generally migrate significantly in natural systems. Instead, it is rapidly precipitated and adsorbed onto suspended particles and bottom sediments. Changes in the chemical and physical properties of an aquatic environment can, however, result in changes to the chromium (III)-chromium (VI) equilibrium (Richard and Bourg 1991).

In soils, chromium (III) is relatively immobile due to its strong adsorption capacity onto soils. In contrast, chromium (VI) is highly unstable and mobile, since it is poorly adsorbed onto soils under natural conditions (Mukherjee 1998).

Redox reactions (oxidation of chromium (III) to chromium (VI) and reduction of chromium (VI) to chromium (III)) are important processes affecting the speciation and hence the bioavailability and toxicity of chromium in soils. Conversion can occur in either direction under the appropriate conditions (Mukherjee 1998).

Chromium (III) and (VI) have been shown to accumulate in many aquatic species, especially in bottom-feeding fish, such as the brown bullhead (*Ictalujrus nebulosus*); and in bivalves, such as the oyster (*Crassostrea virginica*) and the blue mussel (*Mytilus edulis*) (Kimbrough *et al.* 1999).

Whilst chromium (III) is an essential trace element in animals, chromium (VI) is non-essential and toxic at low concentrations (Goyer 1996, USPHS 2000). Chromium (VI) compounds are corrosive, and allergic skin reactions readily occur following exposure, independent of dose. Short-term exposure to high levels can result in ulceration of exposed skin, perforations of respiratory surfaces and irritation of the gastrointestinal tract. Damage to the kidney and liver have also been reported (USPHS 2000).

The International Agency for Research on Cancer (IARC) classifies chromium (VI) compounds as known carcinogens (IARC 1998). The US Department of Health and Human Services in its 9th Report on Carcinogens, lists classifies chromium (VI) compounds as “known to be human carcinogens” (USPHS 2001). Long-term occupational exposure to airborne levels of chromium higher than those in the natural environment has been associated with lung cancer. Individuals at most risk include those in chromate-production industries and chromium pigment manufacture and use; and similar risks may exist amongst chromium-alloy workers, stainless steel welders, and chrome-platers (Kimbrough *et al.*1999, USPHS 2001).

3 Lead

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 (Alloway 1990, Sauve *et al.* 1997, USPHS 2000). As with all metals, however, lead speciation is critical when assessing bioavailability and the potential threat to the environment. Many plants and animals can accumulate lead from water, soil and sediment, with organic forms being more easily absorbed than inorganic (USPHS 2000).

Lead has no known nutritional biochemical or physiological function (Goyer 1996). The toxic effects of lead are the same, irrespective of whether it is ingested or inhaled, and blood levels less than 10-100 μg/dl in humans have been associated with a wide range of adverse effects. These include 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 (Bernard *et al.* 1995, Goyer 1993, Nriagu 1988, Pirkle *et al.* 1998, USPHS 2000). It is clear that increased body burden of lead results in decreased scores on measures of intelligence from early infancy through school age. It also results in effects on behaviour of school children, including increased distractibility, short attention span and impulsivity (Rice 1996).

In 1975 the Centre for Disease control (CDC) in Atlanta recommended that the maximum permissible level of blood-lead be 30 μg/dl (for both adults and children). This level was revised downward in 1985 to 25 μg/dl, and again in 1991, defining a blood-lead level of 10 μg/dl as an action or intervention level (USPHS 2000). 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 (Goyer 1993, USPHS 2000).

4 Mercury

Mercury is an extremely toxic, non-essential trace metal, having no biochemical or nutritional function. Biological mechanisms for its removal are poor, and mercury is the only metal known to biomagnify, that is, progressively accumulate as it passes though the food chain (WHO 1989). Mercury can exist in three main forms; metallic (as a liquid or vapour), ionic salts and in organic compounds.

In the atmosphere, elemental mercury is by far the most common form and, as a vapour, it is responsible for the long-range, global cycling of mercury. In addition, to a far lesser degree, mercury may be associated with particulates, which are removed by dry or wet deposition (USPHS 2000, WHO 1989).

In the aquatic environment, mercury is most commonly found in the mercuric (II) state, and is predominantly adsorption to soluble and particulate organic material. Mercury accumulation from sediments may be a dominant pathway for uptake in aquatic organisms and accounts for relatively high concentrations in deposit feeders, in both freshwater and marine systems (Bryan & Langston 1992).

Acute inhalation of high levels of mercury vapour may cause nausea, vomiting, diarrhoea, increases in blood pressure or heart rate, skin rashes, eye irritation, corrosive bronchitis and pneumonitis. And, if not fatal, may be associated with central nervous system (CNS) effects such as tremor or increased excitability (Goyer 1996, USPHS 2000). With chronic exposure, the major effects are on the CNS (tremor, spasms, loss of memory, increased excitability, severe depression, personality changes, even delirium and hallucination), although renal damage, associated with chronically exposed workers, has also been shown (Goyer 1996, Ratcliffe *et al.* 1996). These effects have also been reported in animal studies (USPHS 2000).

Acute exposure to high levels of mercury salts, or chronic low-dose exposure, is directly toxic to the kidney (Zalups & Lash 1994). In addition, nausea and diarrhoea may result after swallowing large amounts of inorganic mercury salts, and some nervous system effects have also been recorded (USPHS 2000, WHO 1989).

Once metallic mercury has entered the environment it can be methylated by micro organisms, found in soils and fresh water and marine sediments, to organic forms of mercury, most commonly methylmercury. Recent studies have demonstrated that newly deposited mercury is more readily converted into methylmercury than mercury already in the ecosystem (Renner 2002).

In organic form, mercury is able to cross cell membranes easily and quickly enters the aquatic food chain. From here it may enter the human food chain. Exposure to methylmercury has resulted in permanent damage to the CNS, kidneys, and the developing foetus. The levels of methylmercury that result in these effects are not usually encountered by the general population, however they were encountered by the population of Minamata, in Japan, who were exposed to high levels of methylmercury from eating contaminated fish and seafood collected from the Bay (USPHS 2000). Symptoms such as brain damage, numbness of extremities, and paralysis, along with the loss of hearing, speech and sight were reported (D'Itri 1991). Whilst only the Japanese cases have been confirmed as Minamata Disease, other populations in Canada (from chlor-alkali discharges) and Brazil (from gold mining) are potentially at risk. The problem of methylation of past and present inorganic mercury discharges continues, and the long retention time of mercury by sediments delays the elimination of contamination for many years (Akagi *et al.* 1995, Bryan & Langston 1992, D'Itri 1991, Harada 1997).

5 Nickel

In the environment, nickel if predominantly present in inorganic forms. It is a fairly mobile metal in natural waters, especially soluble at higher pH values, though concentrations of soluble nickel are generally low compared with nickel associated with suspended and bottom sediments (Mance & Yates 1984, USPHS 2000). Nickel is reasonably mobile in soil and has the potential to leach through soil and subsequently enter groundwater (Alloway 1990, Nriagu 1980, USPHS 2000).

Nickel is significantly bioaccumulated in some, but not all, aquatic organisms (USPHS 2000). 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 (Alloway 1990, USPHS 2000). However, there is sufficient evidence for the carcinogenicity of nickel and certain nickel compounds. The US Department of Health and Human Services, in its 9th Report on Carcinogens, lists nickel and certain nickel compounds as "reasonably anticipated to be human carcinogens" (USPHS 2001).

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 (Goyer 1996, USPHS 2000). Other serious consequences of long term exposure to nickel may include chronic bronchitis and reduced lung function (USPHS 2000). 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).

6 Zinc

Zinc occurs in the environment primarily in inorganic forms, either dissolved or as insoluble complexes and compounds (USPHS 2000). In soils, it often remains strongly sorbed, and in the aquatic environment it will predominantly bind to suspended material before finally accumulating in the sediment (Alloway 1990, Bryan & Langston 1992, USPHS 2000).

Zinc is an essential element, present in the tissues of animals and plants even at normal, ambient concentrations. However, if plants and animals are exposed to high concentrations of bioavailable zinc, significant bioaccumulation can results, with possible toxic effects (USPHS 2000).

Excessive dietary in take in both humans and animals can cause gastrointestinal distress and diarrhoea, pancreatic damage and anaemia (Goyer 1996, USPHS 2000). For example, animal studies involving doses 1,000 times higher than the recommended daily allowance (RDA), taken over a period of a month, resulted in anaemia and injury to the pancreas and kidney; and rats that ate very large amounts of zinc became infertile (USPHS 2000). Humans taking supplements at higher than recommended doses (400-500 mg/day) suffered severe gastro-enteritis (Abernathy & Poirier 1997); and humans who drank water from galvanised pipes, over a prolonged period, suffered irritability, muscular stiffness and pain, loss of appetite and nausea (UNEP 1993).

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

7 References

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