Heavy metal and metalloid content of fly ash collected from the Sual, Mauban and Masinloc coal-fired power plants in the Philippines, 2002

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EXECUTIVE SUMMARY

This study was carried out to determine the content of a range of elements in fly ash produced by three coal fired power plants located in the Philippines;

- Sual 1200MW Coal Power Plant, Pangasinan Province
- Mauban 440MW Coal Power Plant, Quezon Province
- Masinloc 600 MW Coal Power Plant, Zambales Province

All three facilities are equipped with electrostatic precipitators (ESPs) for fly ash collection.

Greenpeace visited the facilities in March and April 2002 and collected a sample of fly ash from each. 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 ashes, the sample from the Mauban plant contained many elements at concentrations significantly above those found in the samples from the Masinloc and Sual plants. The fly ash from the Sual power plant contained the lowest concentrations of elements for the three samples. Although the concentrations of elements detected in the fly ash samples are not significantly higher than those typical found in soil, the ashes pose a potential environmental hazard due to the very large quantities produced, and the tendency for a significant fraction of the toxic and potentially toxic elements contained within them to leach into the immediate environment.

Estimates of the total quantities of toxic and potentially toxic elements contained in the fly ashes produced by the Mauban and Masinloc plants have been calculated from the annual quantity of fly ash produced and the elemental composition of one fly ash samples from each plant. Other than mercury, which almost exclusively escapes pollution control devices, the quantities of toxic elements in the fly ash produced are in the order of tons or tens of tons per year from each plant (Table 5).

Previous scientific studies demonstrate that a significant proportion of the elements detected in the fly ash samples from these facilities can be readily leached from them, posing a threat to the receiving environment. Treatment processes to reduce the quantities of these elements in the fly ashes would simply result in the production of additional contaminated waste-streams.

In addition to their toxic element content, fly ashes produced by these facilities pose a threat due to their very fine particle fraction. 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 ‘respirable’ particles, which can contain higher concentration of toxic elements that the fly ash as a whole.

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

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

- Sual 1200MW Coal Power Plant, Pangasinan Province
- Mauban 440MW Coal Power Plant, Quezon Province
- Masinloc 600 MW Coal Power Plant, Zambales Province

Sual Coal Power Plant

A 1200 MW pulverized coal-fired thermal power plant, consisting of two 600 MW units. The facility is equipped with electrostatic precipitators (ESPs) for fly ash collection and a flue gas desulfurisation plant. Atmospheric emissions are released via a 220m chimney.

Mauban Coal Power Plant

A 440MW pulverized coal-fired thermal power plant consisting of a single unit boiler furnace equipped with ESPs for fly ash collection and flue gas scrubbers. Atmospheric emissions are released via a 150m chimney.

Masinloc Coal Power Plant

A 600 MW coal-fired thermal power plant, consisting of two 300 MW units. The facility is equipped with ESPs for fly ash collection.

Facility		Sual	Mauban	Masinloc
Energy production	(MW)	1200 (2 x 600)	440	600 (2 x 300)
Coal consumption	(tons/hour)	179	181.5-235.1	ND
	(million tons/year)	2.66	1.9	ND
Ash production	(tons/hour)	ND	28.8[a]	44.0[a]
	(million tons/year)	ND	0.252[a]	0.385[a]

Table 1. Summary of consumption and production figures for the three coal burning facilities based upon data obtained from the Environmental Impact Statement (EIS) Reports for the three facilities. ND; no data available from the EIS Report. a; Quantity for all ashes produced

2 SAMPLING PROGRAM

In March and April 2002, one sample of fly ash was collected from each of the three coal fired power plants. 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 captured by pollution control devices within the facilities. Description of the samples collected is given in Table 2.

Sample number	Sample description	Facility
MI02012	fly ash	Sual Coal Power Plant
MI02013	fly ash	Mauban Coal Power Plant
MI02014	fly ash	Masinloc Coal Power Plant

Table 2. Description of samples collected from three coal-fired power plants in the Philippines.

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 the toxic and potentially toxic elements analysed for other than cadmium. Of the three samples, the fly ash from the Mauban power plant (MI02013) contained the highest concentrations of all elements analysed for, other than lead and manganese. The sample from the Sual power plant (MI02012) contained the lowest concentrations of all elements analysed for.

Sample number	MI02012	MI02013	MI02014
Description	fly ash	fly ash	fly ash
Power facility	Sual	Mauban	Masinloc
Element	mg/kg dry weight	mg/kg dry weight	mg/kg dry weight
Arsenic (As)	8.4	41.8	10.4
Cadmium (Cd)	<1	<1	<1
Calcium (Ca)	6090	17195	22434
Chromium (Cr)	6	49	18
Cobalt (Co)	6	25	12
Copper (Cu)	22	34	34
Lead (Pb)	8	15	22
Manganese (Mn)	122	215	308
Mercury (Hg)	1.2	1.9	1.2
Nickel (Ni)	6	50	16
Zinc (Zn)	23	138	51

Table 3. Concentration elements identified in samples of fly ash from the Sual, Mauban and Masinloc coal power plants in the Philippines.

The variation in element concentrations between the samples is likely to be mainly due to the type of coal burned and the pollution control devices employed at the three facilities. The trace element composition of fly ash from a single facility has, however, been reported to vary measurably on a daily basis (Egeman & Coskun 1996).

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

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

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

Estimates of the total quantities of toxic and potentially toxic elements contained in the fly ashes produced at the plants can be calculated from the total quantity of fly ash produced and the elemental composition of the fly ash (see Table 5). These figures are only approximate as they are based upon the composition of only one sample of fly ash and on ash production data given in the Environmental Impact Statement (EIS) reports for these two plants. These data, however, give an indication of the large quantities of these elements produced in one of the waste-streams as a result of coal burning at the Mauban and Masinloc plants.

Element		contained in the fly ash produced (kg/year) Mauban[a]	 Masinloc
Arsenic	(As)	9000	3400
Chromium	(Cr)	10000	5900
Cobalt	(Co)	5400	3900
Copper	(Cu)	7300	11000
Lead	(Pb)	3200	7200
Manganese	(Mn)	46000	100000
Mercury	(Hg)	410	390
Nickel	(Ni)	11000	5200
Zinc	(Zn)	30000	17000

Table 5. Total element quantities produced in the fly ashes of the Mauban and Masinloc coal fired power plants. Data calculated from the composition of fly samples MI02013 and MI02014 and ash production data given in the Environmental Impact Statement (EIS) reports.
a; based upon fly ash constsiuting 85% of total ash production, as for the Masinloc plant

3.1 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. The fraction of certain elements that are emitted in flue gases compared to the amounts in all waste-streams have been estimated; these include mercury (up to 95%), lead (up to 40%) and arsenic (up to 30%) (Llorens *et al.* 2001). The use of flue gas scrubbing with lime (calcium oxide) can significantly reduce the fraction of gaseous arsenic released to the atmosphere through sorption to lime particles (Senior *et al.* 2000).

3.2 Elements detected

Calcium was present at significantly higher concentration in the fly ash samples than all other elements analysed for. This element, however, does not pose a toxic threat to animals or humans.

Fly ash from coal combustion typically contains 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 the Mauban plant, as reflected in the concentration of calcium in the fly ash (MI02013). The high concentrations of calcium in the fly ash sample from the Masinloc plant (MI02014) may be due to the use of this type of pollution control, or the type of coal used.

The use of lime as a scrubbing agent is 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).

Those elements other than calcium detected in the fly ashes exhibit a broad range of toxic effects to humans, terrestrial and aquatic life and plants. These elements cannot be broken down or destroyed in the environment. They can, however, change from one form to another. A number of the elements also have the potential to bioaccumulate, including arsenic, chromium, lead, mercury & zinc (Kimbrough *et al.* 1999, USPHS 2000). Information on key elements detected in the fly ash samples is given below (Sections 3.2.1 - 3.2.6). For additional information on these elements see Appendix 2.

3.2.1 Arsenic

Most arsenic compounds can readily dissolve in water, and so arsenic can enter waterways such as rivers, lakes and by dissolving in rain (USPHS 2000). Bioconcentration of arsenic can occurs in aquatic organisms, primarily in algae and lower invertebrates (USEPA 1980).

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). 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)

3.2.2 Chromium

In the environment, many different forms of chromium can exist, 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 for the analysis of the fly ash samples from Sual, Mauban and Masinloc plants are not able to distinguish the quantities of individual chromium species present, giving data only on the total chromium concentrations. However, studies have shown significant amounts of chromium in leachate from fly ash to be present in the hexavalent form (Lecuyer *et al.* 1996)

3.2.3 Lead

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).

Lead has no known nutritional biochemical or physiological function (Goyer 1996). The toxic effects of lead include damage to the kidneys, cardiovascular and nervous system. 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).

3.2.4 Mercury

The concentrations of mercury in the three fly ash samples were significantly lower than the other elements analysed for. The presented on fly ashes from similar facilities (Table 4) show significantly lower concentrations of mercury than those detected in this study. Other studies, however, have reported similar concentrations to those detected in samples MI02012-14 (Kotnik *et al.* 2000).

A previous study by Greenpeace Southeast Asia found mercury in the fly ash from the Calaca coal power plant in the Philippines in the concentration range 0.02-0.21 mg/kg. Mercury was also detected in fly ash leachate from this facility (Greenpeace 2001).

These data, however, does not fully reflect the quantities of mercury in all waste-streams from coal combustion. The greater proportion is vented via the flue stack gases rather than being trapped in the fly or bottom ashes. The amount released to atmosphere will depend on the end-of-pipe technologies employed. Similar coal burning plants equipped with ESPs have been estimated to emit to the atmosphere up to and above 95% of the mercury liberated upon coal burning, in either gaseous or particulate form (Kotnik *et al.* 2000, Llorens *et al.* 2001)

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 forms of mercury, including about 56% to the global emissions of mercury to the atmosphere (Pacyna & Pacyna 2002).

Mercury is an extremely toxic metal, having no biochemical or nutritional function. The majority of toxic effects that can result from exposure are on the central nervous system (CNS) (USPHS 2000).

Inorganic mercury can be converted into an organic form, 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. the 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).

Recent studies have demonstrated that newly deposited mercury is more readily converted into methylmercury than mercury 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 could be expected from a lower rate of methylmercury production.

3.2.5 Nickel

When released to the environment, nickel can be reasonably mobile, and in the aquatic environment can bioaccumulate in some organisms (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 result 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).

3.2.6 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).

3.3 Element leaching

Elements present in coal fly ash are not fully bound to the particles, and 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 lead to the release of leached metals into soils, surface and ground waters. The majority of these elements are able to build up in soils and sediment, and many are persistent and high toxic to animals, humans and plants through air water and soil uptake.

The concentrations of those elements detected in the fly ash samples are not significantly higher than those typical found in uncontaminated soils (Alloway 1990). These ashes do, however, pose a threat due to the very large quantities of ash produced, and the tendency for a significant fraction of the toxic and potentially toxic elements contained within them to leach into the immediate environment.

The rate and quantity of leaching is dependent on a number of factors including the fly ash source and leaching time (Egeman & Coskun 1996, Hansen & Fisher 1980). Acidity has a major influence, with higher acidity (low pH) tending to result in higher rates and quantities of elements leached. While high alkalinity (high pH) appears to be characteristic of most ashes, leachates can vary from acidic (pH=4.2) to alkaline (pH=12.4) (Page *et al.* 1979).

Reports on the fraction of these elements that are able to leach from the ash vary between methods employed. Studies using sequential extraction methods have demonstrated that a significant fraction of most elements present in fly ash are able to leach from the ash, including arsenic (57%), chromium (17%), cobalt (8%), copper (7%), nickel (8%), lead (13%) & zinc (12%) (Fytianos & Tsaniklidi 1998, Querol *et al.* 1996).

In studies aimed to approximate field conditions, those metals that were generally found to leach to the greatest extent were cadmium, chromium and lead (Fytianos & Tsaniklidi 1998). Even where pure water has been used in leaching studies, appreciable fractions of arsenic, chromium, cobalt, copper, nickel, lead & zinc have been shown to leach from 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).

In a study designed to simulate rainwater leaching of coal fly ash (Praharaj *et al.* 2002), arsenic was detected in the leachate at concentrations up to 260 μ/l, 26 times the US Environmental Protection Agency (EPA) limit and the World Health Organization (WHO) recommended value for drinking water (USEPA 2002b, WHO 1998). The use of lime flue gas scrubbing has been demonstrated to reduce the quantity of arsenic present in fly ash leachate (Lecuyer *et al.* 1996).

Hexavalent chromium (VI) has been determined in fly ash leachate, constituting up to 88% of the total chromium leached where lime flue gas scrubbing was employed, and up to 79% without such scrubbing (Lecuyer *et al.* 1996). Earlier studies, however, indicated that all soluble chromium leached from fly ash under acidic conditions (<pH4.8) was present solely as chromium (III) (Rai & Szelmecka 1990). Due to the analytical methods employed, it was not possible to determine the fraction of hexavalent chromium (VI) in the fly ash samples from the Sual, Mauban and Masinloc plants.

Studies have demonstrated impacts on amphibians inhabiting locations contaminated with coal fly ash. For example, both adult southern toads (*Bufo terrestris*) and freshwater grassshrimp (*Palaemonetes paludosus*) have been shown to accumulate trace elements from coal ash polluted areas, including arsenic and cadmium (Hopkins *et al.* 1999, Rowe 1998). 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, including teratogenic elements such as selenium, chromium, cadmium and copper (Hopkins *et al.* 2000).

The ability of potentially toxic elements to leach from coal fly ashes has serious implications where fly 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 Fly ash and bottom ash

In general, fly ash is by far the major ash waste from coal power production constituting up to 88% of total ash production from coal burning power plants (Sandelin & Backman 2001, Swaine 2000).

Some elements are preferentially retained in either the fly or bottom ashes to varying degrees. The relative enrichment is to some degree dependant on the technologies employed at the facility.

Elements that have been reported to exhibit a small degree of selective retainment in the bottom ashes include copper, manganese. Those reported to be selectively retained in the fly ash include arsenic, cadmium, chromium, lead, mercury and zinc. The degree of enrichment is particularly large for mercury, with over 90% of that retained being found in the fly ash. Other elements show little or no selectivity between the fly and bottom ashes (Querol *et al.* 1995, Sandelin & Backman 2001). The enrichments of these 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.

Certain elements are vapourised to varying degrees during coal combustion and upon cooling of the combustion gases are fully or partially sorbed onto fly ash particles. This process results in their concentrations being higher in those particles less than 10µm (0.01mm) in diameter. This is due, in part, to the high surface area of these very fine particles. 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 for the failure of pollution control devices to capture ultrafine particles, and the threat posed by such particles upon inhalation.

ESPs and fabric filters retain more than 99% of fly ash produced ash, with efficiencies of 99.95% reported for some plants (Querol *et al.* 1993). Due to the considerable quantities of fly ash produced, however, particulate emissions to the atmosphere can still be considerable. Emitted fly ash particles can be deposited at distance several to hundreds of kilometers 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). Particulates in the emission plume can be enriched with elements including arsenic and zinc by 1.5-3.0 times compared with stack particles (Ondov *et al.* 1989). Estimate on the quantities of toxic elements emitted to atmosphere based on the percentage of fly ash retained may underestimate the total quantities due to such enrichment of elements in the very fine particles (Llorens *et al.* 2001, Senior *et al.* 2000).

“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).

The combination of poor capture efficiencies and elevated element concentrations for these fine “respirable” particles produced through coal combustion has clear implications for human health.

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 chemicals, weathering and erosion over time will ultimately cause their release back to the environment.

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 waste-stream to be dealt with.

4 CONCLUSIONS

The production of power through the combustion of coal at the the Sual, Mauban and Masinloc coal power plants in the Philippines produce 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).

Despite the use of highly efficient end-of-pipe pollution control devices such as electrostatic precipitators (ESPs), appreciable quantities of elements bound to fly ash particles and in gaseous form will be released to the atmosphere along with flue gases. This is especially the case for mercury, the vast majority of which is released to the atmosphere in gaseous form.

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.

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.

Treatment processes to reduce the quantities of these elements in the fly ashes will simply result in the production of additional waste-streams.

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.

5 REFERENCES

Alloway B.J. (1990) Heavy metals in soils. John Wiley and Sons, Inc. New York, ISBN 0470215984

Allsopp M., Costner P., Johnston, P. (2001) Incineration and Human Health: State of knowledge of the impacts of waste incinerators on human health. Publ. Greenpeace International, Amsterdam, ISBN 90-73361-69-9: 81 pp

Carpi A. (1997) Mercury from combustion sources: a review of the chemical species emitted and their transport in the atmosphere. Water, Air, and Soil Pollution, 98: 241-254

Coles, D. G. Ragaini R. C. Ondov J. M. Fisher G. L. Silberman D. Prentice B. A. (1979) Chemical studies of stack fly ash from a coal fired power plant. . Environmental Science and Technology, 13(4): 455-459

COMEAP, Committee on the Medical Effects of Air Pollutants (1995). Non-biological particles and health. Department of Health, UK. London: HMSO.

Egemen E., Coskun Y. (1996) Regulatory leaching tests for fly ash: A case study. Waste Management & Research 14: 43–50

El-Mogazi D., Lisk D.J., Weinstein L.H. (1988) A review of physical, chemical, and biological properties of fly ash and effects on agricultural ecosystems. The Science of the Total Environment, 74: 1-37

EPAQS, Expert Panel on Air Quality Standards, (1995). Particles. Published by HMSO. ISBN 0 11 753199 5

Goyer R.A. (1993). Lead toxicity: current concerns. Environmental Health Perspectives, 100: 177-187

Goyer R.A. (1996). Toxic effects of metals. In Casarett & Doull's Toxicology. The Basic Science of Poisons, Fifth Edition, Klaassen, C.D. [Ed]. McGraw-Hill Health Professions Division, ISBN 0071054766

Greenpeace (2001) Coal-fired power plants and the menace of mercury emissions. Greenpeace Southeast Asia, August 2001. Available at: www.greenpeacesoutheastasia.org/ en/rpt/rpt_ce_mercury.pdf

Hall M.L., Livingston W.R. (2002) Fly ash quality, past, present and future, and the effect of ash on the development of novel products. Journal of Chemical Technology and Biotechnology, 77(3): 234-239

Hansen L.D., Fisher G.L. (1980) Elemental distribution in coal fly ash particles. Environmental Science and Technology, 14(9): 1111-1117

Hopkins W.A., Rowe C.L., Congdon J.D. (1999) Elevated trace element concentrations and standard metabolic rate in banded water snakes (*Nerodia fasciata*) exposed to coal combustion wastes. Environmental Toxicology and Chemistry 18(6): 1258-1263

Hopkins W.A., Congdon J., Ray J.K. (2000) Incidence and impact of axial malformations in larval bullfrogs (Rana catesbeiana) developing in sites polluted by a coal-burning power plant. Environmental Toxicology and Chemistry, 19(4): 862-868

Howard C.V. (2000). Particulate aerosols, incinerators and health. In: Health Impacts of Waste Management Policies. Proceedings of the seminar "Health Impacts of Waste Management Policies", Hippocrates Foundation, Kos, Greece, 12-14 November 1998. Eds. P. Nicolopoulou-Stamati, L.Hens and C.V. Howard. Kluwer Academic Publishers.

IARC (1998). IARC monographs on the evaluation of the carcinogenic risk of chemicals to humans. Chemicals, industrial processes and industries associated with cancer in humans. IARC monographs, Vol. 1 to 29

Kaise T., Watanabe S., Itoh K. (1985) The acute toxicity of arsenobetaine. Chemosphere 14: 1327-1332

Kersch C., Van der Kraan M., Woerlee G.F., Witkamp G.J. (2002) Municipal waste incinerator fly ash: supercritical fluid extraction of metals. Journal of Chemical Technology & Biotechnology, 77(3): 256-259

Kimbrough D.E, Cohen Y., Winer A.M., Creelman L. and Mabuni C. (1999). A critical assessment of chromium in the Environment. Critical Reviews in Environmental Science and Technology, 29 (1): 1-46

Kotnik J., Horvat M., Mandic V., Logar M. (2000) Influence of the Sostanj coal-fired thermal power plant on mercury and methyl mercury concentrations in Lake Velenje, Slovenia. The Science of the Total Environment, 259: 85-95

Kress N. (1993) Chemical aspects of coal fly ash disposal at sea: Predicting and monitoring environmental impact. Wat. Sci. Tech., 27(7-8), 449-455

Lecuyer I., Bicocchi S., Ausset P., Lefevre R. (1996) Physico-Chemical Characterization and Leaching of Desulphurization Coal Fly Ash. Waste Manage. Res., 14: 15-28

Llorens J.F., Fernandez-Turiel J.L., Querol X. (2001) The fate of trace elements in a large coal-fired power plant. Environmental Geology, 40(4-5):409-416

Mason B.J. (1992) Acid Rain. Its causes and its effects on inland waters. Science, technology and society series. Clarendon Press, p126. In Querol *et al.* (1993)

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

Nriagu J.O, Pacyna J.M. (1988) Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature 333: 356-389

Ondov J.M., Choquette C.E., Zoller W.H., Gordon G.E., Biermann A.H., Heft R.E. (1989) Atmospheric behavior of trace elements on particles emitted from a coal-fired power plant. Atmospheric Environment, 23(10): 2193-2204

Pacyna E.G., Pacyna J.M. (2002) Global emission of mercury from anthropogenic sources in 1995. Water Air and Soil Pollution, 137(1-4): 149-165

Page, A. L. Elseewi A. A. Straughan I. R. (1979) Physical and chemical properties of fly ash from coal-fired power plants with reference to environmental impacts. Residue Reviews, 17: 83-120

Praharaj T., Powell M.A., Hart B.R., Tripathy S. (2002) Leachability of elements from sub-bituminous coal fly ash from India. Environment International 27: 609–615

Pirkle J.L. Kaufman R.B., Brody D.J., Hickman T., Gunter E.W., Paschal, D.C. (1998). Exposure of the U.S. population to lead, 1991-1994. Environmental Health Perspectives, 106(11): 745-750

QUARG (1996). Airborne Particulate Matter in the United Kingdom. Third Report of the Quality of Urban Air Review Group (QUARG), May. ISBN 0 9520771 3 2.

Querol X., Pares J.M., Plana F., Fernandez-Turiel J.L., Lopez-Soler A. (1993) Fly Ash Content and Distribution in Lake Sediments Around a Large Power Station: Inferences from Magnetic Susceptibility Analysis. Environ. Geochemistry and Health, 15(4): 9-18

Querol X., Fernadez-Turiel J.L., Lopez-Soler A. (1995) Trace elements in coal and their behavior during combustion in a large power station. Fuel 74(3): 331-343

Querol X., Alastuey A., Lopz-Soler A., Mantilla E., Plana F. (1996) Mineral composition of atmospheric particulates around a large coal-fired power station. Atmospheric Environment, 30(21): 3557-3572

Querol X., Umana J.C., Alastuey A., Ayora C., Lopez-Soler A., Plana F. (2001) Extraction of soluble major and trace elements from fly ash in open and closed leaching systems. Fuel, 80: 801-813

Rai D., Szelmeczka R.W. (1990) Aqueous behaviour of chromium in coal fly ash. Journal of Environmental Quality, 19: 378-382

Renner R. (2002) Newly deposited mercury may be more bioavailable. Environmental Science and Technology, 36(11): 226A-227A

Rowe C.L. (1998) Elevated standard metabolic rate in a freshwater shrimp *(Palaemonetes paludosus*) exposed to trace element-rich coal combustion waste. Comparative Biochemistry and Physiology Part A, 121(4): 299-304

Rowe CL, Hopkins WA, Coffman VR (2001) Failed recruitment of southern toads (Bufo terrestris) in a trace element-contaminated breeding habitat: Direct and indirect effects that may lead to a local population sink. Archives of Environmental Contamination and Toxicology, 40 (3): 399-405

Sandelin K., Backman R. (2001) Trace elements in two pulverized coal-fired power stations. Environmental Science and Technology, 35(5): 826-834

Sauve S., McBride M.B., Hendershot W.H. (1997). Speciation of lead in contaminated soils. Environmental Pollution, 98(2): 149-155

Senior C.L., Helble J.J., Sarofim A.F. (2000) Emissions of mercury, trace elements, and fine particles from stationary combustion sources. Fuel Processing Technology, 65–66: 263–288

Swaine D.J. (2000) Why trace elements are important. Fuel Processing Technology, 65–66 : 21–33

USEPA (1980) Ambient water quality criteria for arsenic. Washington, DC: U.S. Environmental Protection Agency, Office of Water Regulations and Standards. EPA 440/5-80-021

USEPA (2002) US Environmental Protection Agency Toxic Release Inventory; http://www.epa.gov/tri/

USEPA (2002b) http://www.epa.gov/safewater/arsenic.html

USPHS (2000). Toxicological profile on CD-ROM. Agency for Toxic Substances and Disease Registry.

USPHS (2001) 9th Report on Carcinogens U.S. Department of Health and Human Services

Wadge A., Hutton M., Peterson P.J. (1986) The concentrations and particle size relationships of selected trace elements in fly ashes from U.K. coal-fired power plants and a refuse incinerator. Science Total Environment, 54: 13-27

Weinstein L.H., Osmeloski J.F., Rutzke M., Beers A.O., McCahan J.B., Bache C.A., Lisk D.J. (1989) Elemental analysis of grasses and legumes growing on soil covering coal fly ash landfill sites. Journal of Food Safety, 9: 291-300

World Health Organisation (1989). Mercury. Environmental Health Criteria 86. ISBN9241542861

World Health Organization (1998) Water, sanitation and health: guidelines for drinking water quality. Geneva, Switzerland: World Health Organisation

APPENDIX 1. ANALYTICAL METHODOLOGY

A1.1 Preparation of samples for analysis

A1.1.1 Heavy metals

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.

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 & 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

Abernathy C.O. & Poirier K.A. (1997) Uncertainties in the risk assessment of essential trace elements: the case of zinc. Human and Ecological Risk Assessment, 3(4): 627-633

Akagi H., Malm O., Kinjo Y., Harada M., Branches F.J.P, Pfeiffer W.C., Kato H. (1995) Methylmercury pollution in the Amazon, Brazil. The Science of the Total environment, 175: 85-95

Alloway B.J. (1990) Heavy metals in soils. John Wiley and Sons, Inc. New York, ISBN 0470215984

Bernard A.M., Vyskocil A., Kriz J., Kodl M. and Lauwerys R. (1995) Renal effects of children living in the vicinity of a lead smelter. Environmental Research, 68: 91-95

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

Chashschin V.P., Artunia G.P., Norseth T. (1994) Congenital defects, abortion and other health effects in nickel refinery workers. The Science of the Total Environment, 148: 287-291

Coles, D. G. Ragaini R. C. Ondov J. M. Fisher G. L. Silberman D. Prentice B. A. (1979) Chemical studies of stack fly ash from a coal fired power plant. . Environmental Science and Technology, 13(4): 455-459

D'Itri F.M. (1991) Mercury contamination: what we have learned since Minamata. Environmental Monitoring and Assessment, 19: 165-182

Goyer R.A. (1993) Lead toxicity: current concerns. Environmental Health Perspectives, 100: 177-187

Goyer R.A. (1996) Toxic effects of metals. In Casarett & Doull's Toxicology. The Basic Science of Poisons, Fifth Edition, Klaassen, C.D. [Ed]. McGraw-Hill Health Professions Division, ISBN 0071054766

Hall A.H. (2002) Chronic arsenic poisoning. Toxicology Letters, 128: 69–72

Harada M. (1997) Neurotoxicity of methylmercury; Minamata and the Amazon. In Mineral and Metal Neurotoxicology. Yasui, M., Strong, M.J., Ota, K. and Verity, M.A.[Eds]. CRC Press Inc., ISBN 0849376645

IARC (1998) Chromium and certain chromium compounds. In: IARC monographs on the evaluation of the carcinogenic risk of chemicals to humans. Chemicals, industrial processes and industries associated with cancer in humans. IARC monographs, Vol. 1 to 29

Kaise T., Watanabe S., Itoh K. (1985) The acute toxicity of arsenobetaine. Chemosphere 14: 1327-1332

Kimbrough D.E, Cohen Y., Winer A.M., Creelman L. and Mabuni C. (1999) A critical assessment of chromium in the Environment. Critical Reviews in Environmental Science and Technology, 29(1): 1-46

Levin-Scherz J.K., Patrick J.D., Weber F.H., Garabedian C. (1987) Acute arsenic ingestion. Annals of Emergency Medicine, 16(6): 702-704

Mance G. & Yates J. (1984) Proposed environmental quality standards for List II substances in water. Nickel. Water Research Centre Technical Report TR211

Mukherjee A.B. (1998) Chromium in the environment of Finland. The Science of the Total Environment, 217: 9-19

Nriagu J.O. (1980) Global cycle of nickel. In Nickel in the Environment, John Wiley and Sons, New York: 1-26

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

Pirkle J.L., Kaufman R.B., Brody D.J., Hickman T., Gunter E.W., Paschal D.C. (1998) Exposure of the U.S. population to lead, 1991-1994. Environmental Health Perspectives 106(11): 745-750

Ratcliffe H.E., Swanson G.M., Fischer L.J. (1996) Human exposure to mercury: a critical assessment of the evidence of adverse health effects. Journal of Toxicology and Environmental Health, 49: 221-270

Renner R. (2002) Newly deposited mercury may be more bioavailable. Environmental Science and Technology, 36(11): 226A-227A

Rice D.C. (1996) Behavioural effects of lead: Commonalities between experimental and epidemiologic data. Environmental Health Perspectives, 104 (Suppl. 2): 337-350

Richard F.C. & Bourg A.C.M. (1991) Aqueous geochemistry of chromium: a review. Wat. Res., 25(7): 807-816

Sauve S., McBride M.B., Hendershot W.H. (1997) Speciation of lead in contaminated soils. Environmental Pollution 98(2): 149-155

Smith A.H., Hopenhaynrich C., Bates M.N., Goeden H.M., Hertzpicciotto I., Duggan H.M., Wood R., Kosnett M.J., Smith M.T. (1992) Cancer risks from arsenic in drinking-water. Environmental Health Perspectives, 97: 259-267

UNEP (1993) Preliminary assessment of the state of pollution of the Mediterranean Sea by zinc, copper and their compounds and proposed measures. Mediterranean Action Plan UNEP (OCA)/MED/WG.66/Inf.3, Athens 3-7 May 1993

USEPA (2002) http://www.epa.gov/safewater/arsenic.html

USPHS (2000) Toxicological profile on CD-ROM. Agency for Toxic Substances and Disease Registry. U.S. Public Health Service

USPHS (2001) 9th Report on Carcinogens U.S. Department of Health and Human Services

Welch A.H., Lico M.S., Hughes J.L. (1988) Arsenic in groundwater of the western United States. Ground Water, 26: 333-347

World Health Organisation (1989). Mercury. Environmental Health Criteria 86. ISBN9241542861

World Health Organization (1998) Water, sanitation and health: guidelines for drinking water quality. Geneva, Switzerland: World Health Organization

Zalups R.K. & Lash L.H. (1994) Advances in understanding the renal transport and toxicity of mercury. Journal of Toxicology and Environmental Health, 42: 1-44