Impacts of mercury contaminated mining waste on soil quality, crops, bivalves, and fish in the Naboc River area, Mindanao, Philippines.

J D Appleton[a,*], Weeks J M[b], Calvez J P S[c] and Beinhoff, C[d]

[a] British Geological Survey, Keyworth, Nottingham, England

[b] Centre for Environment, Fisheries & Aquaculture Sciences (CEFAS), Pakefield Road, Lowestoft, Suffolk, England

[c] Mines and Geosciences Bureau, Quezon City, Philippines

[d] United Nations Development Organisation (UNIDO), Vienna, Austria

Abstract

Rice paddy fields in the Naboc area, near Monkayo on the island of Mindanao, Philippines, have been irrigated four times a year over the last decade using Naboc River water contaminated with mercury (Hg) by artisanal gold mining in the Diwalwal area. Silt containing up to at least 90 mg Hg/kg (d.w.) has been deposited in rice paddy fields during the 1990's and this has been repeatedly mixed into the rice root zone through ploughing. Hg in the rice paddy field soils averages 24 mg Hg/kg and generally exceeds the UK and Canadian soil quality thresholds for agricultural soils as well as the proposed Dutch Intervention value and the USEPA soil ingestion Soil Screening Level (SSL) for inorganic Hg. Much lower Hg concentrations (0.05-0.99 mg/kg) within the range expected for uncontaminated soils, characterise soils on which corn and bananas are cultivated, largely because these are not irrigated with Hg-contaminated water from the Naboc River. The estimated total weekly MeHg intake for a person living in the Naboc area related to the weekly consumption of 2.1 kg of rice grown on Hg contaminated soils (15 µg MeHg) in conjunction with 1

[*] Corresponding author. British Geological Survey, Nicker Hill, Keyworth, Nottingham NG12 5GG, England. Tel.: +44-115-936-3207; Fax: +44-115-936-3200.

E-mail address: jda@bgs.ac.uk (J.D. Appleton)

kg of fish (220 µg MeHg) and 100g of mussels (50 µg MeHg) from the Naboc River, would total

285 µg MeHg (equivalent to 4.75 µg/kg bw for a 60 kg adult), which is nearly three times the

JECFA PTWI of 1.6 µg/kg bw. This will significantly contribute to the population mercury

exposure and might explain why 38% of the local inhabitants were classified as Hg intoxicated

during a mercury toxicity assessment (Drasch et al., 2001).

Keywords: , water quality, sediment quality, rice, mussels, cadmium, lead, human exposure.

1. Introduction

The gold mining centre of Diwalwal (also know as Mt. Diwata), located within the mountainous

east Mindanao Ridge, is one of the largest artisanal gold mining centres on the island of Mindanao

(Appleton et al., 1999). The focus of mining activity at Diwalwal lies in the headwaters of a series

of minor tributaries of the Naboc River, which subsequently joins the north-flowing Agusan River

(Figure 1). Environmental monitoring surveys in the 1990's revealed extensive mercury pollution

of water and sediment in the Naboc River (Appleton et al., 1999). .

Massive, uncontrolled small-scale mining and mineral processing in the headwaters of the Naboc

River in the late 1980's and early 1990's, involving up to 100,000 people resulted in severe

pollution of the irrigated rice paddy fields in the Lower and Upper Naboc Communal Irrigation

Systems, located either side of the Naboc River and serving 600 farmers and their families (Figure

1). Rice yields declined from 6,000 kg/ha in the 1980's to 3,000 kg/ha in the 1990's caused by the

high load of fine suspended silt in the irrigation water. The death of a significant number of water

buffalo was tentatively diagnosed as cyanide poisoning and farmers working in the affected paddy

fields had reported unexplained skin diseases (Appleton, 2000). In response to these reported

problems, the United Nations Industrial Development Organisation (UNIDO) funded studies of (1)

the extent and magnitude of mercury pollution in the Naboc River and neighbouring agricultural

areas (Appleton, 2000); (2) the potential risk to human health from consumption of rice cultivated

in rice paddy fields irrigated by mercury-contaminated mine waste water (Weeks, 2000); and (3) an

evaluation of the influence of mercury on the health of people living in the Diwalwal mining centre and the villages of Naboc, Tubo-Tubo, Babag and Mamonga (Figure 1; Böse-O'Reilly et al., 2000, Drasch et al., 2001). The objective of this paper is to provide a link between earlier regional studies (Appleton et al., 1999) and the detailed health studies (Drasch et al., 2001), which showed that 38% of the local inhabitants were classified as Hg intoxicated. Because consumption of contaminated rice and fish is the primary route of potential exposure to heavy metals, this paper concentrates on mercury in soil, crops, and aquatic biota and assesses the potential hazard to the local people caused by Hg, Cd, and Pb in locally produced food sources. Greater detail on water and sediment quality monitoring is reported by Appleton (2000).

2. Sampling and analytical methods

2.1 Sediment, soil and water

Bottom sediment (BS) samples (Figure 1) were collected by wet screening of river or stream-bed sediment through a 150 µm sieve, using a minimal amount of water to avoid the loss of fine silt and clay fractions. Suspended particulate matter (SPM) samples were obtained by filtering 500 ml water through 47 mm diameter, 0.45 µm Cellulose Nitrate Membrane Filters (Whatman™) using 250 ml and 500 ml capacity Nalgene™ filter holders and receivers and a hand operated vacuum pump. Filter membranes were carefully removed to avoid contamination and stored in 30 ml Sterilin™ tubes.

Soil sampling was carried out in the agricultural terrains adjacent to the Naboc River, comprising (i) the rice paddy fields of the Lower and Upper Naboc Communal Irrigation Systems; (ii) corn fields on non-irrigated land between the paddy fields and (iii) banana plantations adjacent to the Agusan River (Figure 1). Composite soil samples were collected from sites about 10-20 m apart at and immediately below the root depth of the rice, corn, and banana plants. Sediment and soil samples were sealed in plastic securitainers to avoid evaporative losses and oxidation.

Stream and well water pH, temperature, Eh, and conductivity were determined in the field using a series of temperature-compensated electrodes and meters. Water samples for chemical analysis were filtered through 50 mm diameter Sartorius Sartolab P™ 0.45 µm disposable SFCA membranes using 50 ml disposable syringes and collected into 250 ml Nalgene™ LPDE bottles. Some water samples for analysis at the BGS were collected using 25 mm diameter, 0.45 µm Millipore™ cellulose acetate membranes into 30 ml Nalgene™ HPDE bottles. At each site, the suite of water samples collected included: (1) 250 ml filtered water preserved with 1% v/v HNO_3 (*Merck*) for determination of Hg, Cu, Cd, Cr, Pb, Zn, Cd; and (2) 250 ml unfiltered water with pH adjusted to 12 with solid NaOH for CN analysis. A number of 30 ml samples, filtered and preserved with 0.3 ml conc. HNO_3 + 0.3 ml 0.2 vol.% K_2CrO_7 were collected for total Hg analysis at the BGS by a UK Accrediatation Services cold vapour atomic fluorescence spectroscopic (CV-AFS) method to a practical detection limit of 30 ng/L using a PS-Analytical AFS. Quality control

was achieved by analysis of duplicates, blanks, aqueous quality control standards and

AQUACHECK proficiency testing samples. Results for duplicate samples analysed in the BGS and

the Philippines Mines and Geosciences Bureau (MGB) laboratories agreed well (Figure 2).

Bottom sediment (BS), suspended sediment (SS) and soil samples were dried at <40°C. SS samples

were digested with the cellulose filter membrane in aqua regia at <50°C. Dried BS and soil samples

were disaggregated, hand ground in a porcelain mortar and pestle and 1.0g digested overnight in

50% aqua regia at room temperature then gently refluxed for 2 hours at about 106°C, cooled and

made up to 20 ml. For the determination of Hg, organically bound mercury was released by

oxidation with 6% potassium permanganate solution. Mercury in water, sediment and soil at the

MGB was determined by flameless atomic absorption spectrophotometer (Hiranuma HG-1) to a

detection limit of 0.1 µg/L in water and 0.04 mg/kg in sediment and soil using $SnCl_2$ as a reduction

agent (Appleton, 2000). CN in filtered waters was determined by ion selective electrode (ISE)

using a Jenway 3340 Ion Meter. Cu, Cd, Cr, Pb, Zn, Cd in filtered waters and aqua regia soluble

Cu, Cd, Cr, Pb, and Zn in sediments and soils were determined by AAS using a Shimadzu AA-

6800. Quality control of the MGB analysis was achieved by analysis of duplicates, blanks, aqueous

and solid quality control standards (GXR-2), and by comparing MGB results with results for

samples analysed in the BGS laboratories (Figure 2). Mercury analyses of BS and soil samples at

the BGS were carried out on 1 g milled sub-amples, digested overnight in 50% aqua regia at room

temperature then gently refluxed for 2 hours at about 140°C, cooled and made up to 50 ml.

Mercury was then determined by CV-AFS to a practical detection limit for solid samples of 0.02

mg/kg using a PS-Analytical AFS. Cu, Cd, Cr, Pb, and Zn in a 5 ml aliquot of the aqua regia

digestate were determined by ICP-AES using a Varian/Vista AX CCD simultaneous instrument

with dedicated Varian SPS-5 Autosampler. Instrument calibration was achieved using mixed

element standards covering a range of concentrations and the instrument was re-calibrated after not

more than 40 samples. Two quality control standards, high and low, were analysed after each

calibration, during the run, after no more than ten unknown solutions and at the end of each run to

check for drift. Blanks, calibration standards and quality control standards were matrix matched to

the samples to be analysed. All reported measurements are based on the average of three replicate

analyses. National Research Council of Canada marine sediments BEST-1 and PACS-1 were used for quality control. There was good agreement between the MGB and BGS results (Figure 2)

2.2 <u>Rice</u>

Samples of rice (*Oryza sativa* L.) grain from a representative selection of sites within the Naboc, Babag, Mamonga, Tubo-Tubo area (Figure 1) were collected either (1) from the mature rice plants *in situ*, or (2) in the majority of cases, where rice had previously been harvested, samples were collected from concrete drying beds. In the latter case, each sample comprised a composite of at least 6 sub-samples of the rice being dried. Approximately 300g were taken for each location in a randomised fashion. Samples were placed in plastic bags and kept in a fridge (5°C) before being dried and subsequently analysed. Grains were thoroughly washed once only and dried at a low temperature (<40°C) in an oven until a constant weight was achieved. The hull of the rice was removed prior to milling to a fine powder. Additionally, rice samples were cooked in the traditional way to assess the impact of cooking on Hg concentrations. 2 g of rice samples were digested using nitric and sulphuric acids (Adelojou et al., 1994). Organically bound mercury was released by oxidation with 6% potassium permanganate solution and mercury was determined by flameless atomic absorption spectrophotometer (Hiranuma HG-1) using $SnCl_2$ as a reduction agent 5 g subsamples were digested in concentrated HNO_3 and HCl at room temperature overnight, heated on a hot plate, filtered, made up to 100 ml and analysed for Cd and Pb by AAS using a Shimadzu AA-6800.

Duplicates, blanks, and certified international reference materials, including National Research Centre for Certified Reference Materials (NRCCRM) rice (GBW08508; 0.038 µg Hg/g), and National Research Council, TORT-1 (lobster hepatopancreas; 0.2185 µg Hg/g) were used for quality control of rice, banana and aquatic biota analysis. The precision and bias of the chemical analysis was less than 10% with the exception of some Pb results, which were re-determined to achieve the required precision (Weeks, 2000).

2.3 <u>Bananas</u>

Commercial banana plantations between the Naboc and Mamunga Rivers are spray-irrigated with river water. A thin white film of clay-silt was observed on the leaves and trunks of the banana plants at a site adjacent to the Naboc River, close to the confluence with the Agusan River. Other banana plantations were spray irrigated with water pumped from the Agusan River. Nearly ripe bananas were cut from trees growing under protective plastic bags from three areas each under different irrigation regimes. Bananas were taken from plantations in Mamonga (irrigated by the Naboc), and in Babag and Macopa (located 2 km WSW of Babag), both of which were irrigated by waters from the Agusan River. Banana samples were stored at 5°C in a fridge and the edible part analysed for Hg, Cd and Pb (see section 2.2).

2.4 Aquatic biota

Mussels were collected from the Naboc River and a pond fed by the river, near to the village of Naboc (Figure 1). They were rinsed in clean bottled water; the edible soft tissues were carefully removed from their shells and the gut contents discarded. Tissue samples were frozen in self-sealing plastic bags at –18 to -20°C (see Williams et al., 1999). Mussels are considered ideal as biomonitors of heavy metal contamination on account of their limited mobility, widespread distribution and tendency for biomagnification of ambient heavy metal concentrations. These freshwater mussels also formed part of the human diet in the region.

Fish (Tilapia spp.) were collected by hook and line fishing from the Naboc River between Naboc and Babag villages and also from a tributary of the Agusan River. Muscle tissue was removed from the freshly killed fish using stainless steel dissecting tools and frozen in Sterilin tubes at -18 to -20°C. Samples were analysed for Hg, Cd and Pb using the methods described in section 2.2.

3. Results and discussion

3.1 Water quality

Hg in filtered water samples from the Naboc River (Table 1) exceeds the Philippine water quality criteria for both the protection of public health (2 µg Hg/L as total mercury; DENR Administrative Order No. 34, 1990) and fisheries (5µg/L; maximum limit for total Hg; UNEP, 2002). Water from the Naboc River is not abstracted for drinking because it is extremely turbid as a result of discharges from the Diwalwal artisanal mine workings and mineral processing plants. Whereas high Hg loads in solution have been reported previously (Appleton et al., 1999) the general decline in the use of amalgamation for gold extraction suggests that the risk from Hg in solution has declined.

Total Suspended Solids (TSS) in the Naboc River exceed the DENR Class D water quality criteria (100 mg/L) by a factor of 2 to 73, declining to 59 mg/L in the Agusan River, about 5 km downstream of the confluence with Naboc River (Table 1). High suspended sediment load in the Naboc River will effectively prevent the survival of most aquatic macrobiota.

Cyanide exceeded DENR drinking water quality criteria (50 µg CN/l) at the Depot site, but decreased to about 35 µg/L in the lower reaches of the Naboc River. Quality criteria for Hg and CN are not exceeded in water samples from drinking water wells in the Tubo Tubo, Naboc, Mamonga and Babag areas.

Short-term temporal variation was recorded in Hg and CN concentrations in filtered water samples, as well as Hg in SS and TSS (Appleton, 2000). This short-term temporal variation in the chemistry of filtered water and suspended particulate matter is very characteristic of rivers impacted by artisanal and small-scale gold mining areas and is an important factor to consider when setting up a water quality monitoring system. If the temporal variations related to changes in contaminant fluxes and hydraulic regime that have been recorded during the present survey are a common occurrence, then concentrations higher than those recorded are likely to occur and may pose a significant hazard to aquatic biota.

3.2 Sediment quality

Hg in bottom sediment in the Naboc River varies within a relatively restricted range of 13 to 55 mg/kg (Table 2) and is still quite high in SS and BS in the Agusan River, approximately 5 km below the confluence with the Naboc River (20-25 mg/kg; Figure 1). Historical data indicates that Hg declines to 2 mg/kg at a site approximately 60 km further downstream (Appleton et al., 1999). These bottom sediments are a long-term source of Hg contamination and release of Hg into river water may occur as a result of methylation of Hg in bottom sediment. There is also the risk that Hg contaminated sediments will be transferred downstream during periods of high hydraulic flow. Hg concentrations in bottom and suspended sediment in the Naboc and Agusan Rivers (Table 2) exceed the Environment Canada Toxic Effects Threshold for the Protection of Aquatic Life (1 mg/kg; Haines et al., 1994) by factors of up to 55 and 166, respectively.

Significant Spearman correlation coefficients were recorded between (1) pH, Na, Hg, CN and sulphate in filtered water; (2) TSS and (3) Hg and Pb in BS (Figure 3). This reflects the multi-component contamination derived from the Diwalwal mining settlement, comprising Hg from amalgamation, Na and high pH from cyanidation, and Pb from mineralization.

3.3 <u>Soil quality</u>

Rice paddy fields in the Lower and Upper Naboc Communal Irrigation Systems have been irrigated four times a year over the last decade using Hg-contaminated water from the Naboc River. It is reported that 5 to 15 cm of silt has been deposited in rice paddy fields during the 1990's and that in some areas 2 to 5 cm of silt is ploughed into the top 10-20 cm of the soil profile every year. Consequently Hg contaminated silt containing 29-89 mg/kg Hg (Table 3) will be thoroughly mixed into the rice root zone. Hg in rice paddy field soils range between 0.05 to 96 mg/kg (average 24 mg/kg; median 12 mg/kg). There is, as would be expected, lateral variation in the Hg concentration away from where silt laden irrigation water enters a field. For example, Hg declines from 66 mg/kg where irrigation water enters one paddy the field to 4 mg/kg in the centre of the field, a distance of about 250 metres. Cu and Zn exhibit no vertical variation with depth in the soil profile whereas Pb and Hg decrease by a factor of 2 to 4 (Table 4).

Hg in the majority of the rice paddy soils exceeded (1) the maximum permissible concentration of Hg in agricultural soil in the UK (1 mg/kg); (2) the Canadian Soil Quality Guideline for agricultural soils (6.6 mg/kg); (3) the UK soil guideline value for inorganic Hg for allotments (8 mg/kg; Environment Agency, 2002); (4) the proposed Dutch Intervention value (SRC - "serious risk concentration") for inorganic Hg (36 mg/kg; RIVM, 2001); (5) the USEPA soil ingestion Soil Screening Level (SSL) for inorganic Hg (23 mg/kg); and the USEPA SSL for inhalation of volatiles (10 mg/kg; USEPA, 1996). However Hg in the Naboc paddy soils does not exceed either the Dutch proposed human health SRC of 210 mg/kg or the USEPA generic SSL for plant uptake (270 mg/kg), which implies that the plant uptake pathway is not regarded as a major contributor to exposure compared with soil ingestion (USEPA, 1996). Limit values for Cd, Cu, Pb and Zn in agricultural soils adopted by the UK are not exceeded in any of the soil samples (Table 3), neither are the Dutch SRCs for human health or the USEPA SSLs for soil uptake (USEPA, 1996) for Cd (24-28 mg/kg) and Pb (400-622 mg/kg).

Much lower Hg concentrations within the range expected for uncontaminated soils, characterise soils on which corn and bananas are cultivated, largely because these are not irrigated with Hg-contaminated water from the Naboc River. With the exception of one sample (0.98 mg/kg Hg), which was taken from a corn field that appeared to have been used previously for rice cultivation, all corn soils have Hg concentrations below 0.5 mg/kg.

The close correlation between Hg and Pb in the rice paddy soils mirrors a similar correlation in bottom sediments (Figure 3). pH measured in a selection of soils revealed a range of 5.3 to 7.2 but no significant correlations could be detected between pH, Hg, Cd, or Pb.

3.4 <u>Rice</u>

Concentrations of Hg in rice ranged from 0.008 – 0.050 µg Hg/g (wet weight) and between 0.009 – 0.058 µg/g dry weight (Table 5). Both cooking the rice by boiling and polishing reduced the level of total inorganic mercury (Table 5). Hg in rice commonly consumed in Saudi Arabia averages 0.0032 µg/g (range < DL – 0.0436 µg/g; Al-Saleh & Shinwari, 2001), whereas a value of 0.0052µg/g was reported for commercial rice from Italy (Horvat et al., 2003) and 0.005 to 0.034

µg/g in wild rice from northern Wisconsin (Bennett et al., 2000). Rice from the mercury-polluted Niigata area of Japan averages 0.003 µg/g (Nakagawa and Yumita, 1998; soil Hg 0.155 µg/g) and rice cultivated close to a chlor alkali industrial plant in Ganjam, India (Lenka et al., 1992) contained 0.008 µg/g. Much higher concentrations ranging up to 0.57 µg/g were recorded from the mercury polluted areas of Wansham and Quingzhen in Guizhou province of China (Horvat et al., 2003).

No significant correlation could be detected between Hg in rice and soil samples collected from the same general area as where the rice was grown (Figure 4). However, it is difficult to make direct comparison between Hg concentrations in composite soil samples, comprising sub-samples collected from sites about 10-20 m apart and wherever practicable, from two to three adjacent paddy fields, with Hg concentrations in rice grain samples that represent much larger areas. Unfortunately it was not possible to collect soil and rice samples from exactly the same sites because the rice had been harvested shortly before the field programme was carried out.

The relationship between Hg in soil and un-cooked rice from the Naboc area is compared with data from the Wansham and Quingzhen areas (Horvat et al., 2003) in Figure 5. This illustrates the much higher concentrations of Hg in rice from the mercury mining area of Wansham whereas rice samples from the vicinity of the chemical plant at Quingzhen, where mercury is used as a catalyst for the production of acetic acid, are similar to Hg levels in the Naboc rice. There appeared to be no correlation between Hg in rice and soil in either area in China (Horvat et al., 2003).

Cd in Naboc rice ranges from 0.057 to 1.025 µg/g with a mean of 0.29 µg /g whilst Pb ranges from <0.01 to 0.430 µg/g with a mean of 0.0479 µg/g (Table 5). In Korea, rice grain grown on soils developed from cadmium-rich uraniferous black shales ranged between 0.1 to 3.5 µg Cd /g (dry weight) with an average concentration of 0.6 µg/g (Kim & Thornton, 1988). In the Yugu-Kwangcheon Au-Ag Province of Korea, average concentrations of Cd and Pb in the most contaminated paddy soils range up to 8.2 µg/g Cd and 192 µg/g Pb, whereas corresponding Pb

concentrations in rice grain and sesame from these soils ranged between 0.4 µg/g and 6.8 µg/g (Kim et al., 1998). Watanabe et al. (1989) reported geometric mean contents of Cd and Pb in Philippine rice of 0.020 µg Cd/g and 0.016 µg Pb/g (dry weight) respectively compared with world geometric means of 0.02 µg Cd/g (dry wt.) and 0.016 µg/g Pb (Watanabe et al., 1996). Zhang et al. (1996) found that Pb in Philippines rice grain averaged 0.0376 µg Pb/g. Cadmium and lead in 27 rice grain samples commonly consumed in Saudi Arabia have mean concentrations and ranges of 0.02 (range < DL-0.18) µg/g and 0.135 (range 0.02-1.53 µg/g), respectively (Al-Saleh and Shinwari, 2001).

Rice is generally grown under both oxidising and reducing soil conditions and these conditions will influence the metal uptake by plants. Many investigations have demonstrated that the availability of metals decreased under submerged conditions due to processes of precipitation with hydrides, carbonates and sulphide and iron compounds. Factors influencing metal uptake by rice include soil pH, redox potential, organic matter content, phosphorus content, temperature and time and additionally the cultivar of rice grown (Jung & Thornton, 1997; McLaughlin et al., 1999). One of the most important factors affecting metal bioavailability is soil pH. A relatively low metal uptake by rice is found under reducing conditions due to increasing soil pH. Jung & Thornton (1997) showed that metal concentrations in rice plant stalks growing under reducing conditions were lower than those growing under oxidising conditions. Other studies have shown that an increase in soil organic matter content increased the exchangeable Fe and Mn in soils under flooded conditions and thus decreases the availability of metals to plants.

It is also possible that HgS may form in the anoxic layers of rice paddy soils, thereby making the Hg relatively unavailable to plants. However, this is only likely to occur in relatively high sulphur conditions. Equally, adsorption of Hg onto secondary Fe hydroxides when the paddy soil dries out and becomes oxidised will also reduce bioavailability, as will adsorption of Hg onto organic matter in the paddy soils. The availability of metals typically decreases under submerged conditions due to soil metal precipitation, metal sorption and a range of other factors. Lee et al. (1996) reported an increase of soil pH with increases in the duration of the flooding period for acidic soils, and this

results in greater Cd availability reflecting the dynamic change in the chemical forms of Cd in soils under various flooded conditions. Soil Hg generally has a low availability and plant roots act as a barrier to Hg uptake. In addition, demethylation of Hg in the upper 10-15 cm of the soil profile may reduce Hg availability. These factors may together explain why relatively little Hg appears to be taken up by the rice plants in the Naboc area. This is fortunate because significant brain damage in animals (rats) is associated with the consumption of Hg polluted rice (average 0.14 mg/kg) from Guizhou province, China (Wang et al. 2004).

The uptake of Hg is generally much less than for Cd or Zn, which would explain the relatively high soil/rice grain rations for Hg compared with Cd (Tables 3 and 5). Watanabe et al. (1996) reported high Cd contents in rice harvested from paddy fields with elevated soil Cd, whereas Cd in Naboc rice is high in relation to the level of Cd in paddy soils (<1 mg/kg; Table3). Absorption of Cd may be influenced by flooding the paddy fields, which controls the redox potential of the soil, and hence the uptake of Cd by rice plants.

3.5 <u>Banana</u>

Hg, Cd and Pb in banana (Table 6) are low and within appropriate food safety standards for such items. The bananas were commercially grown for export and local consumption is very restricted. The low concentrations are compatible with concentrations in the soils (Table 3).

3.6 <u>Fish and mussels</u>

Hg in <u>Tilapia spp</u>. from the Naboc River (0.277 µg/g) is twice as high as in fish from the Agusan River (0.125 µg/g; Table 7), reflecting differences in water, suspended and bottom sediment chemistry in these two rivers (Tables 1 & 2). Total Hg in fish muscle tissue does not exceed the maximum recommended limit commonly allowed for fish in most countries (0.5 mg Hg/kg wet weight; UNEP, 2002). Hg in the soft edible tissues of 64% of the mussel samples exceeds the 0.5

mg Hg/kg wet weight allowed for fisheries products in the European Community although only 18% of the mussel samples exceed the maximum allowable/recommended level for shellfish in the USA (1 mg methyl Hg/kg; UNEP, 2002). Hg in fish from the Naboc River is much higher than in marine biota (0.004-0.063 µg/g) in the artisanal gold mining impacted area of Libay (Zamboanga del Norte, Mindanao) where sediment Hg concentrations are much lower (0.035 µg/g) (Maramba et al., 2004). Low concentrations of THg in freshwater fish (0.012 µg/g) and clams (0.18 µg/g) (Ramirez et al. 2004) and 0.01 µg/g in Tilapia (Akagi et al., 2000) have been reported also from the Tagum artisanal gold processing area, Mindanao.

3.7 Metal intake related to rice, fish, and mussel consumption

The dietary intake of rice by the local residents in the Naboc area is estimated to be 300g (air-dried) per person per day. The average Hg concentration in rice grain grown in the study area was 0.0149 µg/g (dry wt.), so the amount of mercury entering the body, assuming that locally grown rice is washed and cooked, is 4.47 µg Hg /day. (0.03 mg/week). This value is much lower than the Provisional Tolerable Weekly Intake (PTWI) of 0.3 mg for mercury in the diet set by the WHO and the FAO, of which the maximum intake of MeHg should be no more than 1.6 µg/ kg bw (FAO/WHO, 2003). If 50% of the Hg in Naboc rice were MeHg (see Horvat et al., 2003), then the total weekly MeHg burden from rice would be 15 µg MeHg equivalent to only 0.25 µg/ kg bw for an adult (bw 60 kg). Average total Hg intake for consumers of Naboc rice is also lower than the Japanese safe guideline limit (0.036 mg/day for an adult weighing 50 kg; Nakagawa & Yumita, 1998) as well as the Provisional Tolerable Daily Intake (PTDI) for adults (0.47 µg/ kg bw/day) and for pregnant women and children (0.2 µg/ kg bw/day) in Canada. However, individuals consuming polished and cooked Naboc rice at the upper limit of the Hg concentration range (0.037 µg/g) would have a daily intake of 0.185 µg/ kg bw/day, which is almost equal to the Canadian PTDI for children and pregnant women.

The average Cd concentration in rice grain grown in the Naboc area was 0.2907 µg Cd g^{-1} (wet wt.) so the average daily intake of Cd from consuming 300g of rice is 87.2 µg Cd, or 610 µg per week.

This exceeds the Provisional Tolerable Weekly Intake (PTWI) of 420 µg Cd recommended by the Joint FAO/WHO Expert Committee on Food Additives (JECFA).

The average Pb concentration in rice grain grown in the Naboc area is 0.0479 µg/g (wet wt.) so the average daily intake of Pb from consuming 300g of rice is 14.3 µg Pb, or 100 µg per week. This is only 6.8% of the Provisional Tolerable Weekly Intake (PTWI) of 1470 µg Pb recommended by the Joint FAO/WHO Expert Committee on Food Additives (JECFA).

Fish and fish products are the dominant sources of methyl mercury in the diet and levels greater than 1200 µg/kg have been found in edible marine species such as tuna and swordfish. Similar levels have also been recorded in fish from polluted freshwaters. Consumption of 250g of fish from the Naboc River four times a week would result in an intake of 277 µg Hg/week (Table 7). This value is close to the Provisional Tolerable Weekly Intake (PTWI) of 300 µg for total mercury in the diet recommended by JECFA. If 80% of the total Hg in the Naboc fish is MeHg, then the weekly intake is approximately 220 µg MeHg (3.33 µg/kg bw), which is double the JECFA PTWI of 1.6 µg/kg bw (FAO/WHO, 2003). Consumption of 100g of the edible portions of freshwater mussels from the Naboc River and adjacent ponds (average 0.59 µg Hg/g; Table 7) each week would result in an additional MeHg burden of about 50 µg MeHg/week.

4. Conclusions

Hg in the majority of the rice paddy soils exceeded the UK and Canadian soil quality thresholds for agricultural soils as well as the proposed Dutch Intervention value and the USEPA soil ingestion Soil Screening Level (SSL) for inorganic Hg, although concentrations are less than the Dutch proposed human health value and the USEPA generic SSL for plant uptake. Limit values for Cd, Cu, Pb and Zn in agricultural soils adopted by the UK are not exceeded in any of the soil samples. Much lower Hg concentrations within the range expected for uncontaminated soils, characterise

soils on which corn and bananas are cultivated, largely because these are not irrigated with Hg-contaminated water from the Naboc River.

The estimated total weekly MeHg intake for a person living in the Naboc-Babag area related to the weekly consumption of 2.1 kg of locally grown rice (15 µg MeHg), 1 kg of fish (220 µg MeHg) and 100g of mussels (50 µg MeHg), both from the Naboc River, would total 285 µg MeHg (equivalent to 4.75 µg MeHg/kg bw for a 60 kg adult) which is almost 3 times the JECFA PTWI of 1.6 µg/kg bw. This will significantly contribute to the population mercury exposure and might explain why 38% of the local inhabitants were classified as Hg intoxicated during a mercury toxicity assessment (Drasch et al., 2001). Some local people are reported to eat locally caught fish up to three times a day (Drasch et al., 2001), which would substantially increase their exposure to methyl mercury. Not consuming local fish would produce the greatest reduction in exposure to methyl mercury. Inadvertent ingestion of soil containing 24 mg Hg/kg at a rate of 20 mg/day (WHO, 2001) or 50mg/day (Campbell, 2003) would give an additional estimated weekly intake of between 3 and 8 µg THg. The importance of dermal absorption of inorganic mercury and methyl mercury from paddy soil has not been considered but may be an additional exposure route for farmers and their families in the Naboc area. The same applies to the occasional deliberate consumption of soil (pica) or the persistent and purposeful consumption of soil (geophagia), although geophagia is not known to be practised in the Naboc area. A more comprehensive assessment of all Hg exposure routes that includes a systematic dietary survey covering the full range of food types is now required, especially as no plans to remediate the mercury contaminated soils of the Naboc Irrigation Systems have yet been reported. We further recommend the development of a set of water quality criteria specific for this site that would serve as a basis for controlling discharges or releases of heavy metals in the water. These recommended human health water quality criteria would not impose legally binding requirements but would serve to protect the health of consumers of non-commercial freshwater fish. In addition it is recommended that no change of land use from rice to other crops, such as corn, should be permitted unless it can be demonstrated that the alternative crops do not absorb Hg to levels that could further enhance the level of human exposure to mercury.

Postscript

The government took control of the mining and mineral processing activities at Diwalwal in 2002 following which mineral processing by mini-CIP plants and ball mills was required to follow environmental and safety rules. Miners constructed their own mini mine tailings dam to temporarily store mine wastes instead of dumping them directly into the Naboc River. The government also terminated the operation of three big mineral processors thereby reducing production from 500-700 tons to just 100 tons per day. It is reported that attempts will be made to rehabilitate the Naboc River once the Mabatas tailings dam has been constructed. Recent DENR-EMB monitoring has shown that these changes have produced a significant improvement in the water quality of the Naboc River with Hg below the permitted level of 0.002 µg/L and cyanide below the water quality criteria for fresh waters of 0.05 mg/L. Siltation in the lower Naboc has declined to a third of previous levels and TSS in the rest of the river system is now within the public water supply quality standard of 50 mg/L.

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Table 1. Chemistry of filtered water samples from the Naboc River compared with historical data from the Diwalwal artisanal mining area (concentrations in µg/L)

	Depot site, Naboc River, 1 km below Diwalwal	Naboc River (at and below NIA dam)[1]	Mamunga R. & tributaries	Agusan R above Naboc R	Agusan R below Naboc R	Well waters	Diwalwal[2]
No. of samples	2	14	3	2	3	9	Max.
Cu	100-120	<20	<20	<20	<20	<20	344
CN	440-445	20-40	10-30	10-20	8-30	6-46	nd
Hg	7-37	<0.1-42	<0.1	<0.1	<0.1	<0.1	1539
TSS[3] (mg/L)	5055-7357	200-929	57-110	42-57	59-316	16	nd
Zn	<50	<50	<50	<50	<50	80-1160	81

[1] Drainage samples sites on Naboc River in Figure 1

[2] Appleton et al., 1999; Breward et al, 1996

[3] TSS = Total Suspended Solids

nd = not determined

Table 2. Chemistry of suspended (SS) and bottom (BS) sediment samples and concentration of Total Suspended Solids (TSS) for the Naboc River area (concentrations in mg/kg, except TSS).

	Depot site, Naboc River, 1 km below Diwalwal	Naboc River (at and below NIA dam) [1]	Mamunga R. & tributaries	Agusan R above Naboc R	Agusan R below Naboc R
No. of samples	2	14	3	2	3
Cd SS	<1	<1-2	<1-2	2-5	<1-5
Cd BS	<1	<1	<1	<1	<1
Cu SS	46	35-55	53-83	108-126	69-268
Cu BS	67-76	39-57	65-74	73-85	61-74
Hg SS	28-37	52-166	5-84	<0.04-2	27-124
Hg BS	13-17	13-55	2-51	0.1	17-33
Pb SS	33-38	57-120	<10-65	<10	14-186
Pb BS	37-40	20-32	<10-25	<10	17-19
TSS (mg/L)	5055-7357	200-929	57-110	42-57	59-316
Zn SS	70-82	64-145	135-275	157-254	136-642
Zn BS	75-89	49-121	57-112	57-61	66-79

[1] Drainage sample sites on Naboc River - see Figure 1

Table 3. Mean and range of Cd, Cu, Hg, Pb and Zn in surface soils from the rice paddy soils of the Lower and Upper Naboc Irrigation Systems and adjoining areas of banana and corn cultivation compared with silt deposited in irrigation canals and soil quality criteria (concentrations in mg/kg).

	Rice paddy soil	Banana soil	Corn soil	Irrigation canal silt	EC (UK) Limit Values[1]
No. of samples	58	9	9	3	
Cd	<1	<1	<1	<1	1 - 3 (3)
Cu	63 (35-105)	65 (49-118)	61 (46-84)	56 (41-67)	50 - 140 (135)
Hg	24.3 (0.05-96)	0.12 (0.05-0.3)	0.27 (0.08-0.99)	82 (29-89)	1 - 1.5 (1)
Pb	14 (<10-56)	<10	<10	22-38	50 - 300 (300)
Zn	72 (37-121)	67 (45-86)	64 (43-82)	67 (48-80)	150 - 300 (200)

[1] Limit values for concentrations of heavy metals in soils (EC Directive 86/278/EEC on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. Permitted range (value adopted by the UK in brackets))

Table 4. Cu, Pb, Zn and Hg in two rice paddy field soil profiles (concentrations in mg/kg; see Figure 1 for location of profiles P1 and P2)

Profile	Depth of sample	soil type	Cu	Pb	Zn	Cd	Hg
P1	2-8 cm	brown clay silt	69	23	87	<1	40.0
	10-20 cm	grey clay silt	62	<10	84	<1	12.4
P2	5-10 cm	grey silt	57	29	85	<1	49.6
	15-20 cm	mottled brown clay-silt	57	11	85	<1	12.8

Table 5. Mean concentrations and ranges of Hg, Cd and Pb in rice grains sampled in the vicinity of the communal irrigation area (metal values are µg/g dry weight, unless otherwise stated).

Rice grain	Mean	Range
Hg		
Polished + cooked	0.015	0.006-0.037
Polished + not cooked	0.018	0.008-0.050
Unpolished	0.020	0.001-0.043
Dry weight	0.021	0.009-0.058
Wet weight	0.016	0.008-0.050
Cd (wet wt.)	0.291 (0.020)[a]	0.057-1.025
Pb (wet wt.)	0.0479 (0.038)[b]	0.043-0.430

[a]Geometric mean value for the Philippines based on 26 samples from Watanabe et al. (1996)

[b]Geometric mean value for the Philippines based on 26 samples from Zhang et al. (1996).

Table 6. Mean concentrations (µg/g wet wt.) of Cd, Hg and Pb banana.

Site (Source of irrigation water)	n.	Cd	Hg (range)	Pb
Mamonga (Naboc River)	5	0.27	0.016 (0.007-0.039)	<0.01
Makopa (Agusan River)	5	0.17	0.011 (0.008-0.066)	<0.01
Babag (Anaan River)	5	0.13	0.016 (0.008-0.016)	0.03

Table 7. Mean concentrations (µg/g wet wt.) of Cd, Hg and Pb in fish (*Tilapia* spp.) and mussels collected from the Naboc and Agusan Rivers.

Species Sample Site	No.	Cd	Hg (range)	Pb
Fish (Tilapia spp.)				
Agusan tributary	7	0.13	0.125 (0.109-0.156)	0.16
Naboc River	3	0.13	0.277 (0.146-0.494)	<0.01
Mussels (Taiwan clam)				
Naboc River	8	0.12	0.315 (0.233-0.554)	0.22
Pond adjacent to Naboc River	14	0.16	0.869 (0.296-1.208)	0.24

Figure captions

Figure 1. Hg in drainage (bottom sediment and canal silt) and soil in the Naboc River and adjoining areas (see Figure 1 in Appleton et al., 1999 for location of survey area; all soil samples are from rice paddy fields except those marked **b** (banana soil) and **c** (corn soil); **P1** and **P2** are soil profile locations).

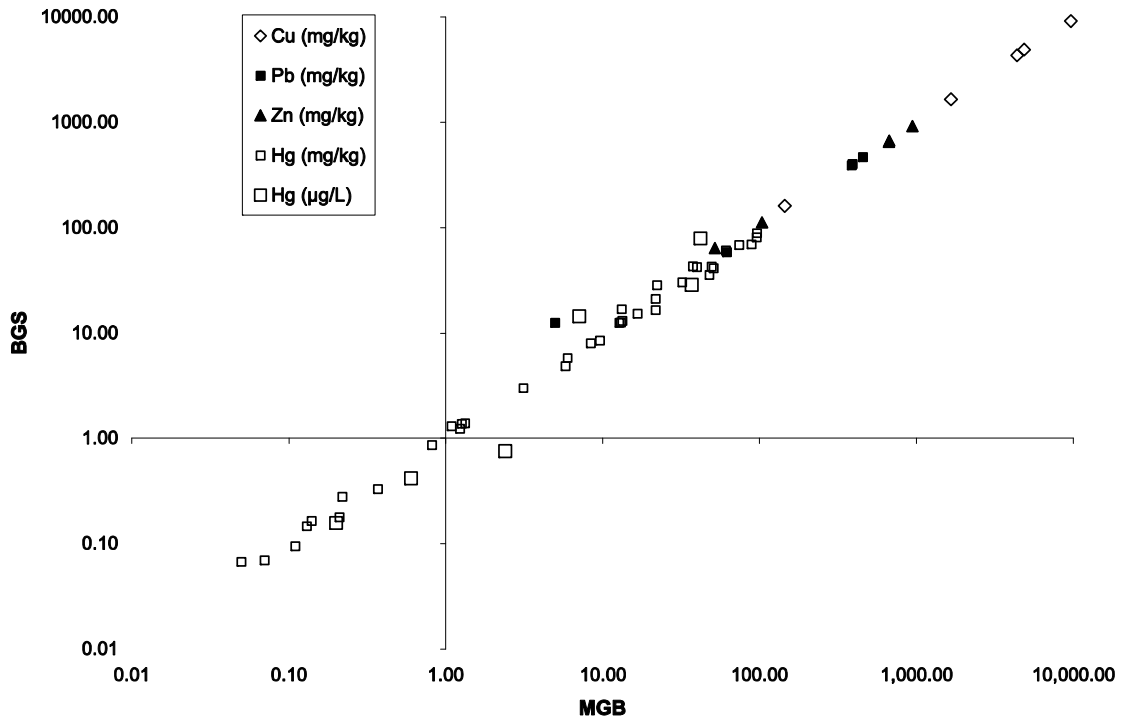Figure 2. Comparison of analytical results for water (µg/L) and sediment (mg/kg) samples analysed at the MGB and BGS laboratories.

Figure 3. Correlation between Hg and Pb in soil and bottom sediment, Naboc area.

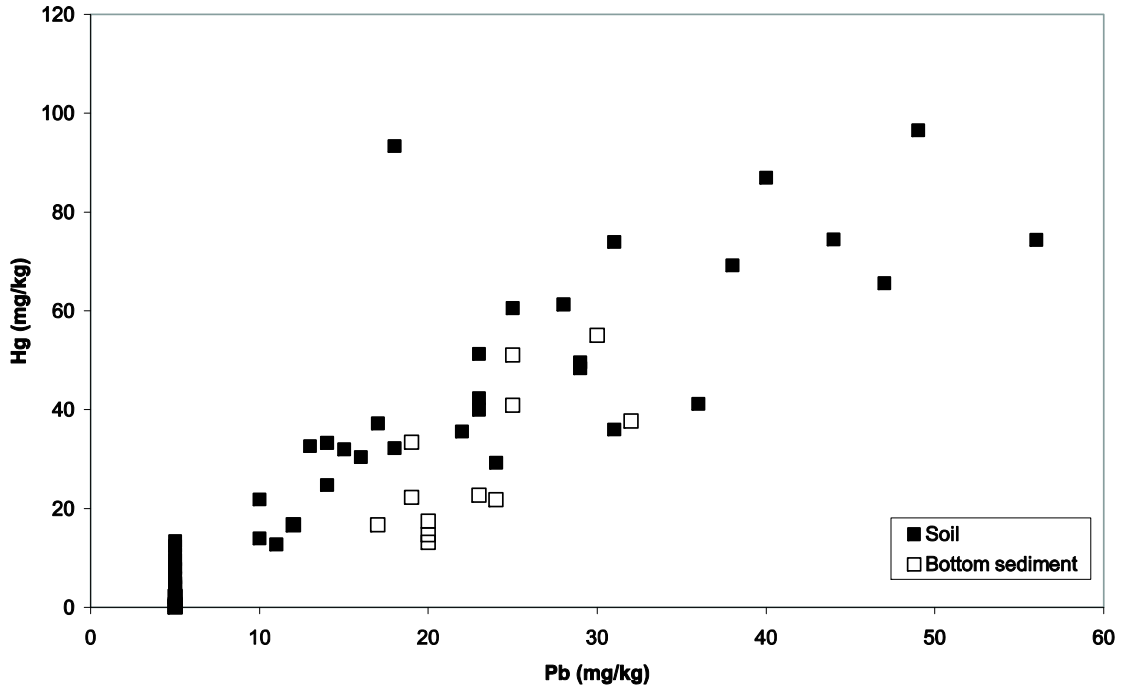Figure 4. Relationship between Hg in soil and rice, Naboc River area

Figure 5. Concentration of Hg in soil and rice from the Naboc area compared with the Quingzhen and Wanshan areas in China (Horvat et al., 2003)
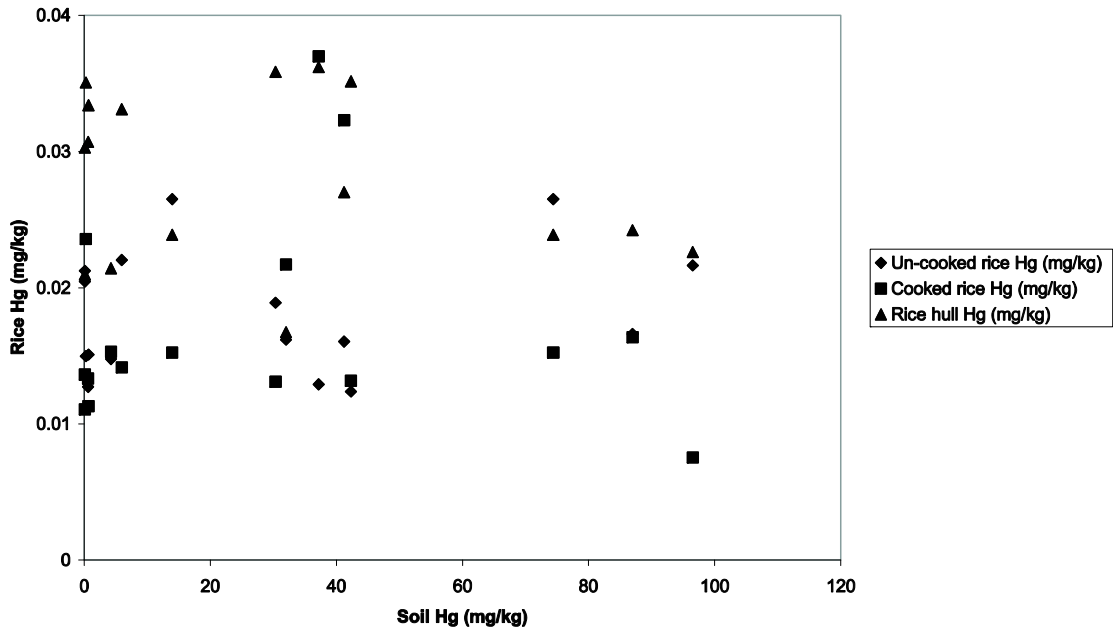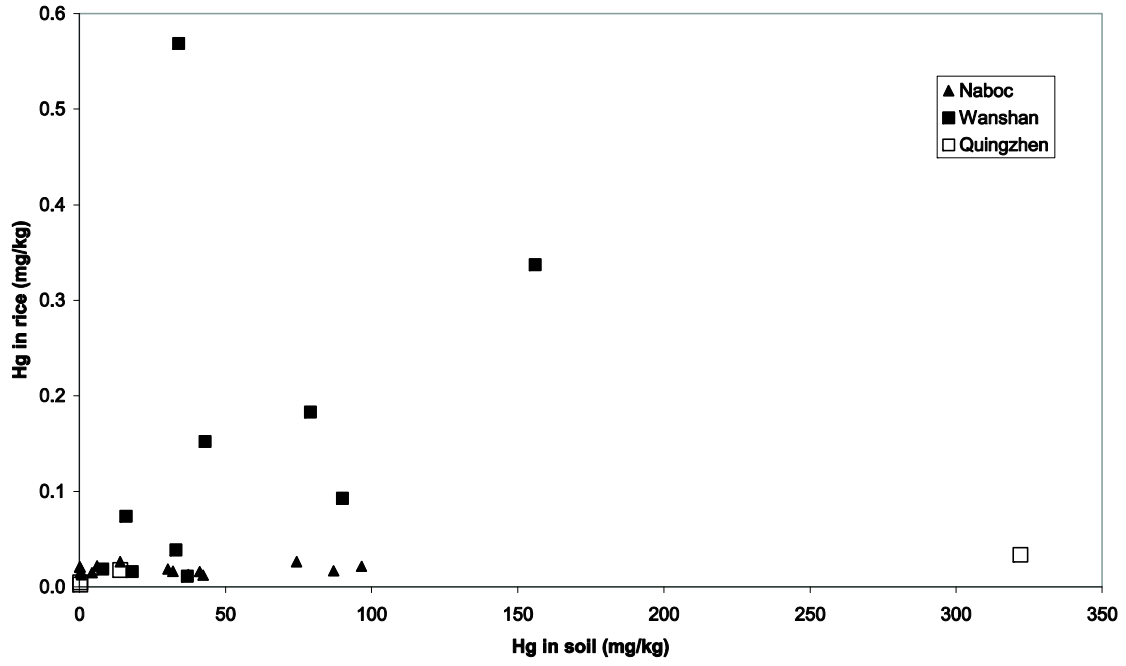
Appleton Naboc Figure 1

Appleton Naboc Figure 2

Appleton Naboc Figure 3

Appleton Naboc Figure 4

Appleton Naboc Figure 5