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ABSTRACT

This study was conducted to assess the impact of gold mining activities on the nearby marine bay. We investigated the fate of mercury (hg) among the different environmental compartments (water, sediment, suspended particulates, organisms) and its relative distribution among 10 of the most common invertebrate species found in the bay.

Sampling was done from October 25-29, 1999 in 10 sampling stations within the bay. Samples were kept frozen and later analyzed at the Biology Laboratory of the University of Antwerp, Belgium. The mercury discussed in this paper relates to total mercury only.

Results of analyses showed that all the sampling sites in the bay exceeded the allowable Hg limit for seawater (2ppb). Stations nearest in proximity to the mining area tend to acquire higher concentrations in all the compartments. Among the species, *Modiolus philippinarum*, *Nerita planospira* and *Trachycardium flavum* were within the allowable limit of 0.5 ppm. *Tectus fenestratus*, *Strombus sp*, *Placuna ephippium* and *Circe scripta* had as much as a factor of 5 more than the allowable limit. From regression analysis, this study has shown that mercury concentration in tissues of 3 out of 4 species studied correlated with dissolved mercury and suspended particles or sediments. Lack of consistent correlations between dissolved or particulate Hg and tissue concentrations were observed in *Modiolus philippinarum* (a bivalve) though it showed high levels of mercury.

This study has shown that there are some interactions/associations among metals during accumulation process in several species. However, we were not able to establish the mechanism that control these interaction/associations.

I. Introduction

Heavy metals such as mercury, lead, arsenic, cadmium, tin, chromium, zinc, and copper are among the most dangerous pollutants in the marine environment (Goldberg, 1975; Philips, 1980; Cossa, 1988; Ross, 1988; Schuhmacher and Domingo, 1996; Nebel and Wright, 1996). Due to its unique properties, mercury is used in medical and scientific instruments like thermometers, manometers and barometers, jewelry making, for coating the back of mirrors, in dental amalgams, as catalyst in the production of polyurethane foams, in printing and in the extraction of gold and silver (Dugan, 1972; Sittig, 1980; Bunce, 1991; Huber, 1997; STAO, 1992; USEPA, 1997; ATSDR, 1999).

Mercury cycles in the environment as a result of natural processes such as volatilization of mercury in marine and aquatic environments, from vegetation, degassing of geologic materials and volcanic emissions and anthropogenic activities, dominated by industrial processes and combustion sources (Tinggi and Craven, 1996; Park and Curtis, 1997). Most of the mercury in the atmosphere is

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elemental mercury vapor, which circulates in the atmosphere for up to a year, and hence can be widely dispersed and transported thousands of miles from main sources of emission (Sang and Lourie, 1995; Park and Curtis, 1997; Sigel and Sigel, 1997). Most of the mercury in water, soils, sediments, or plants and animals is in the form of inorganic salts and organic forms of mercury (methyl mercury). Once in the water surface, mercury enters a complex cycle in which one form can be converted to another. It enters the sediment compartment by particle settling and is later released by diffusion or resuspension into the water column where it can enter the food chain or it can be released back to the atmosphere by volatilization (Sigel and Sigel, 1997). In terms of human exposure to mercury, fish consumption dominates the pathway for human and wildlife (Joiris et al., 1995; Sigel and Sigel, 1997; USEPA, 1997). All forms of mercury are toxic to humans but methyl mercury is of special concern because our bodies have less well developed defense mechanism against this toxin (USEPA, 1997). Effects on the nervous system are the most prevalent in humans.

Small-scale gold mining activity contributes significantly to gold production and rural employment in the country. Foreign studies cited high production levels for small- scale gold mining in the Philippines (Israel and Asirot, 2000). The production of small-scale gold mining in 1992 was estimated at 6,826 kilograms, which is about 25 percent of the total gold production in the country. This contribution is certainly large considering that it is coming from a non-mechanized and generally artisanal form of mining activity. While economically significant, small-scale gold mining has been the target of strong oppositions in the Philippines in recent years mainly due to its various adverse environmental and social side-effects, foremost of these is mercury pollution (Breward, 1996; DENR, 1999; Israel and Asirot, 2000; DENR, 2000).

Mercury gets into the picture in small-scale mining because it is the main agent used to separate the gold from the mined ore employing the amalgamation method of processing. Amalgamation is popular in small-scale mining since it is simple to apply and requires relatively low investment (USAID, 1997; Israel and Asirot, 2000).

Distribution of mercury in the different marine components will depend on the following: pH, organic matter, temperature, suspended particles and distance from source. In this study we investigated the fate of mercury among the different environmental compartments (water, sediment, suspended particles, organisms) and relative distribution of mercury among 10 of the most common invertebrate species found in the bay. The study also investigated the local distribution of mercury within the bay with reference to the main source of mercury in the bay (point source zones).

II. Objectives

The main objective is of this study is to assess the impact of small scale gold mining activities on the nearby marine bay. Specifically, to determine the extent of heavy metal pollution in the major environmental compartments (water, sediments, suspended particles and marine organisms) and to compare the levels of mercury concentrations in edible marine species whether these animals are fit for human consumption. Though the study includes a wide range of heavy metals, emphasis is on mercury mainly because it is specially used in the gold mining process. In addition mercury is of special interest due to its toxicity to humans. The mercury discussed in this paper relates to total mercury only.

III. Study Area

Murcielagos is a semi enclosed bay and is located 123°33'00" E longitude and 8°39'00" N latitude. It falls under the administrative jurisdiction of Regions IX (Western Mindanao) and X (Northern Mindanao). Sibutad is one of the municipalities under Region IX situated along Murcielagos. The bay is approximately 6547 ha wide and can be reached with motorized boats or by public and private land transportation. The area was once a grazing land and remained unproductive and neglected until the discovery of gold in 1987.

Gold was discovered in two areas in the municipality of Sibutad namely Larayan and Lalab. This resulted in the influx of small-scale miners, panners, gold buyers and prospectors. By 1988, it was estimated that around 10000 people had moved to the area and had occupied 250 ha of the 360 ha land available.150 tunnels were built, and 139 ball mills were installed. The average daily gold production was 150 m^3 (DENR-IX, 1990). After the peak of the mining activity from 1988-1989, only 79 active tunnels remained in the area with 67 ball mills and the average gold production was reduced to only 5 m^3. In this operation, 67 kgs of mercury are utilized per day and 50 kgs of these are monthly wasted. Cyanide is also used for gold extraction through the heap leaching process. This method is utilized by Philex Gold Philippines Inc., the mining firm in the area (DENR, 1998).

The sampling sites were chosen to include stations already established by DENR-IX and only Stations 8-10 were added as control points. Stations 1-9 fall under the jurisdiction of Region IX while Station 10 belongs to Region X.

IV. Sample Collection

Sampling was done from October 25-29, 1999. Both filtered and unfiltered seawater samples were collected. A 0.2 µm membrane filter paper (Schleicher and Schuell) was used for filtration. The filtered water was collected in polypropylene containers, 100 ml each and 1 ml nitric acid was added. These containers were kept frozen at -5°C which was the only freezer available in the area.

The filters were placed in polypropylene tubes and kept frozen. The unfiltered water samples were immediately wrapped with aluminum foil to prevent any photosynthetic activity and were also kept frozen at -5°C.

The most common mollusk species that occurred per station were considered in this study. Samples were randomly collected within a 10 m radius. Some were hand picked while others required diving. At each station, the two most dominant species were collected, 30 specimens each. Soft tissues and shells were transferred to separate vials and kept frozen. A total of 570 specimens were gathered in the area belonging to six orders and ten families.

Sediment samples were collected between 0.5 m and 1.5 m water depth with a 52 mm diameter (height = 13 mm) plastic Petri dish. These were filled completely and tightly sealed with adhesive tape to avoid air spaces. Five replicates were gathered for each station and kept frozen.

To determine Suspended Particulate Matter (SPM), filters were pre-weighed and a known volume of seawater was filtered. Filters were dried at a 110 °C oven for a total of 3 hours and then transferred to a desiccator before taking the final weight. Samples were kept frozen (Hamilton, 1989; Hershelman et al., 1981; Hornung et al., 1981; Joiris et al., 1995; Parker and Curtis, 1997) from the time of collection in the Philippines. Water, suspended particles, sediment and tissue samples were transferred to a cooler (Igloo) packed with dry ice (O'Connor, 1998) and transported to Belgium for analysis.

V. Analytical Methods

Dissolved organic carbon content in filtered seawater were measured using a Shimadzu 5000 TOC analyzer while particulate and sediment organic carbon were measured using the Coulomat carbon analyzer (Coulomat 702-LI, Strohlein Labortechnik).

For sediments, particle size distribution were determined with the use of a Mastersizer particle analyzer (Mastersizer, Malvern Instruments).

An Inductively Coupled Plasma Mass Spectrometer ICP-MS, UltraMass 700 (Varian Australia Pty Ltd) was used for metal analysis in the different compartments: water, organisms and sediments.

VI. Results and Discussion

A. Relationship between metal concentrations in the soft tissues of organisms and concentrations in water, suspended particles and sediments.

Metal concentrations in body tissues of mollusk in the bay were related to metal levels found in the three environmental compartments (water, suspended particles and sediments). Two approaches were applied: (i) simple linear regressions were constructed between metal concentrations in the tissues and concentrations in either water suspended particles or sediments. These regressions were performed for four species (*T. fenestratus, A. scapha, M. philippinarum and Strombidae*), which were present at more than three stations. (ii) The second approach was to examine the relationships further by applying a multi-linear regression model with dissolved, suspended particles and sediment metal concentrations as variables. The model was first applied to individual species for each element and later on all the species combined. Both regression analyses were performed with the computer software STATISTICA 6.0.

B. Metal concentrations (dissolved) in seawater

B.1 Mercury and gold

In this section we compared dissolved metal concentrations among the 10 sampling stations. The highest mercury concentration in water was observed at Station 1 with 8.91 µg/l and Station 6 with 12.29 µg/l. High concentrations were also noted in Stations 3 to 5 (6.32 µg/l, 5.40 µg/l, and 7.16 µg/l respectively). Most of the stations that showed high mercury concentration also had high gold content except for Stations 7 and 8 which showed the opposite. Compared with dissolved mercury measured earlier in the bay, our results are generally higher by about an order of magnitude. It is unlikely that these results are erroneous as the results for the reference seawater were in agreement with certified values. Such high dissolved mercury concentrations in mining areas in the Philippines are common. In a study by Williams et al. (1995) in a nearby mining area in the eastern part of Mindanao (Philippines), dissolved mercury ranged between 0.21 - 2906 µg/l within 1 km from the mine fields, and samples taken distant from the site showed concentration range of 0.14 µg/l and 2.84 µg/l. These values are comparable to our study area. A year later Breward (1996) did a follow-up study from Mamunga River, near the mining camp and noted a maximum Hg concentration of 1.539 µg/l. When compared with other parts of the world, our results are higher than what is reported by Kannan et al. (1998) for estuaries in South Florida but lower than in the coastal waters of North Lebanon (Shiber et al., 1978).

B.2 Other metals

For most of the other metals, Station 4 showed the highest concentration (715.41 µg/l for Al (122 µg/l), Fe (63.8 µg/l), Mn (38.9 µg/l), Zn (51µg/l) except for nickel which was highest in Station 7 (27.44 µg/l).

C. Heavy metal concentrations in suspended particles

C.1 Mercury and gold

Mercury and gold concentrations measured in the bay ranged between 3 - 13 µg Hg/g and 1 - 6 µg Au/g dry weight, respectively. The highest mercury and gold concentrations were recorded at Station 4. Other stations, which showed high Hg and Au concentrations, were Stations 1, 2 and 5. These were stations located in the proximity of the mining area. When tested to see whether there were significant differences among all stations, the results from Kruskal-Wallis test showed very high significant differences ($P < 0.001$) all stations combined.

C.2 Other metals

Other metals such as Cd, Co, Cu, Fe, Ni, Pb, and Zn were highest in Station 4 while Ag and Cr, which were highest in Station 6. There are few studies on metal concentrations in suspended particles particularly places close to gold mining fields (Tessier et al., 1984, Fileman et al., 1991).

D. Metal concentrations in the bottom sediments

D.1 Mercury and gold

Sediments serve as sinks for heavy metals and for metals with high affinity for organic particles such as mercury will be elevated in organic rich sediments (Skei, 1978; Luoma, 1989). Generally, as grain size decreases, the concentration of metals adsorbed onto sediments increases, particularly across the transition zone from silt to clay (< 4 – 63 µm) (Deely et al., 1992). Except for Station 8, which exhibited the highest Hg and Au contents (58.15 µg/g & 254.29 µg/g respectively), most of the stations with smaller particle size showed higher concentrations for Hg and Au. Gold was also highest (254.3 µg/g) at station 8 followed by station 4 (21.4 µg/g).

Stations 2, 9 and 10 also serve as monitoring stations for neighboring region (DENR-X) and the results they obtained for their June 1999 sampling (Manzano and Daitia, 1999) were about two orders of magnitude higher than our October samples. This difference may be a result of differences in procedures for the extraction of total metals from the sediments used. In our study, total metal concentrations in the sediments were measured according to the procedure reported by Tessier et al. (1979) and Bervoets et al. (1998). Mercury in river sediments from Eastern Mindanao (Williams et al., 1995) was in the range of 0.02 mg/kg and 23 mg/kg within the mining site, five times higher than what this study measured. Compared with other studies Sasamal et al. (1987), Craig and Moreton (1983), Park and Curtis (1997) recorded similar values.

D.2 Other metals

Even for the other metals, Station 8 had the highest concentration, except for lead which was high in Station 4 (331 µg/g) and Station 5 (286 µg/g). Hamilton (1989) reported similar concentrations for cadmium in the Northeast Pacific.

E. Heavy metal concentrations in invertebrate species in the bay

From the total of 10 species collected during our sampling exercise, only four species were present in more than 3 stations. The other species were either present only at one or two stations. Metal concentrations varied from one station to other and with species.

E.1 Mercury and gold

Among the sampled species in the bay, *Circe scripta* in Station 2 had the highest mercury content, 9.2 µg/g, followed by *Placuna ephippium* also in Station 2 with 4.32 µg/g, *Tectus fenestratus* and *Strombus sp.* in Station 3 with 3 µg/g and 2.74 µg/g respectively. Other species that showed high mercury concentration include *Tectus fenestratus* from Station 2 with 2.72 µg/g; *Anadara scapha* in Station 4 with 1.66 µg/g; and *Littorina scabra* from Station 6 with 1.58 µg/g. The rest of the species had less than 1 µg/g concentration.

For gold, *Isognomon isognomum* in Station 5 had the highest tissue concentration, 5.78 µg/g. Other species like *Modiolus philippinarum* in Station 10, *Isognomon isognomum* in Station 4, *Tectus fenestratus* in Stations 3 and 8 showed greater than 1 µg/g. The rest of the species in various stations had less than 1 µg/g.

When comparing the results of the present study with earlier study by Bayaron et al. (1997) it seems that there is a decrease in the concentration of mercury in the mollusc species in the area. The highest reported concentration was 2.63 µg/g for *Mytillus sp*., which were collected within Station 4 of the present study. The result we obtained from other bivalves collected in Station 4 had on the average 1.16 µg/g. These results are outside the standards set by the Philippine government (0.5 µg/g). However, results from this study are comparable with other studies elsewhere (Denton and Breck, 1981; Meyer et al., 1998, Williams et al., 1999).

E.2 Other metals

The following species were observed to have high concentrations for the other metals considered in this study: *Circe scripta* in Station 2 for Ag and Co; *Placuna ephippium* in Station 2 for Cd; *Isognomon isognomum* in Stations 4 for Cu; *Tectus fenestratus* in Stations 2 and 3 for Cr and Fe respectively; *Nerita planospira* for Ni and *Littorina scabra* for Pb all in Station 6; and *Isognomon isognomum* in Station 4 for Zn.

These results for Ni and Cd are comparable to other studies by Paez-Osuna et al. (1991) while Zn was three times lower than reported by Lopez et al. (1990). Lobel et al. (1982) reported much higher concentration of Cu compared to those found in all the gastropods studied in the bay. His group also found higher Fe content compared to what was detected in *Tectus fenestratus*, which comes from the same order but Zn was comparable to what was measured in this study for *Modiolus philippinarum* which comes from the same genus.

F. Are metal concentrations in organisms correlated with levels measured in water, suspended particles or sediments?

In our study we used linear regression analysis to determine the fraction of metal measured in four mollusk species that can be described by levels found in the three compartments (water, suspended particles and sediments).

F.1 Total Mercury

Mercury tissue concentration showed a linear relationship with all three compartments in only one species (*T. fenestratus*). There were also significant linear relationships between tissue concentrations in *A. scapha* and suspended particles and sediments. However, linear regression models found relationships between tissue concentrations and all three compartments except for *A. scapha* and with sediments for *M. philippinarum* and *Strombus sp*. It is often reported that metal concentrations in tissues of many mollusk species reflects levels found in the environment (Goldberg, 1975; Philips, 1976; Cossa, 1988; Fowler, 1990).

Consequently, linear relationships between environmental and tissue metal concentrations are usually expected within a certain range. But beyond a certain environmental concentration, metals in tissues of organisms tend to reach asymptotic level (Pentreath, 1973; Riisgard et al., 1997; Wang et al., 1997). In addition, this relationship can be modified by a variety of environmental and physiological factors such as salinity, metal speciation, physiological condition body size, sex, species, tidal position and season (Philips, 1997; De Kock and Kramer, 1994; Fisher et al., 1996; Vercauteren and Blust, 1996; Muhaya et al., 1997).

When a multiple linear regression model was applied to mercury concentrations in all the species (10) studied, we observed significant correlation relationship with dissolved mercury and suspended particles ($p<0.0001$). But no significant relationship with either suspended particles or sediment were found. From the coefficient of determination values (r^2) the variation in mercury concentration in the tissues that can be described by dissolved mercury were however very small. The explanation for the unexplained mercury concentration in the tissues has to be related to the effects of factors mentioned above.

Correlation of tissue concentrations with either suspended particles or bottom sediments as recorded in *A. scapha* and *T. fenestratus* are consistent with general knowledge that sources of heavy metals such as mercury for marine invertebrates include particulate bound metals (Luoma, 1989; Fisher et al., 1996; Riisgard et al., 1987; Sigel and Sigel, 1997; Prudente et al., 1997; Olvero et al., 1998; Williams et al., 1999).

The consequences of mercury transformation and speciation in the sediment and tissues may have significant effects on mercury partitioning and eventual accumulation in the organisms. Due to absence of measurements of methylmercury we are not able to discuss in details. However, it is known that mercury in inorganic form when released into the marine environment is transformed into different species of organic mercury by sulfate-reducing bacteria in the sediments (Sigel and Sigel, 1997; Horvat et al., 1999) and naturally by methylation in organisms. In most organisms mercury exists as organic mercury, in fish nearly 90% of mercury is MeHg (Sigel and Sigel, 1997).

F.2 Gold

Gold which is the principal product of the mining activity in the study area also showed relatively elevated values in the bay. In all four species studied, tissue concentrations showed relationships with dissolved gold. However, only one species showed a significant linear correlation with dissolved gold. From the linear regression for gold concentration in the bivalve *M. philippinarum* about 25% of tissue concentrations could be described by the dissolved gold concentration.

Overall, gold concentrations in the tissues of species studies showed some relationship with water and suspended particles. This indicates that the sources of gold for these species in this particular area is both from dissolved and suspended particles. From the calculated coefficients of determinations (multiple linear regression), water is about 10 times higher than suspended particles implying that dissolved gold is relatively more important for accumulation in the organism.

F.3 Other metals

Generally, for all the dissolved metals measured there were significant correlations with tissue metal concentrations. However the variances that could be explained by dissolved fraction were generally low (<50%). When all species are considered, all metals measured except Fe, Zn, and Hg showed no correlations between tissues and suspended particles.

G. Associations of heavy metals in the soft tissues of four species of invertebrates

We studied the correlations of 12 elements measured in four species. No correlations among most elements were observed in all species except in the bivalve, *A. scapha* where most elements showed positive correlations with each other. When looking at metal concentrations in the suspended particles, nearly all metal (except Ag and Zn) showed strong positive correlations. For most elements, there were no correlations in the tissues of other three species and in water as well. Without the influence of other factors the positive correlations observed in suspended particles would be expected to result in similar patterns in the organisms. However, this was not generally the case for most species. Probably this is an indication that the contribution to metal accumulation from suspended particles in the bay is minimum. It is reported in literature that the importance of particles in metal uptake varies with environmental conditions, species and elements (Bryan, 1979; Luoma, 1989; Andersen et al., 1996; Fisher et al., 1996; Riisgard et al., 1987; Wang et al., 1997). Another observation was the absence of consistent correlations between essential elements, or competition with non-essential elements. These correlations did not match with correlations in either water or suspended particles. It is not clear for now what kind of processes or mechanisms control these interactions. It is also possible that processes that affect these kinds of interactions are external (Elliott et al., 1986). What we can say from our results is that interactions among heavy metals in body tissues seem to vary from species to species and environmental conditions.

VII. Conclusions

Mercury concentrations in the three abiotic compartments are higher than what is observed in less contaminated areas, but are similar in concentration, for instance in water, to what is observed in other gold mining areas in other parts of the Philippines.

All the ten sampling sites in Murcielagos bay exceeded the allowable Hg limit for seawater (2ppb). Stations nearest in proximity to the mining area tend to acquire higher concentrations in all the compartments (water, suspended particles, and sediment). Among the species, only Species 3, 8 and 10 were within the allowable limit (0.5 ppm). Species 1 4, 5 and 7, have as much as a factor of 5 more than the allowable limit. Stations 1, 7-9 had organisms just below the tolerable concentration among the stations.

From regression analysis, this study has shown that mercury concentration in tissues of 3 out of 4 species studied correlated with dissolved mercury and suspended particles, and no correlations were observed with either suspended particles or sediments.

VIII. Recommendation

People living around Murcielagos bay depend so much on the seafood in the area for their daily subsistence and considering the effects of metal concentrations such as mercury obtained from this study, it appears that such dependence pose a great risk.

It is perceived that the findings of this study will enable both the DENR together with the Local Government of Sibutad and the province of Zamboanga del Norte, to come up with safety measures for the coastal residents and the small-scale miners for better management of the bay.