LEAD AND ZINC CONCENTRATIONS IN THE VENUS CLAM, *PAPHIA TEXTILE* (GMELIN) IN SOFT-BOTTOM COMMUNITIES OF KATIPUNAN AND ROXAS, ZAMBOANGA DEL NORTE: AN INDICATOR OF HEAVY METAL CONTAMINATION

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ABSTRACT

Infaunal bivalve communities are known to pose potential public health risks as they are bioaccumulators that may be regularly harvested for human consumption. To assess a possible health risk of heavy metal contamination from factory waste output, samples of the locally-consumed venus clam, *Paphia textile* were collected from nearshore soft-bottom communities of Katipunan and Roxas Zamboanga del Norte. They were analyzed for lead and zinc concentrations. The highest levels of lead (mean ± SD = 4.43 ± 1.23 mg/kg) and zinc (mean ± SD = 30.09 ± 9.40) were obtained from the Tuburan site, located nearest the Southern Island Oil Mill Port Area. The concentration levels from our sampling sites indicated that the coastal waters of Katipunan and Roxas, Zamboanga del Norte are contaminated with both lead and zinc. Continued consumption of the clams will lead to biological magnification in human populations, thus posing an unquantified health risk to local coastal communities consuming these animals.

Introduction

Metals are introduced naturally into the aquatic ecosystem as a result of weathering of rocks and volcanic eruption, or from anthropogenic sources such as municipal, industrial, and agricultural wastes, airborne particles emitted from combustion engines, and runoff from mining and highways. Point sources include metal processing plants, dye-making firms, and paper mills. Unlike organic pollutants, heavy metals are not broken down by bacteria. Consequently, they may persist in the water or bottom sediments for many years and eventually enter human food chains via marine animals or plants that consume or absorb them from the environment. This process, known as bioaccumulation, involves sequestering toxic compounds in body tissues by organisms which consume the toxins without detoxifying or excreting them. As these organisms are consumed by animals (such as humans) higher in the food chain, the effects of the toxins are magnified. One of the best-documented examples of the effects of bioaccumulation is Minamata Disease, the poisoning of a large segment of a Japanese coastal population by mercury from pollution effluent in the 1950s. The effects were devastating, affecting an as yet unquantified number of people (Ui, 1992).

Metals such as manganese, copper, iron, and zinc are micronutrients with essential roles in biological systems. Others, such as lead and mercury, are not required even in minute amounts by any organism. However, regardless of whether or not they are essential, metal accumulation can pollute marine ecosystems and can pose an often unquantified health risk. Zinc is a micronutrient associated with enzymes involved in DNA replication and protein synthesis. Hence, it is critical for growth and development. It can, however, reach pollution-level concentrations in water and sediment. Zinc is used in metallurgy, plutonium production for nuclear reactors, and manufacturing. Limited data show that it is processed from tissues relatively slowly by bivalves (Phillips, 1980). When ingested by humans in excess amounts, it may cause diarrhea, abdominal cramps, and vomiting within three to ten hours.

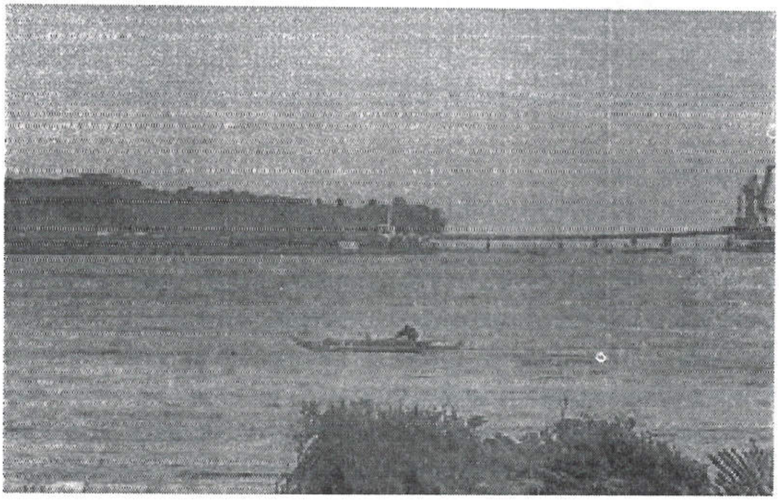
On the other hand, lead compounds are highly toxic, particularly to children (Barry, 1975, 1981; Baghurst *et al.*, 1987; Batuman *et al.*, 1981; Kaul *et al.*, 1999). The US Center for Disease Control considers lead poisoning a major environmental health threat to children (http://epa.gov/waterscience). Most problematic sources of lead are found in home products such as paint, but it is also found in petroleum products, which may end up in coastal waters from runoff or discharge. The human nervous system is particularly vulnerable to lead poisoning, which is why children, whose nervous systems are rapidly developing, are the most susceptible to encephalopathy with high levels of lead exposure (ATSDR, 1999; Fulton *et al.,* 1987; Hawk *et al.,* 1986). Exposure has also been linked with hypertension, reproductive toxicity (Alexander *et al.,* 1996), and developmental defects (Baghurst *et al.,* 1987). It inhibits enzymes critical to the synthesis of heme, causing a decrease in blood hemoglobin. Alexander *et al.* (1996) and Gennart *et al.* (1992) suggested that occupational exposure to lead decreases sperm count and motility, and increases abnormal sperm frequencies (Alexander *et al.,*1996). Thus, sub-lethal long-term exposure can cause serious physiologic effects, but low levels of exposure have also been shown to have many subtle health effects in studied populations. Hence, it is important to identify and quantify all possible sources of lead contamination.

The Venus clam *Paphia textile* is a filter feeder of the family Veneridae. It has a solid, equivalve, inequilateral shell. Its color is externally beige to pale yellow with a characteristic zig-zag pattern in brown (Fig. 1). It commonly burrows on offshore shelf bottoms (Barash and Danin, 1992). *P. textile* has been harvested and consumed by residents of Katipunan and Roxas, Zamboanga del Norte for a decade. Pails of this clam are delivered and sold daily in the two municipalities, as well as in the public market of Dipolog City. Venus clams are collected 200 m from shore at a depth of 18 m (Fig. 2). Traditionally, the clams were harvested by hand from the soft-bottom, 10 cm deep. Currently, a device developed by local fishermen eliminates the necessity of free-diving. The device resembles a grab sampler which scoops up a volume of mud from which the clams can be removed on board a boat.

Like other benthic filter feeders, *P. textile* can be used as a biological indicator of metal pollution. Generally, clams readily accumulate metals by direct transport of water across their gills and from ingestion of suspended particles and bottom sediments and are, therefore, considered to be reliable indicators of heavy metal pollution (Phillip, 1980; Boisson *et al.,* 1998). They are

Figure 1. Photograph of *Paphia textile* clams harvested from the nearshore benthos of Zamboanga del Norte.

Figure 2. Photograph of a local fisher harvesting *P. textile* from the nearshore Tuburan station; the wharf is visible in the background



known to be tolerant to high trace metal concentrations; hence, their metal body burdens can reflect the contamination history of an environment. Data suggest high variation in the rate at which metals may be stored or eliminated both between species and between the metals themselves within species (see review in Denton *et al.,* 1999). As little is known regarding heavy metal toxicity as a health risk for coastal communities in the Philippines, and few Philippine bivalve species have been studied, people regularly consuming these clams are facing an unquantified health risk.

An uncharacteristic black coloration on the clam shells (Fig. 1) triggered this preliminary investigation to determine whether *P. textile* inhabiting the coastal substrates of Katipunan and Roxas, Zamboanga del Norte are contaminated with lead and/or zinc. The presence of both an oil mill and a wharf in the area from which clams are harvested represent possible point sources of pollution. Heavy metal bioaccumulation in the shellfish was suspected because the most probable sources of contaminants in the area (the mill and the wharf) produce or discharge byproducts containing lead (from gasoline) and zinc (from metallurgical operations). At this preliminary stage, water and sediments were not tested as the primary goal was an immediate quantification of a possible public health risk.

Methods

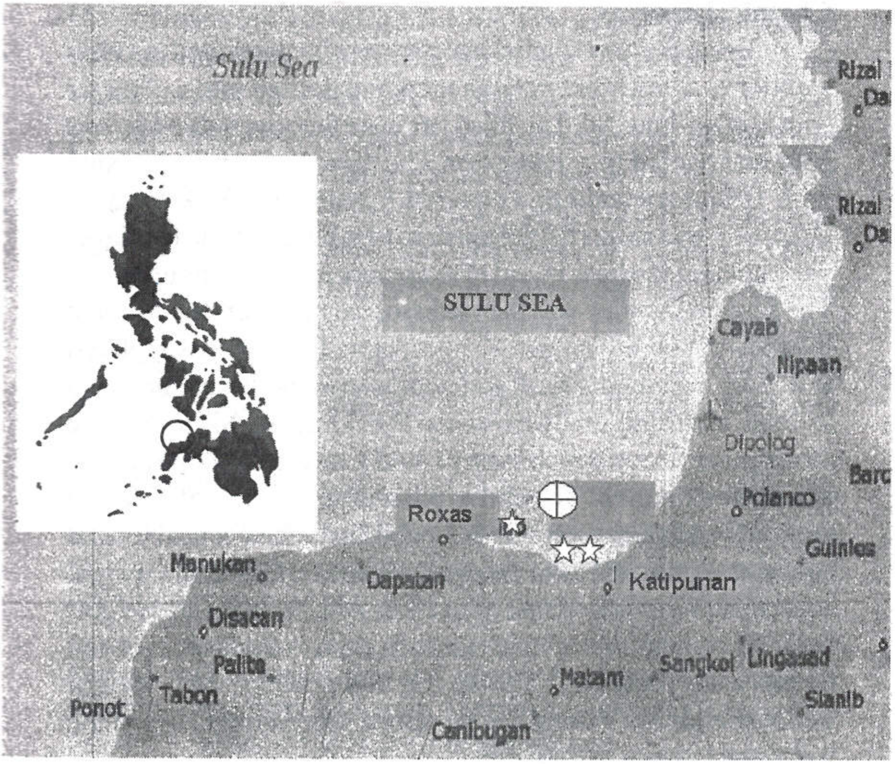
Sampling sites

Sampling was conducted in nearshore sandy/muddy substrates in three coastal barangays: Tambo and Tuburan of Katipunan (8° 30' N; 123° 17' E) and Irasan, Roxas (8° 31' N; 123° 13' E) in Zamboanga del Norte (Fig. 3).

Clam collection and preparation

Samples of *P. textile* were collected on January 30, 2004 from the three sampling sites, 200 m from shoreline at a depth of 9 fathoms in three replications per site, with nine clams per replication (a total of 27 clams per site). Samples were packed in

Figure 3. Map of the study area, showing the three sampling sites in relation to suspected point sources of pollutants.



plastic bags and immediately transported to the Jose Rizal Memorial State College-Katipunan National Agricultural School Chemistry Laboratory for tissue analysis preparation. The clams were thoroughly cleaned by brushing the shells with water and allowed to depurate for at least three hours to remove the silt and sediment from the tissue. The shells were carefully opened to remove the tissue. The tissues were packed in plastic bags and placed in a styropore box with ice, which was immediately shipped to Silliman University Chemistry Laboratory for spectrophotometry.

Chemical analysis

Tissue from each individual clam was homogenized in a glass blender to a paste-like consistency, and poured into a glass jar with a teflon-lined lid. The filled jars were then oven-dried for one hour and cooled in a dessicator. The dried tissue was digested with 10% nitric acid in a covered Erlenmeyer flask for 3 hr. Digestion was extended for another 3 hr, but this time the flasks were opened to allow liquid to evaporate and the residue to dry. The air-dried residue was then redissolved in a 3% nitric acid and filtered through Whatmann 42 filter paper. The filtrate was placed in a 25 ml volumetric flask and diluted to mark. It was subjected to lead and zinc analysis using Pye Unicam SP 9 Atomic Absorption Spectrophotometry (AAS), using the flame atomic absorption method. The above procedure was repeated for all replicates and all stations. As most published values of heavy metal concentrations refer to wet weight, we converted our dry weight concentrations to wet weight equivalents by subtracting dry weights from the original wet weights for each clam to determine a mean tissue water content of 80% for this species. Dry weight concentrations of Pb and Zn, therefore, represented 20% of the wet weight values in fresh tissue.

Results

The average concentrations of lead and zinc in *Paphia textile* are presented in Table 1.

Table 1. The range and mean concentrations (ìg/g dry wt) of Lead (Pb) and Zinc (Zn) in *Paphia textile* individuals collected from three sampling stations. Mean ± SD (upper values); Range (lower values); n=9 samples per site.

METAL	TAMBO	TUBURAN	IRASAN
Pb	4.18 ± 0.80 3.41 - 5.01	4.43 ± 1.23 3.01 - 5.15	3.92 ± 1.38 2.97 - 3.28
Zn	15.11 ± 5.0 9.49 - 19.08	30.09 ± 9.40 20.97 - 39.15	11.66 ± 2.50 8.78 - 13.25

As shown, samples collected from Tuburan (Station 2) registered the highest concentrations of lead and zinc. Samples taken from Irasan (Station 3) showed the lowest concentration for both metals. No significant difference was observed between stations for lead concentration (Fig. 4; ANOVA F (2,6) = 0.146, p=0.867). However, significant between-site differences were observed for the amount of zinc in tissues (Fig. 5, ANOVA F (2,6) = 7.221, p=0.025). Post-hoc comparisons indicated that zinc levels of Tuburan clams were significantly higher than those from Irasan; Tambo values were intermediate between the two, and the differences were not significant. It should be noted that Irasan is situated farthest from the oil mill and wharf area (Fig. 3).

Converting our values to wet weight concentrations allowed us to compare levels found in our study sites with other published concentrations of Zn and Pb in selected bivalve species. These values are presented in Table 2.

Figure 4. Concentration of Lead in *Paphia textile* samples collected from three stations in Katipunan and Roxas Zamboanga del Norte. Mean ± SD; n=9 clams per station.

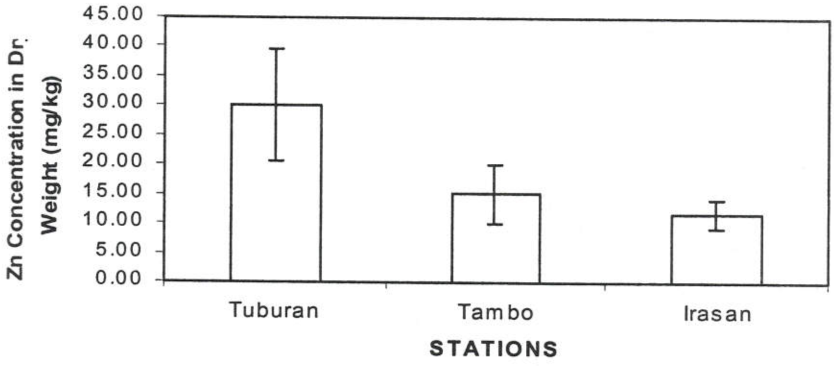
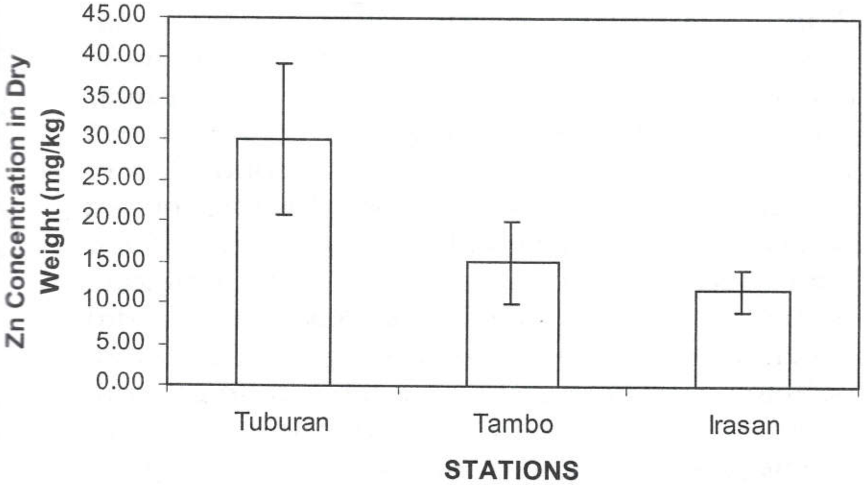


Table 2. Comparisons of the range of concentrations of lead and zinc in selected bivalve species (ig/g wet wt).

Species	Metal	Location	Source	
	Pb	Zn		
Paphia textile	**0.99-1.03**	**1.76-7.83**	**Zamboanga del Norte**	**This study**
Chama iostoma	<0.9	41.0-164	Great Barrier Reef, Austr	Burdon-Jones & Denton 1984
Chama brassica	<0.3-2.0	79.4-387	Apra Harbor, Guam	Denton *et al.* 1999
Crassostrea gigas	0.3	80.5	Hong Kong	Phillips *et al.* 1982
Saccostrea amasa	<0.3-1.8	1163-2443	Australian coastal waters	Burdon-Jones *et al.* 1979
Saccostrea cucullata	<0.2-1.4	1012-2752	Australian coastal waters	Burdon-Jones et al. 1979
Saccostrea cucullata	<0.3-1.1	2262-4722	Apra Harbor, Guam	Denton *et al.* 1999
Spondylus ducalis	3.7-7.5	175-518	Great Barrier Reef, Austr.	Burdon-Jones & Denton 1984

Figure 5. Concentrations of Zinc in *Paphia textile* samples collected from three stations in Katipunan and Roxas, Zamboanga del Norte. Mean ± SD; n=9 clams per station.



Discussion

The highest concentrations of lead and zinc were obtained in Tuburan, which is located nearest the Southern Island Oil Mill Port Area (Fig. 2 & 3). In general, lead levels were not significantly different between sites, though zinc levels varied greatly. Zinc concentrations were significantly higher in Tuburan, and similar for Tambo and Irasan, though these two sites are not adjacent (Fig. 5). Undoubtedly, the large variation in zinc concentration between individual clams accounted for the lack of significance in concentrations between Tambo and Tuburan, even though the sites are close and both are within the proximity of the oil mill (Table 1, Fig. 3). Denton *et al.* (1999) notes considerable between-species variation in metal contents, with zinc being particularly variable.

In interpreting our data to identify a possible health risk, it is important to consider evidence from the literature. The selected studies presented in Table 2 indicate several points. First, heavy metal concentrations can vary greatly within a single species between different sites that have similar levels of pollution (see values for Zn concentrations in *Saccostrea cucullata*, Table 2). Second, closely related species can also vary considerably, and not necessarily in a predictable way; *Chama iostoma* contained much more lead, but much less zinc within the pristine Great Barrier Reef site than did specimens of *C. brassica* coming from the more polluted Apra Harbor, Guam (Table 2). In general, interpreting a lead contamination risk using bivalves can be problematic, as available evidence suggests that bivalves may not be particularly sensitive to lead concentrations in the environment (Denton *et al.,* 1999). However, in general, higher levels of lead in bivalve tissues indicate higher levels of organic lead in the environment. As inorganic lead is almost insoluble in water (Moore, 1991), it can be assumed that high lead concentrations in tissues are from particulate organic forms from industrial and mining activities settling into the substrate. Our values for lead concentration were higher than the upper range of values reported from known polluted waters (Apra Harbor and Hong Kong) but considerably lower than those reported from the Great Barrier Reef (Table 2). This could represent interspecific variation in lead uptake. Little is known regarding sensitivity of *Paphia textile,* and lead concentrations in the water column and substrate were not obtained, making a quantitative assessment of lead pollution difficult. However, considering that *P. textile* is regularly harvested and consumed as food, our data suggest that lead bioaccumulation in human populations consuming this clam is a possibility. Our evidence definitely suggests that a more in-depth study is needed.

Our zinc levels, on the other hand, were considerably lower than those found in other species (Table 2), though it is known that zinc levels fluctuate widely between species (Denton *et al.*, 1999). Oysters (*Saccostrea* spp.) are known to be very sensitive bioindicators of Zn and Cu pollution, but no information exists regarding *Paphia textile* sensitivity. However, our evidence suggests that Zn concentration levels probably do no constitute a health risk at this time.

Our data suggest that both the oil mill and the wharf could be possible sources of both lead and zinc contamination, as the site nearest these structures contained the highest levels of both metals. Unregulated fuel discharges of cargo vessels docked at the wharf could be a primary source of input. Such organic lead compounds are particularly toxic to most life forms (Denton and Burdon-Jones, 1986). In addition, little is known about the composition of the oil mill wastes and it is not known if any pollution control practices are in place. As shown in the map, Tambo and Tuburan are located inside a cove containing these possible point sources (Fig. 3), while Irasan is located on the outer coast. Local circulation patterns could contribute to the transport and deposition of pollutants; Irasan is better flushed and more exposed to open water. This may result in less exposure to heavy metal pollutants deposited from point sources. However, to establish the actual sources of these contaminants, a more focused and in-depth study is required.

This preliminary investigation suggests several lines of inquiry to determine the exact nature and extent of pollution in this area. A study of the surface water, sediments, and infauna would allow determination of correlations between the concentration levels and distance from suspected sources, as well as the extent of geographic contamination. Identifying general sources of pollution, such as municipal waste dumps, sewage outfalls, and the oil mill itself would elucidate sources of these heavy metals. Furthermore, our results suggest the possibility that there may be other metals and other species that should be considered. To assess public health risks, other harvested species (benthic invertebrates, coastal fish, macroalgae) should be surveyed with a broader assay of contaminants.

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