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Mercury Levels in Sediments and Mangrove Oysters, *Crassostrea rizophorae*, from the North Coast of Villa Clara, Cuba

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Abstract Total mercury levels were quantified in sediments and oyster tissues (*Crassostrea rizophorae*) from the Sagua la Grande River estuary and offshore mangrove keys 19 km downstream of a chlor-alkali plant (CAP) in Villa Clara, Cuba. Relatively elevated total mercury levels were found in sediments from the estuary itself, ranging from 0.507 to 1.81 μg g^{-1} dry weight. However, levels were lower in sediments from the keys farther from the estuary. Oyster mercury levels were always acceptable for human consumption, although levels significantly correlated in sediments and oysters across sampling sites ($p < 0.05$), which suggests that mercury from the CAP is impacting coastal water quality conditions.

Keywords Mercury · Sediments · Oysters (*Crassostrea rizophorae*) · Sagua la Grande River

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Large areas of the north coast of Villa Clara Province in Cuba are covered by mangroves (*Rhizophora mangle*) that form natural internal and external keys. Freshwater outputs from rivers that feed these areas, such as Sagua la Grande River, encourage the development of banks of "mangrove oysters" (*Crassostrea rhizophorae*) and harvesting oysters is a major fishing activity. However, oyster catches from the mangrove keys have declined since the mid 1980 s, probably due to salinity increases resulting from damming of local rivers, but also due to pollution from land-based sources that have reduced water quality over recent years (Díaz-Asencio et al. 2009). One major pollution source is the chlor-alkali plant (CAP) on the Sagua la Grande River located 19 km from the coast, which uses mercury (Hg) in electrolytic cell manufacture.

CAPs are among the largest land-based sources of Hg to the environment (UNEP 2002). This CAP began operations in the 1980 s; however, investigations found incipient total mercury (tHg) contamination in the river estuary downstream of the CAP. As such, its treatment plant was redesigned in 1990 s and wastewaters were then discharged directly into Sagua la Grande River. Subsequent studies on the vertical distribution of tHg in estuary sediments, using Pb-210 dating, found progressively increasing tHg levels in sediments since 1978, reaching a maximum of 2.68 ± 0.13 μg g^{-1} in about 1990 (Díaz-Asencio et al. 2009), confirming past anthropogenic causes. However, recent tHg analysis in river fish found tissue levels above recommended limits by the World Health Organization (De la Rosa et al. 2009a, b) and new studies were suggested. In particular, previous work did not examine tHg levels in organisms that reside on the coastline, especially within mangrove keys that retain the active oyster fishery. Therefore, this study was undertaken to quantify tHg levels in estuarine and offshore oysters and sediments to assess

whether influence of the CAP facility extends to the coastline where important marine species also might be impacted.

Materials and Methods

The study area was the north coast of Villa Clara province, Cuba bounded by the following: 23° 01′ 45″N and 80° 05′ 01″W to 22° 48′ 07″N and 79° 42′ 18″W (Fig. 1). Ten sites were sampled in two regions: the Sagua la Grande River estuary near the town of Isabela de Sagua and the coastal zone within local mangrove keys. Both regions are actively fished areas, which include banks of natural and artificial mangrove oysters. Sampling was performed in December 2009 and April 2010, coinciding with the dry and rainy seasons in this area.

Typically, surface sediments were collected to a depth of 10 cm using the Van Veen grab system (total volume of 250 cm^2). Three independent samples were collected per site, taken randomly over an area of about 100 m^2. Dredged contents of the individual samples were placed onto a tray and then homogenized for each site. The samples were then transferred to pre-washed plastic bottles for return to the laboratory and storage at 4°C prior to analysis. In the laboratory, samples were air-dried; stones, shells and other oversized materials removed; and then blended and sieved prior to further processing. Only the <125 μm fraction was used for tHg analysis. Moisture was determined at 105°C using a separate aliquot and all tHg levels are reported per dry weight (DW) of sediment.

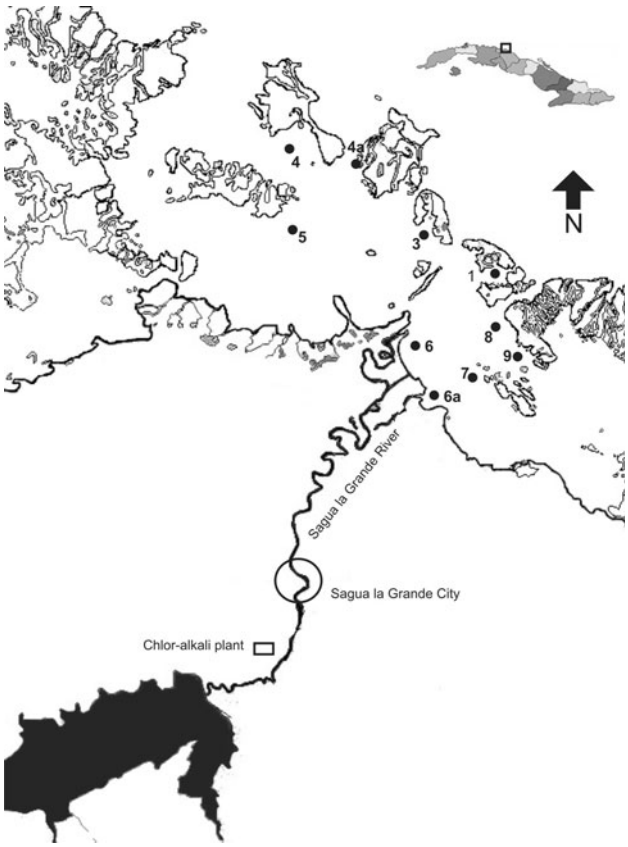

Fig. 1 Sampling sites near the mouth of the Sangua la Grande River relative to the location of Sangua la Grande City and the Chloro-alkali plant (CAP). The CAP facilty is approximately 19 km from the coastline and the map is not to scale

Oysters were randomly collected in parallel with sediment sampling, typically harvesting individuals directly from mangrove roots or artificial collectors at local oyster farms. Individual oysters were measured from the umbo to the posterior edge of the shell and separated in the field by size into three groups of about 25–30 individuals each. The oysters were rinsed with seawater and stored immediately on ice in polyethylene bags. Upon return to the laboratory, the shells were opened using a stainless steel knife and the full contents removed, including water and tissues, into individual clean glass bottles. Samples were weighed fresh and then frozen at −20°C. They were then lyophilized, weighed again, and homogenized with an agate mortar in preparation for tHg analysis.

Mercury analysis was performed using a Direct Mercury Analyzer (DMA-80 Milestone, Italy) following EPA Method 7473. Typically, 40 mg of sample was placed into the capsule crucible in the furnace and thermally decomposed in an oxygen flow. Mercury vapors were trapped in an Hg amalgamator, which was heated to 650°C and released as Hg^0. Actual Hg content was quantified using atomic absorption spectrophotometry at 254 nm.

Detection and quantification limits (0.0002 and 0.0004 μg g^{-1}, respectively) were determined using 17 blanks under the same test conditions as the test samples. Accuracy and precision were obtained by measuring tHg levels in three Certified Reference Materials (CRM); i.e., IAEA-433, IAEA-407 and NIST 1645. No statistically significant differences were found ($p < 0.05$) between measured mean values and defined values for each CRM ($n = 6$). Analytical precision was defined by coefficient of variation, which was always less than 12%. All two-sample and other statistical analyses were performed using SPSS Version 17.

Results and Discussion

Levels of tHg in surface sediments ranged from 0.032 to 1.81 μg g^{-1} DW (mean = 0.375 μg g^{-1} DW), which are summarized in Table 1. Since Cuba has no established sediment quality guidelines, US National Oceanic and Atmospheric Administration (NOAA) guidelines were used for comparative evaluation (PTI 1988). Mercury levels varied across sites, ranging from "uncontaminated"

Table 1 Levels of tHg in the sediments from Sagua la Grande estuary and mangrove keys in the vicinity of oysters

Sampling stations	tHg (μg g^{-1} DW)	
	December 2009	April 2010
1	0.165 ± 0.063	0.160 ± 0.045
3	0.143 ± 0.016	0.135 ± 0.020
4	0.160 ± 0.008	0.109 ± 0.005
4a	0.172 ± 0.029	0.032 ± 0.004
5	0.117 ± 0.023	0.057 ± 0.004
6	***1.81 ± 0.530***	***1.62 ± 0.079***
6A	***0.507 ± 0.357***	***1.07 ± 0.332***
7	0.205 ± 0.031	0.172 ± 0.007
8	0.196 ± 0.024	0.178 ± 0.038
9	0.265 ± 0.163	0.132 ± 0.009
Mean tHg level	0.374	0.384
(Range)	(0.117–1.81)	(0.032–1.62)

Bold italicized stations have sediment Hg levels that exceed the probable effects concentrations (PTI 1988)

to "highly contaminated" according to guideline definitions. The highest tHg levels were found in sediments from stations 6 and 6A near the river estuary with levels of 1.81 ± 0.53 and 1.07 ± 0.33 μg g^{-1}, respectively. These results are consistent with previous work (Díaz-Asencio et al. 2009) where tHg levels ranged from 0.25 μg g^{-1} (before 1978) to 1.84 μg g^{-1} (in 2003) with a maximum of 2.68 μg g^{-1} (in the early 1990 s). Although values from Díaz-Asencio et al. (2009) and those from the current work are not exactly comparable due to different sampling methods, both sets of results imply Hg contamination in the estuary, including levels that exceed Probable Effects Levels (PEL) (i.e., 0.696 μg g^{-1}) and suggest a high probability of toxic effects in resident organisms (PTI 1988).

It is noteworthy that tHg levels are similar to observations have been made in other coastal areas with extensive industrial activity (UNEP 2002). For comparison, data from other locations are provided in Table 2, which further show CAP facilities as a major source of coastal Hg pollution. Sediment tHg levels in the Sagua la Grande River estuary are high relative to other Cuban sites (Gonzalez 1991) except Havana Bay that has extensive industrial and urban development. This confirms that the Sagua la Grande CAP facility is very large source of Hg contamination, which has been recognized previously (UNEP 2002).

Mercury is clearly high in the river estuary, but actual mechanisms of transport from the CAP site are not obvious given the distance of the facility from the coast. However, Hg readily binds to small particles with high organic content, which are often found in tropical rivers. Suspended particle-borne Hg transport is plausible here and is consistent with the fact that the sediment deposition sites farthest from the estuary have the lowest tHg levels, ranging from 0.032 to 0.205 μg g^{-1}; similar to "natural" levels in sediments (UNEP 2002). Further, these "background" levels were typical of sediment conditions prior to the CAP facility (Díaz-Asencio et al. 2009) with the most distant sites having levels even lower than the early twentieth century (i.e., 0.030–0.044 μg g^{-1}). Clearly, Hg is reaching the coastline from the river and the CAP is implicated, although urban, agricultural and other industrial development in the river basin may also be influential of local levels.

In parallel with sediment sampling, oysters also were collected and soft tissues analysed for tHg. Tissue levels ranged from 0.190 to 0.690 μg g^{-1} DW across sites with the highest levels found in the estuary itself (0.404–0.690 μg g^{-1} DW; mean 0.570 μg g^{-1}), which significantly exceed levels found in oysters from the keys ($p < 0.05$; see Fig. 2). Interestingly, tHg levels in tissues from December and April samples did not differ significantly (means of 0.300 vs. 0.260 μg g^{-1}). However, Fig. 3 shows that oyster tissue and sediment tHg levels did

Table 2 Examples of tHg levels in contaminated sediments worldwide

Study sites	tHg range (μg g^{-1} DW)	Source	References
Venice Lagoon, Italy	0.2–2.37	CAP	Bloom et al. (2004)
Santos–San Vicente Bay, Brasil	0.04–1.19	CAP	Hortellani et al. (2005)
Lavaca Bay*	0.005–0.783	CAP	Bloom et al. (2004)
Saguenay Fjord and St. Lawrence estuary	0.145–0.455	CAP	Gagnon et al. (1996)
Havana Bay, Cuba (1983)	0.27–3.24	Urban-industrial	Gonzalez et al. (1991)
Matanzas Bay, Cuba (1983)	0.02–0.4	Urban-industrial	Gonzalez (1991)
Santiago de Cuba Bay, Cuba (1983)	0.21–0.56	Urban-industrial	Gonzalez (1991)
Sagua la Grande River estuary[a] (1990)	2.68	CAP	Díaz-Asencio (2009)
Sagua la Grande River estuary	0.507–1.81	CAP	(this work)
North coast, Cuba (2009 and 2010)	0.032–0.205	CAP	(this work)

[a] Upper 1 cm of sediment

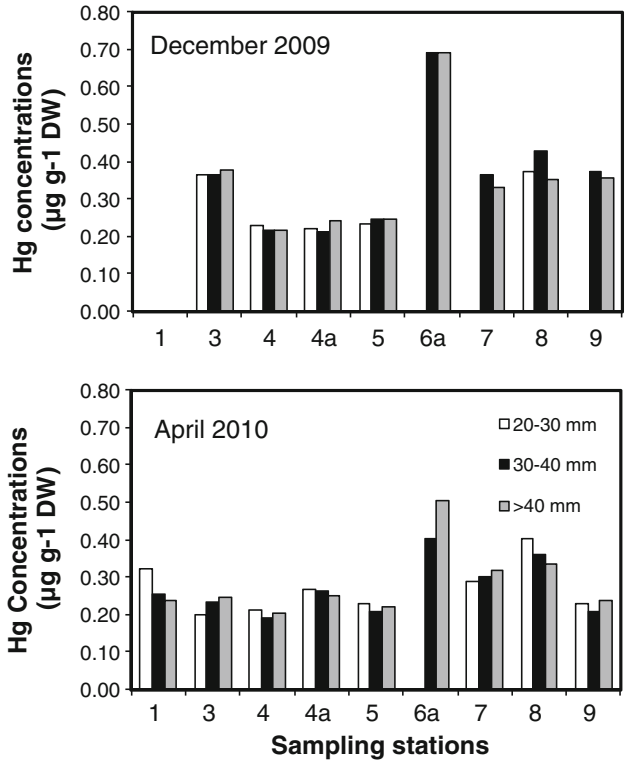

Fig. 2 Mercury concentrations in oysters of different size collected during two field sampling campaigns

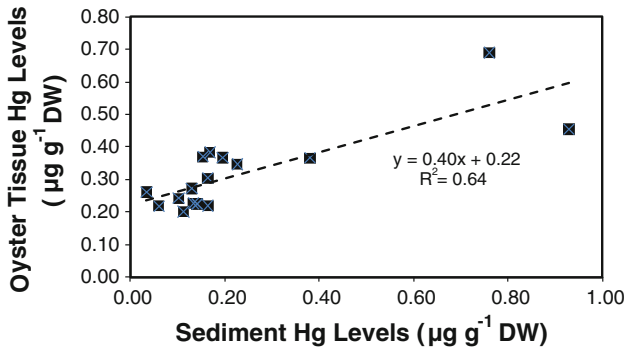

Fig. 3 Relationship between tHg levels in oyster tissues (*C. rhysophare*) and marine sediments in vicinity of the oyster sampling sites. *C. rhysophare* is not a benthic organism; therefore this significant correlation ($p < 0.05$) provides strong corroboration of the impact of Hg pollution on the local environment

significantly correlate among all sampling sites ($p < 0.05$; Fig. 3).

Despite locally elevated tHg levels in the estuarine oysters, detected levels did not exceed maximum allowable levels for shellfish consumption (UNEP 2002), although, because these oysters are low in the marine food web, it is possible that tHg levels in the oysters are lower than associated fish and other top predators, which also may be consumed by humans. Further, observed tissue levels are

Table 3 Levels of tHg reported in oysters (*C. Rizophorae)* from different regions around the world

Study sites	tHg range (µg g^{-1} DW)	Source	References
Ceará River, Brazil	0.094–0.214	Urban-industrial	Vaisman et al. (2005)
Sepetiva Bay, Brazil	0.015–0.023	Industrial	Kehrig et al. (2006)
Sagua la Grande River, Cuba	0.190–0.690	CAP	(this work)

typical of individuals near other CAP discharges (Table 3) and considerably higher than levels seen in oysters that are not impacted by waste sources (Vaisman et al. 2005). It should be noted that there was no significant difference ($p < 0.05$) between tHg levels in oysters as a function of oyster size (Fig. 2). This indicates that variability in detected oyster tHg levels more reflects environmental pressures than age- or size-specific factors related to individuals.

The correlation presented in Fig. 3 is useful because filter feeding oysters tend to accumulate trace metals making them good bioindicators of the pollutants where they reside. Moreover, many countries use shellfish tissues (oysters, mussels, etc.) for monitoring marine ecosystem health, although metal levels in marine mollusks are often dependent on local conditions. Seasonal effects like temperature, salinity, dietary factors and allometric characteristics must be considered, but it is noteworthy that oyster tissue and sediment tHg levels correlate here, which implies both type of sample might be used for monitoring conditions in the estuary.

The chemical form of Hg in oyster tissues was not determined here. However, it is well established that Hg is often transformed to toxic methylmercury (CH_3Hg^+) by environmental microorganisms and can be prevalent in exposed oysters. For example, Kehrig et al. (2006) found between 31.9% and 64.5% of tHg in oysters was present as CH_3Hg^+. This is important because CH_3Hg^+ is harmful to higher organisms (e.g. birds) whose diet is based on shellfish. Further, oyster larvae are sensitive to CH_3Hg^+, which can alter reproductive processes. As such, it is recommended that both CH_3Hg^+ and tHg be measured in future assessments.

In summary, high levels of tHg were found in the sediments of Sagua la Grande River estuary, which suggests possible impacts on organisms residing in or near the sediments. However, sediment tHg levels in the most actively oyster-farmed areas in the mangrove keys were close to background levels, although tHg levels were very high in the estuary. Although tested tHg levels in oysters were always acceptable for human consumption, concern

exists for wildlife that feed on shellfish because of their greater dependency on oysters for food. Overall, results show that Hg from the CAP facility on the river is impacting coastal sediments and resident organisms; although data away from the estuarine zone show the impact of the facility does not extend far along the coastline.

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References

Bloom NS, Moretto LM, Ugo P (2004) A comparison of the speciation and fate of mercury in two contaminated coastal marine ecosystems: the Venice Lagoon (Italy) and Lavaca Bay (Texas). Limnol Oceanogr 49:367–375

De La Rosa D, Lima L, Olivares-Rieumont S, Graham DW, Enriquez I, Díaz O, Bastias JM, Munoz O (2009a) Assessment of total mercury levels in *Clarias gariepinus* from the Sagua la Grande River, Cuba. Bull Environ Contam Toxicol 82:101–105

De La Rosa D, Olivares-Rieumont S, Lima L, Díaz O, Moyano S, Bastías JM, Muñoz O (2009b) Estimate of mercury and methyl mercury intake associated with fish consumption from Sagua la Grande River, Cuba. Food Addit Contam Part B 2:1–7

Díaz-Asencio M, Alonso-Hernandez CM, Bolanos-Alvarez Y, Gomez-Batista M, Morabito R, Pinto V, Hernández-Albernas JI, Eriksson M, Sanchez-Cabeza J (2009) One century sedimentary record of Hg and Pb pollution in the Sagua estuary (Cuba) derived from Pb-210 and -137 Cs chronology. Mar Poll Bull 59:108–115

Gagnon C, Pelletier E, Mucci A (1996) Diagenetic behavior of methylmercury in organic-rich coastal sediments. Limnol Oceanogr 41:428–434

Gonzalez H (1991) Heavy metal surveys in sediments of five important Cuban Bays. Biogeochem 14:113–128

Hortellani MA, Souza JE, Bonetti J, Bonetti C (2005) Evaluation of mercury contamination in sediments from Santos -São Vicente estuarine system, São Paulo State, Brazil. J Braz Chem Soc 16: 1140–1149

Kehrig H, Costa M, Moreirac I, Malma O (2006) Total and methyl mercury in different species of mollusks from two estuaries in Rio de Janeiro State. J Braz Chem Soc 17:1409–1418

PTI Environmental Services (1988) Sediment quality values refinement: 1988 update and evaluation of Puget Sound AET. PTI Environmental Services, Bellevue, Washington

UNEP (2002) Global mercury assessment. UNEP Chemicals, Geneva

Vaisman A, Marins R, Lacerda L (2005) Characterization of the mangrove oyster, *Crassostrea rhizophorae*, as a biomonitor for mercury in tropical estuarine systems, Northeast Brazil. Bull Environ Contam Toxicol 74:582–588