Journal of Environmental Protection, 2024, 15, 379-400
https://www.scirp.org/journal/jep
ISSN Online: 2152-2219
ISSN Print: 2152-2197

Antimony, Arsenic and Thallium Bioaccumulation in Asiatic Clam (*Corbicula fluminea*) Transplanted along the Manadas Creek, Laredo, Texas

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How to cite this paper: Garcia, N., Thomas, V. and Addo-Mensah, A. (2024) Antimony, Arsenic and Thallium Bioaccumulation in Asiatic Clam (*Corbicula fluminea*) Transplanted along the Manadas Creek, Laredo, Texas. *Journal of Environmental Protection*, **15**, 379-400.
https://doi.org/10.4236/jep.2024.154022

Received: February 28, 2024
Accepted: April 14, 2024
Published: April 17, 2024

Abstract

Manadas Creek is an urban tributary of the Rio Grande that flows past a decommissioned antimony smelter and processing plant. This antimony plant is associated with heavy metal contamination in the creek and still poses a threat to the surrounding aquatic environment. *Corbicula fluminea* was used to determine bioaccumulation from the water column and sediments in Manadas Creek. The metals arsenic (As), antimony (Sb) and thallium (Tl) were analyzed in the water, sediments, gills, mantle, foot, digestive (DI) tract, gonads and shell of clams being monitored at eight sites between March and August 2013. Sediment, water, and dissected *Corbicula fluminea* samples from different sites in the Creek were acid-digested and analyzed by Inductively Coupled Plasma Optical Emission Spectroscopy. High levels of antimony (25.88 ug/L; 75.96 mg/kg) and arsenic (8.26 ug/L; 6.41 mg/kg) in the water and sediments were observed at the site downstream from the smelter. There were no detectable concentrations of arsenic, antimony, or thallium in the shell of *C. fluminea*. Arsenic and antimony were detected in the tissues of *C. fluminea* but thallium was not detected. Based on the results, the organotropism for arsenic is DI tract > gills > gonads > foot > mantle > shell and the organotropism for antimony is gills > DI tract > gonads > mantle > foot > shell. This study shows that the Asiatic clam (*Corbicula fluminea*) is a useful bio-monitor to provide data on the status of metal pollution in Manadas Creek, Laredo, Texas.

Keywords

Biomarker, Manadas Creek, Rio Grande, Heavy Metals, *Corbicula fluminea*, Biota Sediment Accumulation

1. Introduction

Heavy metals are metals or metalloids with high atomic weight (>63.5 $g \cdot mol^{-1}$) and atomic density (>5 $g \cdot cm^{-3}$). Examples include lead, arsenic, cadmium, mercury, silver, and thallium [1]. Heavy metals can be classified as essential and non-essential. This classification is based on their functions in biological processes. For instance, vanadium and manganese are essential for enzymatic functions; selenium is essential for hormone production and functions; and nickel for cellular growth [2] [3]. These metals are, however, needed only in trace quantities because they are toxic to the body at higher concentrations [4]. Non-essential metals like lead, mercury, and cadmium do not have any known biological functions and are toxic to the body at trace concentrations [5] [6] [7] [8]. Heavy metals are also used as raw materials in electronic devices, automobiles, machinery, and construction [9] [10] [11] [12]. Heavy metals are released into aquatic environments through industrial activities such as mining and metal smelting, metal fabrication, combustion of fossil fuels, and electroplating [5] [13]. The increase in demand for metal-based goods has led to an increase in metal pollution. This pollution often finds itself in public water supplies and currently presents itself as a serious problem to local and ecological communities. Metals are found dissolved in the water column and in the sediment, increasing variability in the uptake routes of organisms. The effects of exposure to contaminated water include health, environmental and ecological problems [14] [15]. Increased urbanization is linked to the rise in water pollution, which stems from point and non-point sources [16] [17]. To reduce pollution in the aquatic environment, it is important to identify the source of contamination.

Manadas Creek is an urban tributary of the Rio Grande. It flows along residential, recreational, and business areas, a major highway, heavily traveled roads, warehouses, a ready-mix cement factory, a major railroad, and an antimony smelter [18]. Because water from the Rio Grande is an important natural resource, there is much concern about protecting this river from urban pollution. Located near the banks of the creek are two slag sites and a retention pond, which is used to prevent contaminants from entering the creek. All of these contain antimony byproducts. This is the site of the now inactive antimony smelting and processing operation, known as Anzon Inc. (currently, known as Al Divestitures, Inc.). This operation is associated to the heavy metal contamination in Manadas Creek and still poses a threat to the surrounding aquatic environment [19]. A study by Baeza *et al.*, 2010 sampled six different sites in Manadas Creek that were upstream and downstream from the antimony site [18]. Higher than normal antimony and arsenic levels were measured in both water and sediments from the creek. In addition, an antimony gradient was observed. The site near the antimony plant had the highest concentration, which the levels decreased downstream. There is the need for constant monitoring of the creek to determine the fate, transport, and bioavailability of heavy metal and the presence of alternate point sources.

Geochemical analysis of water and soil parameters does not predict bioavailability or bioaccumulation of contaminants in a system. Therefore, using aquatic

organisms as bio-monitors to directly measure the abundance and availability of these contaminants in the environment is beneficial [20] [21] [22]. Additionally, using live organisms will reveal concentration levels that are harmful as well as aid in providing information on the effects of metal pollution as aquatic organisms have been observed to accumulate metals in their tissues several times above the levels in the surrounding environment [23] [24] [25]. The main purpose of biomonitoring is to relate metals accumulated in an organism's tissues to bioavailable levels found in the surrounding environment. *Corbicula fluminea*, a freshwater mussel native to Southeast Asia was used in this study. This clam is a suitable biomonitor because they are filter feeders and accumulate heavy metals in their tissues in proportion to the degree of environmental contamination [25] [26] [27]. They feed from both the water column and the substrate. As a result, concentrations in their tissues should be higher at contaminated sites and lower at uncontaminated sites.

In studies using clams, metals were observed to accumulate in the kidney, gills, and/or digestive glands [20] [23] [28]. The kidneys are known sites for excretion, which may account for this increased concentration. The digestive gland also may have increased concentrations due to its role in digestion, where food and water particles from the environment enter the mantle cavity through the incurrent siphon. In studies conducted on bivalves, arsenic was seen to accumulate more in the gills than any of the other tissues as the gills have a large surface area that metals taken up from the environment bind to [29] [30]. The shells of mussels have been observed to accumulate metals from the environment in high concentrations where pollution occurred [31] [32] [33]. However, some studies have indicated that soft tissues accumulate more metals than the shell matrix [30]. In this study, *Corbicula fluminea* (**Figure 1**) transplanted from the Rio Grande mainstem into Manadas Creek were used to detect levels of the trace metals antimony, arsenic, and thallium in the gills, mantle, foot, digestive tract, gonads, and shell at different sites throughout the creek. These metals were chosen because they were found in high concentration levels in Manadas Creek [19].

The objectives of this study are 1) to determine and compare the concentrations of antimony, arsenic and thallium in the various body tissues and shell, 2) examine the relationships between metal concentration in specific organs and shell and the metal concentration in the water column and sediments, and 3) verify if the freshwater mussel, *Corbicula fluminea* is a viable biomonitor for antimony, arsenic, and thallium in the aquatic environment.

Figure 1. *Corbicula fluminea*, the asiatic clam.

2. Materials and Methods

2.1. Sampling Sites

Eight sampling sites were chosen throughout Manadas Creek to determine the levels of antimony, arsenic, and thallium in the water column, sediments, tissues, and shells (Figure 2). Sites were chosen based on location, accessibility, and presence of water (Table 1). Site 1 is located on the west side of a busy road near businesses and downstream from a residential and recreational area. Site 2 is along another heavily traveled road. The water in this tributary of the creek comes from storm drains as well as effluent from the North Laredo Wastewater Treatment Plant. This part of the creek contains building metals and broken pieces of cement slab. Site 3 is located on the west side of I-35, which is downstream from a cement ready mix plant. Site 4 is in a part of the creek that has been channeled below a large body of water and is surrounded by warehouses. Oil was observed on the water surface in this part of the creek. Site 5 islocated downstream from the inactive antimony plant and is known to be polluted by chemicals released from that plant. Site 6 is located downstream of site 5 and is located on the west side of Mines road. The bottom of the creek here contains pieces of asphalt, cement slab and large rocks. Site 7 is in a part of the creek that is located along a major road between a boat sales and service business and truck repair shop. Site 8 is upstream of site 7. Site 8 looks cleaner compared to site 7 as water from the North Creek Plaza pushes all the garbage to the back of the creek where it eventually gets caught in hanging trees or under the railroad bridge.

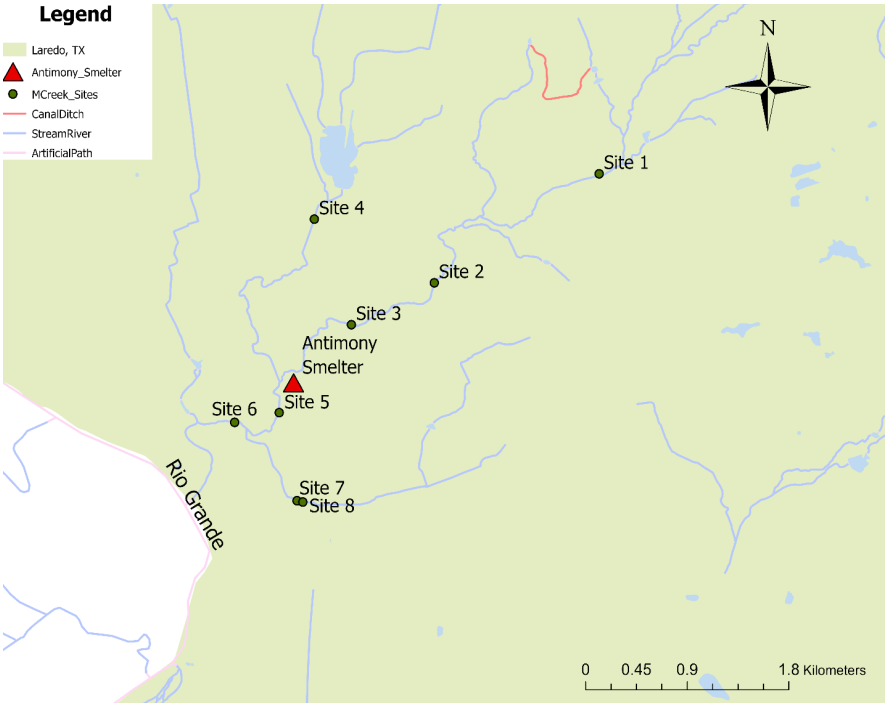

Figure 2. Map of sampling sites along Manadas Creek, Laredo, Texas.

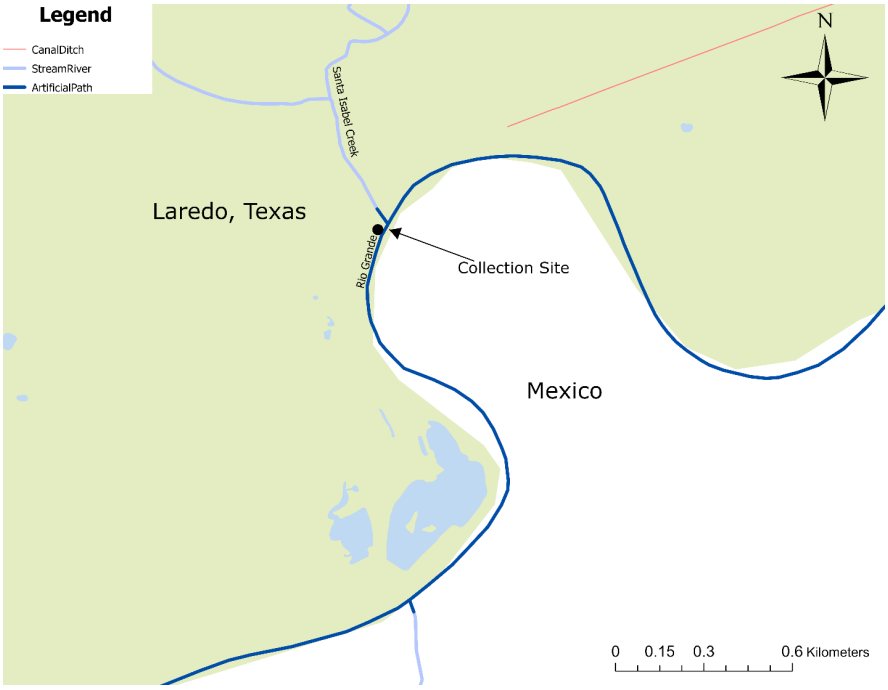

Figure 3. Map of collection site.

Table 1. Coordinates and depth of Manadas Creek sampling sites

Sites	Latitude (N)	Longitude (W)	Depth (m)
1	27˚35'39.48"	−99˚28'48.95"	0.36 - 0.48
2	27˚35'9.08"	−99˚29'36.18"	0.41 - 1.22
3	27˚34'57.42"	−99˚29'59.93"	0.94 - 1.12
4	27˚35'26.82"	−99˚30'10.55"	0.48 - 0.64
5	27˚34'32.94"	−99˚30'20.64"	1.19 - 1.65
6	27˚34'30.24"	−99˚30'33.4"	1.14 - 1.52
7	27˚34'8.39"	−99˚30'15.54"	1.07 - 1.17
8	27˚34'8.02"	−99˚30'13.87"	1.12 - 1.30

Note: Depths were recorded on sampling days.

2.2. Sample Collection

In March 2013, 1000 clams were collected from a gravel bar above the confluence of the Rio Grande and Santa Isabel Creek (**Figure 3**). These clams were analyzed as controls and concentration of metals (As, Sb, and Tl) were below detection limits. An additional 400 mussels were collected on March 30, 2013, for the addition of Site 8 as well as to replace mussels at Site 7. When transporting the clams to the lab, they were placed in buckets filled with river water. In the lab, mussels were rinsed with deionized water to remove any particles from their shell. After they were air dried, the mussels were measured for their length (24 - 36 mm), width (14 - 19 mm), height (20 - 32 mm) and weight (6.3 - 10.4 g).

The mussels were housed in aquariums with filtered river water until they were put in cages out in the field. About 150 clams were placed in stainless-steel cages (15 cm × 15 cm × 17 cm) at the different sites on March 16, 2013. In April, 200 mussels were added to the cages at Site 7 and Site 8 due to the high mortality at that part of the creek. Each cage was about 1/2 filled with gravel substrate. Cages were suspended midstream from T-post at the sites. At Sites 1 and 4, cages were placed on the sediment bed of the creek and secured with rebar due to the shallow water. Cages were checked once a week to ensure they were still in their location, submerged and that the mussels were alive.

For analysis, 3 specimens from each site were collected bi-weekly. Specimen samples were taken back to the lab in ice. Clam shells were cleaned with deionized water to remove any algae or sediments and then depurated in distilled water for 24 hours. After 24 hours, they were frozen at −80˚C until they were dissected.

Water samples were collected midstream at all sites using whirl-paks and then taken back to the lab in ice. Sediment samples were collected on one occasion at all sites. Grab samples were collected at three different spots at each site upstream of the cages. About 6 cm of the upper sediment layer was removed. Samples were stored in whirl-paks, mixed and placed in ice to be taken back to the lab.

2.3. Chemicals and Instrumentation

Ultrapure water (Millipore, United States) was used to prepare the standards, blanks, and dilution of acid digested samples. Triton™ X-100, Nitric acid (HNO_3, 70%), Hydrogen peroxide (H_2O_2, 30%) and Hydrofluoric acid (HF, 51%) were purchased from Sigma-Aldrich (St. Louis, MO, United States). Standard reference material (SRM) 1566b oyster tissue, 2710a Montana I Soil, and 1643f -trace elements in water were purchased from National Institute of Science and Technology, Gaithersburg, MD, United States. A calibration curve method was used to quantify the heavy metal concentrations. 100 mg/L analytical grade stock solution of metals was purchased from VWR (Radnor, PA, USA) and used to prepare standards for calibration. Trace metal analysis was done with an Agilent ICP-720 Inductively coupled plasma-optical emission spectrometer (Agilent Technologies, Santa Clara, California, USA).

2.4. Sample Preparation

Tissue, shell, water, and sediment samples were collected for metal analyses. Clams were dissected frozen. The gills, mantle, foot, digestive tract, and gonads were each isolated using stainless-steel instruments. Once all the soft tissues were removed, the tissue was cleaned and rinsed. After dissection, the clam tissues and shell were put into crucibles and dried to a constant mass for 2 hours at 100˚C. Each of the tissue and shell samples were ground into a fine powder to evenly mix the samples before digestion.

Water samples were immediately filtered after being taken back to the lab using a syringe filter with a 0.45 μm pore diameter membrane filter and acidified with nitric acid before being stored. Sediment samples were evenly mixed, dried at 100˚C for 24 hours, and ground into a fine powder.

2.5. Acid Digestion of Samples

For water samples, 10 mL of acid mixture (7 mL HNO_3 and 3mLHF) was added to 100 mL of water sample in a beaker and digested using U.S. EPA method 3052 [34]. The beaker was covered with an evaporating disc, and allowed to reflux for 15 minutes on a hotplate at 80˚C. After 15 minutes, the beaker was allowed to cool and 5 mL of HNO_3 was added. The beaker was refluxed for 30 minutes and cooled again. 2 mL of water and 5 mL of hydrogen peroxide was added. The beaker was refluxed for 30 minutes, followed by removing the evaporating disc to let the solution evaporate to about 5 mL of volume. Once cooled the solution was diluted to 50 mL in a volumetric flask with MilliQ water. The solution was filtered with a 0.45 μm filter disc into a centrifuge tube and then capped for later analysis. Samples were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES). In the case of sediments, 0.5 g of prepared sediment was weighed into a beaker and 10 mL of acid mixture was added and digested using U.S. EPA method 3052 described above. Pooled tissue and shell samples of 3 - 5 individuals from each site were analyzed for As, Sb, and Tl using U.S. EPA method 3052. The samples were digested by adding 10 mL of acid mixture to an analytical amount of 10 - 500 mg of pooled sample and digested using U.S. EPA method 3052 as was done for water samples.

2.6. Quality Control

All glassware and plastic containers used were soaked in an acid-wash bath (0.1% Triton X-100 and 5% HNO_3) for 24 hours and then triply rinsed with deionized water. Analyses of the samples were carried out in triplicates. A calibration blank, and a reference standard were used to ensure the accuracy of the ICP-OES. Blanks and standards were run after every ten samples. To avoid memory effects between samples, MilliQ water was run through the analysis tubing to remove any traces of metals that remained. Certified SRM1566b oyster tissue, 2710 a Montana I Soil, and 1643 f-trace elements in water were digested using U.S. EPA method 3052 to check accuracy of the digestion protocol adopted. Method blanks were employed to check for background contamination. The analytical values were within the range of certified values and the recoveries of the metals across the sampling sites varied from a low of 90% to a high of 105%.

2.7. Statistical Analysis

ANOVA was used to determine differences in the metal distribution in the water column of Manadas Creek at the different sites as well as to see differences in the

metal distribution in the soft tissues of the clam ($p < 0.05$). A Kruskal-Wallis test was used to determine variability in the metal concentrations at the different sites. Also, Pearson correlation was used to determine any correlations between the metal concentrations in the mussel and the water column.

2.8. Metal Pollution Index (MPI)

The metal pollution index (MPI) was used to assess the load of metals (As, Sb, and Tl) in the gills, DI tract, gonads, foot, and mantles of C. fluminea. MPI was calculated according to the equation (1) [35].

$$MPI = \left(M1 \times M2 \times M3 \times \cdots \times Mn\right)1/n \tag{1}$$

M_n = The concentration of metal n (mg/kg) in a certain tissue.

2.9. Bioaccumulation Studies

Bioaccumulation factor (BAF) and biota-sediment accumulation factor (BSAF) were calculated for each site to evaluate the efficiency of As, Sb, and Tl accumulation in the tissues and shell. Water, sediment, and sample concentrations for a site were averaged together. BAFs and BSAFs were calculated using the following equations (2) and (3): [36] [37] [38].

$$\text{BAF} = \frac{\text{metal concentration in the organism}}{\text{metal concentration in the water}} \tag{2}$$

$$\text{BSAF} = \frac{\text{metal concentration in the organism}}{\text{metal concentration in the sediment}} \tag{3}$$

3. Results and Discussion

All metals studied (arsenic, antimony, and thallium) were observed at all sites in both the water and sediments of Manadas Creek.

3.1. Heavy metal Concentration in Water

Figure 4 shows the mean concentrations of metals (As, Sb, and Tl) in the water column from each sampling site collected from March 2013 to August 2013. Statistical analysis reveals variability in the concentrations of As (ANOVA, $df_1 = 5$, $df_2 = 66$, $F = 31.412$, $p < 0.000$), Sb (ANOVA, $df_1 = 5$, $df_2 = 66$, $F = 62.337$, $p < 0.000$), and Tl (ANOVA, $df_1 = 5$, $df_2 = 66$, $F = 5.373$, $p < 0.000$) in the water at the sampling sites. The range of Sb (4.36 - 13.45 μg/L) and Tl (3.63 - 7.47 μg/L) across all eight sampling sites were above the US EPA maximum contaminant level (MCL) in water (Sb, 6 μg/L; Tl, 2 μg/L) [39].

On the other hand, the range of As (5.73 - 10.33 μg/L) were all below the MCL (10 μg/L) except at Site 5 (10.33 μg/L) which is adjacent to the decommissioned antimony plant. Site 5 had the highest arsenic concentration (10.33 μg/L), while the lowest arsenic concentration (5.29 μg/L) was recorded at Site 2. The highest antimony concentration, 13.45 μg/L, was observed at Site 5, while the lowest antimony concentration, 4.36 μg/L, was recorded at Site 1. The highest thallium

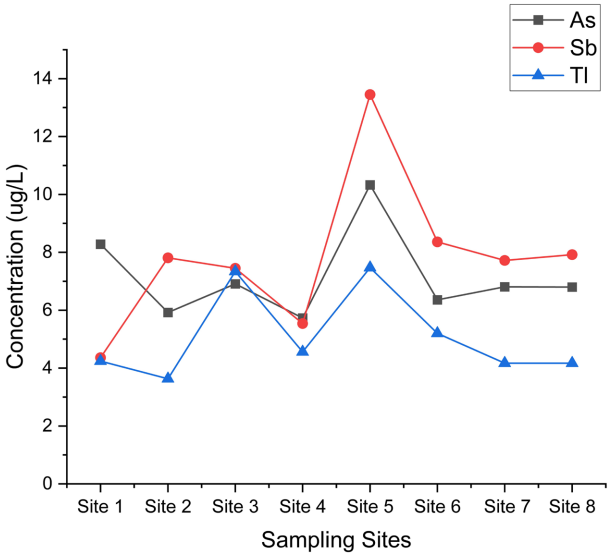

Figure 4. Concentration of As, Sb and Tl in water.

concentration, 7.47 μg/L, was observed at Site 5, while the lowest concentration, 3.63 μg/L, was recorded at Site 2. Tl concentrations measured in this study exceed the concentration of Tl in uncontaminated waters (1 μg/L) [40]. Overall, the highest arsenic, antimony and thallium mean concentrations in the water column were observed at site 5, which is the site closest downstream to the decommissioned antimony smelter. This observation implies that activities at the smelting plant led to the release of heavy metals into the creek. The higher concentration of metals in the water around the decommissioned plant area points to the coexistence of other metals in antimony ores.

Table 2 shows results from this study compared with previous studies in the creek. A study conducted by the United States International Boundary and Water Commission (USIBWC) in March 1993 recorded mean concentrations of arsenic, antimony, and thallium as 10 μg/L, 78 μg/L, and 2.2 μg/L respectively [19]. Mean As and Tl concentrations were within the MCL set by the EPA. However, mean Sb concentration in that study exceeded the MCL by 12-fold. A follow up study by the same organization in May 1995 recorded concentrations of arsenic, antimony, and thallium in the water as 6.3 μg/L, 36.4 μg/L, and 1.9 μg/L respectively [19].

The second study shows a reduction of metal concentration especially Sb which was recorded at about 50% reduction. A study in Feb-May 2008 recorded As and Sb concentrations in the creek as 20.6 and 219.3 μg/L respectively, and a study in in February 2010 recorded mean As and Sb concentrations 47.99 μg/L and 22.80 μg/L respectively [18] [41]. These results highlight fluctuations over the years of study which can be attributed to seasonal variations in geochemical conditions [42]. A trend of an overall reduction in the metal load in the creek is also observed. The reduction in mean As and Sb concentrations can be attributed to the effectiveness of the containment steps taken by the city to stop/reduce the release of Sb into the surrounding ecosystems.

Table 2. Comparison of results with previous studies.

	1993[19]	1996[35]	2008[18]	2010[43]	2013-this study
As (ug/L)	10	6.3	20.6	47.99	10.33
Sb (ug/L)	78	36.4	219	22.80	13.45
Tl (ug/L)	2.2	1.9	-	-	7.47

- was not measured in the study.

Higher Sb concentrations observed points to the sediment acting as a sink and source of metal in the water column [43] [44]. Since metals are non-biodegradable, they are sorbed in particles and settle down on the sediment. Seasonal fluctuations in water flow and occasional disturbance can remobilize the metals trapped in the sediment and serve as source of metal. This was evidenced by the higher bioaccumulation of Sb in *C. fluminea* in the 2010 study by Addo-Mensah *et al.* [41]. The presence of antimony, arsenic and thallium in the creek are mostly due to the antimony smelter. Thallium and arsenic are by-products of these operations. These toxic chemicals are naturally found in very small amounts in the earth's crust, but in higher concentrations, they are carcinogens and a threat to human health [45]. Antimony enters the water from weathering of rocks, effluents from agricultural, industrial, and mining/smelting processes [19]. Arsenic easily dissolves in water and enters the waters by erosion, use as a pesticide, and from industrial, municipal, and smelting effluents [19]. Thallium usually enters the water from effluents of smelting [19].

3.2. Heavy Metal Concentration in Sediment

Figure 5 shows the arsenic, antimony, and thallium concentrations in the sediments of Manadas Creek collected at the end of the sampling period, August 31, 2013. The highest mean concentration of arsenic (6.41 mg/kg) and antimony (5.77 mg/kg) in the sediments of Manadas Creek were observed at Site 5, while the highest mean concentration for thallium (3.00 mg/kg) was recorded at site 3. Site 2 had the lowest mean concentrations for arsenic (3.29 mg/kg) and antimony (1.77 mg/kg) in the sediment. Site 8 had the lowest mean concentration for thallium (1.95 mg/kg). Kruskal-Walllis test reveals differences in metal concentrations in the sediments for As ($p < 0.025$) and Sb (0.007) among the sites, while there is no variability of Tl ($p > 0.315$) among the sites. Site 5 had the highest concentration values of antimony (75.77 mg/kg) and arsenic (6.41 mg/kg). Site 3 had the highest concentration value for thallium (3.00 mg/kg). Site 2 had the lowest concentration values of arsenic and antimony (3.29 and 1.77 mg/kg), while Site 8 had the lowest concentration value for thallium (1.95 mg/kg). Concentration of Tl across the sampling sites were not significantly different from each other ($P < 0.05$). Concentration of As and Tl across the sampling sites were comparable to mean arsenic and thallium concentrations in rivers across the United States of America and other parts of the world [40] [46] [47] [48]. The concentration of As in the sediments in this study was comparable to As concentration

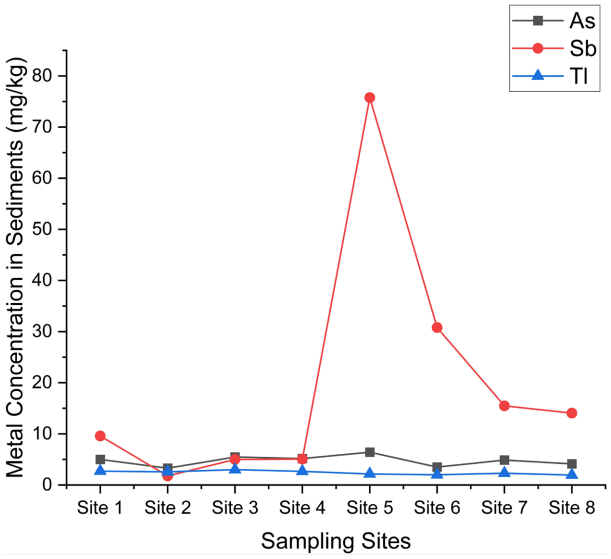

Figure 5. Concentration of As, Sb and Tl in sediment.

in previous study by Baeza *et al.*, 2010 [18]. The concentration of all metals studied at site 1 - 4 were comparable to that observed in uncontaminated soils and sediments in the USA [48] [49] [50] [51].

Site 5 which is adjacent to the antimony smelter had antimony concentrations higher than that of uncontaminated sediments but comparable to that observed in antimony mining sites or smelter plants [52] [53]. The Sb concentration gradient observed from Site 5 to 8 points to the smelting activities as a likely point source of contamination [54].

The average concentration of As in the sediments at all the sampling sites (4.73 mg/kg) was not statistically different at the 0.05 level from the previous studies by USIBWC in 1993 and 1996 (5.2 mg/kg 7.6 mg/kg respectively [19]. The average Tl in the sediments of the sites studied is 2.42 mg/kg and it is not significantly higher at the 0.05 level than previous studies by USIBWC in 1993 and 1996 (0.25 mg/kg and 0.17 mg/kg respectively). Mean Sb concentration is 19.69 mg/kg, but the highest Sb concentration is 75.77 mg/kg. The concentration recorded is significantly lower than that observed in the study by Baeza *et al.*, 2010 (470 mg/kg [18]. This general trend of decrease and stability of metal concentration in the sediment has been observed in European rivers since the 1970s. This trend is attributed to sound environmental policies. In the case of this smelter plant, remediation measures have been effective [55].

3.3. Metal Pollution Index

MPIs of the tissues are represented in **Figure 6**. Gills and DI tract had the highest MPIs 13.92 and 13.66 respectively. The gills of bivalve clams like *C. flumineaare* used for respiration and filtering food [56]. These activities allow them to be in close contact with metal enriched sediments thereby having high MPI as seen in the results. The DI tract of the clam consists of the mouth, esophagus, and stomach (which is within the liver) is used for food digestion and waste excretion.

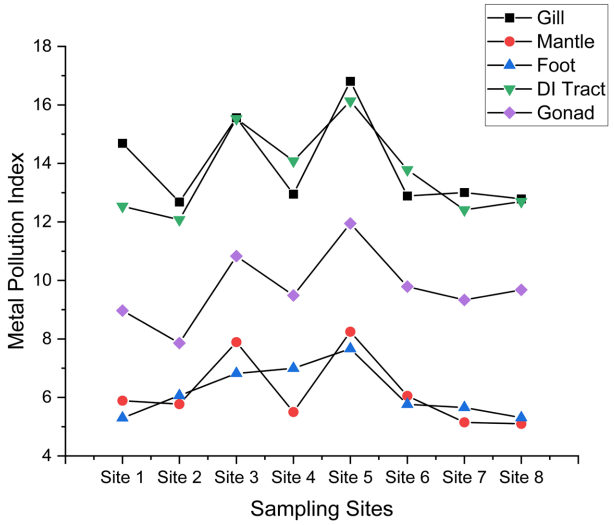

Figure 6. Metal Pollution Index of Tissues.

These two major metabolic organs had the highest MPI and the accumulated metals the most. The mantle which covers the visceral mass, and the foot are not involved in metabolic activities of the clam and hence have low MPI. Site 5 which is adjacent to the decommissioned plant had the highest MPI when compared with the other sampling sites. This supports the observation that abandoned smelting and processing sites are point sources of heavy metal pollution [57] [58].

3.4. Bioaccumulation As, Sb and Tl in Organs of *Corbicula fluminea*

Distribution of the bioaccumulation of the metals in different parts of *C. fluminea* throughout the sampling period is shown in **Table 3**.

Analysis of the shell showed As, Sb and Tl values were all below the detection limit. The shells therefore did not bioaccumulate the metals studied. Also, mean thallium concentration in the organs of *C. fluminea* were below detection limit. The distribution of arsenic (ANOVA, $df_1 = 4$, $df_2 = 355$, $F = 349.502$, $p < 0.000$) and Sb (ANOVA, $df_1 = 4$, $df_2 = 355$, $F = 100.313$, $p < 0.000$), in the tissues of *Corbicula fluminea* varied. The average antimony concentrations recorded in the tissues of the clam were the highest followed by arsenic. The DI tract tissue had the highest arsenic concentration, followed by the gills, then gonads, then foot, and finally the mantle. For antimony, the gills had the highest concentration, followed by the DI tract, then gonads, then mantle, and finally the foot. This order mirrors that which was observed in the MPI. Based on the results, the organotropism for arsenic is DI tract > gills > gonads > foot > mantle > shell and the organotropism for antimony is gills > DI tract > gonads > mantle > foot > shell. The organotropism order agrees with similar studies where they also observed that metabolically active organs accumulated most metals whereas muscular organs like the foot had low metal affinity [59].

3.4.1. Bioaccumulation Factor and Biota Sediment Accumulation Factor

Bioaccumulation factors (BAF) and biota sediment accumulation factor (BSAF)

are methods used to estimate contaminant loads in organisms. BAFs are used to estimate the proportion in which the metal occurs in the organism and in the surrounding water. Table 4 displays the BAF for each tissue at each site for arsenic and antimony. BAFs and BSAFs for thallium for the soft tissues were not calculated because the thallium levels in the mussel were not detected. Also, no BAFs and BSAFs for shells were calculated as the metal levels in the shells below the detection limit of the analysis.

The criteria set by Arnot and Gobas 2006 (less than 1000 = less probable to bioaccumulate; 1000 < BAF < 5000 = bioaccumulative; > 5000 = highly bioaccumulative) was used to analyze the BAF data [36]. All tissues of *Corbicula fluminea* studied can be considered as bioaccumulative with respect to Sb. The gill, DI tract and gonads showed probability of bioaccumulating As. The foot and mantle however were less probable to bioaccumulate. The highest BAF values for arsenic were observed in the digestive tract with values ranging from 1460 to 2800

Table 3. Concentration of As and Sb in the soft tissues of *C. fluminea.*

	Concentration of Metals in *C. fluminea* parts (mg/kg)									
	Gill		Mantle		Foot		DI Tract		Gonads	
	As	Sb	As	Sb	As	Sb	As	Sb	As	Sb
Site 1	13.39	16.12	4.95	7.01	5.00	5.62	12.1	12.99	6.92	11.63
Site 2	12.45	12.92	4.35	7.66	5.80	6.34	11.34	12.86	6.11	10.11
Site 3	14.87	16.29	5.65	11.02	6.38	7.29	17.57	13.73	8.54	13.74
Site 4	13.46	12.46	4.29	7.06	6.06	8.08	16.06	12.35	7.94	11.34
Site 5	16.15	17.50	5.79	11.75	6.59	8.92	18.06	14.41	9.97	14.32
Site 6	13.82	12.02	4.45	8.23	5.15	6.45	16.45	11.55	8.76	10.94
Site 7	13.52	12.51	4.48	5.92	5.07	6.31	13.94	11.05	6.33	13.76
Site 8	13.06	12.52	4.68	5.55	4.74	5.94	14.22	11.34	6.70	13.98

Table 4. Bioaccumulation factors of metals in the tissues and shell of *Corbicula fluminea* collected from March 2013 to August 2013.

	Bioaccumulation Factor									
	Gill		Mantle		Foot		DI Tract		Gonads	
	As	Sb	As	Sb	As	Sb	As	Sb	As	Sb
Site 1	1620	3700	600	1610	600	1290	1460	2980	840	2670
Site 2	2100	1650	730	980	980	810	1920	1650	1030	1290
Site 3	2150	2190	820	1480	920	980	2540	1840	1240	1840
Site 4	2350	2250	750	1270	1060	1460	2800	2230	1390	2050
Site 5	1560	1690	560	1140	640	860	1750	1390	970	1390
Site 6	2170	1440	700	980	810	770	2590	1380	1380	1310
Site 7	1990	1620	660	770	740	820	2050	1430	930	1780
Site 8	1920	1580	690	700	700	750	2090	1430	990	1770

and in the gills with values ranging from 1560 to 2350. On the other hand, the highest BAF values for antimony were observed in the gills with values ranging from 1440 to 3700. BAF values for antimony were also high in the digestive tract with values ranging from 1380 to 2980 and gonads with values ranging from 1290 to 2670. The lowest BAF values for antimony were observed in the mantle and foot. Both the digestive tract and gills are good bioaccumulators of antimony and arsenic from the water column.

A Pearson correlation was conducted to determine any correlation between the metal concentration accumulated in *C. fluminea* and the metal concentration levels in the water column. There was no Pearson correlation calculated for the metal concentrations in the sediments and tissues because of the few soil observations. Based on the water analysis done, there was little to no correlations between the arsenic levels in the water column and the gills ($r = -0.202$), mantle ($r = 0.012$), foot ($r = 0.135$), digestive tract ($r = 0.104$), and gonads ($r = 0.014$). For the antimony levels, there was also little to no correlation between the concentration levels in the water column and the gills ($r = -0.126$), mantle ($r = 0.156$), foot ($r = 0.153$), digestive tract ($r = -0.034$), and the gonads ($r = 0.00$).

3.4.2. Biota Sediment Accumulation Factor

BSAFs are used to estimate the proportion in which the metal occurs in the organism and in the surrounding sediments. BSAF for soft tissue from the sampling sites at the end of the study is recorded in Table 5. BSAF values were used to classify the soft tissues of *C. fluminea* using the criterion established by [60] [61]: BSAF > 2 = macroconcentrator;

1 < BSAF < 2 = microconcentrator; BSAF < 1 = deconcentrator. Table 5 displays the BSAF for soft tissues at the end of the sampling period.

The highest BSAF values for arsenic were observed in the digestive tract and gills with values ranging from 2.42 to 4.67 and 2.52 to 3.93 respectively making

Table 5. Bioatasediment factors (BSAF) of metals in the tissues and shell of *Corbicula fluminea* at the end of the sampling period, August 31, 2013.

	BSAF									
	Gill		Mantle		Foot		DI Tract		Gonads	
	As	Sb	As	Sb	As	Sb	As	Sb	As	Sb
Site 1	2.68	1.68	0.99	0.73	1	0.59	2.42	1.36	1.39	1.21
Site 2	3.78	7.3	1.32	4.33	1.76	3.58	3.45	7.27	1.86	5.71
Site 3	2.71	3.26	1.03	2.21	1.16	1.46	3.21	2.75	1.56	2.75
Site 4	2.6	2.46	0.83	1.39	1.17	1.59	3.11	2.44	1.54	2.24
Site 5	2.52	0.23	0.9	0.16	1.03	0.12	2.82	0.19	1.56	0.19
Site 6	3.93	0.39	1.26	0.27	1.46	0.21	4.67	0.38	2.49	0.36
Site 7	2.78	0.81	0.92	0.38	1.04	0.41	2.86	0.71	1.3	0.89
Site 8	3.15	0.89	1.13	0.39	1.14	0.42	3.43	0.81	1.62	0.99

these tissues a good concentrator of arsenic from the sediment. Also, the gonads were good concentrators of arsenic from the sediments with values ranging from 1.30 to 2.49. The lowest BSAF values for arsenic were observed in the mantle and foot with values ranging from 0.83 to 1.32 and 1.00 to 1.76 respectively. The mantle ranged from being a microconcentrator to a deconcentrator of arsenic, while the foot is a microconcentrator of arsenic. The BSAF values for antimony for all tissues from each site varied from low values to high values. The BSAF values for the gills ranged from 0.23 to 7.30, the values for the mantle ranged from 0.16 to 4.33, the values for the foot ranged from 0.12 to 3.58, the values for the digestive tract ranged from 0.19 to 7.27 and the values for the gonads ranged from 0.19 to 5.71. The variability of the BSAF values suggests that the tissues might not concentrate antimony from the sediment beds at the bottom, but rather when antimony is bound to the particulate phase in the water column [62].

Monitoring heavy metal pollution in the environment using biomarkers is more relevant than water and sediment analysis alone [63] [64]. Biomarkers provide information about the bioavailability of contaminants in the ecosystem and relative ability of an organism to bioaccumulate select contaminants (metals) from their environment. It also gives some knowledge on the integrated influence and harmfulness of the contaminants on to the organisms and ecosystem [65]. *Corbicula fluminea* lives near the sediment-water interface and therefore, is a good biomarker to assess the influence of contaminants in both the water and sediment.

The concentration of metals in water samples at the sampling sites along Manadas Creek throughout the sampling period was not constant. This can be due to factors such as variability in water and sediment chemistry, activity in the biological organism, temporal variability in metal inputs into the creek, and changes in dilution, dispersion, or other hydrologic properties [16] [66] [67]. Also, sediment beds are metal depositories, which when disturbed can pollute the surrounding water [68]. Site 5, which was adjacent to the decommissioned antimony plant had high values of arsenic, antimony, and thallium in both the water and the sediments, which was reflected in the tissues of the clam. Site 3, which is upstream of the antimony smelter had high concentrations of all three metals as well in the water column and sediments. This increase could be due to pollution from the highway or weathering and dispersal from the mounds of contaminated soil at the decommissioned antimony site. Similar effect was observed in a study by Addo-Mensah *et al.*, 2023 [41].

Because there are other factors to consider when measuring concentrations in water and sediments using a biomonitor, the metal concentrations in the organism will not always be reflective of those measured in the ambient environment [62]. In this study, there were no correlations between the concentrations of the metals (arsenic, antimony, and thallium) and the tissues and shell of *Corbicula fluminea*. However, concentrations of metals such as cadmium, copper and lead

from the sediments have been observed to correlate with the concentrations in the tissues of *Corbicula fluminea* [69]. Also, other factors such as age, body size, nutrition and reproductive status may play a role in how much metal an organism accumulates in their tissues [40].

The distribution of the metals in the tissue groups of the biomonitor provides data that can give insight into the contamination routes. When observing the metal distributions in the tissues and shell of *Corbicula fluminea*, arsenic concentration rankings were DI tract > gills > gonads > foot > mantle > shell. For antimony concentration, the rankings were gills > DI tract > gonads > mantle > foot > shell. Metals were highly accumulated from both food and water [70]. The gills of mussels serve as an interface for the uptake of dissolved metal ions and have been observed to contain the most metal concentrations. Gills have large surface areas and are exposed to large amounts of water when feeding or respiring. Also, the digestive tract accumulated high levels of arsenic, this is consistent with studies that have shown mussels can accumulate high levels of metals from ingested food [71]. The shells had the lowest concentrations of all the metals, which agrees with previous studies that have concluded there were no detectable levels of arsenic and antimony in shells [72]. Although the shell can store metals, when mussels are stressed, they resorb shell material, making the metals become mobilized [30]. The concentration of metal in the tissues and shell is a net balance between metal uptake and metal loss.

4. Conclusion

Knowledge of concentration factors of metals in *Corbicula fluminea* is useful for recognizing the relative ability of organisms to bioaccumulate select metals from their environment. Bioaccumulation factors (BAF) and biota sediment factors (BSAF) were employed. Based on the results observed, each tissue accumulated the metals arsenic and antimony from both the water and sediments. Because the metals were accumulated in all tissues, it is useful to recognize the mussel *Corbicula fluminea* as a biomonitor. There was a difference in the distributions of the tissues and shell. Gills and digestive tract had the highest concentrations, while the shell had the lowest concentrations. There was no relationship observed between the metal concentrations in the water and the metal concentrations in the tissues. Lastly, *Corbicula fluminea* is a good biomarker to use to evaluate the levels of arsenic, antimony, and thallium in Manadas Creek.

Acknowledgements

Center for Earth and Environmental Studies of Texas A & M International University for their help to produce the image (**Figure 2**) for this paper.

Fund

Welch Foundation Grant No. BS-0051.

Author Contributions

TV: Conceptualization; Methodology, Writing-original draft preparation. AAM: Conceptualization, methodology, Formal analysis, Writing-review editing. NG: Methodology, Formal analysis, Writing-original draft preparation.

Data Availability

The datasets generated during and/or analyzed during the current study are available from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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