

Report

Estuarine Environmental Indicators for the San Juan Bay Estuary: Assessment of Sediment and Fish Tissue Contaminants

Prepared for: The San Juan Bay Estuary Program, and the
 United States Environmental Protection Agency, Region 2

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List of Acronyms

CCMP	Comprehensive Conservation and Management Plan
EMAP	Environmental Monitoring and Assessment Program
EPA/USEPA	United State Environmental Protection Agency
NCA	National Coastal Assessment

NCCA	National Coastal Condition Assessment
NEP	National Estuary Program
NOAA	National Oceanic and Atmospheric Administration
USGS	United State Geological Survey
SJBE	San Juan Bay Estuary
SJBEP	San Juan Bay Estuary Program
SOPs	Standard Operating Procedures

1 INTRODUCTION

This report contains the results and conclusions of a contamination assessment of sediments and biota conducted in the San Juan Bay Estuary (SJBE) under the Project entitled - *Estuarine Environmental Indicators for the San Juan Bay Estuary: Assessment of Sediment and Fish Tissue Contaminants* (the “Assessment” or “Study”). The field components of the Assessment were completed in July 2011.

The Study was commissioned by the San Juan Bay Estuary Program (SJBE) under funding from the National Estuary Program of the United States Environmental Protection Agency (USEPA). The SJBE selected the Project Consultants following a bid process. The Assessment was completed under contract with the SJBE.

The Study was carried out per procedures described in the Quality Assurance Project Plan (QAPP), which was approved by the USEPA and SJBE in March 2011. The QAPP describes the experimental design, sampling station and environmental indicator selection criteria, sampling and analytical methods, and quality assurance and quality control procedures, among others.

1.1 OVERVIEW OF THE ESTUARY

The SJBE is located on the northern coast of the island of Puerto Rico (**Figure 1**). The SJBE consists of nine major water bodies; these are: the San Juan Bay, San Antonio Channel, Condado Lagoon, Martín Peña Channel, San Jose Lagoon, Los Corozos Lagoon, Suarez Channel, La Torrecilla Lagoon, and Piñones Lagoon (**Figure 2**). The total area and coastal lineal extension for the water bodies of the SJBE system are presented in **Table 1**.

Table 1. Dimensions of the San Juan Bay Estuary Water Bodies

Water body	Area (acres)	Lineal extension
San Juan Bay	3,280	6.5 miles (10.5 km)
San Antonio Channel	114	1.2 miles (2 km)
Condado Lagoon	102	NA
Martín Peña Channel	69	3.8 miles (6 km)
San Jose and Los Corozos Lagoons	1,129	NA
Suarez Channel	63	2.4 miles (3.9 km)
La Torrecilla Lagoon	608	NA
Piñones Lagoon	236	NA



Figure 1. Location of The San Juan Bay Estuary (Source: USEPA National Estuary Program Website)



Figure 2. The San Juan Bay Estuary System and Watershed Estuary (Source: SJBEP)

The SJBE is vital to the regional economy given that it harbors within its boundaries important resources such as ports for cruise and cargo ships, beaches, recreational parks, and historical and natural areas, among others.

The area's growing population has resulted in exploitation of the system's natural resources and degradation and destruction of many of the components of the estuarine system. The main impacts to the SJBE system – land development, illegal sewage discharges, and aquatic debris – are all a result of human settlement and human uses.

In 1992, the SJBE was included in the National Estuary Program (NEP) of the United States Environmental Protection Agency (USEPA), and therefore, was designated as “an estuary of national significance”. The SJBE is the only tropical estuary in the NEP, and the only NEP site outside the Continental United States.

The Comprehensive Conservation and Management Plan (CCMP) for the SJBE contains four Action Plans describing forty-nine specific actions to improve the environmental health of the estuary (Villanueva *et al.*, 2000). The CCMP Action Plans are as follows: (1) Water and Sediment Quality, (2) Habitat, Fish and Wildlife, (3) Aquatic Debris, and (4) Public Education and Involvement.

The San Juan Bay Estuary Program (SJBE) is a non-profit organization responsible for the management and implementation of the CCMP. Projects to address specific components of the CCMP are funded through USEPA National Estuary Program.

In 2010, the SJBE and other SJBE stakeholders awarded contracts to environmental firms to complete the environmental-planning phase in preparation for the implementation of the following CCMP Actions: (1) Improve flow in the Martín Peña Channel through cleanup and dredging activities (Action WS-5), (2) Relocate families living adjacent the Martín Peña Channel (Action WS-2), (3) Fill artificial depressions and restore seagrass beds in the Condado Lagoons (Action HW-2), and (4) Improve the flow of water between La Esperanza Peninsula Cove and the San Juan Bay (Action WS-7). Other CCMP Actions have already been implemented (e.g., Plant mangroves along the shores of the Condado Lagoon (Action HW03), or are underway (e.g., Eliminate unauthorized raw sewage discharges to the Publicly Owned Sewage Treatment Plant (Action WS-3), and to the stormwater sewer system (Action WS-4).

In order to assess the effectiveness of CCMP Actions at the SJBE, the SJBE has proposed the development of a Long-Term Environmental Indicator Program (LTEIP). The indicators to be monitored under the LTEIP have been classified into four groups as follows: (1) Water and Sediment Quality, (2) Biological Productivity and Respiration, (3) Biota Distribution, and (4) Biota-Pollutant Interactions (USEPA, 2006). The LTEIP Program will consist of an integrated approach in which various standard and non-standard methodologies will be used to evaluate among others: contamination assessment of estuarine waters, sediments and biotic tissues, trace element distribution, water column productivity and respiration, and distribution of benthic organisms and submerged aquatic vegetation.

As part of the LTEIP, the SJBE has begun water-quality monitoring at 21 monitoring stations corresponding to locations of high potential for environmental degradation, and has completed a benthic index assessment (PEBS&J, 2009).

1.2 STUDY SCOPE AND PURPOSE

To address the LTEIP components of “Water and Sediment Quality” and “Biota-Pollutant Interactions”, the SJBE required completion of sediment-quality and fish-tissue contamination assessments. To that end, the SJBE formulated a scope of work under the Project entitled: *Estuarine Environmental Indicators for the San Juan Bay Estuary: Assessment of Sediment and Fish Tissue Contaminants* (the “Assessment” or “Study”; available at www.estuario.org/rfp_pdf/rfp_sjbe.pdf).

The purpose of the Study is two fold:

- To assess the effectiveness of ongoing and future conservation and restoration efforts per the CCMP; and
- To evaluate the appropriateness of the selected environmental indicators (i.e., bottom sediments, and mojarra fish and blue crab tissues).

The Assessment was conducted in the summer of 2011 per procedures described in the Quality Assurance Project Plan (QAPP) prepared for this Study. The QAPP was approved by the USEPA and SJBE in March 2011, prior to field implementation.

1.3 SELECTION OF ENVIRONMENTAL INDICATORS

Sediment chemistry was selected as a direct-measurement indicator for the SJBE given that previous site investigations have confirmed the presence of various trace metals and organic pollutants in bottom sediments of the SJBE.

Tissue-chemistry analyses of mojarra fish and blue crab were chosen as environmental indicators for the SJBE, because these organisms are known bottom feeders, are widespread in the estuary, and inhabit the SJBE throughout the year. Further, the meat of these organisms is prepared in foods for human consumption (e.g., the meat of mojarra and blue crab may be consumed by itself in turnovers, or mixed with other fish or shellfish meat during food preparation). Previous site investigations have also shown the presence of trace metals and organic pollutants in fish and shellfish of the SJBE (USEPA, 2008b).

2 PREVIOUS STUDIES

Previous studies conducted in the SJBE may be classified into three categories:

1. Studies published by the EPA in collaboration with other agencies to generate index-indicators of environmental condition, which are expressed as “good”, “fair” or “poor”. These indicators may be used to directly compare the environmental condition of the coastal waters of the United States. The EPA surveys have been conducted by the Environmental Monitoring and Assessment Program (EMAP) under the National Coastal Assessment (NCA; for surveys conducted from 2001 to 2004) and the National Coastal Condition Assessment (NCCA; for surveys conducted after 2004). These studies include:
 - Reports comparing the environmental condition of the nation’s coastal waters (including NEP estuaries) have been published (USEPA 2001b; 2005; 2008a). Further, a nationwide study was conducted under the NCA Program comparing the environmental conditions of the 28 NEP estuaries (USEPA, 2006).
 - A 2008 fish-tissue contaminant assessment conducted by EPA Region II, completed as a surrogate to NCA methodology. This contamination assessment was conducted from fish and blue crab tissue-samples collected from the San Jose Lagoon in the SJBE and in Joyuda Lagoon in western Puerto Rico (USEPA 2008b). Results were expressed as “good”, “fair” or “poor”, based on comparison to EPA Advisory Guidance values.
2. Studies conducted under the SJBEP to help assess the effectiveness of estuary-specific conservation and restoration efforts being implemented per the estuary’s CCMP. At present, the SJBEP has conducted water quality and benthic studies that are intended to address specific concerns at the SJBE.
3. Independent studies conducted by organizations, or individuals, other than EPA or the SJBEP. These studies have been completed to address numerous concerns (e.g., basic research, environmental assessments and environmental permits, among others), and have employed various methods for sampling and analyses.

Following is a summary of the results of previous studies conducted in the SJBE concerning sediment and biotic-tissue chemistry. These are divided per the aforementioned study categories under the headings of “Sediment Chemistry” and “Biotic-Tissue Chemistry”, respectively.

Sediment Chemistry

National Coastal Condition Assessment

The Sediment Quality Index calculated for the coastal waters of Puerto Rico was deemed to be “poor” according to NEP CCR (USEPA 2001b, 2005, 2008a). The Sediment Quality Index was based on data results from sampling stations randomly distributed throughout the coastal waters of Puerto Rico (including stations located throughout the SJBE). The Sediment Quality Index was based on the cumulative score from three sediment-quality indicators: sediment toxicity (10-day

toxicity test to the amphipod *Ampelisca abdita*), sediment contaminants (metals, PAHs, PCBs, and organochlorine pesticides), and sediment Total Organic Carbon (TOC) contents. Regarding sediment contaminants in samples from the SJBE, it was found that more than five analytes exceeded the Effects Range Low (ERL) guideline (i.e., the concentration that potentially could result in a biological effect). Another NCCA sampling event was conducted for Puerto Rico in 2004. However, the results are not available yet for publication and will be presented in the NCCR IV.

In 2002, EPA Region II conducted a survey (under NCA) in which 34 sampling stations were randomly distributed throughout the SJBE (USEPA, 2006). The Sediment Quality Index was rated as “poor” (based on the cumulative scores of sediment toxicity, sediment contaminants and sediment TOC contents).

SJBEP Studies

Webb and Gómez-Gómez (1998), of the USGS, conducted a synoptic survey of water quality and bottom sediments of the SJBE. The survey was conducted in cooperation with the Puerto Rico Environmental Quality Board (PREQB) and USEPA, for the SJBEP.

Webb and Gómez-Gómez (1998) measured the concentrations of seven trace metals (arsenic, barium, cadmium, chromium, lead, mercury, and selenium) in sediment core samples representing the deposition time periods of 1925-1949, 1950-1974, and 1975-1995. Analytical results revealed that of these metals, only mercury and lead concentrations had increased in the most recent sediment strata (1975-1995), compared to levels in older sediment strata (1925-1949 and 1950-1974). The highest concentrations of mercury and lead were encountered in sediment samples collected from the Martin Peña Channel (4.7 and 750 micrograms per gram [$\mu\text{g/g}$], respectively). Whereas mercury levels were homogeneous throughout the remaining study area (ca. 0.15 $\mu\text{g/g}$), lead levels varied with location from an average of 370 $\mu\text{g/g}$, in samples collected from San Jose and Los Corozos Lagoons, to concentrations ranging from 20 to 50 $\mu\text{g/g}$, in samples collected at the remaining sampling stations.

Independent Studies

In 2001, sediment samples were collected at ten sampling stations in the San Antonio Channel and analyzed for aluminum, arsenic, barium, cadmium, chromium, copper, iron, lead, mercury, nickel, selenium, silver, thallium and zinc (PERM, 2001). Only lead and mercury were detected at elevated concentrations. The concentration of lead in the sediment samples ranged from 30 to 100 $\mu\text{g/g}$, whereas mercury concentrations ranged from 0.5 to 3.1 $\mu\text{g/g}$.

A recent comparison between trace metal concentrations in sediments of the San Jose Lagoon and the Joyuda Lagoon in western Puerto Rico (Acevedo-Figueroa *et al.*, 2005) indicated higher concentrations in the San Jose Lagoon compared to those in Joyuda Lagoon, as follows: cadmium 1.8 vs. 0.1 $\mu\text{g/g}$, copper 105 vs. 22 $\mu\text{g/g}$, mercury 1.9 vs. 0.17 $\mu\text{g/g}$, lead 219 vs. 8 $\mu\text{g/g}$, and zinc 531 vs. 52 $\mu\text{g/g}$. In general, the concentrations of lead and mercury in this study were within the range of concentrations previously reported for the San Jose Lagoon.

Polychlorinated Biphenyls (PCBs), DDT, lead and mercury, were the most abundant contaminants encountered in bottom sediments from the SJBE (Villanueva *et al.*, 2000). Bis (2-ethylhexyl) phthalate, a common plasticizing agent, was encountered in bottom sediments from the Martín Peña Channel. This compound had been found in concentrations up to 20,000 micrograms per kilogram (mg/kg) in sediments of the Martín Peña Channel. Webb and Gomez-Gomez (1998) found significant levels of PCBs, organochlorine pesticides and semi-volatile organic compounds. They found a total PCB concentration of 20 µg/g in samples collected from Piñones Lagoon, and at levels in excess of 450 µg/g in the Martín Peña Channel and the San Jose Lagoon. Significant levels of Polycyclic Aromatic Hydrocarbons (PAHs) were detected in the San Antonio Channel (PPB Environmental Laboratories 1999).

A survey of organic pollutants in the San Antonio Channel (PERM, 2001) indicated low concentrations of most of the semi-volatile organic compounds (SVOCs), and polychlorinated naphthalenes (PCNs). Seven PAHs were detected, of which only benzo[a]pyrene was above the accepted threshold effects level (TEL) according to MacDonald *et al.* (1998). Aroclor 1260 was the only PCN detected in the study area at levels below 0.7 µg/g.

Biotic-Tissue Chemistry

National Coastal Condition Assessment Studies

Analytical results of contaminants in fish and crab tissues from a 2008 EPA Survey of the San Jose Lagoon (USEPA, 2008b) were used to calculate a fish tissue contaminant index for the SJBE. The fish tissue contaminant index was calculated by comparing contaminant levels in biotic-tissue samples to EPA Advisory Guidance values. The fish tissue contaminant index for the SJBE was rated as “poor” because 40% of the samples analyzed for contaminants exceeded EPA Advisory Guidance values (USEPA, 2006). The study revealed that PCBs, dieldrin, total PAHs, and total DDT were of potential public health concern. The concentrations of these compounds in fish and crab-tissue samples were found to exceed those of human health screenings values (USEPA, 2008b). Except for the mean concentration of dieldrin in crab hepatopancreas, the mean concentrations for the tested species did not exceed their respective human screening values (USEPA, 2008b).

SJBEP Studies

Currently, the SJBEP has not conducted biotic-tissue contamination assessments of the SJBE, other than participating in the 2008 Survey of the San Jose Lagoon.

Independent Studies

Analysis of seven trace metals in tissues of blue crab, mojarra and false mussel in the San Jose Lagoon (Delgado Morales *et al.*, 1999; and Rodriguez Sierra and Jimenez, 2002) had indicated moderately elevated levels of mercury. However, mercury concentrations in some samples approached or exceeded the Food and Drug Administration’s (FDA) action level for human consumption of 1 µg/g in edible fishes. Similarly, lead concentrations were moderately high with some samples exceeding the FDA action level of 0.5 µg/g. Sampling locations showing action-level

exceedances appeared to correspond to areas with high potential for receiving human-derived pollution.

3 FIELD METHODS

3.1 SAMPLING-STATION LOCATIONS

Sampling of bottom sediments and biota (fish and blue crab) at the SJBE was conducted from 31 May to 11 June 2011 as two consecutive events for the western and eastern portions of the estuary, respectively.

The western portion of the SJBE, designated here as WSJBE, was sampled from 31 May to 3 June 2011, and from 10 to 11 June 2011, and consisted of Sampling Stations located in the Condado Lagoon, the main basins of the San Juan Bay and Cataño, Puerto Nuevo River, and the Martin Peña Channel. The eastern portion of the SJBE, designated here as ESJBE, was sampled from 7 to 9 June 2011, and consisted of Sampling Stations located in the San Jose, Torecilla and Piñones Lagoons, Canal Suarez, Boca de Cangrejos, and near the eastern entrance to the Martin Peña Channel.

Figures 3 show the targeted Sampling Stations, whereas **Figures 4** and **5** show the actual Sampling Stations for WSJBE and ESJBE, respectively (some Stations had to be moved based on field conditions). **Table 2** summarizes information pertaining to the samples collected at these locations.



Figure 3. Targeted Sampling Station Locations. Stations for the collection of bottom-sediment samples are marked with a square, whereas those for tissue samples are marked with a circle

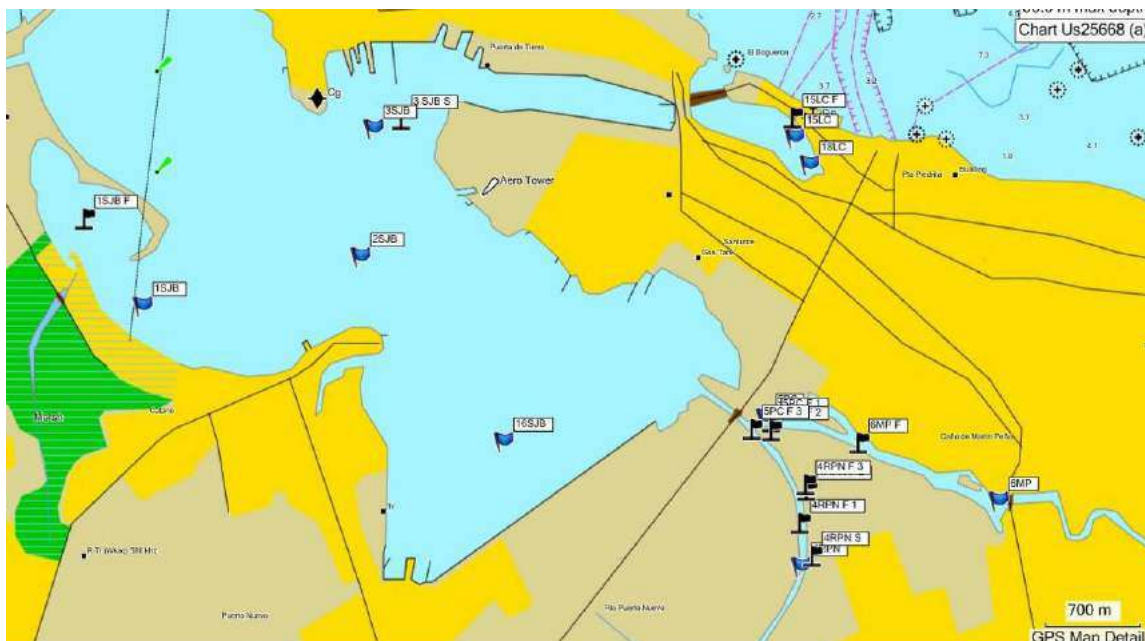


Figure 4. West San Juan Bay Estuary Sampling Stations. Positions and samples collected are indicated in Table 1. Original stations are indicated as blue flags. Black flags indicate position of alternate stations.



Figure 5. East San Juan Bay Estuary Sampling Stations. Positions and samples collected are indicated in Table 1. Original stations are indicated as blue flags. Black flags indicate position of alternate stations.

Table 2. Sediment and Biotic-Tissue Sample Designation

Station ID	Date Collected	Sediment Sample ID	Fish Tissue Sample ID	Blue Crab Tissue Sample ID
1 SJB	May-31-11	SJBE-BS-1SJB		SJBE-CT-1SJB
1SJB F	June-2-11		SJBE-FT-1SJB	
1 SJB	June-10-11	SJBE-CT-1SJB	SJBE-FT-1SJB	
2SJB	May-31-11	SJBE-BS-2SJB		
3SJB S	May-31-11	SJBE-BS-3SJB		
4RPN S	May-31-11	SJBE-BS-4RPN		
4RPN F	June-2-11			SJBE-FT-4RPN
4RPN F	June-10-11		SJBE-CT-4RPN	
5PC	May-31-11	SJBE-BS-5PC		
5PC F	June-2-11			SJBE-CT-5PC
5PC F	June-3-11			SJBE-CT-5PC
5PC F	June-9-11			SJBE-CT-5PC
6MP	May-31-11	SJBE-BS-6MP		
6MP F	June-2-11			SJBE-FT-6MP
16SJB	May-31-11	SJBE-BS-16SJB		
18LC	May-31-11	SJBE-BS-18LC, 2X LAB QC (18LC)		
15LC	May-31-11	SJBE-BS-15LC		
15LC F	June-2-11		SJBE-CT-15LC	SJBE-FT-15LC
15LC F	June-3-11		SJBE-CT-15LC	
15LC F	June-10-11		SJBE-CT-15LC	
15LC F	June-11-11		SJBE-CT-15LC	SJBE-FT-15LC
7MPSJ	June-7-11	SJBE-BS-7MPSJ		
7MPSJ F	June-8-11		SJBE-CT-7MPSJ-A, B	SJBE-FT-7MPSJ-A, B
8SJC S	June-7-11	SJBE-BS-8SJC		
8SJC F	June-8-11		SJBE-CT-8SJC	SJBE-FT-8SJC
9SJ	June-7-11	SJBE-BS-9SJ-A,B		
9SJ	June-7-11	2x LAB QC (9SJB)		
10CS S	June-7-11	SJBE-BS-10CS		
10CS F	June-9-11	18.42344	SJBE-CT-10CS	SJBE-FT-10CS
11LT	June-7-11	SJBE-BS-11LT		
11LT F	June-8-11		SJBE-CT-11LT	SJBE-FT-11LT
12BC S	June-7-11	SJBE-BS-12BC		
13PS	June-7-11	SJBE-BS-13PS		
14PN	June-7-11	SJBE-BS-14PN		
17SJ	June-7-11	SJBE-BS-17SJ		

Sampling locations, and collection and preparation methods were according to the EPA-approved QAPP, except as otherwise noted.

Table 3 show a comparison of Sampling Station in the present Study with those in previous studies, whereas **Table 4** shows the Sampling Station selection criteria.

Table 3. Comparison of Sampling-Station Locations in the Proposed Study to those of Previous Investigations

Proposed Study	WQVMPP ^W	Web and Gomez-Gomez 1998 ^S	Acevedo-Figueroa 2005 ^S	PERM 2001 ^S	Delgado-Morales et al 1999 ^T	Rodriguez-Sierra and Jimenez, 2002 ^T	SJBE 2008 ^W	Rivera 2005 ^B
1SJB	SJB6							32 SJBEP2000
2SJB	SJB3						BSJ2	3, 50 SJBEP2000
3SJCA	CSA			SAC-G-38-177				68 SJBEP2000
4RPN	RPN						RPN	1 SJBEP2000
5PC								
6MP	CMP	500449850					CMP	
7MPSJ			11			IV	LS1	
8SJC	SJ3	50049710	3,4,5		M5, FC3	III	LLC	70,56 REMAP2002
9SJ	SJS300	50049755			M3, FC2			41 SJBEP2000
10CS					M2, FC1		CS1	9, 114REMAP2002
11LT	TL3							
12BC	TL1						LT1	
13PS		50050344						39 REMAP2002
14PN	PL2							41,43 REMAP2002
15LC							LC1	13 REMAP2002
16SJB		500049935S					BSJ3	19 SJBEP2000
17SJ			8		M7			10, 46 SJBEP2000
18LC							LC1	15 REMAP2002

Types of samples collected in previous studies: W= water; S= sediments; T= tissue; B=meiobenthos

Table 4. Sampling-Station Selection Criteria

Station	Description
1SJB	Subjected to inputs from Peninsula La Esperanza and southwestern Bahia de San Juan.
2SJB	Middle station integrating inputs and dilution from inner San Juan Bay.
3SJCA	Subjected to water flow from Canal San Antonio, and integrating other possible sources San Juan Passenger Terminal
4RPN	This station is indicative of inputs from Rio Puerto Nuevo and Rio Piedras, which encompass an important source of pollution to the system.
5PC	Endpoint of pollution sources within the channel communicating Caño Martin Peña and San Juan Bay proper, thus integrating inputs and dilutions of pollutants within the channel.
6MP	Represents western output of Martin Peña channel (MPC) another important source of pollutants into the estuary. This station is included in order to maintain records of pollutant levels prior to the proposed cleanup of MPC, as identified in the CCMP.
7MPSJ	Station closely associated to the eastern exit of Martin Peña and Juan Mendez Creek (this last drains urban sources from Rio Piedras.
8SJC	This station was selected to represent the Corozos Lagoon, a sub-basin of San Jose Lagoon.
9SJ	Represent shallower areas in southwestern San Jose Lagoon.
10CS	Selected to evaluate conditions in Canal Suarez, a tidal creek connecting La Torrecilla and San José Lagoons.
11LT	Selected to indicate conditions at La Torrecilla Lagoon, impacted by local development.
12BC	Seaward endpoint of environmental conditions in this sub-basin of SJBE.
13PS	Southern station of Piñones Lagoon, a semi-enclosed basin in the SJBE, within Piñones Reserve.
14PN	North Station at Piñones Lagoon, serve as replicate in conjunction to PS.
15LC	Represent eastern central portion of Condado Lagoon, site related to seagrass restoration project of Condado Lagoon that was dredged decades ago.
16SJB	Selected to represent southern portion of San Juan Bay.
17SJ	Represent deeper areas of San Jose Lagoon dredged decades ago and reported as being anoxic. This specific area is the target of one of the CCMP actions to restore the conditions in the San José Lagoon by depositing sediments dredged from other sites as a means to eliminate anoxia and restore water flows.
18LC	Eastern Portion of Condado Lagoon. Selected as a station with minimum circulation potential.

3.1.1 West San Juan Bay Estuary (WSJBE)

Sediment Sample Collection

On 31 May 2011, nine stations were sampled at WSJBE for sediment contaminants (See **Figure 4**). Sampling Station 3SJB was moved to Lat N18.45825 and Lon W66.10926 degrees (see **Table 5**), given that abundant shell-cover at the original location prevented penetration of the Petite Ponar sampling dredge.

Fish and Crab Sampling

Fish and crab specimens were collected from 1 to 3 June and from 10 to 11 June 2011 using cast nets and traps at or near the designated Biota Sampling Stations. During 1-3 June 2011, environmental conditions were mostly cloudy with heavy rains. During 10-11 June 2011, conditions were mostly sunny. Fishing at preselected stations (**Figure 3**) was first attempted.

Table 5. Sampling Locations at the Western and Eastern Portions of the San Juan Bay Estuary¹

SJBE	Station Number	Station Designation	Position (Lat, Lon)	Sediments	Fish captured	Blue Crab captured	Planned Location
West	1	1SJB	N18.44589, W66.13032	YES	YES	YES	YES
West		1SJB F	N18.45116, W66.13530	NO	YES	NO	NO
West	2	2SJB	N18.44914, W66.11256	YES	NO	NO	YES
West	3	3SJB	N18.45762, W66.11152	NO	NO	NO	YES
West		3SJB S	N18.45825, W66.10926	YES	NO	NO	NO
West	4	4RPN	N18.42865, W66.07702	NO	NO	NO	YES
West	4	4RPN S	N18.42937, W66.07612	YES	NO	NO	NO
West	4	4RPN F	N18.43154, W66.07710; N18.43373, W66.07657; N18.43409, W66.07664	NO	YES	YES	NO
West	5	5PC	N18.43851, W66.07987	YES	NO	NO	YES
West		5PC F	N18.43826, W66.07942; N18.43767, W66.07941; N18.43774, W66.08098	NO	NO	YES	NO
West	6	6MP	N18.43299, W66.06108	YES	NO	NO	YES
West		6MP F	N18.43685, W66.07237	NO	YES	NO	NO
West	7	15LC	N18.45701, W66.07754	YES	NO	NO	YES
West		15LC F	N18.45836, W66.07771	NO	YES	YES	NO
West	8	16SJB	N18.43692, W66.10102	YES	NO	NO	YES
West	9	18LC	N18.45531, W66.07632	YES	NO	NO	YES
East	10	7MPSJ	N18.42780, W66.03410	YES	NO	NO	NO
East	10	7MPSJ F	N18.4242, W66.0292; N18.4244, W66.0231; N18.4311, W66.0230	NO	YES	YES	NO
East	11	8SJC	N18.44131, W66.03891	NO	NO	NO	YES
East	11	8SJC S	N18.4405, W66.0380	YES	NO	NO	NO
East	11	8SJC F	N18.43221, W66.03102	NO	YES	YES	NO
East	12	9SJ	N18.42428, W66.02023	YES	NO	NO	YES
East	13	10CS	N18.42680, W65.99709	NO	NO	NO	YES
East	13	10CS S	N18.4261, W65.9974	YES	NO	NO	NO
East	13	10CS F	N18.42344, W66.01073; N18.41802, W66.01308	NO	YES	YES	NO
East	14	11LT	N18.43906, W65.98006	YES	NO	NO	YES
East		11LT F	N18.4450, W65.9815	NO	YES	YES	NO
East	15	12BC	N18.45777, W65.99200	NO	NO	NO	YES
East	15	12BC S	N18.4563, W65.9900	YES	NO	NO	NO
East	16	17 SJ S	N18.41925, W66.01615	YES	NO	NO	NO
East	17	14 PN	N18.44280, W65.95259	YES	NO	NO	YES
East	18	13PS	N18.43431, W65.95844	YES	NO	NO	YES

¹Sampling stations designation including "S" (sediment) or "F" (fish/crab) indicate alternate locations for sediment, and fish/crab sampling, and that the original selected station had to be abandoned for the specified matrix. An absence of "S" or "F" flags indicates that the original selected location was sampled successfully. Positions are given in decimal degree N or W. Sampling of sediments or collection of specimens at each station is indicated as "YES".

However, depending on catch success, fishing efforts were moved to nearby locations to obtain the necessary quantity of biotic sample. To maximize catch potential, fishing efforts were concentrated along the banks of the lagoons and channels within the estuary where mangroves and seagrasses provided habitat for biota. Regarding Sampling Station “1SJC”, located in Cataño, at the western end of the San Juan Bay (i.e., no mangroves), fish specimens had to be collected also from the nearby Peninsula La Esperanza Lagoon to increase the quantity of fish necessary for sample analysis.

Sampling of biota at Station 6MP (i.e., Martin Peña Channel) was unsuccessful due to the prevailing anoxic conditions present at that Station. The Station was initially moved to an alternate location 150m across the entrance of the Martin Peña Channel, but no catch was retrieved. The Station was then moved 1.3Km westward along the navigation channel to a location frequented by fishermen.

Fishing efforts at the Rio Puerto Nuevo (4RPN) Station covered areas up to 500m to the north along the river edge, given that dredging operations were being conducted during this period and precluded safe navigation within areas adjacent to the pre-selected Sampling Station.

Fishing effort at the Condado Lagoon was concentrated along its north-northeastern bank, which contained seagrass and mangrove habitats. Therefore, Station 15LC was offset 150m northward from its pre-selected location. The degraded environmental conditions at Station 18LC prevented the establishment of seagrasses thus minimizing fishing potential. Furthermore, traps deployed at Station 18LC were stolen.

3.1.2 East San Juan Bay Estuary (ESJBE)

Sediment Sample Collection

On 7 June 2011, nine Sediment Sampling Stations at ESJBE were visited of which three were moved due to field conditions. Station “8SJC” was moved to the southeast (N18.4405, W66.0380) due to the presence of dense beds of the false mussel *Mytilopsis* sp. that prevented the proper penetration of the dredge at the original location. Station “10CS” was moved ca. 60m to the southwest (N18.4261, W65.9974) due to existing boat traffic, whereas Station 12BC was moved southeast ca. 200m (N18.4563, W65.9900) since the bottom at the original Station location was mostly compact sand and dredge penetration could not be achieved.

Fish and Crab Sampling

Tissue sampling at ESJBE was fully accomplished from 8 to 9 June 2011, using mainly trammel net for fish and trammel net and hook for blue crabs. Sampling was attempted at all original locations. However, fishing efforts were expanded to adjacent areas as guided by local fishermen to increase sample to adequate amounts needed for analysis, or moved from locations away from existing boat traffic that prevented sample collection. The fishing station “8SJC” was moved 1 km southeast (N18.43221, W66.03102) from the original location. Specimen catch at “7MPSJ” was limited to a few specimens of fish and no blue crabs, so additional catch from three adjacent

locations (N18.4242, W66.0292; N18.4244, W66.0231; N18.4311 W66.0230) were pooled to get the necessary tissue for analysis. These samples cover the central portion of the San Jose Lagoon Basin. No catch was retrieved at “10CS” and at other locations within Canal Suarez. The fishing effort was afterwards moved to the inland entrance of Canal Suarez and the mouth of San Anton Creek (N18.42344, W66.01073; N18.41802, W66.01308). Fishing for fish and blue crab was attempted in the shallows, 100m northwest of “11LT”, but with no success. After several attempts at adjacent sites, moderate catch of both species of interest was caught about 700m NE of “11LT” (N18.4450, W65.9815).

3.2 SEDIMENT SAMPLE COLLECTION

The completed field forms for sediment sample collection are included in **Appendix A**.

Overall, sediment collection methods followed those described in the EPA-approved QAPP. A handheld GPS unit (Garmin 76csx) with nautical charts was used to reach pre-selected station coordinates. Samples were collected within a 5m radius of the preselected location with the few exceptions mentioned above (Sub-Section 3.1).

The Petite Ponar dredge sampler, fitted with SS screens, was used in conjunction with a stabilizer A-frame (see **Figure 6**) to maintain the dredge at a horizontally leveled position while sampling and, therefore, retrieve acceptable sample grabs. Originally, sediment samples were to be retrieved from the top of the dredge after removal of screens. However, to facilitate retrieval of sediment samples from the Petite Ponar dredge, samples had to be retrieved from the bottom of the dredge (representing the top 8 cm of the sediment layer) as sample collection from the top was hindered by partially blocked upper doors (due to the configuration of the stabilizer A-frame).



Figure 6. Sediment Sampling Rig Including Petite Ponar Dredge Mounted on Stabilizing Frame. The dredge was lowered by the side of the boat using a portable pulley and frame system constructed for this study. The system allows for the retrieval of sediment and collection of sediments in glass bowls and can be easily installed in different small boats.

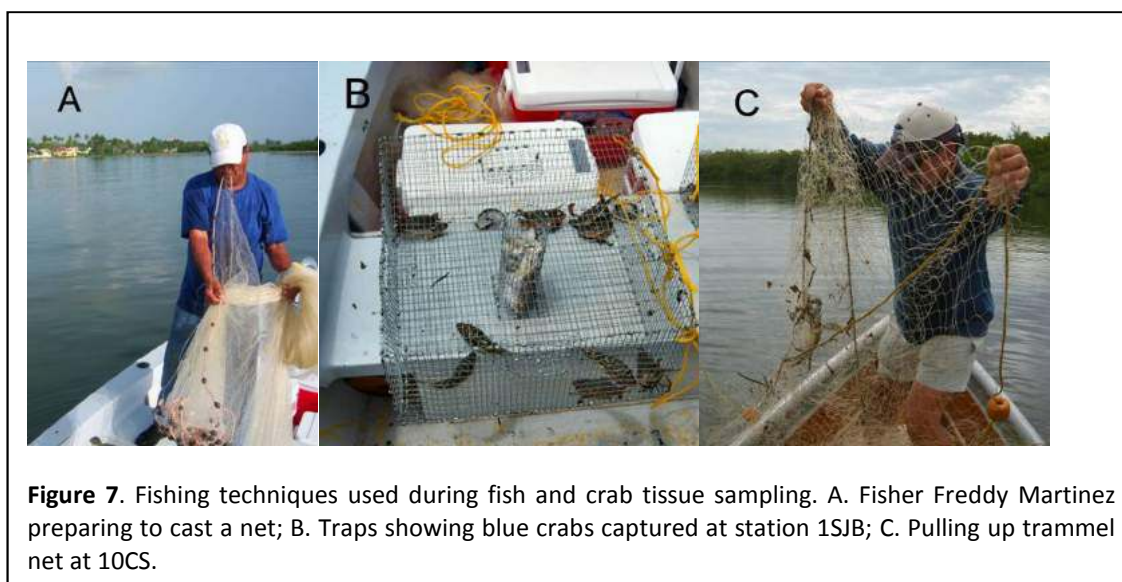
Sediment from the dredge was transferred into a pre-cleaned Pyrex bowl, homogenized with a pre-cleaned stainless-steel spoon and then transferred to laboratory-supplied, labeled jars (avoiding any headspace). The samples were placed inside re-sealable plastic bags and immediately placed in an iced chest. Sediment samples were transported within 24 hours of

collection to Pace Analytical Center in Guaynabo, Puerto Rico. Samples were shipped via overnight carrier to Pace Analytical in New Orleans, Louisiana.

The dredge was cleansed using a low-phosphate soap solution, brush, tap water, 10% HCl, DI water, and Pesticide grade methanol between each station. The equipment blank was collected towards the end of each sampling day.

3.3 COLLECTION OF FISH AND CRAB-TISSUE SAMPLES

The completed field forms for biotic sample collection are included in **Appendix B**. Fishes were collected either using fish traps, cast nets or trammel nets (**Figure 7**).



Fishes from each sampling station were placed separately into cleaned buckets stored inside iced coolers to keep them cold, while avoiding direct contact with ice to minimize the potential for contamination. Once on shore, fishes were organized by size, weighted and measured. Dorsal, anal and pectoral fin spines were clipped with cleaned scissors. The exterior of the fish was washed with DI water, wrapped with several layers of heavy-duty aluminum foil and doubled bagged in plastic re-sealable bags. A label was adhered to the internal bag and a second label was added inside the exterior bag. A third label was attached to the external bag. Samples were then frozen (-20°C) until delivery to Pace laboratory facilities. Samples were packed with dry ice and shipped via overnight carrier to Pace Analytical in Green Bay, Wisconsin, for analysis.

Blue crab tissue was extracted within six hours of landing and the extracted meat was shipped frozen in double bags labeled as the fishes. The tissue was extracted on site in order to verify the amount of meat needed for the analysis. The method of extraction consisted of extrusion of meat from the body cavity 4-6 hours after being killed on ice. In order to accomplish this, crabs were put in clean buckets, capped and put in ice. After being killed, the crabs were washed with distilled water, identified, measured, sexed and their chelae and shell were removed followed by the gills

and innards. The inside of the crab was washed with cleaned nylon brushes and tap water, followed by a DI water rinse. Afterwards, crabs were sectioned sagittally and the meat of each half was extruded using a cleaned Crab Master™ (**Figure 8**). Each portion was transferred to a pre-weighted re-sealable bag where meat was pooled until reaching a minimum weight of 80 to 100g. Sample-container labeling, packing and transportation were as for fish tissue samples.



Figure 8. Extruding raw blue-crab meat.

Biotic samples were transported within 24 hours of collection to Pace Analytical Center in Guaynabo, Puerto Rico (Pace-Guaynabo). Samples were stored at -20°C inside the freezer located at Pace-Guaynabo until all biotic samples had been collected. Temporary sample storage at -20°C did not exceed two weeks. Samples were then packed with dry ice in an ice chest and shipped via overnight carrier to Pace Analytical in Green Bay, Wisconsin.

4 ANALYTICAL METHODS

4.1 SEDIMENT SAMPLES

Pace Analytical Services, Inc. (Pace Analytical), in New Orleans, Louisiana, analyzed sediment and quality control samples for the parameters listed in **Table 6**.

Analyte concentration in sediment samples were corrected for percent moisture and expressed on a dry weight basis.

Table 6. Analytical Methods, Holding Times, Sample Quantity and Preservation for Bottom Sediment Samples

Parameter	Method	Holding Time ¹	Container Type	Preservation
Antimony ³	EPA 6010B	6 months	4 oz. Glass Jar	2°C - 6°C ⁴
Arsenic	EPA 6010B	6 months	4 oz. Glass Jar	2°C - 6°C
Beryllium	EPA 6010B	6 months	4 oz. Glass Jar	2°C - 6°C
Cadmium	EPA 6010B	6 months	4 oz. Glass Jar	2°C - 6°C
Chromium	EPA 6010B	6 months	4 oz. Glass Jar	2°C - 6°C
Copper	EPA 6010B	6 months	4 oz. Glass Jar	2°C - 6°C
Lead	EPA 6010B	6 months	4 oz. Glass Jar	2°C - 6°C
Mercury	EPA 7471A	28 days	4 oz. Glass Jar	2°C - 6°C
Nickel	EPA 6010B	6 months	4 oz. Glass Jar	2°C - 6°C
Selenium	EPA 6010B	6 months	4 oz. Glass Jar	2°C - 6°C
Silver	EPA 6010B	6 months	4 oz. Glass Jar	2°C - 6°C
Thallium	EPA 6010B	6 months	4 oz. Glass Jar	2°C - 6°C
Zinc	EPA 6010B	6 months	4 oz. Glass Jar	2°C - 6°C

Semi-Volatile Organic Compounds and PAHs ⁵	EPA 8270C	14 days/ 40 days ²	4 oz. Glass Jar	2°C - 6°C
Organochlorine Pesticides	EPA 8081A	14 days/ 40 days	4 oz. Glass Jar	2°C - 6°C
PCBs ⁶ (Aroclor Equivalents)	EPA 8082A	14 days/ 40 days	4 oz. Glass Jar	2°C - 6°C
Total Organic Carbon	EPA 9060	28 days	4 oz. Glass Jar	2°C - 6°C
Percent Solids	SM 2540G	7 days	4 oz. Glass Jar	2°C - 6°C
Grain Size	ASTM D422	1 year	8 oz. Glass Jar	2°C - 6°C

¹ Holding time before sample extraction.

² Holding time for analysis after sample extraction.

³ All 13 metals listed in the table are included in the Priority Pollutant Metals.

⁴ C = Degrees Celsius

⁵ PAHs = Polycyclic Aromatic Hydrocarbons

⁶ PCBs = Polychlorinated Biphenyls

4.2 BIOTIC-TISSUE SAMPLES

Pace Analytical in Green Bay, Wisconsin, analyzed fish and crab-tissue samples for the parameters listed in **Table 7**.

Except for fish specimens captured at Sampling Station “1SJB”, fish specimens were filleted as part of sample preparation. Given that the size of the specimens captured at Sampling Station “1SJB” were too small for filleting, whole fish extract was prepared and extracted for sample SJBE-FT-1SJB.

Table 7. Analytical Methods, Holding Times, Sample Quantity and Preservation for Fish and Crab-Tissue Samples

Parameter	Method	Holding Time ¹	Container Type	Preservation
Antimony ³	EPA 6020A	6 months	Polyethylene Bag	Frozen (Dry Ice)
Arsenic	EPA 6020A	6 months	Polyethylene Bag	Frozen (Dry Ice)
Beryllium	EPA 6020A	6 months	Polyethylene Bag	Frozen (Dry Ice)
Cadmium	EPA 6020A	6 months	Polyethylene Bag	Frozen (Dry Ice)
Chromium	EPA 6020A	6 months	Polyethylene Bag	Frozen (Dry Ice)
Copper	EPA 6020A	6 months	Polyethylene Bag	Frozen (Dry Ice)
Lead	EPA 6020A	6 months	Polyethylene Bag	Frozen (Dry Ice)
Mercury	EPA 7471A	28 days	Polyethylene Bag	Frozen (Dry Ice)
Nickel	EPA 6020A	6 months	Polyethylene Bag	Frozen (Dry Ice)
Selenium	EPA 6020A	6 months	Polyethylene Bag	Frozen (Dry Ice)
Silver	EPA 6020A	6 months	Polyethylene Bag	Frozen (Dry Ice)
Thallium	EPA 6020A	6 months	Polyethylene Bag	Frozen (Dry Ice)
Zinc	EPA 6020A	6 months	Polyethylene Bag	Frozen (Dry Ice)

Parameter	Method	Holding Time ¹	Container Type	Preservation
Semi-Volatile Organic Compounds and PAHs ⁴	EPA 8270C	14 days/ 40 days ²	Polyethylene Bag	Frozen (Dry Ice)
Organochlorine Pesticides	EPA 8081A	14 days/ 40 day	Polyethylene Bag	Frozen (Dry Ice)
PCBs ⁵ (Aroclor Equivalents)	EPA 8082A	14 days/ 40 days	Polyethylene Bag	Frozen (Dry Ice)

¹ Holding time before sample extraction.

² Holding time for analysis after sample extraction.

³ All 13 metals listed in the table are included in the Priority Pollutant Metals.

⁴ PAHs = Polycyclic Aromatic Hydrocarbons.

⁵ PCBs = Polychlorinated Biphenyls.

5 QUALITY CONTROL

Mrs. Daliz Estades, Project QA Officer, conducted QC Audits of field activities and of the laboratory report data packages.

On 7 June 2011, Mrs. Estades conducted a Field QC Audit of sampling activities. During the field audit, she accompanied the sampling crew to Sampling Station "8SJC" and witnessed the collection of the sediment sample and the equipment blank, as well as sampling equipment decontamination procedures. The completed Field QC Audit Form is included in **Appendix C**.

The QA Officer conducted verification and validation of the analytical data packages for sediment and biotic-tissue analyses. The completed Data Validation Review Reports for sediment and biotic-tissue analyses are included as **Appendix D**.

Results regarding the QC acceptance criteria for accuracy, precision, sensitivity and completeness are summarized in **Appendix E**.

6 RESULTS AND DISCUSSION

6.1 METHOD DETECTION LIMITS

Table 8 presents the target and average method detection limits (MDLs) for sediment and biotic tissue for the following analyses: metals, organochlorine pesticides (including DDTs), PCBs, SVOCs and PAHs. Sample-specific MDLs for sediment and biotic-tissue samples can be found in the Laboratory Report Packages (**Appendices F and G**).

6.1.1 Sediment Samples MDLs

Analytical results of chemical constituents in sediment samples are expressed on a dry weight basis.

The contaminants of concern in bottom-sediment samples were compared against the Threshold Effects Level (TEL) and the Probable Effects Level (PEL) for marine sediments. The TEL represent an estimate of the concentration below which adverse effects only rarely occur in biota. The PEL represent an estimate of the concentration above which adverse effects frequently occur in biota (MacDonald *et al.*, 1996).

In general, the average MDLs for metals, organochlorine pesticides, SVOCs and PAHs, achieved during sediment sample analysis, were between two to three-fold higher than the target MDLs listed in the QAPP (**Table 8**). In contrast, the average MDLs for PCBs were between eight to 13-fold higher than the target MDLs (**Table 8**).

Regarding organic analytes, matrix interference was likely the main cause in the rise of MDLs relative to the targeted levels. Evidence of matrix interference is seen in the “out of control”.

Table 8. Target and Average Method Detection Limits (MDLs) Achieved During Sediment and Biotic-Tissue Sample Analyses.

	Sediment Samples		Biotic-Tissue Samples	
	Target MDL	Actual MDL (Average)	Target MDL	Actual MDL (Average)
Metals (mg/kg)				
Aluminum	ND ¹	11.89	ND	ND
Antimony	0.08931	0.27	0.004	0.004
Arsenic	0.09754	0.30	0.029	0.027
Beryllium	0.01742	0.05	0.031	0.029
Cadmium	0.01432	0.04	0.008	0.007
Chromium	0.15389	0.47	0.0219	0.047
Copper	0.45887	1.43	0.027	0.040
Lead	0.09885	0.30	0.005	0.010
Mercury	0.00161	0.0045	0.008	0.007
Nickel	0.06559	0.20	0.026	0.024

Selenium	1.13872	3.46	0.070	0.066
Silver	0.02545	0.08	0.003	0.003
Thallium	0.11768	0.36	0.011	0.010
Zinc	0.23334	0.71	0.843	0.779
Polycyclic Aromatic Hydrocarbons (µg/kg)				
PCB-1016 (Aroclor 1016)	16.65	210.9	19.6	25
PCB-1221 (Aroclor 1221)	16.65	210.9	19.6	25
PCB-1232 (Aroclor 1232)	16.65	210.9	19.6	25
PCB-1242 (Aroclor 1242)	16.65	210.9	19.6	25
PCB-1248 (Aroclor 1248)	16.65	210.9	19.6	25
PCB-1254 (Aroclor 1254)	26.04594	210.9	19.6	25
PCB-1260 (Aroclor 1260)	16.65	210.9	19.6	25
Organochlorine Pesticides (µg/kg)				
4,4'-DDD	1.67	6.2	1.04	1.06
4,4'-DDE	1.67	6.2	1.61	1.69
4,4'-DDT	2	6.2	0.796	0.84
Aldrin	0.85	3.1	1.25	1.27
alpha-BHC	0.85	3.1	0.539	0.57
alpha-Chlordane	0.85	3.1	0.609	0.64
Chlordane	0.85	ND	8.54	1.37
beta-BHC	0.85	3.1	1.32	8.98
delta-BHC	0.85	5.9	1.43	1.48
Dieldrin	1.67	6.2	2.50	2.64
Endosulfan I	0.85	3.1	0.724	0.76
Endosulfan II	1.67	6.2	0.665	0.71
Endosulfan sulfate	1.67	6.2	1.196	1.27
Endrin	1.67	6.2	2.50	2.64
Endrin aldehyde	1.67	6.2	2.297	2.43

	Sediment Samples		Biotic-Tissue Samples	
	Target MDL	Actual MDL (Average)	Target MDL	Actual MDL (Average)
Endrin ketone	1.67	6.2	1.073	1.16
gamma-BHC (Lindane)	0.85	3.1	0.646	0.69
gamma-Chlordane	0.85	3.1	0.936	0.99
Heptachlor	0.85	3.1	0.725	0.76
Heptachlor epoxide	0.85	3.1	1.36	1.47
Methoxychlor	8.5	30.8	6.73	7.08
Toxaphene	33.3	120.7	24.0	25.33
Polycyclic Aromatic Hydrocarbons (µg/kg)				
Acenaphthene	28.218	102.0	34.99	102.0
Acenaphthylene	26.454	95.6	52.36	95.6
Anthracene	26.743	96.7	44.74	96.7
Benzo(a)anthracene	27.932	101.1	40.39	101.1

Benzo(a)pyrene	32.053	116.5	47.58	116.5
Benzo(b)fluoranthene	38.637	115.9	53.58	115.9
Benzo(g,h,i)perylene	32.183	103.4	55.93	103.4
Benzo(k)fluoranthene	28.588	139.7	70.54	139.7
Chrysene	27.55	99.7	50.17	99.7
Dibenz(a,h)anthracene	124.763	451.2	70.95	451.2
Fluoranthene	30.811	111.5	49.82	111.5
Fluorene	29.995	108.4	57.35	108.4
Indeno(1,2,3-cd)pyrene	42.161	152.5	128.74	152.5
Naphthalene	30.751	111.2	42.29	111.2
Phenanthrene	26.835	97.1	46.52	97.1
Pyrene	26.77	96.9	81.64	96.9
Semi-Volatile Organics Compounds (µg/kg)				
1,2,4-Trichlorobenzene	28.007	92.6	55.14	92.6
1,2-Dichlorobenzene	28.003	101.3	50.95	101.3
1,3-Dichlorobenzene	27.397	99.1	45.74	99.1
1,4-Dichlorobenzene	25.444	92.0	35.15	92.0
2,2'-Oxybis(1-chloropropane)	33.989	123.0	57.50	123.0
2,4,5-Trichlorophenol	30.407	110.0	56.57	110.0
2,4,6-Trichlorophenol	26.874	97.2	66.12	97.2
2,4-Dichlorophenol	31.329	113.4	67.95	113.4
2,4-Dimethylphenol	34.755	125.7	77.04	125.7
2,4-Dinitrophenol	58.226	210.6	137.0	210.6
2,4-Dinitrotoluene	29.36	106.2	84.74	106.2
2,6-Dinitrotoluene	29.482	106.6	59.39	106.6
2-Chloronaphthalene	26.934	97.3	42.98	97.3
2-Chlorophenol	32.111	116.2	45.9	116.2
2-Methylnaphthalene	28.477	102.9	50.24	102.9
2-Methylphenol (o-Cresol)	29.276	105.8	45.43	105.8
	Sediment Samples		Biotic-Tissue Samples	
	Target MDL	Actual MDL (Average)	Target MDL	Actual MDL (Average)
2-Nitroaniline	33.558	121.4	175.85	121.4
2-Nitrophenol	31.946	115.6	54.2	115.6
3&4-Chloroaniline	165.782	599.7	1,014.36	599.7
3&4-Methylphenol	29.644	107.2	68.07	107.2
3,3'-Dichlorobenzidine	38.256	138.4	73.03	138.4
3-Nitroaniline	37.077	134.1	41.56	134.1
4,6-Dinitro-2-methylphenol	35.626	128.9	68.95	128.9
4-Bromophenylphenyl ether	27.777	100.5	48.43	100.5
4-Chloro-3-methylphenol	31.55	114.1	82.47	114.1
4-Chlorophenylphenyl ether	31.595	114.4	61.80	114.4
4-Nitroaniline	46.885	169.6	109.95	169.6
4-Nitrophenol	33.067	119.5	144.56	119.5
Benzoic acid	99.36957	359.6	ND	359.6

Benzyl alcohol	38.583	139.6	39.02	139.6
bis(2-Chloroethoxy)methane	33.673	121.8	52.83	121.8
bis(2-Chloroethyl) ether	31.392	113.6	56.68	113.6
bis(2-Ethylhexyl)phthalate	35.213	127.4	149.17	127.4
Butylbenzylphthalate	34.594	125.1	75.12	125.1
Carbazole	31.418	113.7	77.71	113.7
Dibenzofuran	25.862	93.5	48.41	93.5
Diethylphthalate	33.36	120.7	83.8	120.7
Dimethylphthalate	31.573	114.2	55.05	114.2
Di-n-butylphthalate	32.22	116.5	99.57	116.5
Di-n-octylphthalate	41.374	149.7	89.10	149.7
Hexachloro-1,3-butadiene	43.198	156.3	39.32	156.3
Hexachlorobenzene	28.181	101.9	58.59	101.9
Hexachlorocyclopentadiene	23.213	83.9	3333	83.9
NDHexachloroethane	38.118	137.9	39.49	137.9
Isophorone	36.645	132.6	54.84	132.6
Nitrobenzene	31.903	115.4	55.30	115.4
N-Nitroso-di-n-propylamine	34.116	123.5	162.46	123.5
N-Nitrosodiphenylamine	33.989	126.5	53.28	126.5
Pentachlorophenol	39.652	143.4	64.02	143.4
Phenol	44.891	162.3	43.5	162.3

¹ ND = Not Determined

percent recoveries of surrogate spiked-samples (refer to laboratory data sheets in **Appendix F**). An increase in MDLs also resulted from analyte concentration being corrected to dry weight; particularly, given the high moisture contents in the sediment samples due to its muddy composition (i.e., high contents of silts and clays).

6.1.1.1 MDL Sensitivity of Sediment Samples

The MDLs for metal analytes in sediment samples were sensitive enough to be evaluated against the Probable Effects Levels (PELs), as stated in the QAPP.

The MDLs for organic analytes in sediment samples were, generally, sensitive enough to evaluated against the PEL values, with the exception of a few compounds (i.e., lindane, acenaphthene and dibenz(a,h)anthracene). The MDLs of PCBs (as aroclors) were below the PEL value (189 µg/kg) in samples collected in 13 out of the 18 Sampling Stations. PCB analysis in samples from the following Stations resulted in MDLs above the PEL: Stations 1SJB, 5PC, 6MP, 4RPN and 18LC.

6.1.2 Biotic-Tissue Samples MDLs

The average MDLs for metals, PCBs and organochlorine pesticides, achieved during biotic-tissue sample analysis, generally met the targeted MDLs or remained close to target MDLs (**Table 8**). Generally, the average MDLs for SVOCs and PAHs were 2-fold higher than the target MDLs listed in the QAPP.

Variations in the observed MDLs versus MDL values listed in the QAPP were mainly a function of newly calculated MDL values for laboratory-method validation for the current year (2011).

6.1.2.1 MDL Sensitivity of Biotic-Tissue Samples

The MDLs for metal analytes in biotic-tissue samples were sensitive enough to be evaluated against the Noncancer EPA Screening Values (SVs) for a Hazard Quotient equal to “1” (HQ = 1).

Of the metal species analyzed, As and Be are the only ones classified as carcinogenic. The MDL for As was sensitive enough to be evaluated against the SV for EPA Cancer Risk of 10^{-5} , whereas the MDL for Be was not. Therefore, Be concentrations, which were non-detectable in all sediment samples, were compared to and did not exceed the EPA Cancer Risk of 10^{-4} .

In general, the MDLs for organic analytes were sensitive enough to be compared against the Noncancer SV for HQ = 1, and against EPA Cancer Risk of 10^{-5} (for those analytes considered carcinogenic). The exception was PCBs where the MDL (25 µg/kg) exceeded the SV for EPA Cancer Risk of 10^{-5} (20 µg/kg).

6.2 SEDIMENT SAMPLES

6.2.1 TOC and Grain Size

TOC contents and grain size distribution in sediment samples collected at the 18 Sampling Stations are summarized in **Table 9** and **Figures 10** and **11**. The average concentrations of TOC in sediment samples ranged from 2,455 µg/g (Station 3SJB) to 125,000 µg/g (Station 6MP).

Estuarine areas have been recently rated as “in poor conditions” in the NCCRII (USEPA 2005) if sediment contained >5% TOC since these locations are associated with organic loadings from “untreated wastewaters, agricultural runoff from livestock areas and industrial discharges” in tropical areas. Based on this TOC index, four (Stations 10CS, 8SJC, 18LC, 6MP) out of the 18 samples (ca. 22%) examined could be classified as derived from sites with poor environmental conditions. These areas coincide with sites that have been highly impacted by humans either by increasing nutrient (organic or inorganic) inputs or by decreased mixing rate (increased retention time via dredging) or both. Station 6 MP, located in the western outlet of Martin Peña Channel receives waters from the densely populated area, which are organically and inorganically loaded. Station 10CS was dredged during the construction of the Luis Muñoz Marín Airport that increased the depth of the basin, which restricted light penetration to the bottom while increasing turnover time. These modifications of the Suarez Channel probably induced increased accumulation of

organic carbon by its efficiency as sediment trap and by the creation of predominant anoxic conditions in these already organic rich waters. Similarly, Station 8SJC is located in an area that receives organically rich waters and suffers from restricted water flow due to the narrow entrance to the basin. Station 18LC also contained TOC close to the 5% threshold, which is supported by the observation of sewage inputs that was observed while sampling.

Although in this case, the higher sediment TOC contents seems reasonably associated to anthropogenic impacts, it is important to consider that such threshold may be incorrectly applied under certain conditions. For instance, earlier worked conducted by Otero in mid and late 1980's (Otero 1988 and Otero *et al.* 1989) indicate that coastal sediments experiencing no anthropogenic inputs may contain 5-10% TOC. These unimpacted areas are organically loaded by natural processes common to coastal areas in Puerto Rico, namely organic production by mangroves and plankton in coastal lagoons and adjacent areas.

Mud (silts plus clays) accounted for 64 to 96% of collected sediment samples (**Figure 11**), except for samples collected from Stations 12BC (8.1% mud) and 3SJB (33.3% mud). The latter samples were collected in or near the Atlantic Ocean. Station 12BC was located close to the sea outlet of La Torrecilla Lagoon, a site commonly known to contain sand deposition similar to other sea outlet sites (e.g., Caño Tiburones in Arecibo, and Caño Corazones in Mayaguez). Sampling of sediments at Station 3SJB was especially difficult. Although sandy, the increased mud content made it particularly plastic and difficult for the dredge to penetrate. Compared to other Stations, Station 3SJB was unique in this regard, suggesting that this site has been heavily modified by human activity, probably by dredging. In an earlier work (PERM 2001) sediments of similar consistency were observed during SCUBA diving in areas close to the east, within the San Antonio Channel, which was heavily dredged for navigation of large ships.

Table 9. Total Organic Carbon Contents and Grain Size Distribution Collected at 18 Sampling Stations in the San Juan Bay Estuary.

<u>Location</u>		<u>Total organic carbon</u> <u>($\mu\text{g/g}$)¹</u>			<u>Sediment Fraction (%)</u> ²				<u>mgTOC/g</u> <u>mud</u>
Sub-Basin ³	Station	AVERAGE	SD ⁴	N ⁵	C SAND	M SAND	F SAND	MUD ⁶	
ESJBE	10CS	99450	9263	2	0.8	7.9	19.7	71.6	139
ESJBE	11LT	41550	212	2	0	0.8	7.3	91.9	45
ESJBE	12BC	19300	6788	2	0	62.5	29.3	8.1	238
ESJBE	13PS	34900	1556	2	0.7	2.3	1.5	95.5	37
ESJBE	14PN	32150	5728	2	0.5	1	4.6	93.9	34
ESJBE	17SJ	33350	1768	2	10.1	9.1	5.9	74.9	45
ESJBE	7MPSJ	43300	3253	2	12.2	11.9	10	65.9	66
ESJBE	8SJC	61950	16334	2	0.4	16.3	19.2	64.1	97
ESJBE	9SJ-A	29150	212	2	0.2	0.3	3.9	95.6	30
ESJBE	9SJ-B	30050	3889	2	2.5	1.7	0.8	95	32
WSJBE	15LC	43550	919	2	0	1.7	17.9	80.4	54
WSJBE	16SJB	28650	10536	2	0	2.2	17.8	80	36
WSJBE	18LC	49600	2404	2	0	3.2	14.8	81.9	61

Location		Total organic carbon ($\mu\text{g/g}$)¹			Sediment Fraction (%)²				mgTOC/g mud
Sub-Basin ³	Station	AVERAGE	SD ⁴	N ⁵	C SAND	M SAND	F SAND	MUD ⁶	
WSJBE	1SJB	12050	1202	2	0	0.4	5.9	93.6	13
WSJBE	2SJB	19100	707	2	4.2	2.5	17.2	76.1	25
WSJBE	3SJB	2455	106	2	5	21	40.7	33.3	7
WSJBE	4RPN	26200	5657	2	0	0.9	23.4	75.7	35
WSJBE	5PC	17700	424	2	0	1	5.1	93.9	19
WSJBE	6MP	125000	11314	2	0	2.4	29.2	68.3	183

¹ $\mu\text{g/g}$ = micrograms per gram sediment

² C, M and F refer to coarse, medium and fine sand fractions, respectively.

³ Sub-Basins: ESJBE = East San Juan Bay Estuary; WSJBE = West San Juan Bay Estuary

⁴ SD = Standard Deviation

⁵ n = Number of Measurements

⁶ Mud = Silts plus Clays

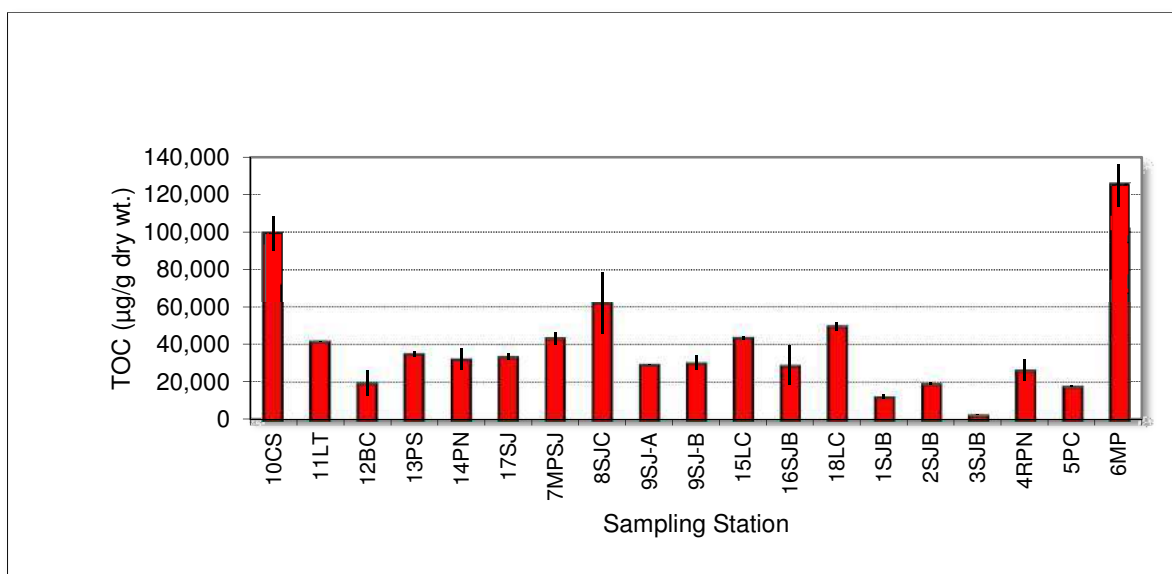


Figure 9. Total Organic Carbon Contents of Sediments Collected at 18 Sampling Stations in the San Juan Bay Estuary (bar indicates standard deviation, n=2).

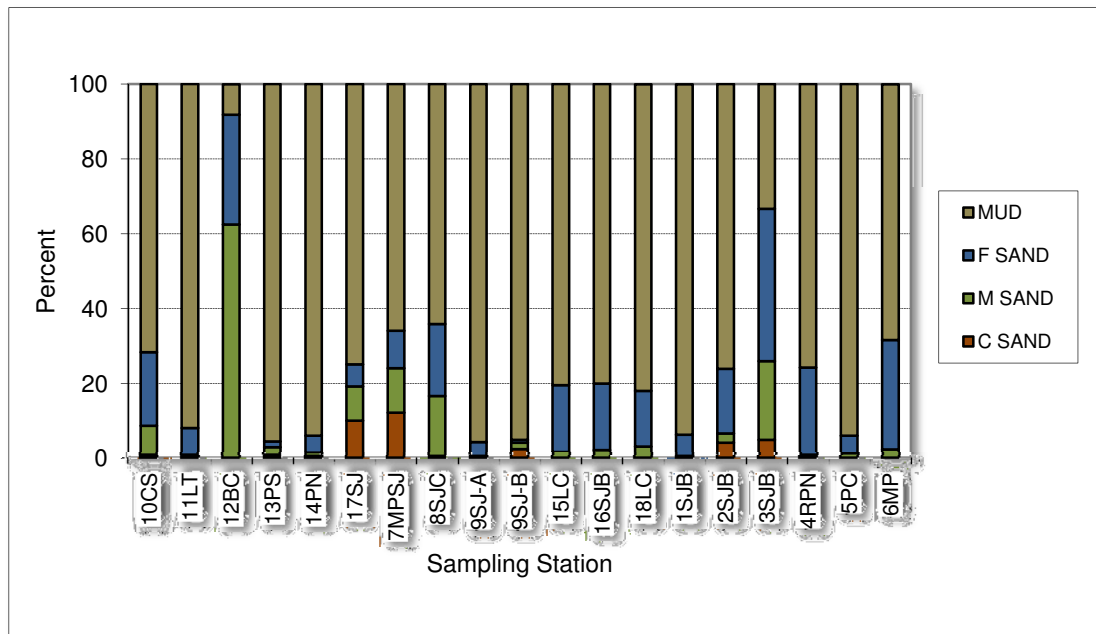


Figure 10. Grain Size Distribution of Sediment Collected at 18 Sampling Stations in the San Juan Bay Estuary.

No correlation between TOC contents and grain size was observed. Mud-normalized TOC values (mg-TOC /g-mud) were ca. 7-238 mg-TOC /g-mud (**Table 9**). Most of these estimates were <70 mg-TOC /g-mud with the exception of Stations 10CS, 12BC, 8SJC and 6MP, suggesting increased organic loading in the larger sediment fraction of these Stations or higher Carbon preservation.

6.2.2 Metals

Table 10 summarizes the trace metal concentrations in sediment samples along with the TEL and PEL values, in order to help evaluate the environmental significance of concentrations found. Concentrations above the TEL are shown in blue font, whereas concentrations above the PEL are shown in red font. For those metals exceeding the TEL, **Figures 11A** through **12B** show a spatial representation of the analytical results of sediment samples collected at the eastern and western portions of the SJBE, respectively. The concentrations of the following metals exceeded the TEL in sediments collected from one or more sampling stations: As, Cd, Cr, Cu, Pb, Ni, Ag, Zn and Hg. The TEL for Cr ($TEL_{Cr} = 52.3 \text{ mg/kg}$) was only exceeded in Sample SJBE-BS-6MP (53.7 mg/Kg), which was collected from the Sampling Station near the western outlet of the Martin Peña Channel (6MP). In contrast, the TEL for Cu ($TEL_{Cu} = 18.7 \text{ mg/Kg}$) was exceeded in 17 Stations (37.9 to 257 mg/kg). The Cu concentration in the sample collected from Station 12BC (4.25 mg/kg) did not exceed the TEL value. Mercury followed Cu in the number of Stations (16 Stations) that showed results exceeding the TEL ($TEL_{Hg} = 0.13 \text{ mg/Kg}$). In addition, Hg exceeded the PEL ($PEL_{Hg} = 0.7 \text{ mg/kg}$) in four stations, namely, stations 6MP, 18LC, 8SJC, and 7MPSJ. In addition, the PELs were

exceeded at Stations 6MP (Ag and Pb) and 18LC (Ni). Of all Stations, 6MP, 18LC, 8SJC and 7MPSJ have the highest incidence of trace metals over the PEL thresholds, thus suggesting the presence of environmental conditions of concern.

Analysis of Al in sediments has been used as a normalization factor when conducting comparisons of locations potentially receiving sediment inputs from geologically distinct watersheds. As discussed in Herut and Sandler (2006), Al is related to aluminosilicates, major components of clays in bottom sediments that are natural adsorption centers of trace metals and, thus, scavengers of trace metals. In addition, Al is derived from terrestrial weathering and has negligible anthropogenic inputs to marine sediments. Therefore, Al is used to normalize for diagenetic processes that may change trace element composition after deposition.

Correlations were conducted between the sample contents of Al, mud fraction, TOC and trace metals. A significant correlation ($R = 0.66$; $n = 20$) was observed between the mud and Al content of samples. No significant correlation was obtained between [Al] and other trace metals, suggesting that factors other than adsorption processes and geological differences among watersheds are stronger modulators of trace element composition in the examined sediments.

Table 10. Analytical Results for Metals in Bottom Sediment Samples of the San Juan Bay Estuary

Analytical Method (concentrations in mg/kg dry weight)														EPA 7471A
EPA 6010B														
	Antimony	Arsenic	Beryllium	Cadmium	Chromium	Copper	Lead	Nickel	Selenium	Silver	Thallium	Zinc	Mercury	
TEL (mg/kg)	NA	7.24	NA	0.68	52.3	18.7	30.2	15.9	NA	0.73	NA	124	0.13	
PEL (mg/kg)	NA	41.6	NA	4.21	160	108	112	42.8	NA	1.77	NA	271	0.7	
Sample I.D.														
SJBE-BS-3SJB	0.567J	5.98	0.574	0.0729J	24.5	39.8	6.35	10.8	ND	ND	ND	40.2	0.0283	
SJBE-BS-2SJB	0.646J	23.5	0.0891J	0.323J	38.9	53.9	16.7	12.1	ND	ND	ND	81.3	0.221	
SJBE-BS-1SJB	0.864J	15.0	ND	0.231J	42.4	47.9	17.5	14.1	ND	0.107J	ND	87.6	0.215	
SJBE-BS-16SJB	0.933J	17.7	0.146J	0.378J	41.1	62.7	21.4	13.1	1.95J	0.484J	ND	108	0.365	
SJBE-BS-5PC	1.49J	14.1	0.344J	0.482J	30.2	94.3	32.7	14.1	ND	1.49J	ND	140	0.348	
SJBE-BS-6MP	3.30J	7.29	ND	1.54J	53.7	257	173	26.6	ND	8.74	ND	907	1.37	
SJBE-BS-4RPN	1.64J	5.62	ND	0.398J	32.1	93.3	27.4	17.0	3.81J	0.187J	ND	171	0.212	
SJBE-BS-15LC	0.672J	10.4	ND	0.561J	41.5	77.6	84	14.5	ND	0.895J	ND	187	0.633	
SJBE-BS-18LC	0.705J	14.0	ND	0.709J	35.5	80.7	83.3	46.2	3.09J	0.531J	ND	272	0.973	
SJBE-BS-14PN	1.60J	4.71	ND	ND	34.6	67.4	11.3	14.1	ND	ND	ND	76.8	0.191	
SJBE-BS-13PS	1.20J	5.80	ND	ND	32.3	72.4	15.9	12.9 J	ND	ND	ND	85.3	0.338	
SJBE-BS-12BC	ND	4.58	ND	0.0222J	4.70	4.25	ND	0.596J	ND	ND	ND	3.44	0.00955J	
SJBE-BS-11LT	0.600J	12.0	ND	0.0967J	24.5	37.9	8.58	7.70J	ND	ND	ND	56.8	0.154	
SJBE-BS-10CS	ND	1.73J	ND	0.156J	18.6	56.0	29.7	9.89J	ND	ND	ND	155	0.140J	
SJBE-BS-8SJC	1.16J	5.85J	ND	1.59J	33.5	96.0	177	17.3J	8.51J	1.50 J	ND	451	2.09	
SJBE-BS-17SJ	1.79J	3.53J	ND	0.224J	29.4	88.0	49.0	13.7J	ND	ND	ND	223	0.345	
SJBE-BS-9SJA	1.02J	6.07	ND	0.297J	27.4	62.0	49.0	10.3J	ND	0.167 J	ND	129	0.159	
SJBE-BS-9SJB*	1.57J	6.44	ND	0.324J	31.0	73.0	65.0	13.2J	ND	0.500 J	ND	150	0.434	
SJBE-BS-7MPSJ	1.46J	7.77	ND	0.840J	37.1	85.0	89.4	12.7	ND	1.30 J	ND	314	0.907	
Equipment Blanks (ug/L)														
EB	ND	0.999J	ND	0.291J	3.49J	ND	ND	8.18J	ND	ND	1.14J	ND	0.0127J	
EB2	ND	0.662J	ND	ND	4.72J	ND	ND	7.91J	ND	ND	ND	ND	0.00589J	

mg/kg = milligrams per kilogram

ug/L = micrograms per Liter

TEL = Threshold Effects Level (i.e., Sediment Quality Guideline from MacDonald *et al.*, 1996).

PEL = Probable Effects Level (i.e., Sediment Quality Guideline from MacDonald *et al.*, 1996).

NA= Not Applicable (i.e., TEL and PEL not available for that metal).

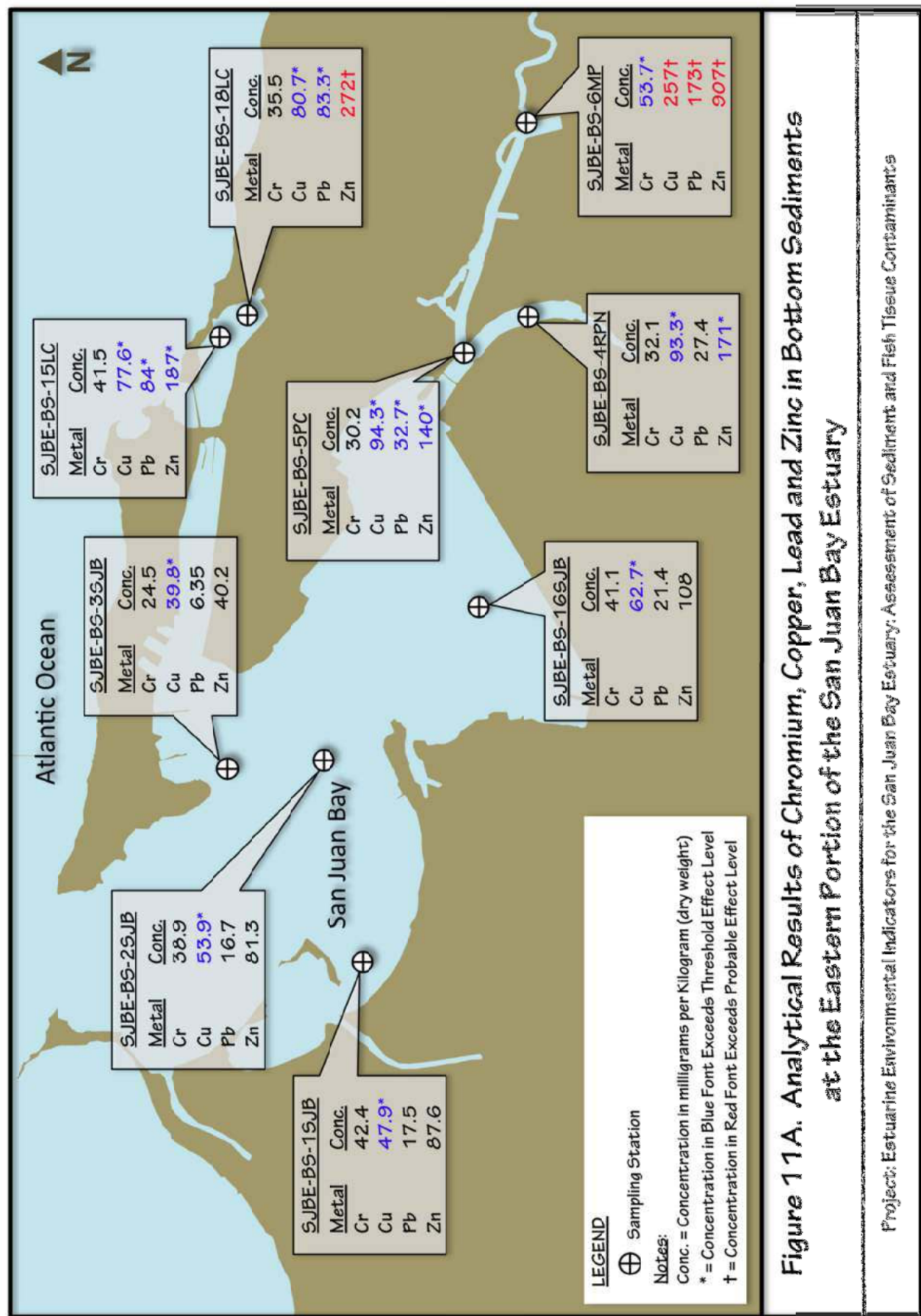
ND = Not Detected below the Method Detection Limit.

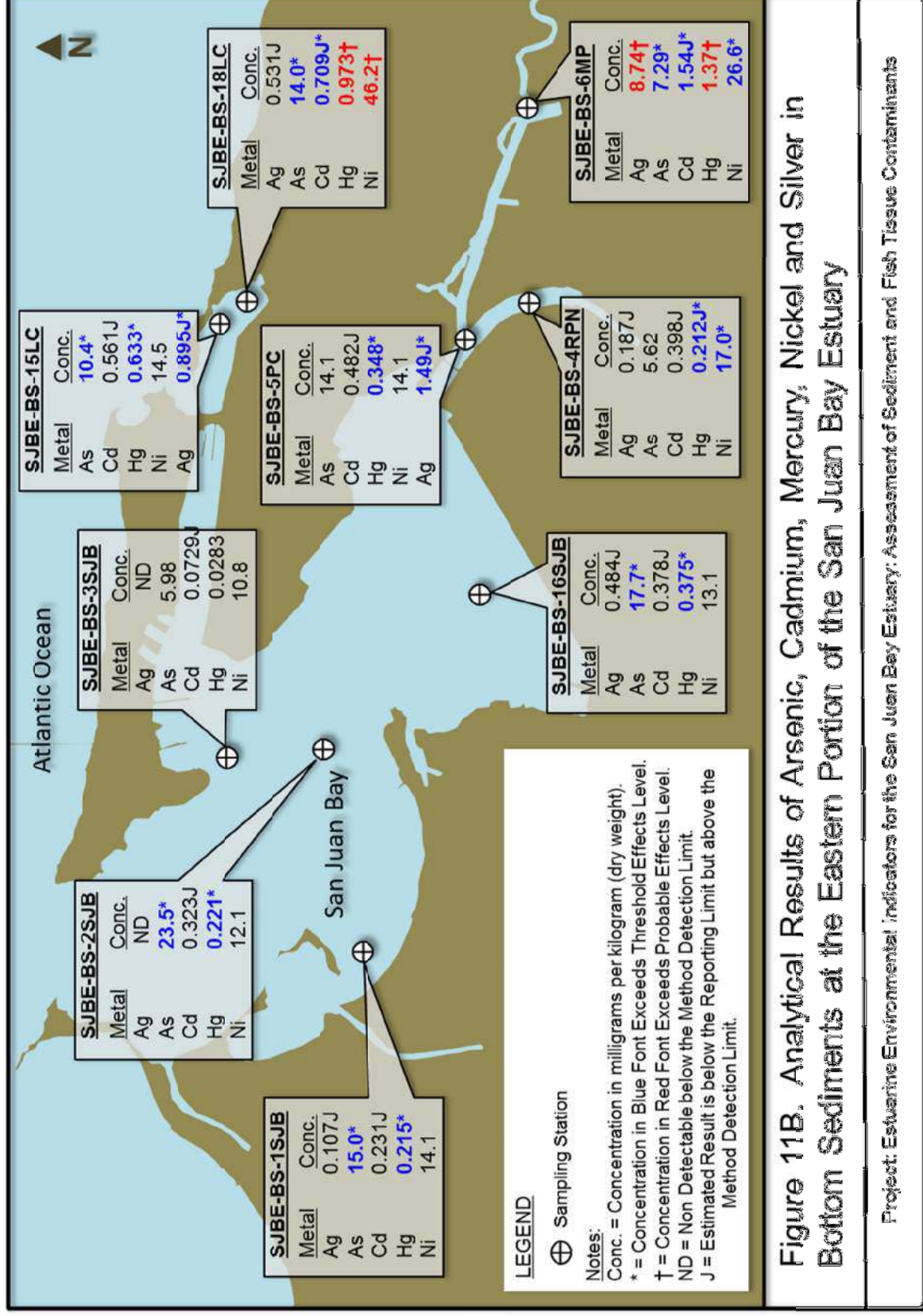
Analytical results in Blue Font exceed the Threshold Effects Level.

Analytical results in Red Font exceed the Probable Effects Level.

J = Estimated value for the analyte is below the laboratory reporting limit but above the method detection limit.

* = Field Duplicate of SJBE-BS-9SJA





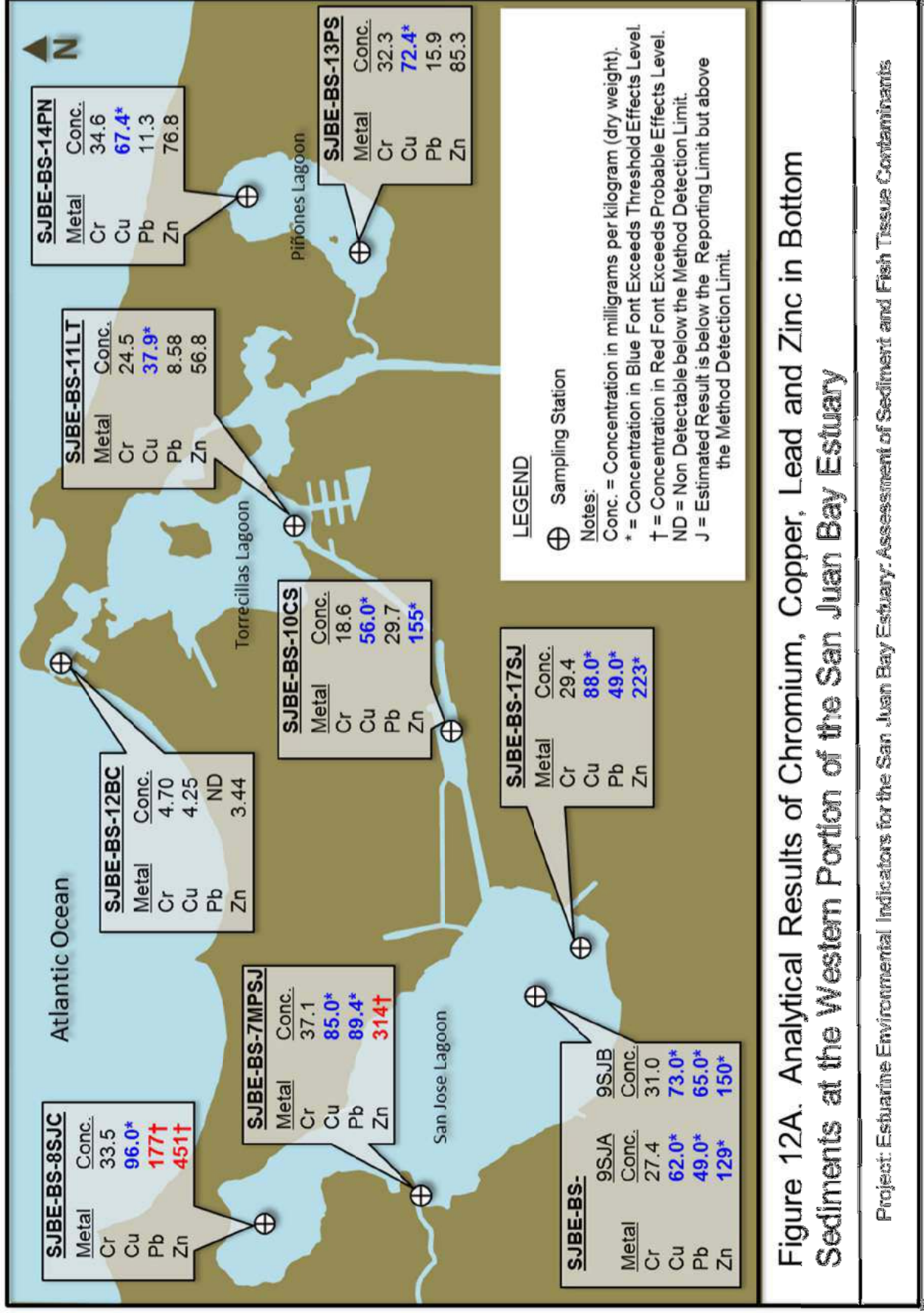


Figure 12A. Analytical Results of Chromium, Copper, Lead and Zinc in Bottom Sediments at the Western Portion of the San Juan Bay Estuary

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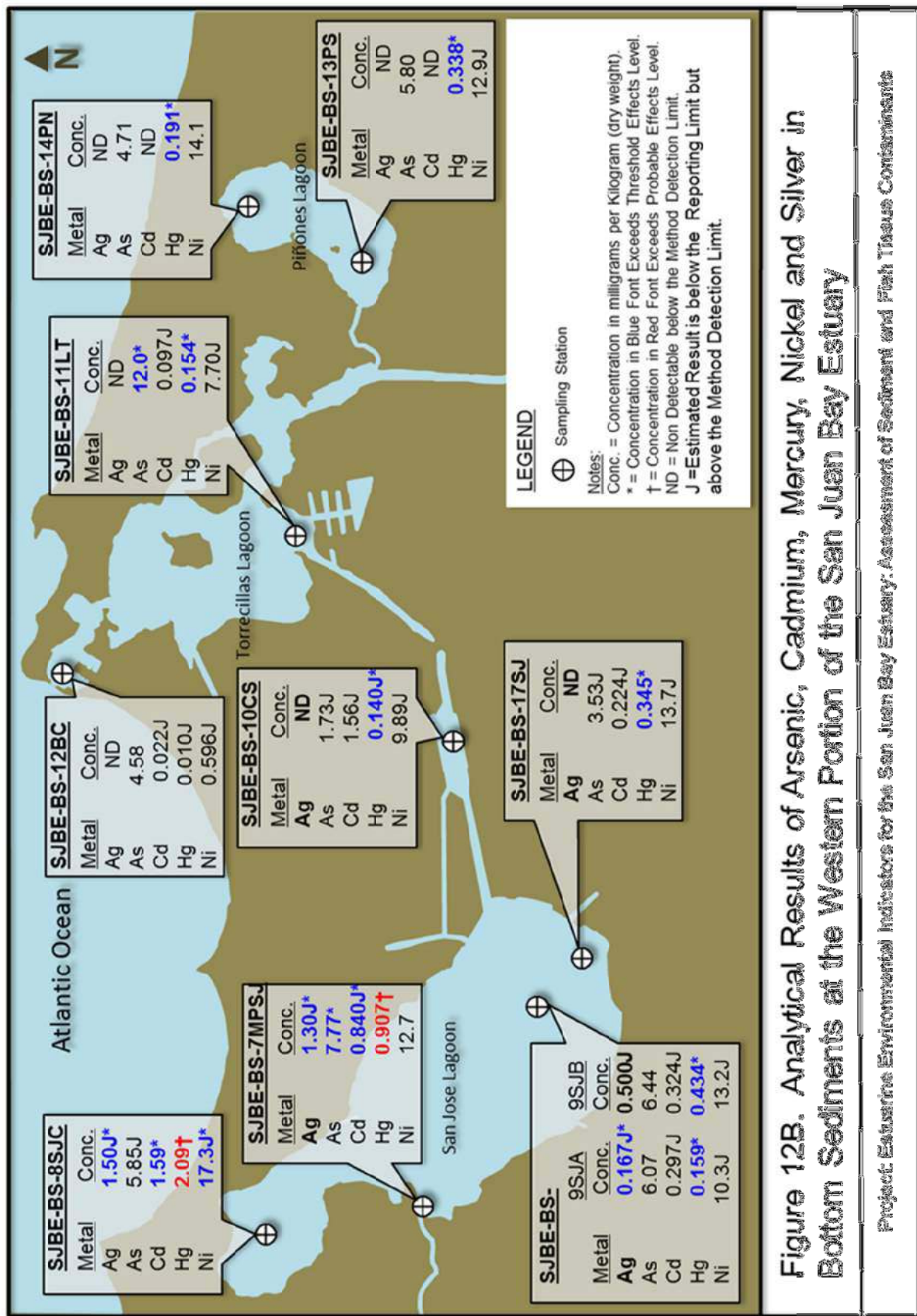
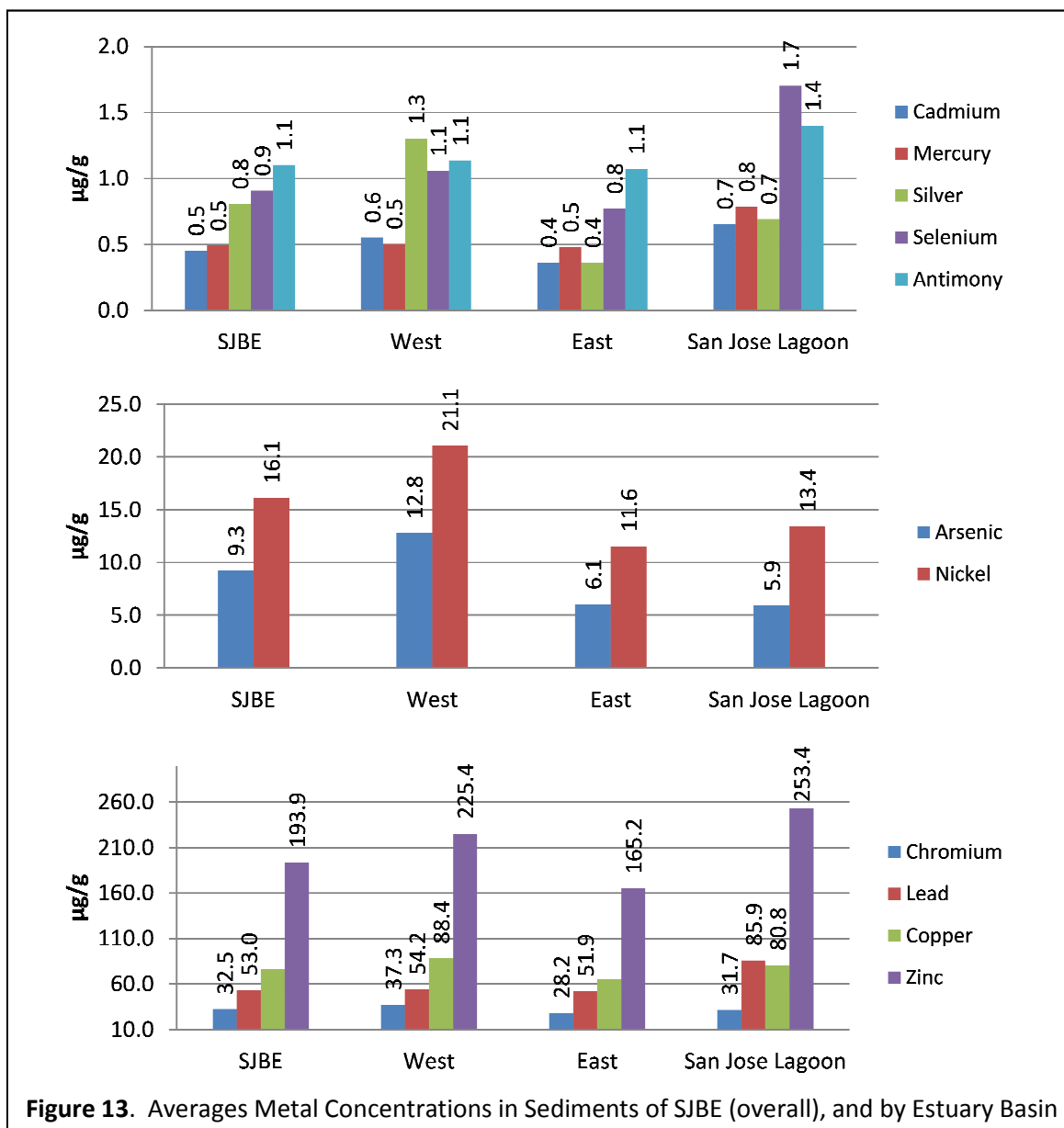


Figure 12B. Analytical Results of Arsenic, Cadmium, Mercury, Nickel and Silver in Bottom Sediments at the Western Portion of the San Juan Bay Estuary

Project Estuarine Environmental Indicators for the San Juan Bay Estuary: Assessment of Sediment and Fish Tissue Contaminants

Figure 13 compares the average metal concentrations for the entire estuary (SJBE), and for separate estuary basins (i.e. WSJBE, ESJBE and San Jose Lagoon). Overall, the average [Cd] and [Cr] was similarly distributed. There was a slight increase in average [Hg] in the San Jose



Lagoon. The concentration of Ag was, in average, higher in the WSJBE. The Se concentration was higher in the San Jose Lagoon in comparison to the WSJBE, a pattern similar to that of [Sb]. Arsenic concentration as well as [Ni] was higher in the WSJBE, and mostly uniform within the ESJBE. Lead concentration was, approximately, 50% higher in the San Jose Lagoon than in other estuary areas. Finally, although the average [Zn] in WSJBE was higher than that of ESJBE, it was slightly lower than that found for the San Jose Lagoon.

Sampling Stations 6MP and 8SJ revealed the highest trace metal concentrations of all Stations sampled. Station 6MP, close to the western outlet of Martin Peña Channel contained the highest concentrations of Cd, Hg, Ag, Sb, Ni, Cr, Cu and Zn in WSJBE. Similarly, Station 8SJC, within the sub-basin of Corozo Lagoon in San Jose Lagoon, contained the highest concentrations of Cd, Hg, Ag, Se, Pb, Cu and Zn within ESJBE (and second highest within the SJBE). These two Stations are located in areas characterized by receiving significant anthropogenic inputs or experiencing restricted water flow.

The concentrations of trace metals in sediments at Stations coinciding with those of previous studies (see **Table 3**, above) were compared to qualitatively evaluate if changes in those Stations had occurred. **Table 11** suggests that increments in trace metals had occurred at Stations 16SJB and 7MPSJ, whereas trace metal concentrations have not changed or are lower at Stations 3SJCA, 13PS, 17SJ, 8SJC and 6MP, with the exception of [Hg]. Mercury concentrations seem to have increased from previous levels in all Stations, except at 17SJ and 13PS where the concentration seems to be stable.

Table 11. Comparison of Average Trace Metal Concentrations (mg/kg dry wt.) in Sediments Collected from Stations Common to the Present Study and Previous Studies. (Black numbers represent concentrations similar within 2SD. Concentrations in red indicate that present concentrations are >2SD those of previous work, whereas those in green indicate that present concentrations are <2SD those of previous work).

Reference	Metal	Station Designation From This Study							2SD*
		16SJB	6MP	8SJC	17SJ	13PS	3SJCA	7MPSJ	
Acevedo-Figueroa et al, 2006	As	-	-	14.60	11.57	-	-	4.50	
PERM, 2001	As	-	-	-	-	-	19.20	-	
This Study	As	17.7	7.29	5.85	3.53	5.80	5.98	7.77	0.52
Webb and Gomez-Gomez, 1998	As	15.00	10.00	9.00	11.00	7.00			
Acevedo-Figueroa et al., 2006	Cd	-	-	3.53	1.63	-	-	0.20	
This Study	Cd	0.38	1.54	1.59	0.22	ND	0.07	0.84	0.04
Webb and Gomez-Gomez, 1998	Cd	0.00	3.00	3.00	1.00	ND	-	-	
PERM, 2001	Cr	-	-	-	-	-	21.70		
This Study	Cr	53.70	53.70	33.50	29.40	32.30	24.50	37.10	4.10
Webb and Gomez-Gomez, 1998	Cr	40.00	55.00	50.00	40.00	30.00	-	-	
Acevedo-Figueroa et al., 2006	Cu	-	-	147.33	96.33	-	-	29.00	15.40
PERM, 2001	Cu	-	-	-	-	-	48.90	-	
This Study	Cu	62.70	257.00	96.00	88.00	72.40	39.80	85.00	15.40
Acevedo-Figueroa et al., 2006	Hg	-	-	2.90	1.17	-	-	0.10	
PERM, 2001	Hg	-	-	-	-	-	0.14	-	
This Study	Hg	1.37	8.74	2.09	0.35	0.34	0.03	0.91	0.38
Webb and Gomez-Gomez, 1998	Hg	0.29	4.70	0.18	0.12	0.15	-	-	
PERM, 2001	Ni	-	-	-	-	-	18.30	-	4.10

This Study	Ni	13.10	26.60	17.30	13.70	12.90	10.80	12.70	
Acevedo-Figueroa et al., 2006	Pb	-	-	401.33	218.00	-	-	16.00	
PERM, 2001	Pb	-	-	-		-	16.50	-	
This Study	Pb	21.40	173.00	177.00	49.00	15.90	6.35	89.40	22.60
Webb and Gomez-Gomez, 1998	Pb	50.00	750.00	550.00	180.00	40.00			
Acevedo-Figueroa et al., 2006	Zn	-	-	998.00	539.67	-	-	48.00	
This Study	Zn	108.00	907.00	451.00	223.00	85.30	40.20	314.00	29.60

*Two standard deviations based on replicate analysis conducted in this study. Replicates were collected for station 9SJ. nD= not detected; - = not determined

The present study found higher trace metal concentrations than other studies conducted in Torrecillas Lagoon, Jobos Bay and La Parguera (Martínez-Colón and Hallock, 2010 and Aldarondo-Torres et al. 2010). In contrast, previous studies conducted by Acevedo-Figueroa *et al.* (2006), in San Jose Lagoon, and by Webb and Gomez-Gomez (1998) in the SJBE, found higher concentrations of trace metals with the exception of Zn, which was similar to that found in Acevedo-Figueroa *et al.* (2006), and Se (**Table 11**).

6.2.3 Organic Compounds

The MDLs for organic analytes in sediment samples were, generally, sensitive enough to evaluate against the PEL values, with the exception noted in Sub-section 6.1.1.1.

Except for bis(2-Ethylhexyl)phthalate (a common plasticizer), organic analytes were not detected in sediment samples. Bis(2-Ethylhexyl)phthalate was found at concentrations of 1,510 and 333 µg/kg in Stations 6MP and 17SJ, respectively. The concentration at Station 6MP (1,510 µg/kg) falls midway between the TEL and PEL for this compound. Previous work conducted in San Antonio Channel did not detect organic contaminants of concern and, as in the present Study, only detected low levels of plasticizers.

None of the targeted organic analytes, including PAHs, chlordanes and DDTs, exceeded their respective PEL values indicating that detrimental effects to biota are not probable.

The MDLs for PCBs at 13 Stations did not exceed the PEL value. Even though the MDLs for PCBs were above the PEL in five Stations (i.e., Stations 1SJB, 5PC, 6MP, 4RPN and 18LC), the PCB data, as a whole, suggest that PCB levels in sediments have not reached levels of contamination likely to cause widespread detrimental effects. The MDL average for PCBs, excluding of highest MDL value (i.e., Station 6MP) is 81µg/kg, which lie two-thirds closer to the TEL (21.6 µg/kg) than the PEL (189 µg/kg). Thus, using sample specific MDLs for PCBs, ca. 70% of the stations had MDLs less than PEL_{PCB}, and 56% were less than midway between the TEL and PEL for PCBs.

6.3 BIOTIC-TISSUE SAMPLES

The concentrations of the contaminants of concern in fish and crab-tissue samples were compared against EPA default Screening Values (SV). The SV for each chemical contaminant is defined as the concentration of the chemical in fish or shellfish tissue that is of potential public health concern (USEPA 2004)

6.3.1 Metals

Arsenic, Cu, Se, Zn and Hg were detected in fish tissue of most Stations, whereas Sb, Cr, Pb, Ni, Ag and Tl were rarely detected (**Table 12**). Cadmium was not detected in the fish tissues analyzed. Arsenic exceeded the EPA Noncancer risk (HQ=1) at Station 15LC and exceeded the EPA Cancer Risk 10^{-4} level in samples collected from the following Stations: 15LC, 1SJB, 4RPN, 11LT, and 6MP. **Figures 14A** through **15B** show the spatial distribution of the results in the eastern and western portions of SJBE, respectively. The concentration of Hg exceeded the EPA screening value for subsistence fishers (a more restrictive threshold than the previous; USEPA 2004), in samples collected at Stations 4RPN and 15LC.

Overall, these results suggest low accumulation of the target trace metals with the exception of As, which reached the highest level in the Condado Lagoon. In contrast, samples from Stations 8SJC and 7MPSJ did not contained levels of As or other contaminants of concern according to the above indices.

Table 13 summarizes trace metal results for crab tissue. Similar to fish tissue, As, Cu, Se, Zn and Hg were detected in crab tissue collected from all Stations. Silver was also detected in all crab tissue samples in contrast with fish tissue. Other metals were not or rarely detected. The concentration of As exceeded the EPA Cancer Risk 10^{-4} Level in all Stations and the EPA Noncancer Effects Level (HQ=1) in two Stations, 1SJB and 15LC. Mercury levels were in average slightly higher than those for fish, and were higher than the screening value for subsistence fishers in 5PC.

Arsenic tissue content of crabs and fish correlated significantly ($R=0.93; n=7; P<\alpha= 0.01$) suggesting that environmental variation in SJBE influence the As content in these species. However, no other correlation was observed.

Average trace metal concentrations in fish and crab tissue samples were compared among Stations (**Table 14**). Zinc and Hg concentrations in crab tissue seem to be similar throughout SJBE, whereas only slightly higher levels were found for Pb and Se in WSJBE. Copper concentration was slightly higher in WSJBE, whereas As was ca. five and eight times higher in WSJBE than in ESJBE and San Jose Lagoon, respectively. In contrast to crab results, no apparent changes in tissue trace metal contents among SJBE regions were found in fish tissue. These results suggest that blue crabs may be better differentiator of trace metal bioavailability than mojarra in SJBE.

Table 12. Analytical Results for Metals in Fish Tissue Samples of the San Juan Bay Estuary

Analytical Method (concentrations in mg/kg wet weight) EPA 6020A													
	Antimony	Arsenic	Beryllium	Cadmium	Chromium	Copper	Lead	Nickel	Selenium	Silver	Thallium	Zinc	Mercury
EPA Cancer Risk 10 ⁻⁴	NA	0.26	0.0929	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
EPA Noncancer HQ=1	1.6	1.2	20.1	4	20.1	149	NA	81.7	20	20.1	NA	1,190	0.4
Sample I.D.													
SJBE-FT-1SJB*	0.011J	1.0	<0.030	<0.0079	0.062J	0.42J	0.13	0.029J	0.36	0.0030J	<0.011	36.6	0.014J
SJBE-FT-6MP-A	0.012J	0.21	<0.027	<0.0070	<0.044	0.26J	0.012J	<0.023	0.30	<0.0027	0.018J	9.5	0.024
SJBE-FT-6MP-B**	<0.0042	0.47	<0.029	<0.0076	<0.048	0.23J	<0.011	<0.025	0.26	<0.0029	<0.011	9.3	0.023
SJBE-FT-4RPN	0.0050J	0.60	<0.027	<0.0070	<0.044	0.27J	<0.0097	<0.023	0.43	<0.0027	<0.0099	6.4	0.093
SJBE-FT-15LC	<0.0040	1.2	<0.028	<0.0071	<0.045	0.22J	<0.0098	<0.023	0.28	<0.0027	<0.010	6.2	0.061
SJBE-FT-8SJC	<0.0044	0.25	<0.030	<0.0079	<0.050	0.25J	<0.011	<0.026	0.31	<0.0030	<0.011	13.4	0.028
SJBE-FT-7MPSJ	<0.0039	0.19	<0.027	<0.0070	<0.044	0.26J	<0.0096	<0.023	0.32	<0.0026	<0.0099	13.6	0.014J
SJBE-FT-11LT	<0.0043	0.59	<0.030	<0.0077	<0.049	0.20J	<0.011	<0.025	0.22	<0.0029	<0.011	7.9	0.026
SJBE-FT-10CS	<0.0043	0.19	<0.030	<0.0077	<0.048	0.24J	<0.011	<0.025	0.31	<0.0029	<0.011	11.4	0.017J

mg/kg = milligrams per kilogram

NA= Not Applicable (i.e., EPA Screening Value not available for that metal).

Analytical results in Blue Font exceed EPA Cancer Risk = 10⁻⁴.

Analytical results in Red Font exceed EPA Noncancer Effects Level for a Hazard Quotient=1.

J = Estimated value for the analyte is below the Laboratory Reporting Limit but above the Method Detection Limit.

< = Concentration below the Method Detection Limit

*Whole-body fish, as opposed to fish fillet, was extracted and analyzed due to small size of fishes in sample.

**Field duplicate of Sample SJBE-FT-6MP-A

Table 13. Analytical Results for Metals in Crab Tissue Samples of the San Juan Bay Estuary

Analytical Method (concentrations in mg/kg wet weight) EPA 6020A												
	Antimony	Arsenic	Beryllium	Cadmium	Chromium	Copper	Lead	Nickel	Selenium	Silver	Thallium	Zinc
<i>EPA Cancer Risk 10⁻⁴</i>	NA	0.26	0.0929	NA	NA	NA	NA	NA	NA	NA	NA	NA
<i>EPA Noncancer HQ=1</i>	1.6	1.2	20.1	4	20.1	149	NA	81.7	20	20.1	NA	1,190
Sample I.D.												
SJBE-CT-1SJB	<0.0040	2.6	<0.028	<0.0071	<0.045	9.3	0.018J	<0.023	0.30	0.45	<0.010	32.9
SJBE-CT-5PC	<0.0041	1.1	<0.028	<0.0073	<0.046	5.8	0.015J	<0.024	0.31	0.32	<0.010	30.2
SJBE-CT-15LC	<0.0043	4.8	<0.030	<0.0077	<0.049	10.3	0.033J	<0.025	0.36	0.15	<0.011	28.6
SJBE-CT-4RPN	<0.0043	0.51	<0.030	0.0089J	<0.049	6.9	<0.011	<0.025	0.35	0.20	<0.011	30.3
SJBE-CT-8SJC	<0.0041	0.31	<0.029	<0.0074	<0.047	5.2	<0.010	<0.024	0.20	0.069	<0.010	31.8
SJBE-CT-7MPSJ-A	<0.0043	0.24	<0.030	<0.0076	<0.048	4.5	<0.011	<0.025	0.19	0.045J	<0.011	32.6
SJBE-CT-7MPSJ-B*	<0.0041	0.28	<0.028	<0.0073	<0.046	5.8	<0.010	<0.024	0.21	0.078	<0.010	38.3
SJBE-CT-11LT	<0.0038	1.1	<0.026	<0.0067	<0.043	5.9	<0.0093	<0.022	0.19	0.038J	<0.0096	32.7
SJBE-CT-10CS	<0.0044	0.28	<0.030	<0.0079	0.11	4.7	<0.011	0.042J	0.22	0.059	<0.011	36.8

mg/kg = milligrams per kilogram

NA= Not Applicable (i.e., EPA Screening Value not available for that metal).

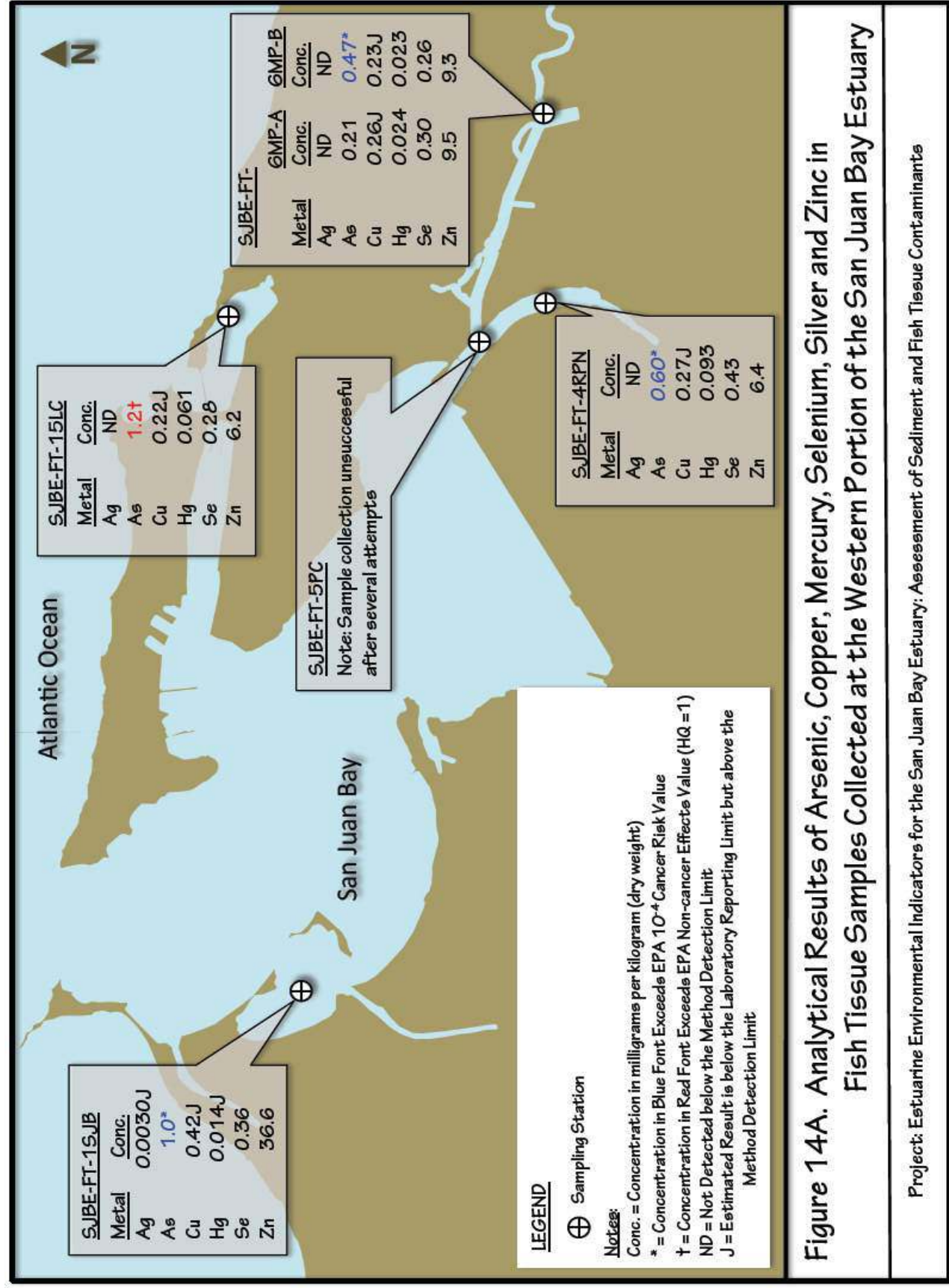
Analytical results in Blue Font exceed EPA Cancer Risk = 10⁻⁴.

Analytical results in Red Font exceed EPA Noncancer Effects Value for a Hazard Quotient=1.

J = Estimated value for the analyte is below the Laboratory Reporting Limit but above the Method Detection Limit.

< = Concentration below the Method Detection Limit

*Field Duplicate of Sample SJBE-CT-7MPSJ-A



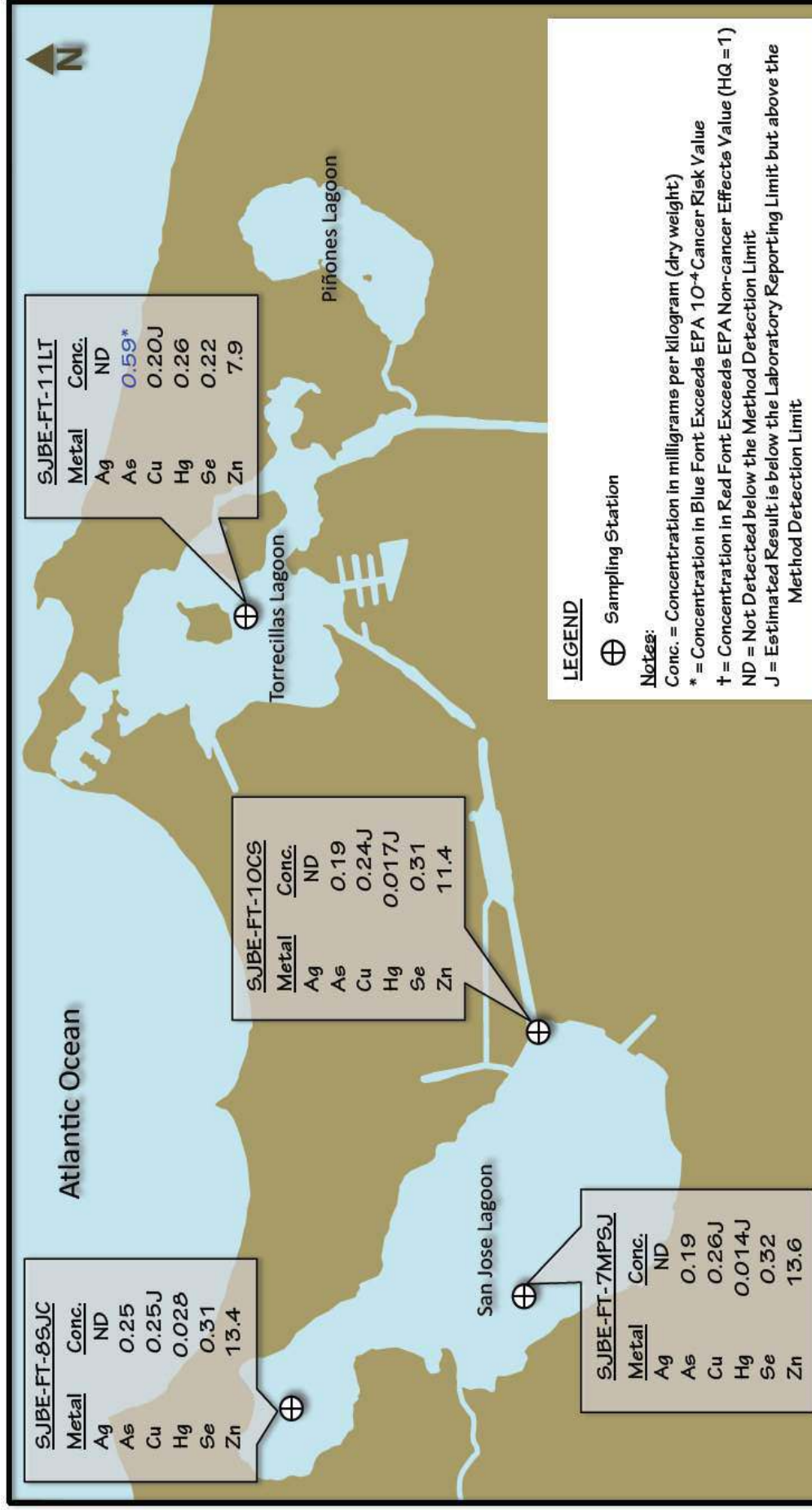
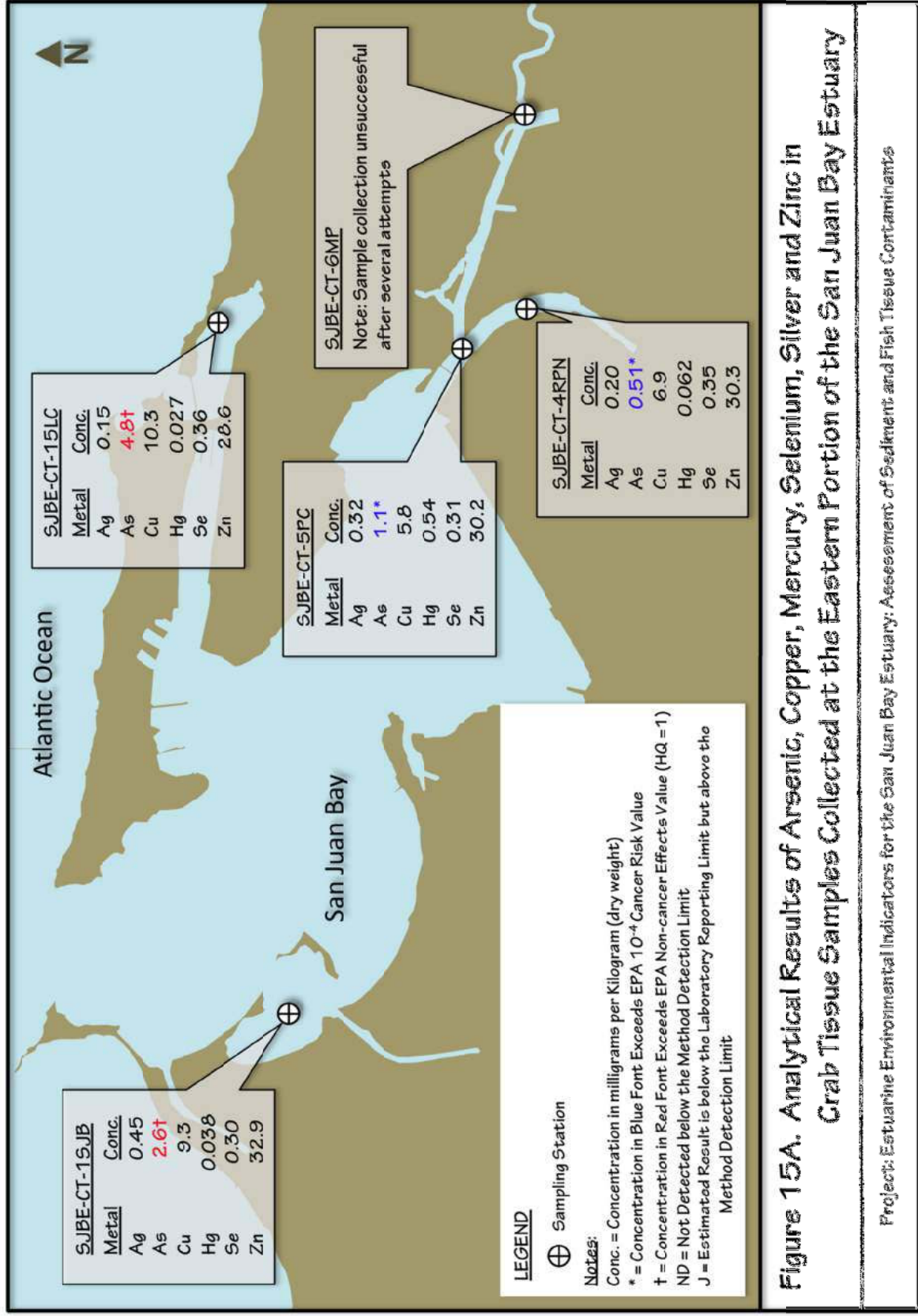
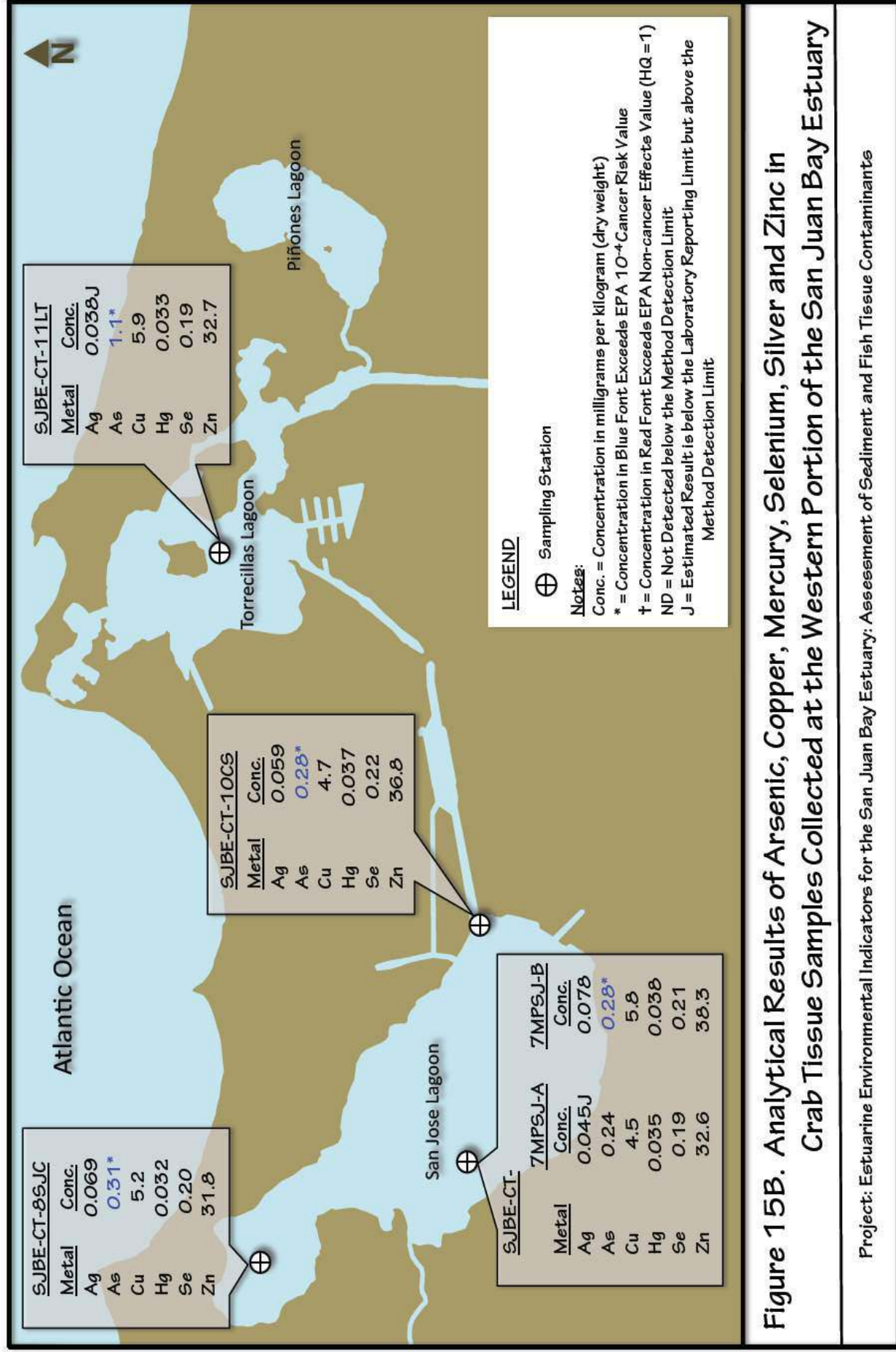


Figure 14B. Analytical Results of Arsenic, Copper, Mercury, Selenium, Silver and Zinc in Fish Tissue Samples Collected at the Western Portion of the San Juan Bay Estuary

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Previous work conducted on trace metal tissue content by Delgado-Morales *et al.* (1999) and Rodriguez-Sierra and Jimenez (2002) indicate that Pb and Hg concentrations were higher in the past in crab and fish tissue. Zinc concentration was higher during the present Study in both tissues, and Cu only in crab tissue. Arsenic and Cd were found in similar concentrations to those in previous work. Overall, the highest trace element values in crab tissue were observed in the western portion of the SJBE, with the exception of Zn, Cd and Hg, when considering historical data.

The levels of As in biotic-tissue samples from this Assessment are about four (crab tissue) to six times (fish tissue) higher than those in a recent study conducted by the USEPA (2008b; **Table 14**).

Table 14. Comparison of trace metal Concentration in Blue Crab and Mojarra muscle from different zones of SJBE and with previous work (concentrations are reported in µg/g dry wt using conversion factor of 5g wet tissue to 1 g dry tissue as in Ref 2. Red values indicate the highest levels within the SJBE system.

Sample Type	Site	As	Cd	Cu	Pb	Se	Ag	Zn	Hg	Ref
CT	average SJBE	6.233	<0.035	32.444	0.071	1.294	0.783	163.444	0.198	1
CT	West SJBE	11.263	<0.035	40.375	0.096	1.650	1.400	152.500	0.226	1
CT	East SJBE	2.210	<0.035	26.100	<0.05	1.010	0.289	172.200	0.175	1
CT	Lag San Jose	1.383	<0.035	25.833	<0.05	1.000	0.320	171.167	0.175	1
FT	average SJBE	2.611	<0.035	1.306	0.120	1.550	<0.015	63.500	0.167	1
FT	West SJBE	2.900	<0.035	1.167	0.144	1.358	<0.015	56.667	0.179	1
FT	East SJBE	1.525	<0.035	1.188	<0.05	1.450	<0.015	57.875	0.106	1
FT	Lag San Jose	1.050	<0.035	1.250	<0.05	1.567	<0.015	64.000	0.098	1
CT	Lag San Jose	2.050	0.050	15.993	0.340	-	-	149.927	0.550	2
CT	Lag Grande	13.380	0.020	103.200	0.120	0.400	-	234.130	-	2
CT	Tiburones	1.360	0.040	24.880	0.250	-	-	152.080	-	2
CT	Rio Blanco	2.400	0.140	60.460	0.130	0.590	-	186.890	-	2
FT	Lag San Jose	-	0.027	12.523	0.960	-	-	22.618	0.473	2
FT	La Parguera	-	0.014	7.590	0.460	-	-	21.350	0.220	2
FT	Lag San Jose	1.340	0.013	2.820	0.130	-	-	28.800	0.130	3
FT	Joyuda	-	-	-	-	-	-	-	-	-
FT	Lagoon	2.150	0.014	4.620	0.470	-	-	23.100	0.050	3
FT	La Parguera	1.070	<0.01	2.160	0.110	-	-	22.000	0.110	3

1= This study

2= Delgado-Morales et al, 1999.

3= Rodriguez-Sierra and Jimenez, 2002.

CT= Blue Crab Muscle

FT= Mojarra muscle

--= Not determined

6.3.2 Organic Compounds

Pesticides found in fish tissue samples were mostly DDT and its degradation products, as well as chlordane related products. DDTs were found up to a concentration of 10 µg/kg (ΣDDTs; **Table 15**). Overall, ΣDDTs were uniformly distributed through all fish tissue samples. Alpha-chlordane was also detected in ca. 50% of the fish tissue samples examined, whereas chlordane was detected only in two Stations (**Table 16**). Endrin and Lindane were only detected in fish tissue from Station 1SJB.

Total PCBs, based on Aroclor equivalents, were detected in fish tissue samples from Stations 1SJB, 7MPSJ, 10CS and 6MP, ranging from 25.9 to 92.2 µg/kg. PAHs were not detected in fish tissue (see **Appendix G**: Laboratory Tissue Analysis Report for detailed information).

DDTs in crab tissue in the present and a previous study (USEPA, 2008b) were within the same order of magnitude, whereas fish tissue levels detected in the previous study are about 3 times higher (Table 17). Alpha-BHC was the only pesticide residue detected in crab tissue ranging from 0.78 to 3.0 µg/Kg (**Appendix G**). PCBs and PAHs were not detected in the crab tissue samples (**Appendix G**).

Table 15. Concentration of DDT and Total PCBs in fish tissue from the SJBE Collected in June 2011.

REGION	STATION	DDTs (µg/kg)				ΣPCBs (µg/kg)
		4,4'-DDD	4,4'-DDE	4,4'-DDT	ΣDDTs	
East	10CS	<1	6.6	1	7.6	25.9
East	11LT	<1	<1.6	<0.8	<1.6	<25
East	7MPSJ	<1	6.9	0.98	7.9	51.3
East	8SJC	<1	7.2	0.96	8.2	<25
West	15LC	<1	<1.6	<0.8	<1.6	<25
West	1SJB	2.0	5.60	2.4	10.0	92.2
West	4RPN	<1	1.9	3.4	5.3	<25
West	6MP-A	<1	3.6	0.93	4.5	<25
West	6MP-B	<1	8.1	1.5	9.6	30.2

Table 16. Concentration (µg/kg wet wt.) of other pesticides found in fish and crab tissues from the SJBE collected in June 2011.

		Fish Tissue				Crab Tissue
SJBE Region	Station	alpha-Chlordane	Chlordane (Technical)	Endrin aldehyde	gamma-BHC (Lindane)	alpha-BHC
East	10CS	0.90	13.80	2.50	<0.65	3
East	11LT	<0.61	<8.5	<2.3	<0.65	1.1
East	7MPSJ	0.65	<8.5	<2.3	<0.65	2.1
East	8SJC	0.76	<8.5	<2.3	<0.65	2.3
West	15LC	<0.61	<8.5	<2.3	<0.65	<0.54
West	1SJB	0.72	<8.5	<2.3	1.20	<0.54
West	4RPN	<0.61	<8.5	4.00	0.67	1.8
West	5PC	-	-	-	-	0.78
West	6MP-A	<0.61	<8.5	<2.3	<0.65	-
West	6MP-B	0.88	12.20	<2.3	<0.65	-

- = not determined

Table 17. Comparison of maximum concentrations of contaminants of concern as defined in USEPA (2008b) for San Jose Lagoon. Concentrations are reported in µg/g dry wt. of tissue.

Analyte	Present Study		USEPA 2008b	
	CT	FT	CT	FT
As ¹	0.031	0.025	0.0067	0.004
PCBs	<.025	0.092	0.0073	0.1
PAHs	<0.100	<0.100	0.00026	0.00019
DDTs	<.0016	0.0082	0.0013	0.025

1= As was multiplied by 0.02 to estimate bioavailable As

The levels of PCBs detected in fish (<25 to 92.2 µg/kg) and crab tissue (<25 µg/kg) approached or exceeded the EPA screening value for recreational fishers (USEPA 200b; 20 µg/kg). Although total DDTs in fish and crab tissue did not exceed the SV for recreational fishers (117 µg/kg), total DDT levels in fish tissue collected from Station 1SJB (10.0 µg/kg) approached the total DDT value for subsistence fisher (14 µg/kg). Chlordane was detected in fish tissue at concentrations approaching the EPA screening value for subsistence fishers (14 µg/kg) at Stations 6MP (12.20 µg/kg) and 10CS (13.80 µg/kg).

7 CONCLUSIONS

7.1 METALS

7.1.1 Sediments

The San Jose Lagoon contains higher concentrations of Se, Sb, Pb and Hg, whereas the WSJBE had higher concentrations of As and Ni. Other metals were approximately uniformly distributed throughout the SJBE.

Two locations were most frequently associated with higher trace metal concentrations, 6MP and 8SJC. However, other locations of concern as indicated by trace metal concentrations exceeding the PEL values are Stations 18LC and 7MPSJ. These locations are associated to outlets of the Martin Peña Channel, and San Jose and Condado Lagoons. Overall, the lowest trace metal concentrations were found in sediment samples collected from Piñones Lagoon (Stations 13PS and 14PN), and from Stations 12BC and 3SJCA. However, the concentration of Hg exceeded the TEL value in Stations 13PS and 14PN, indicating Hg inputs and retention into this Lagoon, possibly through atmospheric deposition. Work examining Hg sources in Piñones Lagoon should be underscored since the Lagoon is part of the Piñones Forest State Reserve.

No co-variation of trace metals with sediment Al content was found suggesting that the distribution of trace metals does not play a major role relative to anthropogenic factors.

Based on results of this Study, analysis of sedimentary trace metals is a useful indicator of changes in environmental conditions throughout the SJBE.

7.1.2 Fish and Crab Tissue

Arsenic, Cu, Se, Zn and Hg were detected in most fish tissue samples. The levels of As reached the EPA Non-cancer Screening Value (HQ = 1) in Station 15LC and EPA 10^{-5} Cancer Risk Screening Value in Stations 1SJB, 4RPN, 11LT and 6MP. None of these screening values were exceeded at Stations 6MP and San Jose Lagoon. Similar to Hg, arsenic did exceed levels of concern for subsistence fishers in samples collected at Stations 4RPN and 15LC. This could be the result of interspecies differences as tissue analyzed in Stations 4RPN and 15LC was dog snappers and not mojaras.

Detection of trace metals in crab tissue was similar to that of fish tissue with the exception of Ag, which was detected in the former but not the latter. Arsenic concentrations exceeded EPA 10^{-5} cancer risk threshold in all Stations, and EPA Non-cancer Screening Value (HQ = 1) in

Stations 1SJB and 15LC. Mercury levels in crab tissue were slightly higher than for fish tissue and exceeded concentrations EPA screening value for subsistence fishers in 5PC.

The variation of As throughout the SJBE was similar for fish and crab tissue, a feature not shared with any of the other metals analyzed. Arsenic levels should be monitored in future sampling events. Comparison to previous works suggests that As concentrations have increase in the WSJBE. The concentrations of Cu, Se, Ag, and Zn have also increased in crab tissue when comparing the present Study with previous ones conducted at the SJBE.

7.2 ORGANIC CONTAMINANTS

7.2.1 Sediments

Organic contaminant detection in sediments was limited to bis(2-Ethylhexyl)phthalate, a common plasticizer, which was detected in Stations 17SJ and 6MP. These Stations are located at the western outlet of the Martin Peña Channel and in the San Jose Lagoon (near the outlet of San Anton Creek), respectively. The concentrations of target organic pollutants were below the PELs.

Contamination of organic compounds in sediments is an important environmental indicator, but its analysis may significantly increase the costs of monitoring. Sediment matrix effects may decrease the power of the analysis by increasing detection limits. Alternative means of analysis, targeting specific analytes, should be examined. For example, ELISA based assays that target PCBs and DDTs are presently available and are a good alternative for general screening and routine monitoring. This method could be employed to identify hotspots prior to more detailed analysis.

7.2.2 Fish and Crab Tissue

Alpha-BHC was the only target organic contaminant detected in crab tissue, whereas DDTs in fish tissue were detected in most of the Stations at similar levels. Total PCBs were only detected in fish tissue at four of the eight Stations sampled. Chlordane, endrin aldehyde and lindane were detected in fish tissue samples collected at Stations 6MP and 10CS (both Stations receive direct inputs from urban sites - i.e., Martin Peña Channel and San Anton Creek).

The levels of PCBs detected in fish (<25 to 92.2 µg/kg) and crab tissue (<25 µg/kg) approached or exceeded the EPA screening value for recreational fishers (20 µg/kg). Although total DDTs in fish and crab tissue did not exceed the SV for recreational fishers (117 µg/kg), total DDT levels in fish tissue collected from Station 1SJB (10.0 µg/kg) approached the total DDT value for subsistence fisher (17 µg/kg).

Comparison of metal concentrations in this Assessment relative to previous studies indicates an increase in fish and crab tissue levels of As, whereas the concentration of DDTs remained at similar levels in crab tissue and decreased in fish tissue.

Evaluation of organic pollutants in biotic tissue is important, as implications for wildlife and humans are serious. However, analytical approaches that are more economical than laboratory analysis (e.g., ELISA testing) may be used for routine monitoring of these contaminants. Further, a subset of organic compounds may be targeted as sentinels of environmental trends.

7.3 COMMENTS ON STUDY GOALS

The purpose of the present work can be stated as:

1. Assessment of effectiveness of ongoing and future conservation efforts.

Based on the above, sediment trace metal contamination indicates that many locations still contain significant amounts of trace metals. Some metals such as As are more abundant in the WSJBE, and strategies to decrease trace metals inputs into WSJBE should be examined.

A significant finding is that sediment samples collected at Stations in the Condado Lagoon were found to contain several trace metals at concentrations high enough to be of concern for management. While sampling in the Condado Lagoon, sewage inputs near the sampling areas were observed, which could account for the input of trace metals into the system. The Condado Lagoon is a protected area where motorized-boat traffic is prohibited, and contains seagrass beds and associated fauna, as well as protected species such as the West Antillean Manati.

Trace metal impacts at Station 1SJB (near La Esperanza Peninsula) are relevant, given plans to fill depressions at the Condado Lagoon with sediments dredged from La Esperanza Peninsula. Sediments from Station 1SJB contain significant levels of As, Cu and Hg, which should be restricted from being mobilized during transport and deposition into depressions at the Condado Lagoon.

Finally, comparison of Assessment results with previous studies indicates that trace metal concentrations have decreased in many Stations (excepting 16SJB and 7MPSJ), whereas the Hg concentration has increased in most Stations. Study findings indicate the importance for evaluating Hg inputs into the Piñones Lagoon, which was assumed to be relatively isolated from inputs of trace metal contamination (given that it is a protected area).

The Study did not show overall high levels of organic contaminants in sediments of the SJBE. However, it is recommended that additional, economic monitoring alternatives of organic target contaminants be continued in the SJBE and its tributaries.

2. To evaluate the appropriateness of the selected environmental indicators (i.e., bottom sediments, and mojarra fish and blue crab tissues).

The concentration of contaminants of concern in sediments is an important indicator of environmental health. In terms of general indices of quality, sediment TOC may be used as an index, but should be evaluated according to specific environmental realities of the system studied. Previous studies conducted throughout Puerto Rico have shown that coastal lagoons that are unlikely to be subjected to anthropogenic organic enrichment may contain TOC up to 9%. Therefore, the present indicator threshold of 5% TOC should be revised. A lower threshold should be applied as sediments with <1% TOC are unlikely to occur naturally in tropical estuarine systems, as was the case of Station 3SJB. In addition, the results of this Study underscore the use of sediments for monitoring trace metal inputs into the SJBE. However, as in the present case, inclusion elemental factors that allow for normalization of geological and/or diagenetic modification of trace metal composition in sediments should also be included along with the contaminants of concern. Suitable choices are Al and Li, as they are considered inert under the conditions found at SJBE. Finally, although organic contaminants in sediments are of interests, analyses are often expensive, and the required detection limits (in the parts per billion) may be upset by matrix effects. Alternative less expensive monitoring methods (e.g., ELISA tests) may be implemented to establish trends in a cost-effective manner.

Mojarra and blue crabs are convenient biological indicators for the SJBE. These species were present in most of the Sampling Stations. The Stations at Puerto Nuevo River and Condado Lagoon did not yield mojarra specimens. Although snapper species were captured at both Stations, the few observations made by others (USEPA 2008b) indicate similar contaminant levels between both types of fish. Blue crabs were the easiest overall catch, but required a large number of specimens (over ten specimens), given that enough meat had to be extracted to assure sufficient material for analysis. Given that during the Study it was confirmed that mojarra and blue crabs are staple products for local fishermen, their tissue should be examined frequently to evaluate trends in trace metal and organic contamination in SJBE. Further, information should be gathered to improve data regarding contaminant trends in these and other species, perhaps complementing future data sets with determinations based on time integrating approaches independent of biota (such as using solvent filled dialysis bags for organic pollutants). In addition, future work should examine the use of organisms with restricted or minimal mobility such as mangroves and bivalves. During the Study, we observed that mangroves are commonplace in many of coastline areas adjacent to the Sampling Stations. Mangroves provide an excellent opportunity to evaluate trace metals, given that some mangrove species concentrate metals in their roots. In addition, stable isotope composition methods may be used to examine the presence of anthropogenic nutrients along with the composition of associated algae. The false mussel, *Mytilopsis dominguensis*, is another organism of potential interest and is widely distributed within the SJBE. The false mussel is an active filter feeder and, therefore, could be used to monitor waterborne contaminants using a similar approach to the Mussel Watch Program.

8 REFERENCES

- Acevedo-Figueroa, D., B.D. Jimenez and C.J. Rodriguez Sierra. 2006. Trace metals in sediments of two estuarine lagoons from Puerto Rico. *Environ. Poll.* 141:336-342.
- Aldarondo-Torres, J.X., F. Samara, I. Mansilla-Rivera, D. S. Aga and C.J. Rodriguez-Sierra. 2010. Trace metals, PAH's and PCBs in sediments from Jobos BAY área in Puerto Rico. *Mar. poll. Bull.* 60: 1350-1358.
- Delgado-Morales, D., C.J. Rodriguez, and B.D. Jimenez, 1999. Heavy Metal Evaluation in Aquatic Organisms from the San Jose Lagoon. Prepared by University of Puerto Rico, Center for Environmental and Toxicological Research, Medical Sciences Campus, San Juan, PR. Submitted to the Puerto Rico Department of Natural and Environmental Resources.
- Herut, B. and A. Sandler. 2006. Normalization methods for pollutants in marine sediments: review and recommendations for the Mediterranean. IOLR Report H18/2006. www.sednet.org/download/0604_herut_and_sandler_report.pdf downloaded on 3 Aug 2011.
- MacDonald, D.D., R.S. Carr, F.D. Calder, E.R. Long, and C.G. Ingersoll. 1996. Development and evaluation of sediment quality guidelines for Florida coastal waters. *Ecotoxicology* 5: 253-278.
- Martinez-Colon, M. and P. Hallock. 2009. Estudio de Metales Trazos en la Laguna La Torrecilla. In. Segundo Informe de la Condición Ambiental del Estuario de la Bahía de San Juan. San Juan Bay Estuary Program. San Juan, PR.
- Otero, E. 1988. Sulfate Reduction Rates in Sediments of La Parguera, Puerto Rico: Effects of Organic Matter Content and Sediment Characteristics. M.S. Thesis. University of Puerto Rico, Mayaguez Campus.
- Otero, E., R.Almodovar-Ferrer and Jose M. Lopez. December 1989. Distribution of trace elements in Coastal Mangrove Sediments. American Chemical Society XIII Senior Technical Meeting, Humacao, Puerto Rico.
- PBS&J. 2009. Development of the Benthic Index for the San Juan Bay Estuary System. SJBEP. San Juan, PR.
- PERM. 2001. Sampling and analysis of bottom sediments in the San Antonio Channel, San Juan Bay, San Juan, Puerto Rico.

- PPB Environmental Laboratories, Inc. 1999. Final Report for San Juan Harbor, Puerto Rico 1999 Evaluation of Dredged Material for Ocean Disposal, Volumes I and II, Gainesville, Florida.
- Rivera , J.A. 2005. Findings on the Benthic Assessment of the San Juan Bay Estuary, Puerto Rico. Final Report Submitted to NOAA Fisheries, Southeast Fisheries Science Center, Miami.
- Rodriguez Sierra, C.J. and B. Jimenez. 2002. Trace metals in striped mojarra fish (*Diapterus plumieri*) from Puerto Rico. Mar. Poll. Bull. 44: 1039-1045.
- SJBEP 2008. Quality Assurance Project Plan for the San Juan Bay Estuary Water Quality Volunteer Monitoring Program. San Juan Bay Estuary Program, San Juan PR.
- USEPA 2000a. Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories. Vol. 1. Fish Sampling and Analysis. 3rd Edition. EPA 823-B-00-007.
- USEPA 2000b. Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories. Vol. 2. Risk Assessment and Fish Consumption Limits. 3rd Edition. EPA 823-B-00-008.
- USEPA 2001a. EPA Requirements for Quality Assurance Project Plans (EPA QA/R-5). EPA/240/B-01/003.
- USEPA 2001b. National Coastal Condition Report. EPA-620/R-01/005. (Available online at <http://water.epa.gov/type/oceb/assessmonitor/nccr/downloads.cfm>).
- USEPA 2004. Screening Values for Chemicals in Sediments and Fish Tissue. The Incidence and Severity of Sediment Contamination in Surface Waters of the United States. National Sediment Quality Survey. 2nd Edition. EPA-823-R-04-007.
- USEPA 2005. National Coastal Condition Report II, EPA-620/R-03/002. (Available online at http://water.epa.gov/type/oceb/2005_downloads.cfm).
- USEPA 2006. National Estuary Program Coastal Condition Report. EPA-842-B-06-001 (Available online at <http://www.epa.gov/owow/oceans/nepccr>).
- USEPA 2008a. National Coastal Condition Report III. EPA/842-R-08-002. (Available online at http://water.epa.gov/type/oceb/assessmonitor/upload/nccr3_entire.pdf)
- USEPA 2008b. Puerto Rico Fish Tissue Analysis, Final Report. EPA Region 2. Division of Environmental Science and Assessment. USEPA. Office of Water. Washington DC.

USEPA 2008c. Indicators Development for Estuaries. EPA842-B-07-004.

Villanueva, E., L.J. Rivera-Herrera, S. Rivera-Colón, M. Tacher-Roffe, C. Guerrero-Pérez, and C. Ortiz-Gómez. 2000. Comprehensive Conservation and Management Plan for the San Juan Bay Estuary. Volume I, U.S. Army Corps of Engineers, San Juan, PR.

Webb, R.M.T. and F. Gómez-Gómez. 1998. Synoptic Survey of Water Quality and Bottom Sediments, San Juan Bay Estuary System, Puerto Rico, December 1994-July 1995. U.S. Geological Survey, Water Resources Investigations Report 97-4144, San Juan, PR.

9 APPENDICES

Please see electronic files.