2012 BIOLOGICAL MONITORING PROJECT PLAN AND MITIGATION ACTIVITIES

Sediment Quality Component

Exploratory Sediment Sampling and Contaminant Evaluation at Four Locations of Guayanilla Tallaboa Bays Complex.

P.O. S-20632 to Univeristy of Puerto Rico Mayagüez Campus

By

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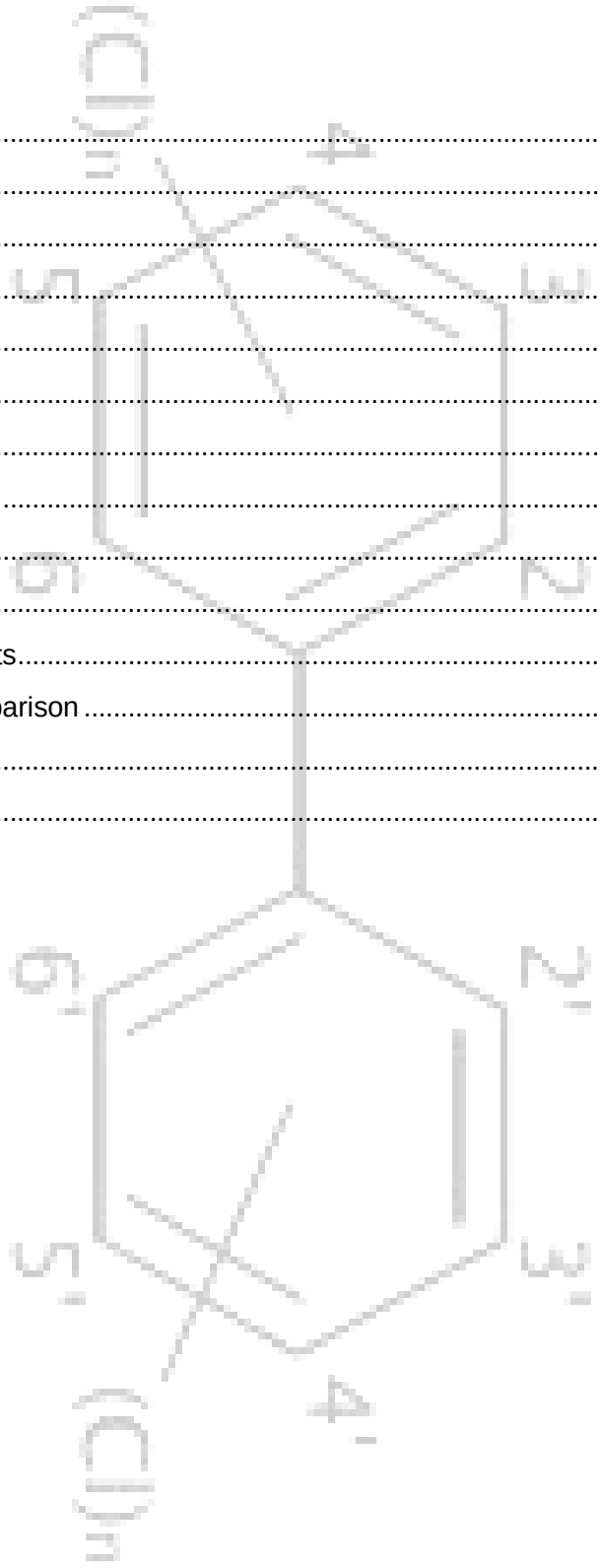

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Introduction

Industrialization at the Guayanilla-Tallaboa Bays System (GTBS) initiated during the late 50's under Operation Bootstrap and resulted in a significant modification of the natural surroundings of this system (Tilly, 1979). A report on extensive samplings conducted during the 1970's (Lopéz, 1979) indicated the accumulation of hydrocarbons and trace elements within the GTBS, to the east of Punta Guayanilla, among other sites. The distribution of these contaminants was attributed to the disposal of cooling water of the then PPG and CORCO operations.

Recently, local stakeholders have demonstrated interest in the topic of toxic contaminants in the area of Guayanilla and Peñuelas, as indicated by news in one of Puerto Rico's most influential newspapers http://www.elnuevodia.com/enelsurlosmas toxicos-1369148.html). Furthermore, recent works have been published in relation to pollutants in marine waters of southwestern Puerto Rico (Lajas and Guanica; Pait et al, 2007) which indicate the presence of some contamination in certain locations, especially those associated to Guánica Bay.

The various contaminants examined in this works include major and trace elements, organochlorine pesticides, butyl tins, polybromylated diphenyl ethers (PBDE's), polycyclic aromatic hydrocarbons (PAH's) and polychlorinated biphenyls (PCB's). The following summary of the characteristics of some of the contaminants examined is taken from Pait et al (2007):

"Growth and reproduction of aquatic life are commonly affected by elements such as copper, cadmium and mercury. Butyltins were used as biocide applications to boat hulls (especially TBT) and is associated with endocrine disruption of mollusks. Larger ships are still allowed to apply this type of antifoulant in US waters. PAH's are associated with combustion of fossil fuels and other organic matter and aquatic organisms are capable of their accumulation. PCB's are synthetic compounds used in various types electrical applications, heat transfer fluids, pesticides and paints. These compounds bioaccumulate and degrade very slowly in the environment. Exposure of fishes to PCB's produce reduced growth, reproductive deficiency and vertebral abnormalities. PBDE's are used widespread as flame retardants in all kinds of plastics, and as PCB's have many congeners. The penta bromylated forms of this type of compounds is of concerns as it is readily absorbed and its concentration is increasing in the environment and humans. Thyroid hormone, liver and neural development impairment have been associated with PDBE's."

The present work focuses attention on a preliminary assessment of contaminants in locations associated to EcoElectrica's pier as well as control sites. This preliminary evaluation will serve as record of extant levels of contamination with regard to the intake and outfall sites of EcoElectrica's cooling water intake and water disposal as seen from the point of view of sedimentary accumulation.

Methods

Study Area

Four stations were sampled during this work (Figure 1). Two replicates were collected at the outfall station (Sample 001DISA and 001DISB and one replicate was collected at the intake (sample 002INT), Maria Langa (sample 003ML) and in Cayo Caribe channel (sample 004CC). Samples at the outfall were collected under the plume.

Figure 1. Sediment sampling locations. Coordinates in decimal degrees are: Discharge, 17.97283N,66.76155W; Intake, 17.97528N,66.75908W; Maria Langa, 17.96838N,66.75724W; Cayo Caribe, 17.96935N, 66.73329W.

Clean-up

All sampling and laboratory equipment that would have direct contact with samples were pre-cleaned with tap water and laboratory grade soap, rinsed with distilled water (DW), rinsed with laboratory grade HCL 10%, rinsed with DW, rinsed with pesticide grade methanol and dried in the oven. Sampling equipment was doubled bagged in plastic before being transported to the field.

Sampling

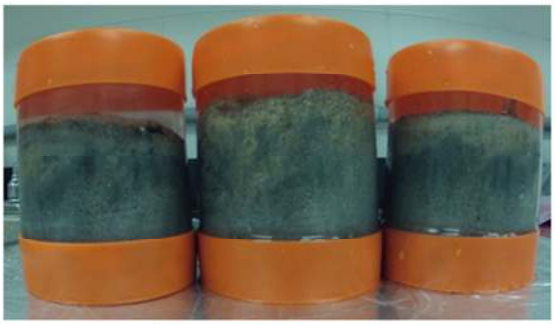
Sampling at each site was conducted by SCUBA divers using tenite butyrate tubing (95.3 mm i.d. x 120 mm H) with beveled lower edges. The tubing was inserted vertically in the sediments using a polyethylene paddle and small cleaned sledge hammer. A polyethylene cap was secured on the top and the sediment adjacent to the core was cleared. The bottom cap was installed while slightly tipping the core and minimizing mixing with the surrounding water. Samples were brought to the surface in an upright position and transported in the boat inside clean buckets containing water from the sampling station in order to avoid pressure differentials that may cause emptying of the corer contents. All samples were collected within a period of 4 hours on 24 October 2012, and transported to the laboratory for further treatment.

Sample Preparation

Once in the laboratory, the working surfaces were covered with aluminum paper and rinsed with pesticide grade methanol between each sample to avoid possible cross contamination (Figure 2). Samples were emptied into Pyrex containers and homogenized with stainless steel spoons using gloves. Once mixed, samples were distributed leaving no headspace into vials provided by the contracted analytical laboratory. Bottles were labeled, doubled bagged and custody forms filled. The process was repeated with all samples. Samples were sent to the analytical

laboratory by overnight air courier using cold backs in sealed coolers. All timelines were met according to the analytical lab (See data Package in Appendix 1).

Buckets with seawater holding sediment cores



Cores (3) from Cayo Caribe just prior to being processed and showing reduced sediments.

Vials, spoons and mixing containers on aluminum wrap covered counter tops.

Top view of sediments from the Intake station still prior to homogenization.

Figure 2. Samples in the laboratory at different stages of preparation.

Analysis

Samples were submitted to Columbia Analytical Services (CAS) for analysis; Table 1 contains the detailed list of analyses. Samples arrived in good condition to CAS laboratories. Custody information can be verified in the Appendix 1. Results were compared with *effective range low*

concentration (ERL= concentrations in which <10% of cases exposed to sediments contaminated with a type of pollutant have been observed to elicit toxicity in test organisms) if such values were available.

Table 1. Analysis conducted by analytical laboratory.

Analysis	Method
Particle Size Determination	ASTM Method D422 Modified
Total Metals	6010C (Al, Sb, Cd, Cr, Cu, Fe, Pb, Mr Ag, Th, Sn, Zn), 7010 (As) and 7471B
Buytyl Tins	Krone
Organochlorine Pesticides	8081B
Polybrominated Diphenyl Ethers (PBDE's)	8270C-SIM
Polynuclear Aromatic Hydrocarbons (PAH's)	8270D SIM
PCB's 209 Congeners	1668C

Results and Discussion

Grain Size Analysis

Sediments at three of the sites can be described as sandy (DIS, ML and CC) while contained up to 40% gravel content and 30 % mud content, the highest of all stations (INT; Figure 3). The higher gravel content of station INT is confirmed by the presence of coral and calcareous algae fragments. The increased mud content at this same station is due to the exposure of this site to turbidity plumes derived from the eastern portion of

eastern Guayanilla peninsula or Tallaboa Bay which is transported in that general direction by water currents (see Canals, 2013).

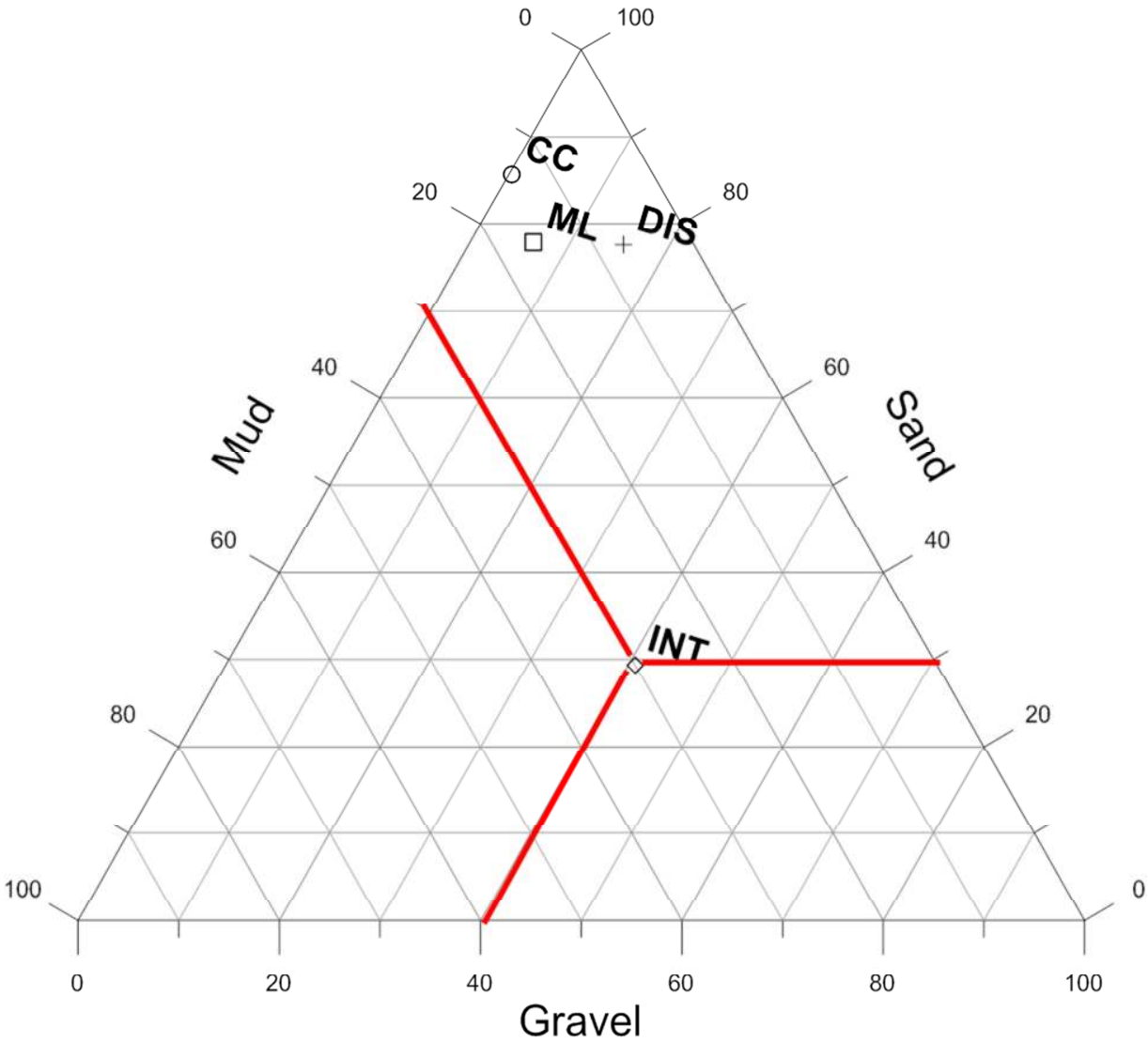


Figure 3. Grain size results from the four locations examined. Lines at INT are drawn as a guide for graph interpretation.

Elements

Aluminum was analyzed to evaluate changes in the geological sources of sediments in the collected samples. Aluminum in sedimentary environments is mostly related to clays and is considered inert. This element has been used for normalization of metal contents in sediments which may depend on weathering and transport of fine sediment constituents from adjacent watersheds (Herut and Sandler, 2006). This agrees well with our observations of finer sediments in station INT where the level of Al was 4X higher than the rest of the stations (Table 2).

Table 2. Concentration of metals (ppm dry wt) at found at different locations. Underlined metal indicate metals for which sediment quality guidelines (SQG's)[*] area available. Numbers light blue represent values over effective range low values (ERL; concentrations with lower 10 percentile probability of causing toxic effects to biota. ND= not detected. MRL(min)= minimum method reporting limit.

Element	Station					
	001DISA	001DISB	002INT	003ML	003CC	MRL(min)
Aluminum	3,340	2,840	13,000	2,970	2,300	10
Antimony	ND	ND	ND	ND	ND	1.9
Arsenic	5.5	5.3	10.2	6.7	2	1
Cadmium	ND	ND	ND	ND	ND	0.1
Chromium	6.3	8.5	19.9	6.5	5	0.5
Copper	5.8	5	29.2	4.3	3.4	0.6
Iron	4720	3980	19000	3850	3030	1.9
Lead	ND	ND	3.4	ND	ND	1.9
Manganese	251	241	673	125	90.4	0.2
Mercury	0.03	0.03	0.06	ND	ND	0.02
Nickel	3.3	4.3	10.9	2.8	1.8	0.4
Selenium	ND	ND	ND	ND	ND	1
Silver	ND	ND	ND	ND	ND	0.5
Thallium	ND	ND	ND	ND	ND	1.9
Tin	ND	ND	ND	ND	ND	1.9
Zinc	10.9	9.1	36.7	5.9	6.6	1

[*] Sediment Quality Guidelines developed for the National Status and Trends Program. 1999. http://archive.orr.noaa.gov/book_shelf/121_sedi_qual_guide.pdf (downloaded on 19 March 2013).

No Cd, Sb, Ag, Th, Sn, and Se was detected at any of the stations at reporting limits of 0.5-2 ppm dry wt basis. The maximum detected metals were observed at INT, coinciding with the highest aluminum and mud concentration. Lead was only detected at the intake station and the highest concentration of mercury was detected also at this station. *Thus, the next discussion will focus on findings at station INT since this station contained 2-6 times the levels of metals that the rest of the stations.*

Guidelines have been established for certain pollutants through different programs in order to evaluate the potential for toxicity of pollutants found in sediments. Sediment quality guidelines (SQG's) used by NOAA's National Status and Trends (NS&T) Program were used throughout this report as to help in the interpretation of the results (See Appendix 2 for Tables). According to these SQG's, only Arsenic was found at a level slightly higher than the effective range low value, indicating low probability of toxicity at INT. The other stations showed concentrations similar to those found at Bahia Montalva (Pait et al) and lower than many sampling locations in eastern San Juan Bay (Otero and Melendez, 2011).

Chromium and Ni concentrations at INT were well within the intermediate values found at Bahia Montalva, while the level of Cu at this station was higher than those found in all stations examined by Pait and collaborators, with the exception of those found within Guanica Bay. Although mercury was not found in all stations of Montalva and La Parguera sampled by Pait et al (2007), low levels were found at Guayanilla, comparable to those of Guanica Bay. In comparison, considering 90 % of the sites sampled in San Juan by Otero and Melendez (2011), Pb, Cr, Ni,

Cu, and Hg were up to 57, 3, 5, 9 and 33 times higher in San Juan than at INT, respectively.

Organic Contaminants

No organichlorine pesticides or butyltins were detected at the 1 ppb detection limit levels. The detection limits achieved by the analytical laboratory for pesticides was sufficient for most of the pesticides (except for Lindane and Dieldrin) and suggest a low probablility for toxicicity on bottom dwellers due to this type of contaminant (Buchman, 2008).

Of the 17 polybromylated ethyl ethers (PBDE's) examined, only three were detected at stations INT (PDBE 47 =15 ppt), DIS (PBDE 206 = 1 and PBDE 209 = 34 ppt at DIS) and CC (PBDE 209= 1.1 ppt). Although only a subset of the total analyzed by Pait et al. was analyzed here (17 out of ca. 30 congeners), a comparison with their totals found at the Parguera/Montalva/Guanica southwestern complex (PMG-SC) suggests that levels of 1-2 ppb are common in the region, while levels of ≥7 ppb were only found within Guánica Bay. Thus, levels of total PBDE's found at DIS and INT stations may be at similar or higher levels as found in Guánica Bay (Figure 4). Since no SQG have been established for these compounds, further evaluation and conclusions on the presence of these compounds at the study site should be made with caution. However, a recent report by USEPA (2010) indicates that the PBDE's found in this study are among the ones more commonly accumulated by some marine fishes and birds and probably derived from fire-retarded plastics and airborne particles.

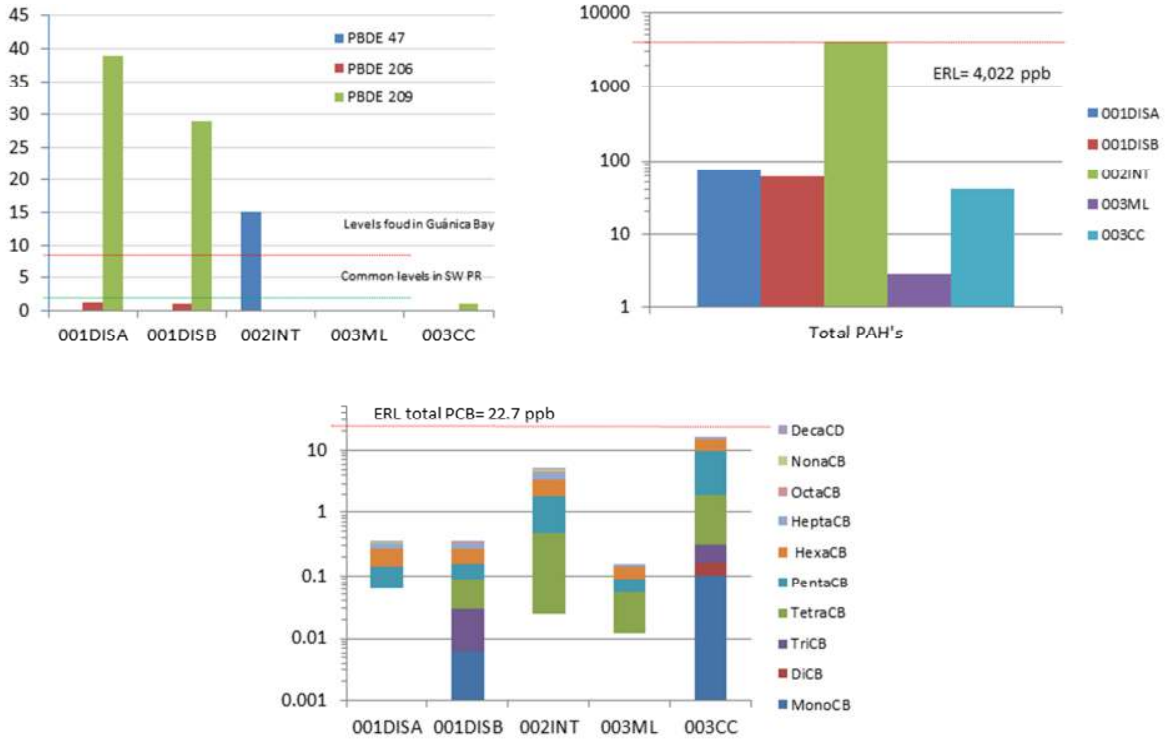


Figure 4. Concentration of organic contaminants (ng/g dry wt) from different stations. Dotted horizontal lines represent PBDE's concentrations found at other locations during previous work. Dotted lines for PAH's and PCB's represent ERL's. PCB data is grouped by 1-10 chlorine substitutions.

The concentration of total PAH's was 2.8 in ML , 41-68 (CC and DIS) and >4100 ppb dry wt at INT, consistent with higher accumulation of contaminants at the latter station (Figure 4). The concentration of PAH's at INT is about 4X higher than the concentration found by Pait (2007) in all sediments sampled at the PMG-SC and slightly over the ERL for total PAH's (4,022 ppb dry wt; USEPA, 2010). Considering 5 of the specific PAH's for which ERL's and ERM's are available in USEPA's SQG's (acenaphthylene, anthracene, naphthalene, benzo(a)pyrene and

dibenzo(a,h) anthracene), all but naphthalene followed the pattern of total PAH's and only dibenzo(a,h) anthracene was found at concentrations higher than its ERL.

Pait et al (2007) evaluated possible sources of these contaminants using the fingerprint of PAH's from their study with those observed from different sources. They suggest a similar fingerprint between the proportions of fluoranthene, pyrene, benz(a)anthracene, benzo(a)pyrene and benzo(g,h,i)perylene in their samples and that of automobile emissions, as per Kimbrough and Dickhut (2006). Our results disagree with the conclusions of Pait and collaborators as no covariation of these compounds with the cited fingerprint was found at the stations where these PAH's were detected. Another comparison was conducted with the average proportion of selected PAH's from outboard engines (Ballofett and Quinn, 2004) and similar to Pait and collaborators, no correspondence was found at the INT station, where most of the compounds were found.

The concentration pattern of total PCB's showed higher values at INT (5.1ppb) in comparison to DIS and ML (0.3-0.2 ppb; Figure 4). However, the highest concentration was found at CC (15 ppb). None of the total PCB's concentrations found exceeded the ERL threshold of 22.7 ppb. Considering the proportion of mono- to nona-substituted PCB's found at the different locations, it is observed that 83-98% of all PCBs are found within the tetra- to hepta- substituted congeners. Also, a large shift to penta substituted PCB's was observed at CC (49% of PCB's) vs the other sites (20-26% of total PCB's) suggesting that the history and source of the PCBs' found at higher concentration in CC differs from that of the other stations. The findings of Cayo Caribe were unexpected since this site is

farther away than the other stations from most of the potential land derived sources of PCB's.

Historical Data Comparison

As mentioned earlier, the historical data from the late 1970's (Lopez, 1979) indicated a spatial pattern of sediment contaminants that increased towards the eastern bottom sediments of Punta Guayanilla. Unfortunately, only contour maps showing the general distribution of metals and petroleum hydrocarbons are available. However, these coincide with our findings of generally higher concentrations at the INT station, suggesting that the higher concentrations at this station may be part of legacy contaminants mobilized by sediment resuspension.

Conclusions

- Overall, sediments from Int contained the highest proportion of fine and terrestrially derived material based on granulometry and aluminum content. These indicators coincide with the finding that this station contains the highest concentrations of contaminants from the sites examined (with the exception of total PCB's).
- No organochlorine and butyltins were detected.
- PBDE's at the discharge and intake sites were found at levels similar to those found in Guánica Bay during previous studies. No guidance is available for these contaminants.

- Total PAH's concentration at the Intake zone was 4X higher than those found recently by previous studies in southwestern Puerto Rico. The levels of PAH's at this site were slightly higher the ERL's and thus low to moderate toxicity on benthic biota may occur according to SQG's.
- Polychlorinated biphenyls were not found at concentrations higher than ERL's, but higher concentrations were found at CC, the farthest station from the cost.
- Overall, the distribution of contaminants found in this small scale survey supports the idea that contaminants accumulated at these sites are not derived from sources related to the operation of EcoElectrica.
- Additional work should include low level analysis of metals and PAH's and PCB's at some potential water point sources as well as an expansion of sediment analysis to confirm the present results. These analyses may consist in a combination of analytical approaches including chemical and immunoassays for major groups of organic compounds including off site control sites.

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