ANALYSIS OF IN-PLACE CONTAMINANTS IN MARINE SEDIMENTS FROM FOUR HARBOR LOCATIONS ON GUAM

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A PILOT STUDY

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ABSTRACT

During 1997, a preliminary survey was carried out to determine concentrations of heavy metals, polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) in sediment core composites (5 x 30 cm) from four harbor locations on Guam (Agana Boat Basin, Outer Apra Harbor, Agat Marina, and Merizo Pier). Overall, a total of 46 sub-tidal sites were examined. The survey clearly demonstrated enrichment of all contaminant groups in Agana Boat Basin, Outer Apra Harbor and Merizo Pier, although by world standards, the majority of sites within each location were considered to be relatively clean. The highest levels of all three chemical groups were found at Apra Harbor, the largest and oldest port on Guam. Here, moderate to heavy enrichment of various heavy metals, PCBs and PAHs were identified in sediments collected in the vicinity of Hotel Wharf, Commercial Port, and Dry Dock Island. The lowest contaminant levels were almost always encountered at Agat Marina, a recently constructed small boat harbor to the south of Agana.

The range of mean heavy metal concentrations (μ g/g dry wt.) for all 46 sites were as follows: silver (Ag): all <0.2; arsenic (As): 1.00-10.7; cadmium (Cd): <0.2-2.18; chromium (Cr): 3.61-39.5; copper (Cu): 0.56-142; mercury (Hg): 0.004-0.403; nickel (Ni):<0.2-71.0; lead (Pb):<0.6-96.3; tin (Sn):<0.1-7.37, and zinc (Zn): 2.3-130. Mean total PCB and PAH concentrations ranged from <0.04-341 ng/g dry wt. and <10-8,140 ng/g dry wt. respectively.

Heavy metal levels in Outer Apra Harbor were generally well below those reported earlier by the U.S. Navy for sediments from the Naval Reservation Area, within Inner Apra Harbor. Most notable from this particular study were the excessively high levels of total Sn (148-1055 μ g/g dry wt) and Hg (0.4-2.4 μ g/g dry wt.) recorded. The impact of these elements on the indigenous biota, within Inner Apra Harbor and immediately adjacent waters of the outer harbor area, is currently unknown.

PCB enriched sediments from Outer Apra Harbor were dominated by Cl₄-Cl₇ homologues while those from lightly contaminated sites frequently contained proportionately higher amounts of the lower chlorinated members suggesting transport from relatively distant sources. PCB profiles, determined in sediments from Hotel Wharf and the Commercial Port area, closely resembled those of Aroclor 1254, a commercial PCB mixture that was once widely used as a dielectric fluid in electrical transformers. In contrast, PCBs in sediments from the southeastern end of Dry Dock Island were similar in profile to Aroclor 1260, another popular ingredient of transformer fluids of the past.

PAH profiles varied substantially between sites, although there was a tendency for some of the lighter components (e.g. acenaphthylene and anthracene) to dominate in sediments from relatively clean areas. Sedimentary fluoranthene/pyrene and pyrene/benzo(a)pyrene ratios were indicative of petrogenic hydrocarbon spillages at Hotel Wharf, the Shell Fox-1 Fuel Pier at the western end of Commercial Port, and Cabras Power Plant. Fossil fuel combustion was considered to be the primary source of PAH at most other sites examined.

The data for all three chemical groups are further discussed in relation to possible sources of input, and are compared and contrasted with findings reported by other researchers elsewhere in the world. Guidelines are proposed for classifying Guam's harbor sediments according to their contaminant loading, and the issue of open water disposal of dredged sediments is briefly addressed. Future directions for continued research are recommended.

INTRODUCTION

Sediments are a major sink for many of the more persistent organic and inorganic chemicals introduced into the aquatic environment (Ingersoll 1995). They also play an important role in releasing sorbed contaminants back to the overlying water and to the indigenous biota (Baudo and Muntau 1990). In highly polluted situations, contaminated sediments may be directly toxic to certain organisms (Swartz *et al.* 1985) and/or bioaccumulate to excessive levels within others (Mac *et al.* 1984). Commonly offending contaminants in this regard are heavy metals, polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs). The partitioning behavior of these contaminants is such that they tend to accumulate in sediments to levels that are several orders of magnitude higher than in the surrounding water. Moreover, their deposition rates are generally related to their rates of input into the immediate area (Förstner 1990). The chemical analysis of sediments can, therefore, provide the investigator with a useful and convenient measure of environmental quality and is frequently incorporated into pollution monitoring surveys.

In the following study, we examined surficial sediments from four harbor locations in Guam. Chemical analysis was carried out to determine levels of the above three groups of pollutants. Some brief notes on the sources and significance of these contaminant groups are given below. More detailed comments on specific elements and compounds within each group are included in the discussion of results.

1. HEAVY METALS

Heavy metals are natural components of the lithosphere and are released into the environment via volcanism, weathering of rocks, and the activities of man. A comparison between the natural and anthropogenic rates of metal mobilization from the earth's crust falls indicates the latter to exceed the former, by an order of magnitude or more, for several elements of environmental importance (e.g., Ag, Cd, Cr, Cu, Hg, Ni, Pb, Sn, Zn) (Bryan 1976, Baudo and Muntau 1990).

Primary industrial processes that release a variety of metals into waterways include mining, smelting and refining (Bryan 1976). In fact, almost all industrial processes that produce wastewater discharges are potential sources of heavy metals to the aquatic environment (Klein *et al.* 1974, Barnhart 1978). Domestic wastewater, sewage sludge, and urban runoff are also major sources of heavy metals into rivers, estuaries and coastal waters (Connell and Miller 1984). Likewise, the burning of fossil fuels releases considerable quantities of heavy metals that frequently account for a significant fraction of the total anthropogenic metal input in sediments in near shore waters adjacent to urban and industrial growth centers (Bruland *et al.* 1974, Topping 1974). Ports, harbors, marinas and mooring sites, are also subjected to heavy metal inputs associated with recreational, commercial, and occasionally, military boating and shipping activities.

While a number of heavy metals are either essential for life (e.g. Cu, Zn) or highly desirable for optimum health (e.g. As, Cr, Ni, Sn), there are those with no known biological function (e.g. Ag, Cd, Hg, Pb). However, irrespective of whether they are essential or not, all heavy

Table 1

Past and Present Industrial Uses of the Heavy Metals Examined^a

Metal	Uses of Metals and Compounds ^b
Arsenic	Component of pesticides; wood preservative; alloys; semi-conductors; medicines; glass and enamels.
Cadmium conductors; biocides	Electroplating (anticorrosion coatings); thermoplastic stabilizers, e.g. in PVC; Ni-Cd batteries; alloys; solders; catalysts; engraving; semi-TV tube phosphors; pigments in paints and plastics; glass ceramics;
Chromium cement	Metallurgy—ferrochromium alloys; refractory bricks; electroplating; industrial dyes; ink; tanning; paint; wood preservative; glass making; production.
Copper	Electrical industry; alloys; e.g. brass; chemical catalyst; anti-fouling paint; algaecide; wood preservative.
Lead	Storage batteries; leaded gasoline; pigments; red lead paint; ammunition; solder; cable covering; anti-fouling paint; glazing; PVC stabilizers.
Mercury preservatives;	Chlorine production; electrical apparatus; anti-mildew paint; instruments; catalyst e.g. for PVC and acetaldehyde production; pesticides; pharmaceuticals; dentistry; anti-fouling paint.
Nickel	Metallurgy—steel and other alloys; electroplating; catalyst; rechargeable Ni-Cd batteries.
Silver	Photography; electric conductors; sterling ware; solders; coinage; electroplating; catalyst; batteries; food and beverage processing.
Tin fungicide—	Tinplate; solder; bronze; white metal; chemical reducing agent; triphenyl tin acetate; anti-fouling paint—tributyl tin.
Zinc	Zinc based alloys; brass and bronze; galvanizing; rolled zinc; paints; batteries; rubber; sacrificial anodes on marine water craft.

 ^a from Bryan (1976), Förstner and Wittmann (1981), Moore (1991), Bryan and Langston (1992)
 ^b importance generally decreasing from left to right.

metals form an important group of enzyme inhibitors when natural concentrations are exceeded (Bryan 1976). Thus, organisms living in or adjacent to sediments contaminated by heavy metals may suffer toxic effects that manifest themselves in the form of mass kills in grossly polluted situations (Carpenter 1924) to the more subtle abnormal metabolic adjustments at the sub-lethal level (Tent 1987). In addition, bioaccumulation processes may be sufficient to diminish or destroy important food resources by making them unacceptable for human consumption.

In the following study we focused on the ten heavy metals mentioned above. It can be seen from Table 1, that all of them have a diversity of uses in industry. As a consequence, they rank among the most common offenders from an environmental contamination standpoint. They also include several of the most toxic elements known to man.

2. POLYCHLORINATED BIPHENYLS (PCBS)

Polychlorinated biphenyls (PCBs) are man-made chemicals that were first described in the literature over a century ago (Schmidt and Shultz 1881). They have the empirical formula $C_{12}H_{10-n}Cl_n$ (n = 1-10) of which there are 209 possible combinations (congeners) divided into nine isomeric groups or homologues (Cl₁-Cl₉) and decachlorobiphenyl (Cl₁₀) (see Fig 1).

PCBs were first produced on a commercial level in 1929 (Hubbard 1964) and were used extensively in industry until the late 1970's when production ceased in many parts of the world following their discovery as global pollutants. Until that time however, they were widely used for a variety of industrial purposes including heat transfer fluids, hydraulic fluids, cutting oils, lubricants for use at high temperature and pressure, flame retardants, plasticizers, adhesives, inks, and dielectric fluids for use in capacitors and transformers.

The unusual industrial versatility of PCBs was related to their physical and chemical properties, namely their high electrical resistance, low vapor pressure and water solubility, compatibility with organic materials, and their thermal and chemical stability (Hutzinger *et al.* 1974). Unfortunately these very same properties, coupled with their widespread use and improper disposal have resulted in the contamination by PCBs of every component of the global ecosystem (Mullin *et al.* 1984, Atlas *et al.* 1986, Tanabe and Tatsukawa 1986).

Routes of entry into the aquatic environment are many and varied. The weathering and incineration of consumer goods containing PCBs releases these compounds into the atmosphere where they may be dispersed far and wide, either as the gaseous phase or adsorbed airborne particulates (Atlas *et al.* 1986). Leakages of contaminated lubricants, hydraulic fluids, heat-transfer fluids, and dielectric fluids may be carried into nearshore waters in rivers and streams (Bopp *et al.* 1981), in urban runoff (Murphy and Carleo 1978), and in domestic and industrial wastewater discharges (Connell and Miller 1984). Other direct sources include dumped sewage sludge (West and Hatcher 1980) and anti-fouling paints (Jensen *et al.* 1972) containing PCB. Once in the aquatic environment, PCBs, by virtue of their low water solubility, quickly become associated with particulate material and ultimately end up in the bottom sediments.

Figure 1. Structure of PCB Showing Numbering in the Biphenyl Ring System and the Number of PCB Congeners Possible



Chlorine Substitution	Number of Possible Isomers
Mono-	3
Di-	12
Tri-	24
Tetra-	42
Penta-	46
Hexa-	42
Hepta-	24
Octa-	12
Nona-	3
Deca-	1
	 Total: 209

In the U.S., PCBs were produced exclusively by Monsanto under the trade name "Aroclor". Commercial Aroclor mixtures contain between 21% and 68 % chlorine by weight depending upon the duration of the chlorination process. The last two digits of the numerical descriptor of each Aroclor indicate the chlorine content of that particular mixture. Thus, Aroclor 1242, Aroclor 1254, and Aroclor 1262, three of the most commonly produced technical mixtures, contains 42%, 54% and 62% chlorine by weight respectively. The only exception to this rule is Aroclor 1016, a special formulation containing 42% chlorine by weight, but without the higher chlorinated components of Aroclor 1242 itself (Stout 1986).

Although 209 different PCB congeners are theoretically possible, the reaction conditions of the commercial process favored specific substitution patterns. For example, 2,4,6-substitution of one or both phenyl rings was very rare whereas 2,4,5-substitution was common. Likewise, the ionic chlorination mechanism produced very little 3- and 3,5-substitution, and 3+0, 4+1, 5+1 and 5+2 substituted congeners (Ballschmiter *et al.* 1987).

At least 20 congeners have never been found in any technical PCB mixture (De Voogt *et al.* 1990) and only about 100 account for all the environmental contamination attributable to PCBs. Still fewer congeners are both prevalent and demonstrably toxic. In fact, if potential toxicity, persistence and relative abundance in the environment are used as criteria, the number of environmentally threatening PCB congeners reduces to about 36 (McFarland and Clarke 1989).

Early work with PCBs demonstrated that these hydrophobic compounds were readily accumulated in the fatty tissues of living organism, often reaching alarmingly high levels in predatory species at the head of food chains (Wasserman *et al.* 1979). Their immunosuppressive effect and ability to induce hepatic microsomal enzyme systems in fish, birds and mammals was also realized fairly early on (WHO 1976). Recent toxicological studies have shown that a few PCB congeners are sterically similar to 2,3,7,8-tetrachlorobenzo-*p*-dioxin (dioxin) and have the ability to induce aryl hydrocarbon metabolizing mixed function oxidases (MFOs). A consequence of this is that relatively nontoxic foreign compounds, e.g., certain PAHs, may be bioactivated within living cells to cytotoxic or genotoxic metabolites (McFarland and Clark 1989, De Voogt *et al.* 1990).

In the following study, congener-specific analysis was undertaken using high-resolution techniques. Emphasis was placed on twenty chlorobiphenyls of greatest environmental importance and included representatives from nine of the ten different isomeric groups (i.e., Cl_2-Cl_{10}).

3. POLYCYCLIC AROMATIC HYDROCARBONS (PAHS)

Polycyclic aromatic hydrocarbons (PAH), or polynuclear aromatic hydrocarbons as they are sometimes called, are a group of hydrocarbons composed of two or more fused benzene rings. They are ubiquitous environmental contaminants derived mainly from anthropogenic inputs with minor contributions from natural sources (Law *et al.* 1997). True PAHs are those compounds containing only hydrogen and carbon atoms and are differentiated here from polycyclic aromatic compounds that contain other atoms such as nitrogen, oxygen and sulfur (McElroy *et al.* 1989).

While PAHs are synthesized by some bacteria, plants and fungi, and are released into the environment by natural processes such as forest and grass fires, and marine oil seeps, anthropogenic activity accounts for most of the PAH released into the environment and is largely associated with the transportation, utilization and incomplete combustion of fossil fuels (McElroy *et al.* 1989). As a consequence, most PAHs enter the marine environment in urban runoff, municipal and industrial waste discharges, in bilge and fuel oil leaks associated with day-to-day shipping operations, in oil spills from maritime accidents and collisions (petrogenic PAHs), and via atmospheric deposition of particulate bound PAH from the burning of coal, oil, petroleum, wood and other organic materials (pyrogenic PAHs). Because of their hydrophobic nature, PAHs are rapidly scavenged out of the water column by suspended particulate material and deposited in the bottom sediments. The importance of sediments as reservoirs of PAH is well known (McElroy *et al.* 1989).

The fused polyaromatic ring system of PAHs renders them relatively resistant to biodegradation although a wide variety of bacteria, fungi and algae residing in aquatic sediments are able to metabolize a number of them. Apparently, degradation occurs most rapidly at the sediment-water interface and proceeds very slowly under anaerobic conditions (Meador *et al.* 1995). As a general rule, the rapidity with which PAHs are degraded is inversely related to molecular weight (Readman *et al.* 1982). Thus, naphthalene, a relatively non-toxic, two-ringed PAH, is readily degraded in natural sediments whereas benzo(*a*)pyrene, a potent five-ringed member, is not (Cerniglia and Heitkamp 1989).

In recent years, the concern about the presence of PAH in the environment has increased, since certain members of this important class of chemicals are carcinogenic in experimental animals and a potential health risk to man (Cerniglia and Heitkamp 1989). In the aquatic environment, some of the higher molecular weight PAHs have been linked with liver neoplasms in bottom dwelling fish (Malins *et al.* 1988).

In the following study, we considered 16 common PAH compounds ranging in size from two to six fused aromatic rings. They included a number of compounds known to be carcinogenic and/or genotoxic.

MATERIALS & METHODS

1. SEDIMENT COLLECTION AND PREPARATION

Sediment samples were collected from four harbor locations on Guam (Fig. 2) between May 16 and June 12, 1997. Six sites were selected at Agat Marina, five at Agana Boat Basin and Merizo Pier, and thirty from Outer Apra Harbor in the vicinity of Hotel Wharf, Commercial Port, Piti Channel, Dry Dock Island and the northwestern section of Sasa Bay (Figs. 3-6). Site selection was based primarily on proximity to potential sources of contamination (e.g., storm water outlet, mooring sites, wharves, piers, fueling stations, electrical substations etc.) along presumed concentration gradients. Site locations were pinpointed using digital orthophoto imagery maps with reference to prominent landmarks.

Sediments were collected by scuba diver at depths ranging from 0.5-17 m, using stainless steel core samplers (5 x 30 cm) fitted with pre-cleaned aluminum liners and Teflon lined plastic end caps. A slide hammer was used to push each corer into the sediment to depths ranging from 15-30 cm depending on the nature of the underlying substrate. Three cores were sampled within a 3 m diameter circle at each site wherever possible. Each core (sub-sites: a-c) was analyzed separately.

Because of difficulties encountered in extracting the charged liners from the body of the corers, the collected sediments were expelled into clean aluminum liners by inversion, wrapped in aluminum foil and stored on ice.

In the laboratory, the entire contents of each liner was dislodged into a glass bowl and thoroughly mixed with a polyethylene spatula following the removal of large rocks, shells and other such bulky materials. Samples for petrographic and particle size analysis were immediately set aside to dry at room temperature. Samples for heavy metal analyses were placed in acid cleaned polyethylene vials and dried to constant weight at 60°C while those for PCB and PAH analyses were air dried in the dark in shallow aluminum pans. Residual amounts of sediment samples were stored in pre-cleaned glass jars at -20°C for further analysis if necessary.

Upon drying, sediments were disaggregated in non-contaminating containers with a heavy Teflon rod. Those samples for metal analysis were sieved through a 1 mm nylon sieve and stored in polyethylene vials at room temperature until required for analysis. Those for PCB and PAH analysis were sieved through a 1 mm stainless steel screen into clean glass vials for storage at -20°C. Appropriate analytical methods for the above contaminants were adapted from the current SW-846 protocols developed by USEPA (1986-1995) for the physical and chemical evaluation of solid waste, in addition to those recommended by the NOAA National Status and Trends Program for Marine Environmental Quality (NOAA 1993a-d). Appropriate quality control and quality assurance procedures including full procedural blanks, matrix spikes, and certified reference materials were built into the analytical protocols.

2. PETROGRAPHIC AND PARTICLE SIZE ANALYSIS

A general petrographic assessment of the collected sedimentary material was performed on air dried samples and included Munsell Color, sorting and description of the dominant constituents. Visual observation, characterizations and measurements were made using a 10x











Hastings Triplet monocular hand lens and a 5x-20x Bausch and Lomb binocular microscope. Grain size was estimated visually and later by a sieving program, the latter performed as follows: Approximately 100 grams of air-dried sediment were gently crushed to break up desiccated clumps. The sample was then sieved for fifteen minutes through a sieve shaker column containing 10-, 18-, and 230-mesh, 8-inch brass screens (U.S. Standard Series). This shortened column produced the following four (4) size fractions:

- >2 mm (gravel)
- 1 mm to 2 mm (very coarse sand)
- 1 mm to 63 μ m (coarse to very fine sand)
- <63 µm (silt and clay or "mud")

The total organic matter content of each sediment sample was estimated following dichromate oxidation as described by Nelson and Sommers (1975).

3. HEAVY METAL ANALYSIS

The digestion of sediments for heavy metal analysis was accomplished by wet oxidation in concentrated hydrochloric and/or nitric acids. The extraction procedures were essentially similar to EPA method 3050A, designed specifically to release weakly to strongly bound metals in the sample without completely destroying the non-carbonate, mineral matrix of the sample. This method is particularly useful for identifying metal enrichment as a result of anthropogenic activities.

All reagents used were analytical grade and all glassware was acid-washed and deionized water rinsed prior to use. Standard stock solutions were purchased from a commercial supplier. Final analysis was carried out by atomic absorption spectroscopy (AAS). All analyses were performed in duplicate and were accompanied by appropriate method blanks and matrix spikes. Heavy metal recoveries from a soil certified standard reference material, were within acceptable limits for all elements examined (see Table 2).

Adopted digestion and analytical procedures varied between metals as dictated by the physico-chemical properties of the elements themselves. A brief description of the different digestion and analytical methods employed is given below.

3.1 Mercury:

Approximately 2 g of dried sediment was accurately weighed into a 125 ml glass Erlenmeyer flask followed by the slow addition of 15 ml of concentrated nitric acid. After all effervescence had subsided, the flask was capped with a Teflon stopper and heated in boiling water bath for 3 h. After cooling, the contents of each flask was diluted to 75 ml with deionized water, thoroughly mixed and set aside to allow residual particulates to settle out. The solutions were then decanted into clean glass vials and stored at 4°C until required for analysis.

Analysis was performed by flameless (cold vapor) AAS and involved the generation of metallic mercury vapor (Hg°) following reduction with 2% stannous chloride (Hatch and Ott 1968). The process was facilitated using the syringe technique described by Stainton (1971).

Table	2
-------	---

Certified Value		This Study		
Mean	Range	Mean	Range	
	<u>Certific</u> Mean	<u>Certified Value</u> Mean Range	Certified ValueThisMeanRangeMean	<u>Certified Value</u> <u>This Study</u> Mean Range Mean Range

Analysis of Standard Reference Materials

Metals (PriorityPollutnTTM/CLP Inorganic Soils [Catalog Nº PPS-46; Lot Nº 233])

	µg/g dry wt			μg/g dry wt	
Arsenic	108	94.1 - 122	112	109 - 121	4
Cadmium	114	91.4 - 137	108	106 - 110	2
Chromium	42.2	37.3 - 47.1	43.1	42.4 - 43.7	2
Copper	68.9	62.9 - 74.9	66.4	64.5 - 68.3	2
Lead	44.3	39.6 - 49.0	47.9	45.4 - 50.4	2
Mercury	1.71	1.42 - 2.00	1.31	1.22 - 1.48	11
Nickel	71.8	63.8 - 79.8	71.9	71.0 - 72.8	2
Silver	59.7	45.1 - 74.3	53.2	50.4 - 56.1	2
Tin	79.0	70.3 - 87.7	79.4	71.9 - 88.0	8
Zinc	85.6	76.1 - 94.8	92.5	91.0 - 94.7	2

PCBs (RTC PCB in Soil [Catalog Nº CRM911-050; Lot Nº J911])

	μg/	g dry wt	<u>µg/g</u>	dry wt	<u>n</u>
Aroclor 1254	1.34	0.61 - 2.07*	0.82	0.77 - 0.90	4

PAHs (RTC PAH Contaminated Soil/Sediment [Catalog Nº CRM104-100; Lot Nº CR12])

	<u> </u>	<u>g/g dry wt.</u>		_µg/g dry wt	<u>n</u>
Naphthalene	0.77	0.0 - 1.57*	nc	<0.65 - <0.70	6
Acenaphthylene	1.21	0.0 - 2.98	0.06	0.04 - 0.08	6
Acenaphthene	0.77	0.27 - 1.28	0.16	0.11 - 0.22	6
Fluorene	0.65	0.25 - 1.05	0.37	0.25 - 0.54	6
Phenanthrene	5.79	2.11 -9.48	4.95	4.00 - 6.45	6
Anthracene	1.44	0.08 - 2.80	1.38	1.14 - 1.81	6
Fluoranthene	24.6	4.53 - 44.6	23.8	20.5 - 30.8	6
Pyrene	15.0	0.0 - 30.7	11.0	9.38 - 14.4	6
Benzo(<i>a</i>)anthracene	7.98	2.09 - 13.9	3.60	3.04 - 4.66	6
Chrysene	8.60	3.39 - 13.8	5.85	4.94 - 7.47	6
Benzo(b)fluoranthene	(9.69)	none given	5.33	4.56 - 6.89	6
Benzo(k)fluoranthene	(5.10)	none given	2.92	2.64 - 3.79	6
Benzo(a)pyrene	5.09	1.56 - 8.63	5.11	4.20 - 6.52	6
Benzo(ghi)perylene	3.58	0.0 - 8.08	2.84	2.50 - 3.68	6
Indenol(1,2,3,-cd)pyrene	4.46	0.0 - 9.09	3.38	2.77 - 4.46	6
Dibenzo(a,h)anthracene	(1.55)	none given	2.72	2.29 - 3.64	6

* Certificate of analysis for PCB and PAH standard reference materials gives only the 95% prediction interval about the certified mean. PAH values listed in parentheses are not certified and are listed for information only.

Calibration standards (5-20 ng/l) were made up in 20% nitric acid containing 0.05% potassium dichromate as a preservative (Feldman 1974).

3.2 Arsenic:

The digestion procedure was identical to that described above for mercury. However, analysis utilized the hydride generation technique whereby inorganic arsenic is converted to arsine gas (AsH₃) by reduction with 3% sodium borohydride in 1% sodium hydroxide. All calibration standards (1-10 μ g/l) and sample dilutions were made up in 10% nitric acid.

<u>3.3 Tin</u>:

The hydride generation technique was also used for tin analysis. However, special precautions were necessary to minimize the problems known to be associated with this element, e.g. pH dependency, poor reproducibility and severe metal interferences (Beach 1992). To this end, sediment samples (~ 2 g) were initially digested with concentrated hydrochloric acid (~ 8 ml) to decompose the carbonates present. Following overnight evaporation to dryness on a hot plate (100°C), the samples were further digested in 10 ml of aqua regia (3:1 HCl and HNO₃) at 100°C for 3 h. Upon cooling, sample volumes were adjusted to 100 ml with deionized water.

The generation of gaseous stannane (SnH₃) was achieved with 3% sodium borohydride in 0.5% sodium hydroxide solution. Matrix interferences were minimized by analyzing small sample volumes (1 ml) in 5 ml of saturated boric acid (50 g/l) together with 0.5 ml of 10% nitric acid. For smaller sample volumes, additional amounts of dilute acid were added as necessary to minimize relative changes in pH. Calibration standards (5-20 μ g/l) were made up in saturated boric acid solution on a daily basis.

<u>3.4 All Other Metals</u>:

Approximately 2 g of the dried sediment samples were weighed into 125 ml Erlenmeyer glass flasks, loosely capped with a Teflon stopper and digested with approximately 15 ml of concentrated nitric acid at 110-135°C for 2 days. The digests were then evaporated to dryness and redissolved in 20 ml of 10% nitric acid with gentle warming. The contents of each flask was thoroughly mixed and allowed to stand for several minutes prior to analysis to permit settlement of residual particulates.

Analysis was performed by flame AAS, the contents of each flask being aspirated directly into the instrument. Corrections for non-atomic absorption were made simultaneously by the instrument using a deuterium continuum lamp. All calibration standards (0.2-10 mg/l) were made up in 10% nitric acid from a commercial mixed stock solution (100 mg/l of each metal).

4. POLYCHLORINATED BIPHENYL ANALYSIS:

Approximately 1 g of air-dried sediment was accurately weighed into a 10 ml Teflon centrifuge tube along with 0.2 g of activated copper to remove elemental sulfur (EPA method 3665A). The samples were extracted with 3 ml of n-hexane in a commercial microwave oven (700 watt-high energy setting) for sequential periods of 60, 30 and 15 seconds (see Ganzler *et al.* 1986). A rotating turntable insured homogeneous distribution of microwave radiation within the unit. Each tube was touched against a Vortex Genie for 5 second between heating

cycles to ensure the extract was thoroughly mixed. After standing overnight the samples were vortexed one last time before centrifuging at 2500 rpm for 5 minutes.

The clear extracts were decanted into 3 ml graduated glass centrifuge tubes, placed in a warm water bath (45° C) and reduced in volume (~0.25 ml) under a gentle stream of nitrogen. Cleanup was accomplished with Florisil (60-100 mesh), activated and stored at 110°C. The Florisil columns (~0.2 g) were made up in disposable glass Pasteur pipettes (see EPA method 3620B) and rinsed with 2 x 1 ml volumes of hexane prior to use. Approximately 0.25 ml of hexane was used to complete the transfer process. Each column was then eluted with hexane under gentle pressure. The PCB fraction was recovered in the first 1.5 ml of hexane through the column. The cleaned up extract was reduced in volume to 0.1 ml and transferred to a clean, glass auto-sampler vial with small volume (250 µl) insert.

Analysis was carried out by Gas Chromatography (Varian 3400CX) using an electron capture detector and a 30 m x 0.53 mm i.d. fused silica SPB-5, polymethyl-5% phenyl-siloxane (1.5 μ m film thickness) 'megabore' column (Supelco). Gas flows (nitrogen) through the column and detector were 4 ml/min and 26 ml/min respectively. The column temperature was programmed to hold at 150°C for the first two minutes, then increased to 260 °C at a rate of 5°C/min and hold for a further 13 minutes. Both the injector and detector temperatures were held constant at 280°C and 325°C respectively.

PCB quantification was accomplished using a 20-congener calibration standard representing PCB homologues Cl_2 to Cl_{10} (NOAA 1993a). The congeners, listed in Table 3, were selected on the basis of their potential toxicity, bioaccumulation and/or frequency of occurrence in environmental samples. Complete chromatographic separation of all congeners was achieved with the exception of PCBs 105 and 153. These were eluted together as a single peak. Method detection limits ranged from around 0.01 ng/g for PCB 195, to 0.11 ng/g for PCB 52.

The "total" PCB content of the sample was calculated from the sum of the individual congener data (\sum_{20} PCB). PCB homologue concentrations were estimated after likely coeluting congeners of significance and different chlorine content were taken into consideration (Table 3). PCB recoveries (as Aroclor 1254) from the standard reference material employed were within acceptable limits of the certified mean (Table 2)

5. POLYCYCLIC AROMATIC HYDROCARBON ANALYSIS:

Sediment samples (1-1.5 g) were subjected to microwave extraction in the same way as described above for PCB, except that methylene chloride (3 ml) was used as the extracting solvent instead of hexane. Also, the heating cycles were of shorter duration (30, 15 and 15 seconds) owing to the lower boiling point of methylene chloride. Following centrifugation, the samples were decanted into 10 ml graduated glass centrifuge tubes, placed in a warm water bath (~45°C) and reduced in volume (~0.75 ml). Solvent exchange into hexane (~1.25 ml) and further reduction in volume (~0.5 ml) was necessary prior to clean up on silica gel (EPA method 3630C). The silica gel (230-400 mesh) was activated at 700°C and stored at 110°C prior to use.

Table 3

CB Congen	ers in Calibratio	on Standard	Co-elut	ting PCB Conge	eners
UPAC ¹ Number	Chlorine Atoms/mol.	Structural Arrangement	IUPAC Number	Chlorine Atoms/mol.	Structural Arrangement
8 ^a (A1221/1242) 2	2,4'	5 ^a	2	2,3
18 ^b (A1016/1242) 3	2,2',5	15 ^a (A1221/1242) 17 (A1242)	23	4,4' 2,2',4
28 ^b (A1016/1242) 3	2,4,4'	31 ^a (A1242)	3	2,4',5
44 ^b (A1242/1254) 4	2,2',3,5'	37 ^a 42 ^a (A1254)	3 4	3,4,4' 2,2',3,4'
52 ^b (A1242/1254) 4	2,2',5,5'	43 ^a	4	2,2',3,5
66 ^b (A1254)	4	2,3',4,4'	80 ^a 95	4 5	3,3',5,5' 2,2',3,5',6
77 ^{a c}	4	3,3',4,4'	110 ^(A1254/1260) 154 ^a	5 6	2,3,3',4',6 2,2',4,4'5,6
101 ^b (A1254/1260) 5	2,2',4,5,5'	79 ^a 90 ^a	4 5	3,3',4,5' 2,2',3,4',5
105 ^b	5	2,3,3',4,4'	132 (A1254/1260) 153 ^b (A1254/1260)	6 6	2,2',3,3',4,6' 2,2',4,4',5,5,
118 ^b (A1254/1260) 5	2,3',4,4',5	106 ^a 135 ^a 144 ^a 149 ^(A1254/1260)	5 6 6 6	2, 3,3',4,5 2,2',3,3',5,6' 2,2',3,4,5',6 2,2',3,4',5',6
126 ^{a c}	5	3,3',4,4',5	129 178 ^a	6 7	2,2',3,3',4,5' 2,2',3,3',5,5',6
128 ^b	6	2,2',3,3',4,4'	167 ^a	6	2,3',4,4',5,5'
138 ^b (A1254/1260) 6	2,2',3,4,4',5'	158 ^a 163 ^a 164 ^a	6 6 6	2,3,3',4,4',6 2,3,3',4',5,6 2,3,3',4',5',6
153 ^b (A1254/1260) 6	2,2',4,4',5,5'	see PCB 105		
170 ^b (A1260)	7	2,2',3,3',4,4',5	190 ^a	7	2,3,3',4,4',5,6
180 ^b (A1260)	7	2,2',3,4,4',5,5'	193 ^a (A1260)	7	2,3,3',4',5,5',6
187 ^b	7	2,2',3,4',5,5',6	159 ^a 182 ^a	6 7	2,3,3',4,5,5' 2,2',3,4,4',5,6'
195 ^a	8	2,2',3,3',4,4',5,6	208 ^a	9	2,2',3,3',4,5,5',6,6'
206 ^a	9	2,2',3,3',4,4',5,5',6	none		
209 ^a	10	2,2',3,3',4,4',5,5',6,6'	none		

PCB Congeners in Calibration Standard used to Quantify PCB Homologues in Sediment Samples from Harbor Sites on Guam

^a not common (<10% occurrence) in environmental samples (from McFarland and Clarke 1989). ^b major component of environmental mixtures (from NOAA 1993a); ^c highly toxic planar PCB. ¹International Union of Pure & Applied Chemistry.Labels in parentheses indicate dominant components (≥ 2% by wt.) of the commercial PCB mixtures: Aroclors 1016, 1221, 1242, 1254 & 1260 (from De Voogt *et al.* 1990) Compilation of chromatographic data from Ballschmiter and Zell (1980); Holden (1986); Ballschmiter *et al.* (1987); De Voogt *et al.* (1990); Rebbert *et al.* (1992); Wise *et al.* (1993); Schantz *et al.* (1993); Bright *et al.* (1995), using 60 m DB-5 (or equivalent) high resolution GC columns. A slurry of silica gel in methylene chloride was loaded into a series of disposable glass Pasteur pipettes. Gentle tapping facilitated settling and even packing of the columns that, on completion, were 4 cm in length and contained approximately 0.5 g of adsorbent. The columns were pre-eluted with 2×1 ml volumes of hexane to remove the methylene chloride and kept under hexane until required.

The sample extracts (~0.5 ml) were transferred to the columns using clean glass pipettes and allowed to drain into the adsorbent. Approximately 0.25 ml of hexane was used to rinse the centrifuge tube and complete the transfer process. The columns were eluted with 1 ml of hexane to remove PCBs, sulfur, and aliphatic hydrocarbons, followed by 2 ml of methylene chloride/pentane (2:3, v/v) to recover the PAHs.

The cleaned up eluates were reduced in volume (~0.5 ml) prior to solvent exchange with acetonitrile (1.0 ml). Further reduction in volume (0.1 ml) preceded transfer to clean, glass auto-sampler vials with small volume (250 μ l) inserts. Full procedural blanks were periodically carried out.

Analysis was carried out by high performance liquid chromatography (HPLC) using a fluorescence/UV (diode array) detector system and a 10 cm x 4.6 cm i.d., stainless steel LC-PAH column (Supelco), containing a porous silica stationary phase (3 μ m particle size). Following sample injection, isocratic elution with acetonitrile/water (4:6, v/v) occurred for the first 0.3 min, followed by a linear gradient to 100% acetonitrile over the next 10 minutes. Elution with 100% acetonitrile continued for a further 5 min before the run was terminated. The solvent flow rate through the column was held constant at 2 ml/min.

Quantification with the more sensitive fluorescence detector was achieved with excitation at 280 nm and emission at 380 nm. The diode array provided a synchronous absorption scan from 190-357 nm, with a wavelength difference of 4 nm, and was used primarily for confirmatory analysis at the higher levels of detection.

The calibration standards were made up containing the 16 PAHs recommended by U.S. EPA (see EPA method 8310). These are listed in Table 4 together with their molecular weights and structural identity. Method detection limits with the fluorescence detector ranged from around 1 ng/g for fluoranthene, benzo(a) anthracene, chrysene, and dibenzo(a,h) anthracene to 38 ng/g for naphthalene. Detection limits for the non-fluorescing PAHs, acenaphthylene and indenol(1,2,3-cd) pyrene, were 6 ng/g and 11 ng/g respectively, using the UV diode array detector.

All calculations were based on peak area comparisons of components sharing identical retention times in both sample and standard. From these data, the "total" PAH (\sum_{16} PAH) content of the sample was calculated. PAH recoveries (from the standard reference material employed were within acceptable limits of the certified means (Table 2).

Table 4

Unsubstituted PAHs in Calibration Standa	ard used to Quantify PAH
Levels in Biota Samples from Harb	bor Sites on Guam

1	IUPAC ¹ Nomenclature	Molecular Wt.	Structur	al Identity
	Naphthalene	128.19	ÔÔ	
	Acenaphthylene	152.21	_	
	Acenaphthene	154.21		
]	Fluorene	166.23		$\hat{\mathbf{O}}\hat{\mathbf{O}}$
]	Phenanthrene	178.24	690	
	Anthracene	178.24		
]	Fluoranthene	202.26		
]	Pyrene*	202.26		
]	Benzo(a)anthracene*	228.30		
	Chrysene*	228.30	Ô	
]	Benzo(b)fluoranthene*	252.32		.~
]	Benzo(k)fluoranthene*	252.32	~ ~	
]	Benzo(a)pyrene*	252.32		
]	Benzo(ghi)perylene	276.34		ŠĒŠ
]	Indeno(1,2,3-cd)pyrene*	276.34		
]	Dibenzo(a,h)anthracene*	278.36		
				\sim

¹ International Union of Pure and Applied Chemistry; * = known carcinogen

6. PRESENTATION OF DATA

All the chemical data accumulated hitherto has been tabulated separately according to category of contaminant and harbor location. This is intended to facilitate quick reference to the concentration and distribution of contaminant levels within and between sites for all locations. All mean values refer to arithmetic means unless stated otherwise.

The tabulated data are preceded by notes on contaminant occurrence in the local sediments examined and to possible contributing sources. Comparisons are also made with levels reported in the literature for marine and estuarine sediments from elsewhere. Much of this published data has been tabulated for easy reference and appears in Tables 5-7 at the end of the current section. From such comparisons a preliminary appraisal of the current situation of the locations studied has been made.

Table	5
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Heavy Metal Concentrations (µg/g dry wt.) in Marine and Estuarine Sediments from Other Areas of the World

Location	Site	Depth (cm)	Fraction	Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Sn	Zn	Reference
Guam	Agana Boat Basin	0-30	<1 mm	all <0.2	1.00-6.00	all <0.2	3.61-28.8	0.56-74.7	0.005-0.107	1.01-19.9	1.99-70.7	<0.1-6.61	3.44-104	This study
Guam	Outer Apra Harbor	0-30	<1 mm	all <0.2	1.16-10.7	0.27-2.18	3.59-17.1	1.00-142	0.011-0.403	<0.2-14.0	<1.00-96.3	<0.1-7.37	2.3-461	This study
Guam	Outer Apra Harbor (Echo Wharf)	surface	bulk sediment	< 0.23	<0.99	< 0.17	16-18				17	<0.66		US Navy (PWC) 1997, unpublished
Guam	Outer Apra Harbor (SRF Industrial)	surface	>65µm			2.0-4.3		30-123	ND-0.43	9.3-21.5	53-129	ND-33	82-3548	Belt Collins Hawaii 1994
Guam	Outer Apra Harbor (SRF Industrial)	surface	<65µm			3.5-6.0		320-1435	0.08-4.6	22.6-51.2	142-395	31-143	234-856	Belt Collins Hawaii 1994
Guam	Outer Apra Harbor	0-10	bulk sediment			1.88-3.12	62.0-113	30.1-211	ND-0.99	10.3-21.4	50.5-132	200-535	34.1-223	Belt Collins Hawaii 1993
Guam	Outer Apra Harbor	70-80	bulk sediment			2.02-2.88	59.8-126	21.6-238	ND-1.74	8.8-190	45.9-138	184-522	16.2-236	Belt Collins Hawaii 1993
Guam	Inner Apra Harbor	0-10	bulk sediment			1.93-3.44	64.0-129	41.0-255	0.14-1.7	7.6-36.9	42.8-139	148-1055	51.9-279	Belt Collins Hawaii 1993
Guam	Inner Apra Harbor	70-80	bulk sediment			2.59-3.76	99.4-112	32.2-176	0.79-2.4	24.1-40.6	54.3-123	726-967	29.5-208	Belt Collins Hawaii 1993
Guam	Inner Apra Harbor (USS Proteus Site)	surface	bulk sediment		6.0*		34.0*	26.0*	0.36*	7.35*	132*		72.2*	Ogden 1996
Guam	Agate Marina	0-30	<1 mm	all <0.2	5.31-9.78	all <0.2	9.85-30.7	2.63-10.3	0.004-0.006	12.3-30.2	all <0.6	all <0.1	4.42-11.2	This study
Guam	Merizo Pier	0-30	<1 mm	all<0.2	2.87-5.19	all <0.2	13.5-39.5	4.34-123	0.008-0.032	14.0-71.0	<1.00-27.1	<0.1-7.06	9.58-130	This study
Philippines	Honda Bay, Palawan	surface	bulk sediment						0.031-570					Benoit et al. 1994
Hong Kong	Pearl River Estuary, Macao	surface	bulk sediment		12.6-34.6	0.36-8.29	4.0-38.6				14.5-66.7			Ferreira et al. 1996
Malaysia	Bintulu	surface	${<}500~\mu m$			2.1-4.8		8.5-12.0			10.3-35.6		40-90	Ismail 1993
Taiwan	Kaohsiung Harbor	surface	<63 µm			0.1-4.64		37.9-505			34.3-138			Chen & Wu 1995
Australia-PNG	Torres Strait	surface	bulk sediment			0.05-0.09								Gladstone & Dight 1994
Australia-PNG	Torres Strait	surface	${<}100~\mu m$					2-17					40-53	Brady et al. 1994
Australia	Halifax Bay, N. Queensland	surface	bulk sediment					6-9.4		8.8-14	14-22		29-44	Knauer 1977
Australia	Halifax Bay, N. Queensland	surface	bulk sediment						0.004-0.016					Knauer 1976
Australia	Sydney Coast	50-80	bulk sediment		9-14	0.1	6-14	5-25	0.05-0.45	3-9	10-90		30-90	Schneider & Davey 1995
Australia	Ninety Mile Beach, VIC	0-5	<63 µm			0.07-1.54	14.6-75.6	1.1-35.0	<0.05-1.20	5.4-20.5	0.1-44.3			Haynes et al. 1995

* only maximum concentration reported; ND = not detectable; dashes indicate no data

Table 5 (cont.)

Heavy Metal Concentrations (µg/g dry wt.) in Marine and Estuarine Sediments from Other Areas of the World

Location	Site	Depth (cm)	Fraction	Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Sn	Zn	Reference
Fiji	Great Astrolabe Lagoon	surface	<100 µm		0.27-12.4	1.2-3.3	17-36	22-88	0.02-90.2	4-25	3-17		10-164	Morrison et al. 1997
Fiji	Suva Harbor (near dumpsite)	surface	<63 µm		0.7-45	0.74-3.04	16-106	59-306	0.2-1.34	17-38	19.3-272		88-670	Naidu & Morrison 1994
Fiji	Suva Harbor (near battery factory)	surface	<63 µm			0.8-198	11-80	64-1151			0.21-26.6 (%)		250-1063	Naidu & Morrison 1994
Antarctic	8 island sites	surface	${<}500\mu m$			4.0-22	2.4-66	3.9-106		5.5-92.2	22.5-128		28.6-271	Alam & Sadiq 1993
Arctic	Beaufort Sea	surface	bulk sediment					16-22						Sweeney & Naidu 1989
UK	Cardiff, Bristol Channel	surface	bulk sediment					40-160			160-300		350-1000	French 1993
UK	19 estuaries	surface	$<\!100\mu m$	0.13-4.13	4.8-1740	0.13-2.17	24-207	7-2398	0.03-3.01	14-58	20-2753	0.4-161	46-2821	Bryan & Langston 1992
UK	Thames Estuary	surface	<63 µm	2.2-22	14-45	0.7-9.8	36-240	24-348	0.2-5.7	21-157	63-1634	13-69	115-1050	Attrill & Thomes 1995
England & Wales	s Various coastal sites	surface	<2 mm				<5-100				3.1-110		3-153	Rowlatt & Lovell 1994
S.W. England	Various estuaries	surface	$<\!100\mu m$		11-3732									Langston 1984
Irish Sea	39 stations in NW	surface	<63 µm				19.4-74.9	8.2-26.9	0.048-0.126	11.3-48.4	17.6-62.3		73.2-210	Service et al. 1996
N. Ireland	Strangford Lough	surface	<63 µm				67-199		0.07-0.29	30.8-62	30.2-65.8		82.6-141.6	Service 1993
S. Ireland	Cork Harbor	surface	<2 mm	< 0.05		< 0.05	3.4-17.2	9.7-18.8	0.053-0.24	11.5-15.8	17.9-44.2		65-1961	Berrow 1991
Denmark	Nissum Broad, Jutland	0-5	bulk sediment						0.58->2.27					Andersen 1992
Denmark	Nissum Broad, Jutland	5-15	bulk sediment						0.119->5.49					Andersen 1992
Denmark	Krikvig, Jutland	0-15	bulk sediment						0.005-0.016					Andersen 1992
Sweden	Baltic Sea	surface	bulk sediment					23-61			21-69			Blomqvist et al. 1992
Poland	Puck Bay, Baltic Sea	surface	<2 mm	11-27		0.7-5.7	120-235	49-122			53-330		195-960	Szefer et al. 1995
Italy	N. Tyrrhenian Sea NW	surface	bulk sediment			1.45-5.04		17.1-39.7			24.2-44.1		39.5-63.3	Fabiano et al. 1994
Italy	Bay of Naples	0-3	bulk sediment						0.09-17.5					Baldi et al. 1983
Italy	Venice Lagoon	surface	<5 mm			0.23-1.92	41-106	7.8-32		14-20	17-40		77-306	Sfriso et al. 1995
Italy	Olbia Bay	surface	<2 mm-65 µm			0.2-10.5	3-27	2-38			0.5-56		14-153	Schintu et al. 1991
Italy	Various coastal sites	surface	<63 µm			0.05-0.58			0.04-2.03		9-172			Giordano et al. 1992

dashes indicate no data

1 a D C J (CO C)	Tabl	le 5	(cont.)
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Heavy Metal Concentrations (µg/g dry wt.) in Marine and Estuarine Sediments from Other Areas of the World

Location	Site	Depth (cm)	Fraction	Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Sn	Zn	Reference
N. Spain	Bidasoa Estuary	surface	<100 µm	0.7-2.4		0.4-1.5	32-79	36-221		22-44	70-298		219-736	Saiz-Salinas et al. 1996
Spain	Pasajes Harbour	3-5	bulk sediment			1.1-14.9	61-299	156-2140		34-162	124-854		420-5620	Legorburu & Canton 1991
Spain	Pasajes Harbour	3-5	<63 µm			1.2-16	25-290	25-539		17-214	45-703		232-995	Legorburu & Canton 1991
Spain	Guipúzcoa	surface	<63 µm			0.37-1.18	45-262	30-101		23-284	18-102		57-487	Legorburu & Canton 1992
Greece	Rhodes Harbour	surface	<63 µm			0.006-0.17	3.7-118	9.1-101			19-230		12-242	Angelidis & Aloupi 1995
Turkey	Izmir Bay	surface	bulk sediment				27-345	11-94	0.06-0.55		49-116			Balci & Turkoglu 1993
Israel	E. Mediterranean coastline	surface	$<\!\!250\mu m$			0.04-1.68		0.84-52.3	0.004-0.462		3.19-48.3		2.40-162	Herut et al. 1993
India	Bay of Bengal	surface	bulk sediment			0.46-6.05	11-394	2-105	0.058-0.56		5-130		13-144	Subramanian & Mohanachandran 1990
S. Pakistan	Arabian Sea	surface	$<\!0.2~\mu m$	0.27-0.73		0.1-0.83	24.3-39.1	20.3-38.4	0.51-2.40	57.2-102	2.4-15.7		24.5-146	Tariq et al. 1993
Jordan	Gulf of Aqaba	0-20	bulk sediment			2-6.2		6.8-9.7		19-90	83-140		32.61	Abu-Hilal & Badran 1990
Kuwaite	Qaruh Island	surface	bulk sediment	0.04	32.6	0.77	2.85	1.2		15.0	1.03		1.28	Fowler et al. 1993
Kuwait & Saudi A	arabia W. Persian Gulf	surface	bulk sediment				4-174	3-41		6-198			13-119	Basaham & Al-Lihaibi 1993
Saudi Arabia	Abu Ali	surface	bulk sediment			1.8-6.4	4.8-25	2.6-8.0		3.2-39.1	8.4-35.8		2.4-20.2	Al-Arfaj & Alam 1993
Saudi Arabia	various sites	surface	bulk sediment	0.12-0.2	4.61-22.7	0.10-0.25	24.6-99.2	3.14-5.53		7.86-27.8	1.70-4.44		3.41-10.2	Fowler et al. 1993
Bahrain	various sites	surface	bulk sediment	0.04-0.04	29.2-35.2	0.01-0.75	3.84-11.9	1.16-17.6		9.4-19.6	0.64-24.0		2.34-3.79	Fowler et al. 1993
UEA	various sites	surface	bulk sediment	0.10-0.13	20.6-22.5	0.02-1.91	71.9-81.8	1.34-7.76		9.40-25.0	0.54-3.6		1.56-3.40	Fowler et al. 1993
Oman	various sites	surface	bulk sediment	0.15-0.73	24.7-32.0	0.07-0.93	66.0-357	1.60-13.9		9.9-439	0.07-25.9		7.70-26.3	Fowler et al. 1993
Africa	Kenyan Coast	surface	bulk sediment			0.01-0.34		3-42			0.5-15.8		2-117	Everaarts & Nieuwenhuize 1995
Canada	Saguenay fjord	surface	bulk sediment				40.4-56.4	20.6-28.2	< 0.05-3.63	25.1-32.8			88-133	Gagnon et al. 1993
USA	Indian River Lagoon, Florida	surface	bulk sediment		0.6-15	< 0.01-0.04	5.1-104	1.0-206	0.006-0.61	0.6-23	0.9-42		2.6-277	Trocine & Trefry 1996
USA	Gulf of Maine	0-5	bulk sediment			0.23-2.6	33.7-97.0	15.1-216		19.7-71.4	10.4-210	17.9-56.8	61.6-287	Larsen & Gaudette 1995
USA	Jamaica Bay, NY	surface	bulk sediment			<0.05-5.2		1.4-450			<0.7-500			Seidemann 1991

dashes indicate no data

Table 5 (cont.)

Heavy Metal Concentrations (µg/g dry wt.) in Marine and Estuarine Sediments from Other Areas of the World

Location	Site	Depth (cm)	Fraction	Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Sn	Zn	Reference
Cuba	Havana City	surface	<150-65 µm				22-225	24-567	0.48-32	3.5-94	50-967		68-3218	Gonzalez & Torres 1990
Cuba	Havana City	surface	<63 µm				22-339	18-716	0.64-76	11-112	44-903		72-3736	Gonzalez & Torres 1990
West Indies	Coast of Tobago	surface	$<\!\!180\mu m$			0.04-2.12		0.06-16			0.3-20.9		0.1-39.3	Rajkumar & Persad 1994
S. America	Coquimbo Coast, Chile	surface	bulk sediment			5-20	50-210							Trucco et al. 1990
S. America	Montevideo coast	surface	<250 µm			0.05-0.231	0.48-57	nd-109	0.011-0.254		0.7-141		2.4-105	Moyano et al 1993
S. America	Guarapina Lagoon, Rio de Janeiro	surface	<63 µm				30-65	18-62		2-45	2-88		62-122	Knoppers et al. 1990

dashes indicate no data

Table 6

Location	Site	Depth (cm)	Fraction	Total PCB (ng/g)	Reference
Guam	Agana Boat Basin	0-30	<1 mm	0.73-11.23	This Study
Guam	Apra Harbor	0-30	<1 mm	0.21-341	This Study
Guam	Agat Marina	0-30	<1 mm	<0.04-0.81	This Study
Guam	Merizo Pier	0-30	<1 mm	0.39-5.12	This Study
Japan	Osaka Bay	0-5	bulk sediment	2.5-240	Tanabe et al. 1991
Japan	Osaka Bay	0-5	bulk sediment	63-240	Iwata et al. 1994
India	Mandovi Estuary, Goa	0-5	bulk sediment	170	Iwata et al. 1994
Thailand	Chao Phraya Estuary, Bangkok	0-5	bulk sediment	11	Iwata et al. 1994
Vietnam	Ho Chi Minh	0-5	bulk sediment	2.3-8.9	Iwata et al. 1994
Papua New Guines	a Port Moresby	0-5	bulk sediment	3.3-24	Iwata et al. 1994
Vanuatu	Efate Island	0-5	bulk sediment	<0.07-0.20	Harrison et al. 1996
Tonga	Tongatapu Island	0-5	bulk sediment	<0.13-12.1	Harrison et al. 1996
Australia	Brisbane River Estuary	surface	bulk sediment	ND-58	Shaw & Connell 1980

PCB Concentrations in Marine and Estuarine Sediments from Other Regions of the World

ND = not detectable
Location	Site	Depth (cm)	Fraction	Total PCB (ng/g)	Reference
Australia	Parramata Estuary, NSW	0-5	bulk sediment	160	Iwata <i>et al.</i> 1994
Australia	Harvey Estuary, WA	0-5	bulk sediment	0.69	Iwata et al. 1994
USA	Elkhorn Slough, CA	5-7.5	bulk sediment	25-147	Rice et al. 1993
USA	Moss Landing Harbor	5-7.5	bulk sediment	158-1782	Rice et al. 1993
USA	Monterey Bay	5-7.5	bulk sediment	2-23	Rice et al. 1993
USA	Chesapeake Bay	surface	bulk sediment	4-400	Sayler et al. 1978
USA	New York Bight	0-40	bulk sediment	0.5-2200	West & Hatcher 1980
USA	New Bedford Harbor, MS	0-41	bulk sediment	1.27-28.8	Brownawell & Farrington 1986
Mexico	San Quintin Bay	surface	bulk sediments	all <10	Gutierrez Galindo et al. 1996
Canadian Arctic	Queen Maud Gulf, NWT	surface	bulk sediment	0.052-0.44	Bright et al. 1995
Canadian Arctic	Cambridge Bay, NWT	surface	bulk sediment	0.14-0.45	Bright et al. 1995
UK	Humber Estuary	surface	<1 mm	ND-72	Tyler & Milward 1996
UK	Humber Estuary	0-10	<63 µm	2.9-19.7	Klamer & Fomsgaard 1993

PCB Concentrations in Marine and Estuarine Sediments from Other Regions of the World

ND = not detectable

PCB Concentrations in Marine and Estuarine Sediments from Other Regions of the World

Location	Site	Depth (cm)	Fraction	Total PCB (ng/g)	Reference
UK	Irish Sea Basin	0-10	<63-3500 μm	0.2-42	Thompson et al. 1996
Sweden	Gulf of Bothnia	surface	bulk sediments	2-14	Van Bavel et al. 1995
Holland	Rhine-Meuse Estuary	surface	bulk sediment	50-1000	Duinker & Hillebrand 1979
E. Spain	Alicante coast	2-3	bulk sediments	0.27-9.69	Prats et al. 1992
Monaco	NW Mediterranean	0-21	bulk sediment	10.5-61.1	Burns & Villeneuve 1983
Italy	Bay of Naples, Tyrrhenian Sea	0-3	bulk sediment	6-3200	Baldi et al. 1983
Italy	Naples Offshore	0-3	bulk sediment	9-170	Baldi et al. 1983
Italy	North Adriatic Sea	0-35	bulk sediment	3-80	Caricchia et al. 1993
Italy	Tiber Estuary	surface	bulk sediment	28-770	Puccetti & Leoni 1980
E. Sicily	Ionian Sea	0-5	bulk sediment	0.8-49	Amico et al. 1982
E. Sicily	Augusta Harbor	0-5	bulk sediment	130-457	Amico et al. 1982
S. Greece	Aegean Sea	surface	bulk sediment	1.3-775	Dexter & Pavlou 1973
Turkey	E. Mediterranean coast	surface	bulk sediment	2-4	Bastürk et al. 1980

Location	Site	Depth (cm)	Fraction	Total PAH (ng/g)	\mathbf{n}^{1}	Reference
Guam	Agana Boat Basin	0-30	<1 mm	20-1900	16	This Study
Guam	Apra Harbor	0-30	<1 mm	20-8140	16	This Study
Guam	Agat Marina	0-30	<1 mm	ND-10	16	This Study
Guam	Merizo Pier	0-30	<1 mm	40-520	16	This Study
USA	Sarasota Bay, Florida	surface	bulk sediment	16-26771	11	Sherblom et al. 1995
USA	Elkhorn Slough, CA	5-7.5	bulk sediment	157-375	13	Rice et al. 1993
USA	Moss Landing, CA	5-7.5	bulk sediment	1470-3080	13	Rice et al. 1993
USA	Monterey Bay, CA	5-7.5	bulk sediment	24-114	13	Rice et al. 1993
USA	San Diego, CA	1-5	bulk sediment	7.1-983	26	Zeng et al. 1997
Caribbean	Guadeloupe Isl. laggons.	3-5	<200 µm	103-1657	9	Bernard et al. 1996
Mexico	San Quintin Bay, Baja, CA	surface	bulk sediment	all <50	?	Gutierrez Galindo et al. 1996
South America	Montevideo Coast	surface	<250 µm	100-940	18	Moyano et al. 1993
Antarctic Peninsula	Arthur Harbor	surface	bulk sediment	ND-14491	14	Kennicutt et al. 1992
Antarctica	Signy Island	surface	fine silt	14-280	12	Cripps 1992

PAH Concentrations in Marine and Estuarine Sediments from Other Regions of the World

 1 n = number of individual PAH's analyzed; ND = not detected

PAH Concentrations in Marine and Estuarine Sediments from Other Regions of the World

Location	Site	Depth (cm)	Fraction	Total PAH (ng/g)	n^1	Reference
Australia	Rowley Shelf Isls., WA	surface	bulk sediment	<5	16	Pendoley 1992
Australia	Perth, WA	surface	bulk sediment	1-3200	11	Burt & Ebell 1995
UK	Humber Estuary	surface	<63 µm	700-2700	13	Klamer & Fomsgaard 1993
Baltic Sea	Various	surface	mud/sand	9.53-1871	15	Witt 1995
Rotterdam	Caland Canal	surface	bulk sediment	2100-3200	16	Van Den Hurk et al. 1997
France	Rhone Delta	surface	bulk sediment	1225-2427	16	Lipiatou & Saliot 1991
France	Gulf of Lions	surface	bulk sediment	182-763	16	Lipiatou & Saliot 1991
France	Lazaret Bay, Toulon	surface	2 μm->500 μm	1440-48090	14	Benlahcen et al. 1997
Monaco	Ligurian Sea	0-2	bulk sediment	599-847	12	Burns and Villeneuve 1983
Italy	N. Adriatic Sea	0-35	bulk sediment	18-577	12	Caricchia et al. 1993
Italy	Spotorno	surface	63-200 μm	1720	14	Benlahcen et al. 1997
Italy	Adriatic Coast	0-20	<63µm	27-527	10	Guzzella & De Paolis 1994
Corsica	Scandola	surface	>500 µm	119	14	Benlahcen et al. 1997
Persian Gulf	Mina Al Fahal, Gulf of Oman	surface	<63 µm	398-787	13	Badawy et al. 1993

¹ n = number of individual PAH's analyzed

Plate 1: Sediment Sampling Devices Three sediment samples were taken at each site using 5×30 cm stainless steel corers, with harden tungsten carbide tips and removable aluminum sleeve inserts. These were driven into the substrate using a detachable slide hammer (held by diver on left of picture).





Plate 2: Sediment Collection Collecting sediments from a shallow, sub-tidal site in Piti Channel, Apra Harbor. Cabras Island Power Plant is shown in the background.

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Plate 3: Sediment Collection

Action close-up of diver collecting sediment samples from a shallow water site in Piti Channel, Apra Harbor. Note the pile-driving action of the weighted slide hammer forcing the corer into the sediment.

Plate 4: Potential Pollution Source: Electric Power Plants

Piti Power Plant, Apra Harbor. Note the effluent water outlet and two oil retention booms. Sediments were collected immediately in front of the outer boom in the center of picture.





Plate 5: Potential Pollution Source: Tour Boats

One of several tour boats ferrying tourists up and down Piti Channel, Apra Harbor, during the sampling expedition. Note Cabras Power Plant shown to leftof boat in the background.

Plate 6: Potential Pollution Source: Fuel Storage Depots

The Mobil Tank Farm, one of several similarly sized fuel storage facilities located in and around the Apra Harbor area.



Plate 7: Potential Pollution Source: Harbor Activities

View from Port Authority Beach, Apra Harbor, looking north across Piti Channel towards Commercial Port. Note the gantry cranes unloading container ships at the dock-side.



Plate 8: Potential Pollution Source: Fuel Piers

Approaching the Fox-1 Fuel Pier at the western end of Commercial Port, Apra Harbor. Sediments collected from this area contained the highest PAH levels.





Plate 9: Field Support Personnel GEPA's intrepid explorers, from left to right: Vance Eflin, Danzel Narcis and Greg Pangelinan - Relaxing after a job well done!

RESULTS & DISCUSSION

A. PHYSICAL ANALYSIS

<u>1. Petrography of Sediments</u>

A visual characterization of dried sediment samples is indicated in Tables 8-11. The data are biased toward sediment larger than fine sand (>0.125mm). More rigorous grain size analyses are indicated in Tables 12-15. None of the petrographic descriptors listed appears to be exceptional in the context of other sediments described and reported from coastal marine sediments around Guam, including sediment collected previously from the general vicinity of the current study sites. (Emery 1964, Randall and Birkeland 1978, Siegrist *et al.* 1991, Randall and Siegrist 1995).

<u>1.1 Color:</u>

Bulk sediment color is caused by the color of the dominant minerals. Unweathered volcanic minerals tend to be dark green and olive, or black; weathered volcanic minerals tend to be tan, yellows, reds, purples, and pinks. The former colors are those associated with ferrous iron minerals; the latter with mixtures of ferric iron phases and clay minerals.

Color was estimated from comparisons with the standard Munsell soil color chart (Munsell, 1975), other descriptors by gross comparisons with samples of previously sieved and analyzed carbonate and volcaniclastic sediment collected from beaches, reef platforms, and reef-front environments around Guam. Color on many gravely samples that have high percentages of both brownish-olive-green volcanics and white and gray bioclastics is too non-uniform to be a useful descriptor and the term "speckled" is added to the comments. Munsell color notation is based on three parameters: hue, value and chroma. The symbol for hue is the letter abbreviation of a spectral color, e.g. Y for yellow, R for red, YR for yellow-red, etc., preceded by a number 1 to 10. Within each color, the hue becomes more yellow and less red as those numbers increase. Value numbers (darkness index) are designated as 5/, 6/ etc., and range for 0 for absolute black to 10 for absolute white. The notation for chroma (saturation index) consists of numbers ranging from 0 for neutral gray to 20 for most vivid colors.

<u>1.2 Composition</u>:

In general, the composition of shallow marine sediments around Guam reflects the contributions of weathered silicates and oxides from nearby volcanic uplands and biogenic carbonates from the reef system. Silicates and oxides are represented by volcanic minerals such as augite, hornblende, labradorite, and magnetite and their weathered derivatives, clay minerals and oxyhydroxides. Biogenic carbonates are the minerals aragonite (corals, *Halimeda*, and some mollusks) and magnesium calcite (forams, red algae, echinoids, and some mollusks). Proportions of terrigenous and reef-derived sediment vary from nearly 100 percent carbonate north of Agana to a binary mixture in the south that ranges from about 90% volcanic detritus, to about 90% carbonate depending upon local factors. The principal variable controlling this ratio appears to be proximity to river mouths, but the size and slope stability in the adjacent watershed, vigor and diversity of the reef community, and physical variables such as wave energy and local bathymetry are obviously locally important factors in determining compositional makeup of Guam's coastal marine sediments.

No.	Depth	Munsell	Texture	Visual Composition
	(m)	Color		
1a	3.5	5Y 5/2	p-sort slty sd	volcs and bioclasts: molluscs, echin, org muds
1b	3.2	5Y 5/2	p-sort slty sd	volcs and bioclasts: molluscs, echin, org muds
1c	3.2	5Y 5/2	p-sort slty sd	volcs and bioclasts: molluscs, echin, org muds
2a	2.8	5Y 5/2	mw-sort slty sd	olive gray, bioclast fragms, org muds, volcs, glass
2b	2.8	5Y 5/2	mw-sort slty sd	olive color, fine bioclsts fragms,, org muds, fine volc grains
2c	2.8	5Y 5/3	mw-sort slty sd	olive color, fine bioclsts fragms,, org muds, fine volc grains
3a	5.9	5Y 6/2	p-sort coarse sd	spckld coquina: forams, molluscs, corals, scatt volcs
3b	7.0	5Y 6/2	p-sort coarse sd	spckld coquina: forams, molluscs, corals, scatt volcs
3c	6.8	5Y 6/2	p-sort coarse sd	spckld coquina: forams, molluscs, corals, scatt volcs
4a	3.5	5Y 7/3	p-sort coarse slty sd	lge coral clasts in uniform pale yellow muddy sds
4b	2.8	5Y 7/2	p-sort coarse sd	spckld coquina sd: molluscs, forams, few volcs, glass
4 c	8	5Y 7/2	p-sort coarse sd	spckld coquina sd: molluscs, forams, few volcs, glass
5a	2.6	5Y 7/3	mw-sort coarse sd	coquina: forams, mollusc, echin, coral, scatt volcs
5b	1.9	5Y 7/3	mw-sort coarse sd	coquina: forams, mollusc, echin, bryoz, coral, scatt volcs
5c	1.5	5Y 7/3	mw-sort coarse sd	coquina: forams, mollusc, echin, bryoz, coral, scatt volcs

Petrographic Description of Agana Boat Basin Sediments (5-20 X Magnification)

Petrographic	Description	of Apra	Harbor	Sediments	(5-20)	X Magnification)
					(

No.	Depth	Munsell	Texture	Visual Composition
	(m)	Color		-
1a	10	5Y 7/3	vp-sort sdy gvl	spckld volcs and lge bioclsts: molluscs, forams, coral, tar
1b	10	5Y 7/3	vp-sort sdy gvl	spckld, volcs, lge bioclsts: molluscs, forams, coral
1c	10	5Y 6/3	p-sort gvly sd	abund molluscs & foram fragms, no volcs
2a	11	5Y 7/2	p-sort gvly sd	abund snails & foram fragms, no volcs, glass
2b	11	5Y 7/3	p-sort coarse sd	abund bioclasts, esp. forams & molluscs, some glass
2c	11	5Y 7/2	p-sort gvl	coquina gvl, abund echin, foram, mollusc & coral
3a	11	5Y 7/3	p-sort coarse sd	mainly bioclsts, few volcs: forams, molluscs, echin.
3b	11	5Y 7/3	p-sort sd	spckld coquina sd, mollusc & encr foram rich
3c	11	5Y 7/3	m-sort coarse sdy gvl	coquina sdy gravel; forams, molluscs, corals, glass
4 a	7.0	5Y 6/2	fw-sort slty-clayey sd	almost no lge detritus, no volcs
4b	7.0	5Y 7/1	fw-sort slty-clayey sd	lge fragms of coral, encr forams, & molluscs, no volcs
4c	7.0	5Y 7/2	fw-sort slty-sd	aggreg, homogen. few mollusc fragms
5a	6.5	5Y 7/2	fw-sort med sd	v uniform color, no lge bioclsts
5b	6.5	5Y 7/2	vp-sort silty sd	abund shells: molluscs, whole and fragms forams
5c	6.5	5Y 7/3	p-sort slty sd	scatt shells, whole and fragm forams, no volcs.
6a	16	5Y 6/3	vp-sort sdy grvl	scatt lge shells in fine mud matrix,
6b	16	5Y 6/3	p-sort clayey sd	v little shelly material, aggreg
6c	16	5Y 6/2	vp-sort med sd	large calc. shelly clasts
7a	6.5	5Y 6/3	p-sort med. sd	abund mollusc, foram fragms
7b	6.5	5Y 6/2	p-sort med. sd	abund shelly det; mollusc, echin, forams
7c	6.5	5Y 6/3	p-sort. coarse sdy gvl	ang fragms mollusc, encr forams, & sev sticks wood
8a	7.0	5Y 6/3	p-sort, coarse sdy gvl	abund coral, mollusc, foram, algae fragms and glass
8b	7.0	5Y 6/2	p-sort, coarse sd	molluscs, forams, green algae, and echin
8c	7.0	5Y 6/2	p-sort, coarse sd	abund fragms of molluscs & encr forams
9a	9.5	5Y 7/2	vp-sort, coasre sd	abund bioclastic debris, predom molluscs and forams
9b	9.5	5Y 6/2	p-sort gravelly sd	aggreg shelly; mollusc, echin, coral
9c	9.5	5Y 7/2	p-sort, shelly med sd	abund mollusc, forams, coral, echin. fragms
10a	16	5Y 7/2	p-sort slty sd	abund forams and molluscs
10b	16	5Y 7/2	vp-sort sdy gvl	abund. mollusc and coral fragms, some glass, volcs
10c	16	5Y 7/2	mw-sort med sd	small grains volcs, few lge shells

Petrographic Description of Apra Harbor Sedimen	ts (5-20 X Magnification)
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No.	Depth	Munsell	Texture	Visual Composition
	(m)	Color		-
11a	14	5Y 7/2	ep-sort slty sd & gvl	molluscs & coral fragms, volcs
11b	14	5Y 7/2	p-sort sd	well-aggreg, few foram and echin fragms.
11c	14	5Y 7/2	p-sort clayey sd	scatt fragms molluscs, echin, forams
12a	11	5Y 7/2	vp-sort. sd & gvl.	Acropora fingers, snails, bivalves, forams, & r. algae
12b	11	5Y 7/2	mw-sort slty sd	occas. mollusc fragms
12c	11	5Y 7/2	mw-sort slty sd	few gvl sized grains of mollusc fragms.
13a	12	5Y 7/2	mw-sort slty sd	uniform, lacks gvl sized detritus, few shells
13b	12	5Y 7/2	fw-sort fine slty sd	no observ coarse detritus
13c	12	5Y 6/2	fw-sort clayey-slty sd	no observ coarse detritus and no shells
14a	11	5Y 7/2	vp-sort clyey sd	abund shells and well-aggreg
14b	11	5Y 7/3	w-sorted cly sd	few scatt. bioclastic grains
14c	11	5Y 7/2	w-sorted, cly, m-sd	v. few fragms encr forams
15a	1.8	2.5Y 7/2	fw-sort slty-fine sd	mollusc fragms, volcs in smaller grains
15b	1.8	5Y 7/2	w-sort, slty sd	abund small grains of volcs
15c	1.8	5Y 7/3	w-sorted slty sd	abund volc grains, coral & encrust. forams
16a	9.5	5Y 7/3	fw-sort. fine sd	v few scatt fragms molluscs, forams, glass
16b	9.5	5Y 7/2	fw-sort clayey-slty sd	uniform, powdery, few bioclasts
16c	9.5	5Y 7/2	fw-sort slty sd	v. uniform color, slightly aggreg, no bioclsts noted
17a	12	5Y 6/3	p-sort coarse sdy gvl.	abund volcs, bioclastics and woody debris
17b	12	5Y 6/3	ep-sort slty sdy gvl	abund fragms coral, molluscs, xlline ls, and sev pottery
17c	12	5Y 6/3	ep-sort sdy gvl	lge mollucs fragms, forams, volcs grains, woody
18a	1.5	5Y 6/3	mw-sort coarse sd	spckld, bioclsts and volcs
18b	1.5	5Y 7/2	vp-sort shelly gvl	spckld "coquina" of mollucs, foram, coral, & echin
18c	1.5	5Y 6/3	vp-sort shelly sd	spckld, small volc grains, coarser bioclasts
19a	3.4	5Y 6/2	mw-sort coarse sd	spckld bioclsts and volcs, no large clasts
19b	3.4	5Y 6/2	vp-sort shelly sd	spckld gvly sd, volcs and bioclasts
19c	3.4	5Y 6/2	p-sort coarse sd	spckld, high percent bioclastics

Petrographic	Description	of Apra	Harbor	Sediments	(5-20)	X Magnification)
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No.	Depth	Munsell	Texture	Visual Composition
	(m)	Color		
20a	2.4	5Y 5/2	p-sort, coarse sd	abund reef bioclasts and volcs, scatt wood
20b	2.4	5Y 6/2	p-sort shelly sd	abund bioclstic grains, molluscs, echin, coral, forams
20c	2.4	5Y 6/2	p-sort sd & gvl	50% coral, corall algae, mollusc, encr forams fragms
21a	0.8	5Y 5/3	p-sort coarse sd	40% bioclastics, 60% volcs sd and terres. carbon
21b	0.8	5Y 5/2	m-sort, coarse sd	spekld sd, volc rich, with abund bioclasts
21c	0.8	5Y 5/2	m-sort, coarse sd	spekld sd, volc rich, with abund. bioclasts, tar ball
22a	1.5	5Y 5/3	vp-sort, sdy gvl	spckld, volcs and bioclsts: molluscs, forams & wood
22b	1.5	5Y 6/2	vp-sort gvl	spckld shelly gvl, molluscs, forams, echin, few volcs
22c	1.5	5Y 6/3	p-sort gravely sd	coarse bioclast. fragms and finer volc grains, wood
23a	2.4	5Y 7/2	p-sort coarse sdy gvl	encr forams, molluscs, echin, wood, scatter. volcs
23b	2.4	5Y 8/3	p-sort coarse sdy gvl	few volcs, bioclasts: molluscs, forams, echin
23c	2.4	5Y 8/2	vp-sort coarse sd	domin coarse bioclasts: molluscs, forams, scatt volcs
24a	2.4	5Y 7/2	p-sort gvly sd	mollusc, encr. forams, coral, echins & volcs
24b	2.4	5Y 7/2	vp-sort sdy gvl	spckld. volc and bio sd and gvl, echin, molluscs, forams
24c	2.4	5Y 7/3	vp-sort gvl	spckld, volcs, bioclsts: molluscs, forams, echin, wood
25a	7.6	5Y 6/3	p-sort med sd	lge Pocillipora stick and other calc. detritus
25b	7.6	2.5 Y5/2	vp sorted, sdy gvl	abund lge coralgal, mollusc, foram, & xlline ls, bioclasts.
25c	7.6	5Y 5/3	ep-sort, sdy gvl	Porites, echin, bivalves, wood and xlline ls det., volcs
26a	0.7	5Y 7/2	vp-sort sdy gvl	abund coral, mollusc, echin, and forams, wood
26b	0.7	5Y 7/2	vp-sort sdy gvl	whole and fragm forams, echin, coral, & mollucs
26c	0.7	5Y 7/3	p-sort sdy gvl	coquina, considerable glass, some wood
27a	2.4	5Y 7/2	m-sort coarse sdy gvl	well-aggreg cly balls, scattered bioclasts
27b	2.4	5Y 7/2	m-sort coarse sdy gvl	well-aggreg cly balls molluscs, wood, echin, forams
27c	2.4	5Y 6/3	p-sort coarse sdy gvl	mollusc detritus, wood
28a	1.5	5Y 7/3	mw-sorted slty sd	few, scatt encr foram and mollusc fragms
28b	1.5	5Y 7/2	mw-sort slty sd	uniform color, few bioclasts noted: molluscs
28c	1.5	5Y 7/3	mw-sort slty sd	aggreg, uniform color, muddy sd, few volcs
29a	1.5	5Y 7/2	mw-sort slty sd	bioclastics and volcs sd grains
29b	1.5	5Y 7/3	p-sort coarse sd	spckld bioclastic sd, echin, molluscs, forams, scatt wood
29c	1.5	5Y 7/2	p-sort coarse sd	spckld, volcs & bioclsts, incl mollusc and foram frgms
30a	8.4	5Y 6/3	ep-sort, sdy gravel	coarse bioclastic gvl, high % volcs sd and gvl
30b	8.4	5Y 6/3	ep-sort sdy gravel	coarse bioclastic gvl, high % volcs sd and gvl
30c	8.4	5Y 6/3	ep-sort sdy gravel	coarse bioclastic gvl, high % volcs sd and gvl

No.	Depth	Munsell	Texture	Visual Composition
	(m)	Color		
1a	4.6	5Y 6/3	p-sort slty sd	uniform pale olive color, scatt mollusc shells
1b	4.6	5Y 7/2	p-sort slty sd	uniform lt gray color, sev lege coral fragms
1c	5.5	5Y 7/3	p-sort slty-cly sd	uniform pale yellow color, aggreg clays
2a	2.4	5Y 5/2	p-sort coarse sd	olive-gray, bioclasts fragms, org muds, weath volcs
2b	3.7	5Y 5/2	p-sort med sd	olive, fine fragms bioclasts, weath volcs & org muds
2c	4.6	5Y 5/3	p-sort coarse sd	olive, fine fragms bioclasts, weath volcs & org muds
3a	2.6	5Y 5/3	p-sort coarse sd	spckled volcs, bioclasts
3b	2.4	5Y 6/3	p-sort v coarse sd	spckled volcs, bioclasts: molluscs, forams, echin & wood
3c	2.7	5Y6/3	p-sort v coarse sd	spckled volcs, bioclasts: molluscs, forams, glass & wood
4a	2.7	2.5Y 6/4	vp-sort gvly sd	spckled volcs, bioclasts: corals
4b	2.7	5Y 7/2	mw-sort slty sd	uniform lt gray, aggreg clays, molluscs and forams
4 c	2.7	5Y 7/2	mw-sort slty sd	uniform lt gray, aggreg clays, molluscs, forams, tar
5a	3.5	5Y 7/2	mw-sort cly-slty sd	uniform lt gray, aggreg clays, scatt bioclasts
5b	4.2	5Y 7/2	mw-sort cly-slty sd	uniform lt gray, aggreg clays, scatt bioclasts, wood
5c	4.5	5Y 7/2	mw-sort cly-slty sd	uniform lt gray, aggreg clays, scatt bioclasts
6a	3.2	5Y 6/3	vp-sort coarse sd	spckld volcs and bioclasts: mollusc shells
6b	3.4	5Y 6/3	p-sort coarse sd	spckld volcs and bioclasts: mainly mollusc shells, glass
6c	2.9	5Y 6/3	p-sort coarse sd	spekld volcs and bioclasts: molluse shells

Petrographic Description of Agat Marina Sediments (5-20 X Magnification)

Petrographic Description of Merizo Pier Sediments (5-20 X Magnification)

No.	Depth	Munsell	Texture	Visual Composition
	(m)	Color		
1a	25	5Y 6/2	p-sort coarse sd	spckled volcs & bioclasts: forams, molluscs, corals, echin
1b	25	5Y 6/2	vp-sort coarse sd	spckled volcs & bioclasts: forams, molluscs, corals, echin
1c	24	5Y 6/2	p-sort coarse sd	spckled volcs & bioclasts: forams, molluscs, corals, glass
2a	5.2	5Y 5/2	p-sort coarse sd	spckled volcs & bioclasts: molluscs
2b	5.1	5Y 6/2	p-sort v coarse sd	spckled volcs & bioclasts: corals, molluscs, echin
2c	5.1	5Y 6/2	p-sort coarse sdy gvl	spckled volcs & lge angular bioclasts: corals, molluscs
3a	3.7	5Y 6/2	p-sort gvly sd	spckled volcs & coarse bioclasts: corals, xlline ls
3b	4.9	5Y 5/2	p-sort gvly sd	spckled volcs & bioclasts: coral fingers
3c	3.0	5Y 5/2	p-sort coarse sd	spckled volcs & bioclasts: molluscs
4a	3.7	5Y 5/3	mw-sort coarse sd	spckled volcs & subordinate bioclasts
4b	4.6	5Y 6/2	p-sort coarse sd	spckled volcs & gvly bioclasts:
4c	4.5	5Y 5/3	mw-sort coarse sd	spckled volcs & gvly bioclasts:
5a	2.4	5Y 5/2	mw-sort coarse sd	spckled volcs & subord bioclasts, wood
5b	2.1	5Y 5/2	p-sort coarse sd	spckled volcs & subord bioclasts: corals
5c	0.6	5Y 5/2	mw-sort coarse sd	spckled volcs & subord bioclasts: molluscs

Abbreviations **from** Tables 8-11:

abun	abundant
aggreg	aggregated
echin	echinoid spines and plates
encr	encrusting
ep-sort	extremely poorly sorted
forams	tests of Foraminifera
frgms	fragments
fw-sort	fairly well sorted
gvl, gvly	gravel, gravely
lge	large
lt	light
m	medium
m-sort	moderately sorted
mw-sort	moderately well sorted
org	organic
p-sort	poorly sorted
scatt	scattered
sd, sdy	sand, sandy
slt, slty	silt, silty
spckld	speckled ("salt & pepper")
volcs	grains of volcanic detritus
vp-sort	very poorly sorted
xlline ls	grains of crystalline limestone

In addition to the principal minerals, many samples, especially in the very coarsest size fractions near beaches and launching ramps, contained minor to trace amounts of non-mineral manufactured and natural products. Especially notable were wood, glass, plastic, and metal.

For this study, sediment composition was estimated from visual comparisons with sediments curated from several published studies of coastal marine sediments in the Mariana Islands, especially from Siegrist et al (1991) and Randall & Siegrist (1995)

1.22 Texture

Grain size, sorting, and grain shape collectively and operationally define the concept of sediment texture. Texture of terrigenous marine sediments normally reflects the size and shape of starting material in the uplands, current velocity maxima in the transporting media (rivers and longshore currents) and distance and time traveled. Texture of the biogenic fractions, however, are primarily a function of the reef community structure, architectural design and skeletal strength of dominant reef organisms, and nature of the bioeroder populations, but only secondarily is related to physical parameters such a energy and depth.

Grain size was estimated visually (Tables 8-11) and later by a sieving program, the latter performed as follows: Approximately 100 grams of air-dried sediment were gently crushed to break up desiccated clumps. The sample was then sieved for fifteen minutes through a sieve shaker column containing 10-, 18-, and 230-mesh, 8-inch brass screens (U.S. Standard Series). This shortened column produced: >2mm (gravel), 1mm-to-2mm (very-coarse sand), 1mm-to-0.0625mm (coarse to very-fine sand), and <0.0625mm (silt and clay) fractions indicated in Tables 12-15.

1.3 Study Sites:

Sediment petrography from the four study areas is summarized in Tables 12-15 below. In general, with the exception of the muddy samples found in deeper parts of the Apra Harbor, they are consistently poorly sorted sands composed of a mixture of weathered volcaniclastic grains in the finer sand sizes and reef carbonate detritus in the coarser sand and gravel grain sizes. Samples with significant fine sand and silt fractions generally were found in deeper holes and many of these changed color from grays and blacks to tans and yellows on drying, indicating appreciable surface oxidation of unstable grains.

Particle Size	e Distribution A	Analysis and	Total Organic	Carbon in Sedi	ments from Agana	Boat Basin
			-			

Site # and Core			Sieved Fractions (%)		Total Organic	
Identity	>2mm	<2mm - >1mm <1mm - >62.5µm		<62.5µm	Carbon (%)	
la 2.27		3 98	87.80	5 91	0 54	
1b	3.58	4.62	83.40	8.40	0.86	
1c	3.98	4.34	85.70	5.95	0.69	
2a	3.85	2.84	78.30	14.98	1.93	
2b	2.85	4.85	83.80	8.50	2.10	
2c	7.39	2.95 82.20 7.49		7.49	1.67	
3a	33.87	16.23	49.70	0.22	0.23	
3b	25.61	17.40	56.60	0.44	0.21	
3c	11.34	19.19	69.40	0.05	0.23	
4a	7.22	9.24	82.00	1.51	0.29	
4b	7.17	10.43	80.60	1.85	0.36	
4c	7.59	13.96	77.50	0.98	0.27	
5a	2.90	14.41	82.40	0.26	0.32	
5b	9.87	14.55	75.40	0.17	0.26	
5c	5.56	13.73	80.70	0.00	0.28	

Site # and Core			Sieved Fractions (%)		Total Organic
Identity	>2mm	<2mm - >1mm	<1mm - >62.5µm	<62.5µm	Carbon (%)
10 12.06		12.86	74 17	0.90	0.33
1a 1b	16.45	14 59	66.85	2.11	0.33
1c	18.09	21.22	59.45	1.24	0.32
2a	1.99	13.91	83.18	0.92	0.18
2b	1.43	15.59	81.97	1.01	0.21
2c	11.81	21.22	66.25	0.72	0.29
3a	2.59	9.94	86.04	1.43	0.32
3b	2.01	8.54	88.19	1.26	0.19
3c	2.66	9.82	86.08	1.44	0.27
4a	3.09	15.86	65.99	15.06	0.49
4b	13.10	13.43	61.24	12.22	0.48
4c	0.52	2.89	76.10	20.50	0.68
5a	3.74	6.16	81.34	8.76	0.45
5b	6.35	11.31	74.59	7.75	0.24
5c	11.63	11.94	69.79	6.65	0.30
ба	42.34	13.39	38.17	6.10	1.26
6b	30.93	21.46	42.54	5.08	1.15
6с	32.96	15.48	46.79	4.77	1.23

Particle Size Distribution Analysis and Total Organic Carbon in Sediments from Apra Harbor

Site # and Core			Sieved Fractions (%)		Total Organic
Identity	>2mm	<2mm - >1mm	<1mm - >62.5µm	<62.5µm	Carbon (%)
7a	2.65	12.13	77.05	8.17	0.66
7b	7.87	10.28	75.53	6.31	0.68
7c	6.96	16.42	71.87	4.76	0.52
8a	18.31	16.87	61.84	2.98	0.58
8b	13.66	15.14	65.74	5.46	0.47
8c	19.26	13.89	62.82	4.03	0.46
9a	13.34	13.73	69.40	3.53	0.45
9b	31.36	16.41	48.46	3.77	0.37
9c	28.86	18.19	49.34	3.62	0.36
10a	9.44	18.62	64.77	7.16	0.47
10b	47.09	18.80	31.49	2.62	0.37
10c	8.49	9.96	68.01	13.54	0.27
11a	5.13	11.56	72.45	10.87	0.62
11b	17.71	25.43	51.40	5.46	0.36
11c	12.49	17.48	63.48	6.55	0.46
12a	15.14	13.78	65.25	5.83	0.61
12b	2.67	6.10	83.03	8.19	0.47
12c	5.44	9.93	74.24	10.40	0.39

Site # and Core		Sieved Fractions (%)						
Identity	>2mm	<2mm - >1mm	<1mm - >62.5µm	<62.5µm	Carbon (%)			
13a	4.05	8.89	78.40	8.65	0.70			
13b	14.62	11.10	66.91	7.37	0.62			
13c	4.49	17.37	69.78	8.37	0.51			
14a	14.04	15.97	61.03	8.95	0.80			
14b	9.65	16.30	64.81	9.23	0.76			
14c	7.82	26.17	57.04	8.96	0.80			
15a	1.87	3.22	81.61	13.29	0.31			
15b	2.15	3.22	86.53	8.10	0.51			
15c	4.31	6.95	83.61	5.13	0.27			
16a	2.29	29.95	62.69	5.07	0.81			
16b	0.13	0.50	66.99	32.38	0.71			
16c	0.11	5.33	69.05	25.51	0.80			
17a	12.24	7.19	69.52	11.05	1.07			
17b	9.77	11.07	71.22	7.95	0.66			
17c	5.29	7.01	77.44	10.25	0.59			
18a	1.44	4.66	93.80	0.10	0.26			
18b	10.39	14.04	74.54	1.03	0.22			
18c	2.88	7.12	89.32	0.69	0.26			

Site # and Core			Sieved Fractions (%)		Total Organic
Identity	>2mm	<2mm - >1mm	<1mm - >62.5µm	<62.5µm	Carbon (%)
19a 1.33		1.62	95.11	1.95	0.37
19b	1.20	5.37	92.66	0.76	0.28
19c	1.57	2.85	93.34	2.24	0.27
20a	4.25	9.19	82.30	4.25	0.37
20b	8.10	10.68	75.55	5.67	0.46
20c	7.48	13.59	73.42	5.51	0.60
21a	6.04	4.73	88.43	0.80	0.52
21b	3.71	5.69	90.56	0.04	0.46
21c	3.95	3.73	90.84	1.48	0.43
22a	10.57	21.59	67.55	0.29	0.55
22b	14.40	21.71	61.30	2.59	0.28
22c	12.29	23.77	62.59	1.36	0.41
23a	4.48	11.59	80.08	3.84	0.33
23b	1.71	9.23	86.52	2.54	0.31
23c	6.57	9.47	77.76	6.20	0.28
24a	4.65	14.11	79.17	2.07	0.34
24b	4.30	8.66	83.76	3.28	0.31
24c	3.64	8.82	84.32	3.22	0.31

Site # and Core			Sieved Fractions (%)		Total Organic	
Identity	>2mm	<2mm - >1mm	<1mm - >62.5µm	<62.5µm	Carbon (%)	
25a	18.00	16.12	63.34	2.47	0.65	
25b	50.14	14.89	34.11	0.86	0.37	
25c	50.28	15.52	33.57	0.63	0.32	
26a	23.25	19.26	54.05	3.44	0.36	
26b	36.85	12.28	46.92	3.95	0.43	
26c	13.79	15.65	66.11	4.44	0.25	
27a	14.72	21.26	51.09	12.93	0.82	
27b	40.25	17.83	31.08	10.84	1.17	
27c	49.93	19.55	24.70	5.83	1.08	
28a	2.95	10.66	75.15	11.24	0.45	
28b	4.72	9.66	72.65	12.98	0.43	
28c	3.72	11.62	70.68	13.98	0.48	
29a	0.66	3.81	88.73	6.81	0.30	
29b	1.32	6.66	88.86	3.16	0.30	
29c	2.18	6.05	90.47	1.30	0.33	
30a	14.89	22.58	61.41	1.11	0.52	
30b	14.53	22.72	61.75	1.00	0.89	
30c	19.22	18.84	61.40	0.54	0.66	

Site # and Core				Total Organic		
Identity	>2mm	<2mm - >1mm	<1mm - >62.5µm	<62.5µm	Carbon (%)	
1a	1.40	3.13	86.60	8.87	0.64	
1b	15.73	4.73	71.90	7.64	0.37	
1c	3.57	0.54	64.10	31.82	0.71	
2a	0.70	1.09	97.20	0.99	0.32	
2b	6.49	3.98	86.70	2.87	0.36	
2c	3.81	2.57	92.50	1.07	0.37	
3a	5.10	8.10	86.60	0.22	0.24	
3b	2.82	5.59	90.00	1.57	0.25	
3c	2.43	6.66	89.40	1.51	0.33	
4a	9.02	5.62	84.10	1.27	0.28	
4b	14.99	4.49	73.90	6.66	0.47	
4c	14.69	10.11	68.70	6.50	0.32	
5a	4.94	1.37	80.00	13.82	0.70	
5b	1.07	0.39	82.30	15.15	0.71	
5c	0.65	0.97	83.80	14.60	0.75	
ба	7.54	11.42	78.00	3.07	0.33	
6b	9.87	13.20	76.40	0.56	0.34	
6с	7.01	9.85	82.50	0.65	0.31	

Site # and Core			Total Organic			
Identity	>2mm	<2mm - >1mm <1mm - >62.5µm		<62.5µm	Carbon (%)	
1a	1.08	7.13	91.69	0.10	0.22	
1b	2.48	6.55	90.86	0.12	0.23	
1c	1.51	9.64	87.92	0.93	0.15	
2a	7.81	3.18	85.56	3.45	0.50	
2b	15.41	8.82	70.98	4.79	0.47	
2c	34.88	11.90	51.34	1.88	0.32	
3a	9.17	5.71	80.24	4.87	0.49	
3b	19.17	8.20	68.14	4.49	0.34	
3c	12.94	4.82	78.42	3.82	0.54	
4a	5.58	5.98	88.33	0.11	0.54	
4b	34.03	14.83	49.93	1.21	0.38	
4c	8.71	5.45	85.73	0.11	0.44	
5a	11.50	4.52	78.05	5.93	1.12	
5b	11.42	8.67	76.96	2.95	1.24	
5c	3.15	5.60	90.72	0.53	0.72	

Particle Size Distribution Analysis and Total Organic Carbon in Sediments from Merizo Pier

B. CHEMICAL ANALYSIS

<u>1. HEAVY METALS IN HARBOR SEDIMENTS</u>

The heavy metal data obtained during the present study are summarized in Tables 16-19. Despite attempts to effectively homogenize sediment samples prior to analysis, high withinsubsite variability was occasionally observed¹. This was attributed to minute metallic or metal containing particles residing in the sediment. For this reason, the geometric mean was used to determine average metal concentrations at each site in order to minimize the influence of such outliers on the true mean. The following discussions are organized on a metal by metal basis and all referenced data are expressed on a dry weight basis unless stated otherwise.

The U.S. EPA, Region V, sediment quality criteria presented in Table 20, and referred to during the following discussions, were developed by the U.S. EPA and the U.S. Army Corps of Engineers to help assess the impact of marine and freshwater dredged materials on the receiving environment (Giesy and Hoke 1990). Along with site-specific bioassays, they have been the standard reference used for regulating contaminated sediments for the past 15 years and, as far as we are aware, are still in effect today.

<u>1.1 Silver (Ag)</u>:

Silver ranks among the most toxic of heavy metals to aquatic organisms (Moore 1991). In uncontaminated sediments, levels are in the order of 0.1 μ g/g (parts per million) (Bryan and Langston 1992). Enrichment is usually associated with inputs from mining wastes or sewage (Thornton *et al.* 1975, Halcrow *et al.* 1973). Contributions from the latter source have placed silver among the heavy metals of greatest concern in the San Francisco Bay Area where levels in excess of 10 μ g/g have been reported (Louma and Phillips 1988). The highest levels reported in the literature, are 40 μ g/g for Acushnet estuary, New Bedford Harbor, Massachusetts (Summerheyes *et al.* 1977), and 190 μ g/g in grossly polluted sediments from Sorfjord, Norway (Skei *et al.* 1972).

Sedimentary silver concentrations determined during the present study were consistently below the limits of analytical detection (~0.2 μ g/g) at all sites visited. Recent sediment analysis undertaken by the US Navy in connection with maintenance dredging at Echo Wharf (see Fig. 4) also failed to find detectable levels of silver in all samples examined (US Navy 1997: unpublished data). It therefore seems reasonably safe to assume that silver is not an element of environmental concern in the coastal waters of Guam.

1.2 Arsenic (As):

Arsenic, in the form normally encountered in the environment, does not appear to be particularly toxic to aquatic organisms (Moore 1991). The most important source of this element to the aquatic environment is domestic wastewater, reflecting the use of arsenic in household preparations and in small industries that discharge effluents to municipal waste

¹ As a general rule, sample analysis was repeated if the variation between replicates was greater than 50%

Heavy Metals in Sediments from Agana Boat Basin

	Heavy Metals (µg/g dry wt.)										
Site	Statistic	Ag	As	Cd	Cr	Cu	Hg*	Ni	Pb	Sn	Zn
1 (a-c)	mean**	nc	3.31	nc	12.0	74.7	61.2	6.96	30.7	2.93	47.7
	range	<0.21 - <0.24	2.47 - 3.98	<0.07 - <0.08	10.9 - 14.2	65.2 - 88.5	45.8 -98.3	5.67 - 8.96	25.4 - 50.1	2.03 - 3.86	41.2 -58.9
2 (a-c)	mean	nc	6.00	nc	28.8	64.6	107	19.9	70.7	6.61	104
	range	<0.18 - 0.36	4.63 - 7.19	<0.13 - 0.27	26.4 - 31.2	48.0 - 96.1	95.8 - 123	18.9 - 21.2	54.6 - 113	4.57 - 10.9	86.3 - 126
3 (a-c)	mean	nc	1.35	nc	3.99	1.91	9.16	1.45	11.1	3.11	4.45
	range	<0.18 - <0.25	0.92 - 2.18	<0.14 - <0.16	3.16 - 4.83	0.81 - 38.0	5.14 - 15.9	1.19 - 1.79	3.35 - 324	1.65 - 7.36	2.61 - 7.77
4 (a-c)	mean	nc	1.03	nc	4.25	3.01	4.59	1.48	1.99	nc	4.57
	range	<0.19 - <0.24	0.92 - 1.23	<0.12 - <0.17	3.65 - 5.05	0.78 - 15.1	4.01 - 5.85	0.56 - 2.47	1.02 - 3.08	< 0.09 - 0.22	1.79 - 37.0
5 (a-c)	mean	nc	1.00	nc	3.61	0.56	4.77	1.01	3.46	nc	3.44
	range	<0.22 - <0.24	0.81 - 1.30	<0.14 - <0.14	3.18 - 4.08	0.49 - 1.01	3.10 - 6.46	0.56 - 1.67	2.72 - 4.35	<0.09 - <0.10	3.05 - 4.12

Heavy Metals in Sediments from Apra Harbor

Heavy Metals (µg/g dry wt.)											
Site	Statistic	Ag	As	Cd	Cr	Cu	Hg*	Ni	Pb	Sn	Zn
1 (a-c)	mean**	nc	10.7	0.59	12.4	142	403	4.04	96.3	7.37	461
	range	<0.16 - <0.2	7.11 - 17.0	0.27 - 2.18	8.61 - 14.1	85.8 - 181	137 - 741	2.34 - 10.0	80.2 - 107	6.54 - 7.91	404 - 552
2 (a-c)	mean	nc	2.01	nc	3.59	3.12	14.3	nc	4.81	1.00	8.35
	range	<0.17 - <0.22	1.77 - 2.32	<0.08 - <0.10	3.09 - 4.20	1.60 - 12.6	10.69 - 18.6	<0.22 - <0.28	3.47 - 9.61	0.20 - 4.93	6.39 - 11.7
3 (a-c)	mean	nc	1.24	nc	3.74	2.79	20.2	nc	6.07	0.54	12.9
	range	<0.18 - <0.21	1.00 - 1.40	<0.08 - <0.10	3.28 - 4.42	2.15 - 3.96	16.7 - 23.5	<0.28 - 1.05	4.76 - 8.33	0.19 - 2.52	9.38 - 17.7
4 (a-c)	mean	nc	3.70	nc	9.58	8.35	127	3.10	7.68	0.76	20.9
	range	<0.17 - <0.22	3.29 - 4.01	<0.08 - <0.10	8.55 - 10.6	7.74 - 9.15	83.5 - 174	2.61 - 3.78	6.25 - 9.04	0.60 - 0.95	19.9 - 22.8
5 (a-c)	mean	nc	3.77	nc	7.46	8.70	68.3	2.74	15.7	1.05	23.5
	range	<0.19 - <0.21	3.43 - 4.43	<0.09 - <0.10	7.11 - 7.78	8.15 - 10.0	56.7 - 74.7	2.36 - 3.38	14.4 - 18.5	0.91 - 1.23	22.4 - 24.6
6 (a-c)	mean	nc	8.64	nc	13.7	29.0	219	6.83	36.5	2.73	88.3
	range	<0.17 - <0.22	8.07 - 9.75	<0.08 - <0.10	12.2 - 16.6	27.9 - 30.3	202 - 256	6.42 - 7.06	32.8 - 41.9	1.98 - 3.50	78.6 - 104
7 (a-c)	mean	nc	4.67	nc	13.5	91.6	144	5.28	63.9	2.29	159
	range	<0.16 - <0.19	3.88 - 5.19	<0.07 - 0.21	10.1 - 21.0	72.7 - 127	107 - 264	4.57 - 6.03	52.6 - 86.7	2.06 - 2.79	144 - 188
8 (a-c)	mean	nc	3.73	nc	10.3	40.2	87.7	3.73	39.2	1.90	142
	range	<0.16 - <0.20	3.31 - 4.36	<0.07 - 0.36	8.28 - 13.4	33.7 - 57.1	67.9 - 107	3.36 - 4.18	30.1 - 53.3	1.70 - 2.26	112 - 227
9 (a-c)	mean	nc	4.45	nc	9.02	21.8	41.9	4.21	31.3	0.91	109
	range	<0.18 - 1.80	3.96 - 4.81	<0.07 - 0.31	7.68 - 13.5	14.2 - 47.2	35.9 - 48.4	3.88 - 4.61	23.2 - 48.2	0.84 - 1.02	75.7 - 182
10 (a-c)	mean	nc	3.81	nc	7.09	3.43	31.2	3.85	4.46	0.25	9.45
	range	<0.20 - <0.22	3.44 - 4.23	<0.08 - <0.09	5.33 - 8.46	1.57 - 4.81	18.0 - 47.3	3.13 - 4.59	3.00 - 5.77	0.15 - 0.39	4.62 - 14.4

Table 17 (continued)

Heavy Metals in Sediments from Apra Harbor

		Heavy Metals ($\mu g/g dry wt$.)										
Site	Statistic	Ag	As	Cd	Cr	Cu	Hg*	Ni	Pb	Sn	Zn	
11 (a-c)	mean**	nc	3.50	nc	7.77	7.32	68.5	4.73	7.49	0.71	22.3	
	range	<0.18 - <0.22	3.17 - 4.00	<0.07 - <0.09	6.72 - 9.48	5.26 - 10.2	39.1 - 473	4.13 - 5.49	6.62 - 8.38	0.47 - 1.25	14.9 - 27.7	
12 (a-c)	mean	nc	4.00	nc	7.36	9.43	25.4	4.54	9.42	0.64	36.4	
	range	<0.17 - <0.22	3.46 - 4.73	<0.07 - <0.17	6.53 - 8.29	7.94 - 11.8	23.8 - 27.2	3.08 - 11.0	6.97 - 19.9	0.35 - 1.92	24.3 - 109	
13 (a-c)	mean	nc	3.79	nc	8.41	8.27	38.1	4.27	5.82	0.38	21.6	
	range	<0.17 - <0.22	3.02 - 4.54	<0.12 - <0.16	7.86 - 9.48	7.49 - 9.24	32.1 - 45.5	3.57 - 4.93	5.07 - 6.74	0.33 - 0.43	19.9 - 23.1	
14 (a-c)	mean	nc	3.30	nc	9.27	10.8	41.9	5.58	7.19	0.54	24.7	
	range	<0.19 - <0.20	2.61 - 3.88	<0.14 - <0.16	8.46 - 10.7	9.99 - 11.9	38.7 - 45.5	5.24 - 5.96	5.80 - 8.07	0.47 -0.67	23.4 - 26.8	
15 (a-c)	mean	nc	2.81	nc	6.04	3.65	14.0	3.87	2.72	nc	11.9	
	range	<0.19 - <0.21	2.24 - 3.15	<0.15 - <0.16	5.61 - 6.29	3.36 - 4.20	11.4 - 21.2	3.42 - 4.33	2.11 - 3.30	<0.08 - <0.09	9.53 - 16.9	
16 (a-c)	mean	nc	3.81	nc	10.7	14.5	45.4	7.43	9.27	0.62	31.2	
	range	<0.18 - <0.22	2.92 - 4.90	<0.14 - <0.17	10.1 - 11.1	13.3 - 17.0	43.1 - 46.8	7.16 - 7.93	8.26 - 10.4	0.49 - 0.74	29.6 - 34.8	
17 (a-c)	mean	nc	5.12	nc	17.1	57.8	47.3	8.87	65.0	5.65	143	
	range	<0.17 - <0.22	4.27 - 6.16	<0.13 - 0.37	13.6 - 20.1	46.6 - 73.6	44.9 - 52.4	7.83 - 11.0	41.0 - 123	2.18 - 35.7	115 - 179	
18 (a-c)	mean	nc	1.53	nc	4.95	1.00	6.18	2.39	nc	nc	2.30	
	range	<0.19 - <0.22	1.30 - 1.81	<0.13 - <0.17	4.66 - 5.29	0.81 - 1.26	4.82 - 7.23	2.19 - 2.55	<0.58 - 1.41	<0.07 - <0.08	1.66 - 2.78	
19 (a-c)	mean	nc	2.38	nc	5.04	4.71	14.2	2.85	4.51	nc	6.74	
	range	<0.19 - <0.21	2.20 - 2.63	<0.15 - <0.17	4.16 - 5.52	3.73 - 5.98	11.9 - 18.1	1.81 - 3.83	3.33 - 6.91	<0.09 - <0.10	4.77 - 8.46	
20 (a-c)	mean	nc	3.15	nc	6.13	6.34	21.1	7.33	4.38	nc	11.4	
	range	<0.19 - <0.22	2.96 - 3.55	<0.14 - <0.17	5.52 - 6.64	5.00 - 8.03	19.3 - 23.5	6.05 - 8.61	3.47 - 5.73	<0.10 - 0.32	10.3 - 13.3	

Table 17 (continued)

Heavy Metals in Sediments from Apra Harbor

			Heavy Metals (µg/g dry wt.)										
Site	Statistic	Ag	As	Cd	Cr	Cu	Hg*	Ni	Pb	Sn	Zn		
21 (a-c)	mean**	nc	3.26	nc	9.50	18.0	13.7	14.0	6.63	0.24	34.3		
	range	<0.17 - <0.20	2.91 - 3.75	<0.13 - <0.16	7.98 - 10.8	14.3 - 22.0	9.23 - 17.0	11.4 - 19.6	5.55 - 7.41	0.17 - 0.44	28.4 - 43.8		
22 (a-c)	mean	nc	2.96	nc	7.38	5.28	23.1	5.48	12.8	3.06	23.9		
	range	<0.18 - <0.22	2.59 - 3.51	<0.14 - <0.17	5.12 - 9.61	3.61 - 9.33	19.8 - 26.7	3.41 - 8.75	3.54 - 53.9	0.38 - 44.0	12.7 - 47.3		
23 (a-c)	mean	nc	1.16	nc	3.91	2.23	15.7	1.66	2.18	nc	5.67		
	range	<0.17 - <0.22	0.98 - 1.73	<0.13 - <0.17	3.49 - 4.54	1.89 - 3.17	11.9 - 50.7	1.45 - 1.98	1.50 - 2.85	<0.10 - <0.10	4.86 - 7.74		
24 (a-c)	mean	nc	4.60	nc	9.62	15.8	88.1	2.56	22.0	1.02	43.0		
	range	<0.19 - <0.22	4.25 - 4.88	<0.15 - <0.17	7.81 - 14.3	10.5 - 34.3	70.9 - 111	1.98 - 4.76	15.0 - 34.9	0.90 - 1.24	31.6 - 53.4		
25 (a-c)	mean	nc	9.05	nc	10.2	48.7	263	8.12	48.9	2.09	117		
	range	<0.19 - <0.24	6.91 - 12.5	<0.11 - <0.14	8.68 - 13.2	35.7 - 75.4	160 - 428	5.70 - 17.4	33.6 - 85.5	2.08 - 2.10	85.1 - 163		
26 (a-c)	mean	nc	5.73	nc	7.71	13.8	16.9	4.04	17.4	0.33	35.6		
	range	<0.19 - <0.23	4.35 - 10.2	<0.11 - 0.19	6.87 - 8.87	10.2 - 20.1	14.6 - 20.3	3.34 - 5.30	10.4 - 22.8	0.18 - 0.50	29.0 - 45.2		
27 (a-c)	mean	nc	7.36	nc	14.4	52.0	110	7.14	48.6	1.89	148		
	range	<0.19 - <0.24	4.93 - 9.69	<0.14 - 0.60	11.1 - 21.9	21.5 - 153	64.3 - 167	6.28 - 8.29	17.9 - 194	0.56 - 4.21	45.7 - 451		
28 (a-c)	mean	nc	3.67	nc	7.27	4.83	22.0	4.17	2.28	nc	8.64		
	range	<0.21 - <0.22	3.46 - 3.91	<0.13 - <0.13	6.71 - 7.84	4.41 - 5.26	18.9 - 26.0	3.65 - 4.48	1.73 - 2.98	<0.09 - <0.10	7.70 - 9.88		
29 (a-c)	mean	nc	2.27	nc	5.07	2.22	10.5	2.54	1.63	nc	3.22		
	range	<0.20 - <0.24	2.08 - 2.47	<0.12 - 0.20	4.25 - 5.94	1.66 - 2.78	8.27 - 14.5	1.95 - 2.90	1.09 - 2.22	<0.10 - 2.28	2.40 - 3.83		
30 (a-c)	mean	nc	4.07	nc	10.9	10.9	43.6	8.90	6.26	0.29	27.2		
	range	<0.20 - <0.24	3.84 - 4.68	<0.12 - <0.15	9.89 - 12.7	9.24 - 13.8	32.5 - 55.5	8.01 - 10.9	4.88 - 8.79	0.17 - 0.46	23.1 - 35.5		

Heavy Metals	in Sediment	s from Agat	Marina
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		Heavy Metals (µg/g dry wt.)									
Site	Statistic	Ag	As	Cd	Cr	Cu	Hg*	Ni	Pb	Sn	Zn
1 (a-c)	mean**	nc	6.92	nc	20.7	7.68	4.96	23.4	nc	nc	7.54
	range	<0.19 - <0.23	5.74-9.44	<0.06 - <0.08	17.7 - 28.5	6.1 - 10.6	4.17 - 6.42	19.2 - 32.2	<0.46 - < 0.56	<0.09 - <0.10	6.36 - 10.2
2 (a-c)	mean	nc	6.37	nc	12.5	5.13	3.83	16.4	nc	nc	7.64
_ ()	range	<0.19 - <0.24	5.84 - 7.12	<0.06 - < 0.08	10.9 - 16.4	4.37 - 6.45	2.75 - 6.47	14.4 - 21.0	<0.44 - <0.57	<0.09 < 0.10	6.57 - 9.94
3 (a-c)	mean	nc	5.85	nc	12.2	2.63	3.93	10.8	nc	nc	4.80
	range	<0.18 - <0.23	5.57 - 6.21	<0.06 - < 0.08	9.13 - 14.6	2.19 - 3.16	2.72 - 6.16	9.70 - 11.7	<0.40 - <0.49	<0.09 - <0.10	4.14 - 6.47
4 (a-c)	mean	nc	6.21	nc	10.3	3.20	4.18	12.4	nc	nc	4.94
	range	<0.20 - <0.22	5.74 6.65	<0.07 - <0.07	8.17 - 11.9	2.77 - 3.79	3.15 - 7.30	11.4 - 13.5	<0.43 - <0.48	<0.09 - <0.10	4.24 - 5.74
5 (a-c)	mean	nc	9.78	nc	30.7	10.3	5.62	30.2	nc	nc	11.2
	range	<0.20 - <0.25	8.58 - 11.1	<0.07 - < 0.08	27.5 - 33.2	9.37 - 11.0	4.22 - 7.05	26.8 - 32.8	<0.43 - <0.54	<0.09 - <0.1	10.7 - 11.9
6 (a-c)	mean	nc	5.31	nc	9.85	3.14	4.19	12.3	nc	nc	4.42
	range	<0.21 - <0.24	4.57 - 6.49	<0.07 - <0.08	7.98 - 11.2	2.51 - 3.45	3.17 - 5.64	9.72 - 13.8	<0.46 - <0.53	<0.09 - <0.09	3.29 - 5.07

Heavy Metals in Sediments from Merizo Pier

	Heavy Metals (µg/g dry wt.)											
Site	Statistic	Ag	As	Cd	Cr	Cu	Hg*	Ni	Pb	Sn	Zn	
1 (a-c)	mean**	nc	2.87	nc	13.5	4.34	8.02	14.0	nc	nc	9.58	
	range	<0.20 - <0.25	2.43 - 3.11	<0.12 - <0.16	12.2 - 15.2	3.55 - 5.21	7.53 - 8.32	12.4 - 15.5	<0.38 - 10.6	<0.08 - 0.13	7.17 - 13.7	
2 (a-c)	mean	nc	4.62	nc	28.3	33.2	16.1	59.4	43.2	7.06	57.8	
	range	<0.23 - <0.25	3.27 - 6.23	<0.14 - 0.22	23.5 - 38.6	27.2 - 39.8	12.6 - 20.5	45.3 - 88.5	14.4 - 129	2.00 - 43.1	54.0 - 62.2	
3 (a-c)	mean	nc	4.82	nc	21.1	43.1	12.0	43.3	12.7	1.76	68.1	
	range	<0.17 - <0.25	3.54 - 5.85	<0.12 - 0.24	17.1 - 26.2	30.8 - 123	9.96 - 13.7	36.8 - 46.9	8.92 - 40.1	1.32 - 3.11	49.7 - 92.9	
4 (a-c)	mean	nc	4.41	nc	20.4	25.8	12.9	35.5	8.40	0.86	44.7	
	range	<0.19 - <0.25	3.55 - 5.58	<0.12 - <0.15	14.4 - 32.2	12.0 - 45.0	11.1 - 15.2	23.7 - 57.8	5.36 - 11.9	0.80 - 0.91	26.8 - 65.6	
5 (a-c)	mean	nc	5.19	nc	39.5	123	32.0	71.0	27.1	1.74	130	
	range	<0.20 - <0.25	4.70 - 5.68	<0.12 - <0.15	33.0 - 52.7	83.1 - 168	20.4 - 73.3	58.1 - 102	16.3 - 58.8	1.54 - 1.93	93.8 - 167	

U.S. EPA, Region V, Guidelines for Classifying Sediments According to Levels of Selected Heavy Metals^a (µg/g dry wt.)

Metal	Non-Polluted	Moderately Polluted	Heavily Polluted
Arsenic	<3	3-8	>8
Cadmium	-	-	>6
Chromium	<25	25-75	>75
Copper	<25	25-50	>50
Lead	<90	90-200	>200
Mercury ^b	<1	-	>1
Nickel	<20	20-50	>50
Silver	-	-	-
Tin	-	-	-
Zinc	<90	90-200	>200

^a Anon (1977); ^b as total mercury. Dashes indicate no data

systems. Other major sources include sewage sludge, manufacturing process, smelting and refining (Moore 1991).

Arsenic levels determined in UK estuaries ranged from 5 μ g/g in uncontaminated sediments from the Axe Estuary to 3732 μ g/g in polluted sediments from Restronguet Creek, Cornwall, which receives drainage from metal mining areas (Langston, 1984, 1985). It would appear, therefore, that levels of less than 10 μ g/g, as determined in the great majority of sediments during the present study, are fairly typical of a relatively clean environment in terms of arsenic contamination.

<u>1.3 Cadmium (Cd)</u>:

Cadmium, particularly as the free cadmium ion, is highly toxic to most plant and animal species (Moore 1991). The main anthropogenic sources of cadmium relate to metallurgical industries, municipal effluents, sewage sludge and mine wastes. Other sources are fossil fuels and some phosphorus containing fertilizers (UNEP 1985).

Recent literature values for this element in coastal sediments range from $<0.01-33 \ \mu g/g$ (see Table 5). Apparently, concentrations in relatively pristine areas are around 0.2 $\mu g/g$ or less with levels exceeding 10 $\mu g/g$ at heavily contaminated sites (Bryan and Langston 1992). Reviewing the data obtained during the present study, it is clear, then, that cadmium is not a problem metal at any of the sites examined although notable enrichment was evident in sediments from the Hotel Wharf area (Site 1) within Apra Harbor. At this site, levels ranged from 0.27-2.18 $\mu g/g$ with an overall mean of 0.59 $\mu g/g$.

From Table 5, it can be seen that relatively high sedimentary cadmium levels have previously been recorded from within Inner Apra Harbor, as well as from the immediately adjacent waters of Outer Apra Harbor in the vicinity of the Naval Ship Repair Facility (SRF) industrial area (Belt Collins Hawaii 1993, 1994).

<u>1.4 Chromium (Cr)</u>:

Chromium is only moderately toxic to aquatic organisms (Moore 1991). Coastal marine sources of this element are dominated by input from rivers, urban runoff, domestic and industrial wastewaters and sewage sludge (Moore 1991). In harbor locations, additional contributions from the metallic components of watercraft, anti-fouling paints, and wood preservatives can also be expected.

Some recently reported levels for chromium in marine sediments are presented in Table 5 and extend from 2.4 at the cleanest site to 749 μ g/g at the most contaminated. The U.S. EPA classifies sediments with chromium levels of less than 25 μ g/g as non-polluted whereas sediments with 25-75 μ g/g and >75 μ g/g are considered to be moderately polluted and heavily polluted with chromium respectively (Table 20). On this basis alone, virtually all of the sites examined during the present study fall into the "non-polluted" category. The exceptions were Site 2 at Agana Boat Basin, Site 5 at Agat Marina, and Sites 2 and 5 at Merizo Pier, where some mild enrichment was noted. Interestingly enough, at Apra Harbor, where the greatest amounts of chromium enrichment was expected, average levels were less than 10 μ g/g for the

great majority of samples analyzed. In marked contrast, chromium levels determined earlier by the U.S. Navy (1993), for sediments from within Inner Apra Harbor and connecting waters of the outer harbor area, are about an order of magnitude higher (Table 5).

<u>1.5 Copper (Cu)</u>:

Copper is highly toxic to most aquatic plants and invertebrates (Brown and Ahsanulla 1971, Denton and Burdon-Jones 1982) and is one of the most toxic heavy metals to fish (Denton and Burdon-Jones 1986, Moore 1991). Inputs of this element into natural waters are derived from numerous sources including mining, smelting, domestic and industrial wastewaters, steam electrical production, incinerator emissions, and the dumping of sewage sludge (Moore 1991). While coastal waters are generally dominated by inputs from rivers and atmospheric sources (Nriagu 1989), algaecides and anti-fouling paints remain a primary source of copper to harbor areas.

Copper has a high affinity for clays, iron and manganese oxides, and carbonate materials (Moore 1991). As a consequence residues are often elevated in sediments near localized sources of input. In reviewing the literature, it is apparent that copper levels in clean, non-geochemically enriched sediments are in the order of 10 μ g/g or less (see Table 5). In contrast, levels in excess of 2000 μ g/g have been reported for copper polluted sediments (Legoburu and Canton 1991, Bryan and Langston 1992).

In the current study, localized pockets of copper contamination were encountered at all locations except Agat Marina where mean levels ranged from 2.63 μ g/g at Site 3, to 10.3 μ g/g at Site 5. At the Agana Boat Basin, Sites 1 and 2 were classified as "heavily polluted" according to U.S. EPA's criteria (Table 20) as were Sites 1, 7, 17, 25 and 27 at Apra Harbor, and Site 5 at Merizo Pier. "Moderately polluted" were Site 6 at Apra Harbor and Sites 2-4 at Merizo Pier. All other sites examined fell into the "non-polluted" category.

Interestingly, maximum copper levels reported earlier for surface sediments taken from within Inner Apra Harbor and adjacent waters of the outer harbor area, are appreciably higher than those noted here (Belt Collins Hawaii 1993; see Table 5). To what extent this is influenced by grain size differences between our respective samples is unknown. However, we do know from earlier work that copper in Apra Harbor sediment is predominantly associated with the clay and silt fraction (Belt Collins Hawaii 1994, Table 5).

<u>1.6 Mercury (Hg)</u>:

Mercury is highly toxic to aquatic organisms, particularly in the organic form (Moore 1991). The number one anthropogenic source of mercury to the environment is discharge from coalburning power plants followed by atmospheric fallout from other sources (e.g. incineration of municipal refuse), chemical manufacturing processes, and discharge of domestic wastes (Moore 1991). Mercury levels in urban runoff are generally very low (Marsalek and Schroeter 1988) although relatively high concentrations have been found in oil and other petroleum products (Patterson *et al.* 1987). Thus, some enrichment can be expected in harbor areas. It is also pertinent to note here that mercury was once extensively used in anti-fouling paints to prevent the growth of marine organisms on ships hulls. In 1969, for example, 12% of the mercury used in the U.S. went into such paints (Gerlach 1981). Baseline levels of total mercury in uncontaminated sediments are reportedly in the order of 30 ng/g (parts per billion) (Bryan and Langston 1992, Benoit *et al.* 1994). However, values published for pristine sediments from the tropical north Queensland coast of Australia were somewhat lower than this and ranged from 4-16 ng/g (Knauer 1976). Based on these data, levels found at Agat Marina (mean: 3.83-5.62 ng/g) all fall into the "pristine" category. Likewise the outer harbor area of Agana Boat Basin is also clean although some mercury enrichment was noted in the inner harbor area (61.2-107 ng/g) and presumably is a reflection of the greater number of permanent mooring sites coupled with restricted water movement in this area. The data for Merizo Pier also indicated a very clean environment, apart from some mild enrichment at Site 5 adjacent to the refueling station.

As expected, the highest levels of mercury encountered during the present study were at Apra Harbor, although, from the data, it is clear that contamination is not universally distributed; rather, it is restricted to localized areas within the harbor confines. The highest levels encountered were in sediments taken from Site 1 adjacent to Hotel Wharf area (mean: 403 ng/g); Site 4 adjacent to the Mobil tank farm (mean: 127 ng/g); Sites 6 and 7 adjacent to the Shell Fox-1 fuel pier (mean: 219 ng/g and 144 ng/g respectively), and Sites 25 and 27 on Dry Dock Island (mean: 263 ng/g and 110 ng/g respectively). Mercury levels determined in sediments from all other Apra Harbor sites were less than 100 ng/g and, in several instances, fell within either the "pristine" or "uncontaminated" category noted above.

Although sedimentary mercury concentrations at certain sites were relatively high by local standards, they pale in comparison to levels encountered in severely polluted waters from other parts of the world. For example, up to 6 μ g/g mercury was recorded by Langston (1986) for sediments taken from the Mersey Estuary in the UK, while Benoit *et al.* (1994), reported a maximum mercury concentration of 570 μ g/g in sediments from Honda Bay in the Philippines. Perhaps the all-time highest values reported for mercury in marine sediments (in excess of 2000 μ g/g) are from samples collected from the grossly contaminated Minimata Bay area in Japan (Tokuomi 1969).

This notwithstanding, some mention should be made here of the relatively high mercury levels of up to 2.4 μ g/g encountered earlier, by the U.S. Navy (1993), in unsorted sediments from Inner Apra Harbor (Table 5). Such elevated levels are indeed worrisome in view of the high toxicity of this metal and its propensity to be taken up within the biota and concentrated up the food chain.

From earlier findings it appears that mercury, like copper, is also primarily associated with the silt and clay fraction of Apra Harbor sediments (Belt Collins Hawaii 1994). Thus, the elevated mercury levels found in the Inner Apra Harbor sediments are, at least in part, a reflection of their finer texture (\sim 10-40% mud) when compared with the majority of sediments examined during the current investigation.

1.7 Nickel (Ni):

Although nickel is moderately toxic to most species of aquatic plants, it is one of the least toxic inorganic agents to invertebrates and fish (Denton and Burdon-Jones, 1986, Moore 1991). The

major source of discharge to natural waters is municipal wastewater (Sung *et al.* 1986) followed by smelting and the refining of nonferrous metals. Total nickel residues in sediments typically range up to 100 μ g/g or higher but may fall below 1 μ g/g in some unpolluted coastal waters (Table 5). Maximum values are usually associated with nickel bearing geological formations and/or the discharge of industrial and municipal wastes (Moore 1991).

Nickel concentrations determined during the present investigation were generally well below the 20 μ g/g maximum, established by U.S. EPA, for non-polluted sediments (Table 20). The notable exceptions were Sites 2-5 at Merizo Pier where moderate to heavy contamination was encountered according to EPA criteria. Levels encountered in Apra Harbor were considerably lower than the maximum values reported earlier by the U.S. Navy (1993) for sediments from within Inner Apra Harbor and the adjoining outer harbor waters of the Naval Reservation area (Table 5).

<u>1.8 Lead (Pb)</u>:

Inorganic lead is moderately toxic to aquatic plants and ranks behind mercury, cadmium, copper and zinc in order of toxicity to invertebrates and fish (Denton and Burdon-Jones 1986). In contrast, organolead compounds, particularly the alkyl-lead compounds used as antiknock agents in gasoline, are highly toxic to all forms of life (Moore 1991).

Primary sources of lead into natural waters include manufacturing processes (particularly metals), atmospheric deposition (e.g. from pyrometallurgical nonferrous metal production; the combustion of leaded fuels; the burning of wood and coal; and the incineration of municipal refuse), domestic wastewaters, sewage and sewage sludges (Nriagu and Pacyna 1988).

Lead is barely soluble in seawater and is readily adsorbed by hydrous metal oxides, clay minerals and organic materials. Consequently, it is not highly mobile in the aquatic environment and tends to accumulate in sediments in the immediate vicinity of its point of entry into the hydrosphere. Harbor sediments are typically enriched (Table 5) owing to the long-term use of alkyl-lead compounds in boat fuels, the use of anti-corrosion lead-based paints, lead containing biocides (used as lead "boosters" in copper-based paints), and lead pipe, sheet and fittings used in water craft construction (UNEP 1985).

Residues in the 15-50 μ g/g range are frequently reported for coastal and estuarine sediments worldwide (Moore 1991). However, levels may be 1-2 orders of magnitude higher, or more, in polluted sediments near wastewater outfalls (Louma and Phillips 1988) or lead mining operations (Bryan and Langston 1992). Lead levels in clean coastal environments are around 25 μ g/g or less (Schafer and Bascom 1976, UNEP 1985, Bryan and Langston, 1992).

Based on the date gathered during the present study for Agat Marina, it would appear that baseline levels for lead in uncontaminated carbonate sediments are $<1 \mu g/g$. If this assumption is correct, then some lead enrichment is apparent at all other harbor locations studied. The highest mean lead level recorded was 96.3 $\mu g/g$ at Site 1 in Apra Harbor. This value just falls within the "moderately polluted" sediment category set by U.S. EPA (Table 20). Relatively high levels were also detected at Apra Harbor Sites 6-9, 17, 25 and 27 although none exceeded the U.S. EPA established maximum for non-polluted sediments.
The U.S. Navy (1993) reported lead levels of 42.8-139 μ g/g for sediments from within Inner Apra Harbor (Table 5). Their data suggests a much greater and more widespread enrichment of lead throughout this area compared with sections of Apra Harbor that we focused on.

1.9 Tin (Sn):

Naturally occurring inorganic tin is relatively harmless to aquatic organisms in direct contrast to anthropogenic organotin compounds, which are highly toxic (UNEP 1985, Bryan and Langston 1992). The primary sources of inorganic tin to surface waters are base metal mining and smelting operations; municipal wastewater and sewage sludge; combustion of fossil fuels, particularly oil and, to a lesser extent, coal; steel and tinplate manufacture; tanning; and atmospheric deposition, particularly near municipal incinerators (Moore 1991, Bryan and Langston 1992). The number one source of organotins is the dissolution of tributyltin (TBT) and related compounds used in anti-fouling paints (Moore 1991). Apart from being highly toxic, TBT is very persistent with an estimated half-life of about 2 years (de Mora *et al.* 1989). As a consequence, levels of this compound are frequently elevated in the sediments and water of harbors, ports and marinas.

All forms of tin are relatively insoluble and hence are readily sorbed by suspended solids upon entry into the hydrosphere. As a consequence they are quickly transported to bottom sediments. This notwithstanding, levels of TBT in the water column of harbors, ports and marinas can exceed 600 ng/l (parts per trillion) (Langston *et al.* 1987, Waldock *et al.* 1987)

Comparatively, little data exists regarding natural tin concentrations in uncontaminated marine sediments. Inorganic tin, as cassiterite (SnO₂), is usually the predominant form in sediments of estuaries associated with tin mining. In such areas, levels in excess of 1000 μ g/g have been reported (Bryan *et al.* 1985). In non-mineralized areas, levels are normally two to three orders of magnitude lower (Bryan and Langston 1992).

Typical surface sediment values for TBT reportedly range from 0.005-0.5 μ g/g (as Sn) depending on the proximity to areas of high boating/shipping activity, and usually accounts for less than 5% of the total tin present (Bryan and Langston 1992). However, Maguire (1987) found an extremely high TBT-Sn level of 10.3 μ g/g in the sediments of Vancouver Harbor, Canada, while Stewart and de Mora (1992) determined an all time high of 38 μ g/g in Suva Harbor, Fiji.

In the current study, we were unable to detect tin in sediments from the recently constructed Agat Marina area. It would appear, then, that baseline levels of naturally occurring, inorganic tin in the calcareous sediments around Guam are below $0.1 \ \mu g/g$. Levels over and above this are thought to represent contributions from anthropogenic sources. Thus, enrichment factors of between 10 and 100 are apparent for several sites within each of the other three harbor locations studied. However, what proportion of this additional loading represents TBT and other organotin compounds is currently unknown.

The extraordinarily high total tin levels reported earlier by the US Navy for sediments from Inner Apra Harbor, and the adjoining waters of the outer harbor area (Belt Collins Hawaii 1993), are especially noteworthy here since they rank among the highest ever recorded (Table 5). Very likely, paint chips associated with the cleaning and maintenance of naval ships, including hull sand-blasting activities, are the principal source of this element. Thus, TBT and other highly potent organotin compounds are probably in high concentrations in sediments from this location. Ballpark estimates are in the order of 1-10 μ g/g assuming TBT to account for 1% of the total tin present.

The potential effects of such high TBT concentrations on the local infauna is currently unknown and ultimately will depend on how quickly it is released from the anti-fouling paint particles incorporated in the sediment. In addition, the characteristics of the local sediments will very likely play a key role in determining the bioavailability and possible toxicity of TBT to the indigenous biota.

Just how much TBT exists in the water column of Inner Apra Harbor and adjacent areas remains to be evaluated. If a conservative sediment to water ratio of 1×10^5 to 1 (see Cleary and Stebbing 1987) is applied to the sediment TBT estimates given above, a range of 10-100 ng/l is obtained. This is well above toxic thresholds for many organisms. For example, laboratory experiments have shown that levels as low as 1 ng/l can induce deleterious sub-lethal effects in sensitive species (Bryan *et al.* 1989, Chagot *et al.* 1990, Gibbs *et al.* 1991) and 10-100 ng/l is sufficient to kill many embryonic and larval organisms and certain juvenile fish (Ward *et al.* 1981, Bryan and Gibbs 1991).

TBT has been described as the most toxic substance ever deliberately introduced into the aquatic environment (Goldberg 1986). It's dramatic effect on the growth and reproductive success of several invertebrate species, particularly mollusks, is now well documented. In fact, the once flourishing oyster fisheries along the coasts of eastern England and western France were decimated solely as a result of the unrestricted use of TBT-based anti-fouling paints between the early 1970's and mid 1980's (Alzieu *et al.* 1986, Alzieu 1991, Dowson *et al.* 1993).

As small boats and pleasure craft were believed to be the primary source of TBT contamination to the aquatic environment, legislation, banning the use of TBT-based biocides on boats of less than 25 m in length, was introduced in several countries, including the U.S.A., between 1986 and 1989 (Evans *et al.* 1995). There are, as yet, no restrictions prohibiting its use on larger vessels.

In light of the above discussions there is clearly an urgent need to: a) confirm the high tin values previously reported for sediment from within the Inner Apra Harbor area, b) identify the source and dominant chemical forms present, and c) evaluate their bioavailability and potential impact on resident organisms and those that feed upon them, including man.

<u>1.10 Zinc (Zn)</u>:

Although zinc is not regarded as being appreciably toxic, it is sometimes released into the sea in substantial quantities (Bryan and Langston 1992). Major sources of this element to the aquatic environment include the discharge of domestic wastewaters; coal-burning power plants; manufacturing processes involving metals; and atmospheric fallout (Moore 1991). Approximately one third of all atmospheric emissions of zinc are from natural sources, the rest emanating from metal production (smelting and refining); the burning of coal and oil; and from fertilizer and cement production (Nriagu 1989, Nriagu and Pacyna 1988).

Aquatic sediments act as a major repository for zinc and residues in excess of 3000 μ g/g have been found in the vicinity of mines and smelters (Poulton 1987, Bryan *et al.* 1985). Enclosed harbors, with restricted water circulation, are particularly prone to zinc contamination from a variety of localized sources including brass and galvanized fittings on boats, wharves and piers; zinc-based anti-corrosion and anti-fouling paints; zinc sacrificial anodes; and numerous metallic structures. Other important sources in these areas are contaminated windblown dust and surface runoff from a multitude of contributing harbor activities. Not surprisingly, then, some of the highest sedimentary zinc levels ever reported come from harbor areas. For example, Legorburu and Canton (1991) found a maximum of 5620 μ g/g in sediments from Pasajes Harbour in Spain, while Poulton (1987) recorded a high of 5,700 μ g/g for Hamilton Harbour in Canada.

Sediments from uncontaminated waters typically contain zinc levels of 5-50 μ g/g depending upon local geology (Moore 1991). World average values for shallow water sediments are given as 92 μ g/g (Wedepohl 1980) and the U.S. EPA classify sediments with zinc levels below 90 μ g/g as "non-polluted" (Table 20).

Zinc concentrations found in sediment samples during the present study spanned two orders of magnitude ranging from baseline levels of 3-5 μ g/g at uncontaminated sites to a maximum of 461 μ g/g off Hotel Wharf (Site 1) in Apra Harbor. Based on the U.S. EPA's criteria for zinc-contaminated sediments, this was the only site classified as "heavily polluted". Sites 7-9, 17, 25 and 27 in Apra Harbor; Site 2 in Agana Boat Basin, and Site 5 at Merizo Pier were classified as "moderately polluted" while the remainder fell into the "non-polluted" category.

Zinc levels determined during the present investigation were reasonably comparable with those reported earlier for sediments from Inner Apra Harbor and adjacent waters (U.S. Navy 1993), in sharp contrast to the other metals common to both studies.

2. POLYCHLORINATED BIPHENYLS IN HARBOR SEDIMENTS

Tables 21-24 summarize the PCB data obtained during the present study. Each table presents the total PCB (Σ_{20} PCB) concentrations (sum of the detectable congeners from the standard mix) and rank order of abundance of PCB homologues in sediment samples from each harbor site. The following discussions deal with each of these components separately. The probable identification of dominant PCB congeners in contaminated samples is also considered. All referenced data are expressed on a dry weight basis unless stated otherwise.

PCBs in Sediments from Agana Boat Basin

Site	Σ_{20} PCB	Concentration (ng	/g dry wt.)	Overall Order of Abundance of Detectable
	Mean	Median	Range	PCB Homologues (Cl_2B to $Cl_{10}B$)
1 (a-c)	11.23	13.6	6.48 - 13.7	$Cl_4B \!\!>\!\!Cl_6B \!\!>\!\!Cl_5B \!\!>\!\!Cl_7B \!\!>\!\!Cl_2B \!\!>\!\!Cl_9B \!\!>\!\!Cl_{10}B \!\!>\!\!Cl_3B \!\!>\!\!Cl_8B$
2 (a-c)	29.33	16.2	7.66 - 64.1	$Cl_5B \!\!>\!\!Cl_6B \!\!>\!\!Cl_4B \!\!>\!\!Cl_7B \!\!>\!\!Cl_2B \!\!>\!\!Cl_9B \!\!>\!\!Cl_8B \!\!>\!\!Cl_{10}B \!\!>\!\!Cl_3B$
3.(a-c)	1.16	1.17	0.07 - 1.60	$Cl_3B > Cl_2B > Cl_4B > Cl_5B > Cl_6B$
4 (a-c)	0.73	0.75	0.34 - 1.09	$Cl_3B > Cl_2B > Cl_4B > Cl_6B = Cl_7B$
5 (a-c)	4.89	1.56	1.43 - 11.7	$Cl_3B > Cl_2B > Cl_4B > Cl_6B > Cl_5B > Cl_7B$

PCBs in Sediments from Apra Harbor

Site	$\underline{\Sigma}_{20} \mathbf{PC}$	<u>CB Concentration (ng/g c</u>	lry wt.)	Overall Order of Abundance of Detectable
	Mean	Median	Range	PCB Homologues (Cl_2B to $Cl_{10}B$)
1 (a-c)	70.6	27.0	22.8 - 162	$Cl_5B \!\!>\!\! Cl_6B \!\!>\!\! Cl_4B \!\!>\!\! Cl_3B \!\!>\!\! Cl_7B \!\!>\!\! Cl_2B \!\!>\!\! Cl_{10}B \!\!>\!\! Cl_9B \!\!>\!\! Cl_8B$
2 (a-c)	6.86	1.08	0.73 - 18.8	$Cl_{5}B > Cl_{4}B > Cl_{6}B > Cl_{3}B > Cl_{2}B > Cl_{7}B > Cl_{10}B > Cl_{9}B > Cl_{8}B$
3 (a-c)	1.67	1.69	0.94 - 2.37	$Cl_3B > Cl_2B > Cl_4B > Cl_6B > Cl_7B > Cl_5B$
4 (a-c)	3.66	2.73	2.11 - 6.15	$Cl_{10}B \!\!>\!\! Cl_9B \!\!>\!\! Cl_7B \!\!>\!\! Cl_6B \!\!>\!\! Cl_8B \!\!>\!\! Cl_5B \!\!>\!\! Cl_3B \!\!>\!\! Cl_2B \!\!>\!\! Cl_4B$
5 (a-c)	1.16	0.99	0.61 - 1.89	$Cl_4B \!\!>\!\!Cl_7B \!\!>\!\!Cl_2B \!\!>\!\!Cl_6B \!\!>\!\!Cl_{10}B \!\!>\!\!Cl_5B \!\!>\!\!Cl_3B \!\!>\!\!Cl_9B \!\!>\!\!Cl_8B$
6 (a-c)	13.2	13.0	7.41 - 19.1	$Cl_{5}B \!\!>\!\! Cl_{4}B \!\!>\!\! Cl_{6}B \!\!>\!\! Cl_{7}B \!\!>\!\! Cl_{10}B \!\!>\!\! Cl_{2}B \!\!>\!\! Cl_{9}B \!\!>\!\! Cl_{3}B \!\!>\!\! Cl_{8}B$
7 (a-c)	341	244	229 - 549	$Cl_5B \!\!>\!\! Cl_4B \!\!>\!\! Cl_6B \!\!>\!\! Cl_7B \!\!>\!\! Cl_3B \!\!>\!\! Cl_2B \!\!>\!\! Cl_9B \!\!>\!\! Cl_8B \!\!>\!\! Cl_{10}B$
8 (a-c)	11.7	11.6	8.41 - 15.2	$Cl_{5}B \!\!>\!\! Cl_{6}B \!\!>\!\! Cl_{4}B \!\!>\!\! Cl_{7}B \!\!>\!\! Cl_{2}B \!\!>\!\! Cl_{10}B \!\!>\!\! Cl_{3}B \!\!>\!\! Cl_{9}B \!\!>\!\! Cl_{8}B$
9 (a-c)	22.2	16.7	8.19 - 41.7	$Cl_{5}B \!\!>\!\! Cl_{4}B \!\!>\!\! Cl_{6}B \!\!>\!\! Cl_{7}B \!\!>\!\! Cl_{3}B \!\!>\!\! Cl_{2}B \!\!>\!\! Cl_{10}B \!\!>\!\! Cl_{9}B \!\!>\!\! Cl_{8}B$
10 (a-c)	1.09	1.15	0.89 - 1.23	$Cl_{6}B \!\!>\!\! Cl_{10}B \!\!>\!\! Cl_{7}B \!\!>\!\! Cl_{5}B \!\!>\!\! Cl_{4}B \!\!>\!\! Cl_{2}B \!\!>\!\! Cl_{3}B \!\!>\!\! Cl_{9}B \!\!>\!\! Cl_{8}B$

Table 22 (cont.)

PCBs in Sediments from Apra Harbor

Site	Σ_{20} PCB	Concentration (ng/	<u>'g dry wt.)</u>	Overall Order of Abundance of Detectable
	Mean	Median	Range	PCB Homologues (Cl_2B to $Cl_{10}B$)
11 (a-c)	1.03	1.06	0.90 - 1.12	$Cl_{6}B{>}Cl_{7}B{>}Cl_{5}B{>}Cl_{4}B{>}Cl_{2}B{>}Cl_{10}B{>}Cl_{3}B{>}Cl_{9}B{>}Cl_{8}B$
12 (a-c)	2.17	2.01	1.95 - 2.56	$Cl_{6}B{>}Cl_{7}B{>}Cl_{5}B{>}Cl_{4}B{>}Cl_{3}B{=}Cl_{2}B{>}Cl_{10}B{>}Cl_{9}B{>}Cl_{8}B$
13 (a-c)	1.59	1.36	0.87 - 2.55	$Cl_6B \!\!>\!\!Cl_7B \!\!>\!\!Cl_4B \!\!>\!\!Cl_2B \!\!>\!\!Cl_5B \!\!>\!\!Cl_10B \!\!>\!\!Cl_9B \!\!>\!\!Cl_8B \!\!>\!\!Cl_3B$
14 (a-c)	2.12	2.21	1.43 - 2.71	$Cl_6B \!\!>\!\!Cl_7B \!\!>\!\!Cl_5B \!\!>\!\!Cl_4B \!\!>\!\!Cl_2B \!\!>\!\!Cl_3B \!\!>\!\!Cl_{10}B \!\!>\!\!Cl_9B \!\!>\!\!Cl_8B$
15 (a-c)	NC	0.33	BDL - 0.56	$Cl_4B \!\!>\!\!Cl_2B \!\!>\!\!Cl_6B \!\!=\!\!Cl_7B \!\!>\!\!Cl_3B \!\!>\!\!Cl_5B \!\!>\!\!Cl_8B \!\!=\!\!Cl_9B \!\!>\!\!Cl_{10}B$
16 (a-c)	2.58	2.21	1.88 - 3.66	$Cl_{6}B{>}Cl_{7}B{>}Cl_{5}B{>}Cl_{2}B{>}Cl_{3}B{>}Cl_{4}B{>}Cl_{10}B{>}Cl_{9}B{>}Cl_{8}B$
17 (a-c)	14.7	6.20	4.87 - 33.1	$Cl_{6}B{>}Cl_{7}B{>}Cl_{5}B{>}Cl_{4}B{>}Cl_{9}B{>}Cl_{8}B{>}Cl_{3}B{>}Cl_{2}B{>}Cl_{10}B$
18 (a-c)	0.23	0.23	0.19 - 0.26	$Cl_2B \!\!>\!\! Cl_4B \!\!>\!\! Cl_3B \!\!>\!\! Cl_5B \!\!>\!\! Cl_6B \!\!>\!\! Cl_7B$
19 (a-c)	0.52	0.51	0.36 - 0.70	$Cl_2B \!\!>\!\! Cl_3B \!\!>\!\! Cl_7B \!\!>\!\! Cl_6B \!\!>\!\! Cl_5B \!\!>\!\! Cl_4B$
20 (a-c)	1.05	1.02	0.80 - 1.32	$Cl_{6}B{>}Cl_{2}B{>}Cl_{5}B{>}Cl_{7}B{>}Cl_{4}B{>}Cl_{3}B{>}Cl_{8}B{=}Cl_{9}B$

NC = not calculable

BDL = below detection limits

Table 22 (cont.)

PCBs in Sediments from Apra Harbor

Site	Σ_{20} PCB	Concentration (ng/	/ <u>g dry wt.)</u>	Overall Order of Abundance of Detectable
	Mean	Median	Range	PCB Homologues (Cl_2B to $Cl_{10}B$)
21 (a-c)	1.21	1.30	0.94 - 1.40	$Cl_6B{>}Cl_5B{>}Cl_2B{>}Cl_4B{>}Cl_7B{>}Cl_3B{>}Cl_8B$
22 (a-c)	1.56	1.39	1.15 - 2.14	$Cl_7B \!\!>\!\! Cl_6B \!\!>\!\! Cl_5B \!\!>\!\! Cl_2B \!\!>\!\! Cl_3B \!\!>\!\! Cl_4B \!\!>\!\! Cl_8B \!\!>\!\! Cl_9B$
23 (a-c)	0.21	0.21	0.12 - 0.32	$Cl_2B \!\!>\!\! Cl_3B \!\!>\!\! Cl_6B \!\!>\!\! Cl_4B \!\!>\!\! Cl_7B \!\!>\!\! Cl_5B$
24 (a-c)	7.59	1.44	1.02 - 20.3	$Cl_7B \!\!>\!\!Cl_6B \!\!>\!\!Cl_5B \!\!>\!\!Cl_9B \!\!>\!\!Cl_8B \!\!>\!\!Cl_10B \!\!>\!\!Cl_4B \!\!>\!\!Cl_2B \!\!>\!\!Cl_3B$
25 (a-c)	11.7	11.0	6.19 - 18.0	$Cl_{6}B{>}Cl_{7}B{>}Cl_{5}B{>}Cl_{10}B{>}Cl_{4}B{>}Cl_{2}B{=}Cl_{3}B{>}Cl_{9}B{>}Cl_{8}B$
26 (a-c)	91.8	103	39.6 - 153	$Cl_{6}B{>}Cl_{7}B{>}Cl_{5}B{>}Cl_{4}B{>}Cl_{8}B{>}Cl_{9}B{>}Cl_{3}B{>}Cl_{2}B{>}Cl_{10}B$
27 (a-c)	13.9	11.4	7.55 - 27.1	$Cl_{6}B{>}Cl_{7}B{>}Cl_{5}B{>}Cl_{4}B{>}Cl_{2}B{>}Cl_{8}B{>}Cl_{3}B{>}Cl_{9}B{>}Cl_{10}B$
28 (a-c)	0.73	0.59	0.48 - 1.13	$Cl_4B \!\!>\!\! Cl_2B \!\!>\!\! Cl_7B \!\!>\!\! Cl_6B \!\!>\!\! Cl_3B \!\!=\!\! Cl_5B \!\!>\!\! Cl_{10}B \!\!>\!\! Cl_8B \!\!=\!\! Cl_9B$
29 (a-c)	0.22	0.22	0.17 - 0.28	$Cl_4B > Cl_2B > Cl_3B > Cl_5B = Cl_6B$
30 (a-c)	2.17	1.01	0.86 - 4.62	$Cl_{6}B{>}Cl_{5}B{>}Cl_{7}B{>}Cl_{4}B{>}Cl_{2}B{>}Cl_{3}B{>}Cl_{8}B{=}Cl_{10}B$

PCBs in Sediments from Agat Marina

Site	<u>Σ₂₀PCB</u> Mean	<u>Concentration (ng/</u> Median	' <u>g dry wt.)</u> Range	Overall Order of Abundance of Detectable PCB Homologues (Cl ₂ B to Cl ₁₀ B)
1 (a-c)	NC	0.34	BDL - 0.39	$Cl_3B>Cl_2B>Cl_4B$
2 (a-c)	NC	0.48	BDL - 0.91	Cl ₃ B>Cl ₂ B
3.(a-c)	NC	BDL	BDL - 0.04	Cl ₃ B
4 (a-c)	NC	BDL	BDL - 0.25	Cl_2B
5 (a-c)	0.81	0.87	0.61 - 0.95	$Cl_2B > Cl_7B > Cl_3B > Cl_4B > Cl_5B = Cl_6B$
6 (a-c)	0.14	0.15	0.09 - 0.18	Cl ₃ B>Cl ₄ B>Cl ₂ B

NC = not calculable

BDL = below detection limits

PCBs in Sediments from Merizo Pier

Site	<u>Σ₂₀PC</u>	B Concentration (ng/g	dry wt.)	Overall Order of Abundance of Detectable
	Mean	Median	Range	PCB Homologues (Cl_2B to $Cl_{10}B$)
1 (a-c)	0.39	0.38	0.13 - 0.67	$Cl_3B{>}Cl_2B{>}Cl_4B{>}Cl_5B{>}Cl_6B{>}Cl_7B$
2 (a-c)	1.83	1.61	1.40 - 2.47	$Cl_{2}B \!\!>\!\! Cl_{3}B \!\!>\!\! Cl_{7}B \!\!>\!\! Cl_{4}B \!\!=\!\! Cl_{6}B \!\!>\!\! Cl_{8}B \!\!>\!\! Cl_{9}B \!\!=\!\! Cl_{10}B$
3.(a-c)	1.69	1.75	1.53 - 1.80	$Cl_{6}B{>}Cl_{2}B{>}Cl_{5}B{>}Cl_{3}B{>}Cl_{4}B{>}Cl_{7}B{>}Cl_{10}B$
4 (a-c)	1.28	1.41	0.99 -1.44	$Cl_3B > Cl_2B > Cl_6B > Cl_4B > Cl_5B > Cl_7B$
5 (a-c)	5.12	5.52	3.30 -6.53	$Cl_4B > Cl_5B > Cl_6B > Cl_2B > Cl_3B > Cl_7B$

<u>2.1 Total PCB Concentrations (ΣPCB)</u>:

By the time leading manufacturers of PCB had ceased production of these compounds in the late 1970's, the cumulative world production had amounted to a staggering 1.2 million tons (Bletchley 1984). Of this, approximately 65% can still be accounted for in amounts held in storage, contained in landfills and currently in use in older electrical equipment (e.g., large capacitors and transformers, and small capacitors for use in association with fluorescent lights, small electric motors, and compressors such as the types used in refrigerators and air conditioners). Almost all of the remainder, some 370×10^3 t, is bound up in coastal sediments and dissolved in open ocean water (Tanabe 1988). PCBs, by virtue of their recalcitrant nature, are, therefore, likely to be with us for a long time to come. In point of fact, less than 5% of PCB produced worldwide has been destroyed to date.

The ubiquity of PCBs as environmental contaminants is a function of their resilience to chemical attack, and their small but nonetheless significant vapor pressure. Once airborne, they can, therefore, be transported thousands of miles from their original source to remote corners of the planet (Atlas *et al.* 1986, Iwata *et al.* 1993, Tanabe *et al.* 1994). In fact, aerial transport is considered to be the major route of PCBs to the open ocean (Tanabe and Tatsukawa 1986). In contrast, domestic and industrial wastes are the primary sources of PCB to coastal waters adjacent to urban growth centers (Iwata *et al.* 1994).

World baseline levels for Σ PCBs in clean coastal sediments are <1 ng/g (part per billion) and are a reflection of PCB background arising from atmospheric transport (Fowler 1986, Phillips 1986). In grossly polluted situations receiving inputs from localized point sources, levels as high as 61,000 ng/g have been reported (Nisbet 1976). Typical concentrations of Σ PCBs in marine and estuarine sediments from around the world are presented in Table 6. The values are representative of sediments from relatively uncontaminated through to grossly polluted areas.

In the current study, Σ_{20} PCB levels in sediment from all sites in Agat Marina were less than 1 ng/g indicating a very clean environment in this vicinity. Somewhat higher levels were observed at the majority of sites at Merizo Pier, with a maximum mean value of 5.12 ng/g recorded at Site 5 adjacent to the Cocos Island departure point. In the inner harbor area of Agana Boat Basin, still higher values of 11.23 and 29.33 ng/g were recorded at Sites 1 and 2 respectively.

At Apra Harbor, Σ_{20} PCB levels recorded were indicative of clean sediments (<1 ng/g) at Sites 15, 18, 19, 23, 28 and 29; moderately contaminated sediments at Sites 1 and 26 (~70-90 ng/g); and heavily contaminated sediments at Site 7 (~340 ng/g). In fact, the overall data for Apra Harbor reveals very distinct and highly localized point sources of PCB in the Hotel Wharf, Commercial Port and Dry Dock Island areas. Interestingly, the PCB profiles from sediments in these areas closely matched those of the technical PCB mixtures, Aroclor 1254 (at Sites 1 and 7) and Aroclor 1260 (at Site 26) (see Figs 7-9) suggesting that leaking PCB-containing

Figure 7: Polychlorinated Biphenyls in Sediments from Apra Harbor



Figure 8: Polychlorinated Biphenyls in Sediments from Apra Harbor



Figure 9: Polychlorinated Biphenyls in Sediments from Apra Harbor



electrical transformers could be the primary culprits². The fact that heavy contamination was not widespread throughout the harbor is indicative of either an acute incidence of the past, or a very recent event that could possibly be ongoing. Clearly then, careful inspection and continued monitoring is warranted in these areas.

2.2 Dominant PCB Homologues:

PCB profiles in environmental samples are frequently very different from those encountered in technical mixtures (Courtney and Denton 1976, Stalling *et al.* 1987). This largely reflects dissimilarities between individual chlorobiphenyls regarding their water solubility, vapor pressure and resistance to chemical and biological attack. As a general rule, water solubility, vapor pressure and resistance to photochemical breakdown decrease with increased chlorination, whereas the reverse is often the case with respect to biodegradation (Sawhney 1986). Thus, the lower chlorinated chlorobiphenyls tend to be the more mobile congeners in air, sediments and surface waters, and are frequently found in relatively high proportions in remote oceanic areas (Atlas and Giam 1981, Boon *et al.* 1985, Tanabe and Tatsukawa 1986, Iwata *et al.* 1993, Klamer and Fomsgaard 1993, Bright *et al.* 1995) and coastal regions distanced from specific point sources. In contrast, the higher chlorinated biphenyls tend to predominate in sediments near sources of high contamination, particularly in aged samples (Stout, 1986, De Voogt 1990, Caricchia *et al.* 1993, Thompson *et al.* 1996).

This certainly seems to be borne out in the current work. For example, at Agat Marina, where Σ_{20} PCB levels were very low, Cl₂-Cl₃ homologues tended to predominate suggesting longrange transport from comparatively distant sources. Of course, contributions from local sources cannot be ruled out. We saw evidence of this again in the relatively uncontaminated outer harbor sites of Agana Boat Basin. In contrast, the great majority of Apra Harbor sites were dominated by Cl₄-Cl₇ homologues. It is noteworthy, that this latter isomeric group contains 154 of the 209 possible PCB configurations (see Fig. 1) and is found in high proportions in Aroclor 1254 (Hutzinger *et al.* 1974, Brownawell and Farrington 1986). It follows then, that Cl₄-Cl₇ homologues will be prevalent in environmental samples taken near localized point sources of this particular technical mixture.

2.3 Dominant PCB Congeners:

Overall, 182 different chlorobiphenyls have been identified in technical PCB mixtures although individual mixtures probably contain less than half this number (Ballschmiter and Zell 1980, Holden 1986, De Voogt *et al.* 1990). Moreover, each mixture usually contains no more than 15 or so dominant congeners (>2% by weight) with several others present only in trace amounts (De Voogt *et al.* 1990).

As noted above, not all congeners present in technical mixtures are persistent. In fact many are rapidly degraded by microorganisms in soil and sediments and hence disappear within a comparatively short time of entering the environment. This is especially true for lower chlorinated members with unsubstituted *meta* and *para* carbons on one or both biphenyl rings

² It has recently come to our attention that a transformer, located in one of the two electrical substations at the southern end of Dry Dock Island (US Naval Ship Repair Facility (SRF): currently inactive), was retrofilled in March 1997 following the discovery that it contained 360 mg/kg PCB (Ogden 1997).

(Bright 1995). On the other hand, many of the higher chlorinated components that are relatively abundant in technical PCB mixtures are almost always found as major constituents of the total PCB content in abiotic samples (De Voogt 1990). This is particularly so for congeners with no unsubstituted *meta* and *para* carbons on one or both biphenyl rings, e.g., PCBs 28, 110, 118, 138, 153, and 180.

In the present study, several of the congeners used in the calibration standard are major components of various Aroclor preparations and their retention times matched primary peaks on many of the sample chromatograms. However, because of possible interference from coeluting chlorobiphenyls, their unambiguous identification and quantification was not assured. Those co-eluting congeners found in relatively high concentrations in technical PCB mixtures were of greatest concern (see Table 3). Despite these chromatographic limitations, some general conclusions were drawn from the data and are discussed here.

PCB profiles in sediments collected from the most contaminated site in Apra Harbor (Sites 1 and 7) resembled that of Aroclor 1254 (Figs. 7 and 8) and were dominated by six peaks corresponding to PCBs 66, 77, 101, 105/153, 118 and 138 of the calibration standard. Collectively, they accounted for about 94% of the total PCB measured. It seems likely that quantitative estimates for PCB 66 at this site were only minimally affected by co-eluting PCBs 80 and 95 considering that both are minor components of this particular technical mixture. The same argument applies for PCB 101 and co-eluting congeners 79 and 90, and PCB 138 and co-eluting congeners 163 and 164. With PCB 118, however, a substantial portion of the peak measured (~30%) is possibly attributable to PCB 149, a major component of both Aroclor 1254 and Aroclor 1260 (De Voogt *et al.* 1990).

The two other major PCB peaks in sediments from these sites correspond to PCB 77 and the co-eluting pair, PCBs 105 and 153. It is noteworthy that PCB 77 and 105 are highly toxic congeners that, fortunately, are only present in trace amounts (parts per million) in technical PCB mixtures (Jones 1988). Both co-elute with dominant Aroclor 1254 components as indicated in Table 3. Thus, in the case of PCB 105, congeners 132 and 153 are the co-eluting counterparts and represents around 2% and 3% (by wt.) of the technical mixture respectively. For PCB 77, the co-eluting congener is PCB 110, the most abundant component of all (~9% by wt.) in Aroclor 1254. In light of the above, the dominant PCB congeners, in decreasing order of abundance, were most likely as follows: PCB 110 > PCB 101 > PCB 118 > PCB 138 > PCB 138 > PCB 164 > PCB 132

PCB profiles in contaminated sediments from Site 26, on Dry Dock Island in Apra Harbor, resembled that of Aroclor 1260 (Fig. 9). In this particular instance, three major peaks matching the retention times of PCBs 105/153, 138 and 180, dominated the chromatograms. There were also three intermediate sized peaks corresponding to PCBs 118, 170 and 187. Collectively, all six peaks accounted for about 87% of the total PCB measured.

Significant interferences seem only likely for PCBs 118, 153 and 180, with co-eluting congers 149, 132 and 193 respectively. In Aroclor 1260, PCB 149 outweighs PCB 118 by about 5:1 and is the most dominant congener (~10% by wt.) in this particular technical mixture (De Voogt 1990). Likewise, for congener pairs 153/132 and 180/193, the former outweighs the

latter by approximately 3:1 in each case. In all probability then, the dominant PCB congeners at this site, in decreasing order of abundance, were: PCB 153 > PCB 138 > PCB 180 > PCB 149 > PCBs 170 & 187 > PCB 132 > PCB 193 > PCB 118.

The retention times of dominant peaks in sediment chromatograms from other relatively enriched sites within Apra Harbor and Agana Boat Basin, invariably matched one or more major components of the higher chlorinated technical PCB mixtures, although there was often some considerable variability between sites regarding each peak's relative abundance.

All of the dominant PCB congeners referred to above have been found in the environment by other workers according to McFarland and Clarke (1989). These authors examined 59 published accounts of congener-specific analysis in various environmental samples. They found that PCBs 101 and 153 were the most frequently reported congeners, appearing in 36% and 37% of the literature respectively. Of the remaining congeners referred to above, PCBs 118, 138, 170, 180 and 187 were reported in more than 20% of the papers considered, while PCBs 66, 110, 132 and 149 were identified between 10 and 20% of the time. PCB 193, on the other hand, was reported comparatively infrequently and appeared in only 7% of the publications examined.

3. POLYCYCLIC AROMATIC HYDROCARBONS IN HARBOR SEDIMENTS

The PAH data obtained during the present study are summarized in Tables 25-28. Each table presents the total PAH (Σ_{16} PAH) concentrations determined at each harbor site in addition to the rank order of abundance of the individual PAH compounds detected. The significance of the findings is discussed in relation to published data from other parts of the world. All referenced data are expressed on a dry weight basis unless stated otherwise.

3.1 Total PAH Concentrations (ΣΡΑΗ):

Although many PAHs arise from natural sources (volcanoes, forest fires, oil seeps, diagenesis, and biosynthesis), anthropogenic sources of PAH are far more important with some 230,000 t entering the marine environment every year (Law 1986). The incomplete combustion of fossil fuels and other organic materials is generally considered to be the primary source of anthropogenic PAHs (Hites *et al.* 1980, Gschwend and Hites 1981). However, in some areas, notably ports and harbors, pyrolytic PAHs are augmented by petroluem-derived PAH from fuel spills and oil discharges associated with shipping activity (Johnson *et al.* 1985).

 Σ PAH levels in uncontaminated sediments are generally less than 5 ng/g (Pierce *et al.* 1986, Van Fleet *et al.* 1986) although background levels of 10-15 ng/g have been reported for some unimpacted, deep-sea sediments (Hites *et al.* 1980). A selection of data for Σ PAH concentrations in marine and estuarine sediments from various parts of the world is presented in Table 7. It can be seen that levels range from less than 5 ng/g in clean sediments to around 50 µg/g in sediments from heavily contaminated areas.

In the current study, we observed sedimentary Σ_{16} PAH concentrations ranging from nondetectable to around 11 µg/g. The highest mean levels of 6.14 µg/g and 8.14 µg/g were

PAHs in Sediments from Agana Boat Basin

Site	<u>Σ₁₆PAH C</u>	I Concentration (µg/g dry wt.)		Overall Order o	of Abundance of Detectable PAH Congeners	
	Mean	Median	Range			
1 (a-c)	0.21	0.21	0.18 - 0.23	BBF>BPE>INP>P	YR>BKF>ANT>FLU>CHR>BAP>PHE>BAA>ACE	
2 (a-c)	1.90	0.64	0.64 - 4.50	BBF>PYR>FLU>BAP>INP>CHR>BPE>BAA>BKF>PHE>ANT>DBA>ACE		
3 (a-c)	0.02	0.02	0.02 - 0.03	ANT>ACE>BPE		
4 (a-c)	0.05	0.05	0.03 - 0.05	ANT>ACE>BPE		
5 (a-c)	0.02	0.02	0.02 - 0.03	ANT>ACE		
PAH Abbr	eviations (in ord	er of molecula	r weight):			
	NAP	Naph	thalene	BAA	Benzo(a)anthracene	
	ACY	Acen	aphthylene	CHR	Chrysene	
	ACE	Acen	aphthene	BBF	Benzo(b)fluoranthene	
	FLR	Fluor	ene	BKF	Benzo(k)fluoranthene	
	PHE	Phena	anthrene	BAP	Benzo(a)pyrene	
	ANT	Anth	racene	BPE	Benzo(ghi)perylene	
	FLU	Fluor	anthene	INP	Indenol(1,2,3-cd)pyrene	
	PYR	Pyrer	ne	DBA	Dibenzo(a,h)anthracene	

PAHs in Sediments from Apra Harbor

Site	Σ_{16} PAH Concentration (µg/g dry wt.)		on (µg/g dry wt.)	Overall Order of Abundance of Detectable PAH Congeners
	Mean	Median	Range	
1 (a-c)	6.14	4.19	3.79 - 10.4	BBF>PYR>BAP>BKF>BPE>INP>PHE>FLU>CHR>BAA>ANT>DBA>FLR>ACE
2 (a-c)	0.07	0.09	0.03 - 0.09	BPE>ANT>BKF>BBF
3 (a-c)	0.18	0.15	0.13 - 0.25	BPE>ANT>BBF>PYR>BKF>CHR>INP>BAP>BAA
4 (a-c)	0.25	0.25	0.22 - 0.28	BKF>BBF>INP>BPE>BAP>ANT>BAA>PHE
5 (a-c)	0.21	0.17	0.16 -0.30	BBF>BKF>INP>BPE>CHR>BAP>BAA>PYR>ANT>FLU>DBA>PHE
6 (a-c)	8.14	9.12	4.57-10.7	BBF>BAP>BPE>INP>CHR>BKF>BAA>DBA>FLU>PYR>PHE>ANT>ACE
7 (a-c)	0.48	0.48	0.35 - 0.61	BKF>BBF>INP>BPE>PYR>BAP>FLU>CHR>ANT>BAA>PHE>DBA
8 (a-c)	2.07	1.32	0.32 - 4.57	PYR>FLU>BBF>CHR>BAA>BKF>INP>ANT>BPE>BAP>DBA>PHE>ACE
9 (a-c)	1.12	1.45	0.45 - 1.45	BBF>BAP>PYR>BPE>INP>BKF>CHR>BAA>FLU>PHE>DBA>ANT
10 (a-c)	0.15	0.11	0.06 - 0.27	BPE>ANT>BBF>BKF>PYR>BAP>BAA

see Table 26 for key to PAH abbreviations used

Table 26 (cont.)

PAHs in Sediments from Apra Harbor

Site	Σ_{16} PAH Concentration (µg/g dry wt.)		on (µg/g dry wt.)	Overall Order of Abundance of Detectable PAH Congeners
	Mean	Median	Range	
11 (a-c)	0.35	0.35	0.18 - 0.53	BBF>BPE>INP>BAP>BKF>PYR>BAA>FLU>ANT>CHR>PHE>DBA
12 (a-c)	0.14	0.15	0.09 - 0.18	BBF>ANT>BPE>INP>CHR>BKF>PYR>FLU>BAA>PHE>BAP>BPE
13 (a-c)	0.20	0.22	0.13 - 0.25	BBF>BPE>CHR>BKF>BAP>ANT>FLU>PYR>BAA>INP>PHE>DBA
14 (a-c)	0.22	0.23	0.15 - 0.23	BBF>CHR>BPE>BAP>BKF>BAA>FLU>ANT>PYR>PHE>DBA
15 (a-c)	0.02	0.02	0.01 - 0.03	ANT>CHR
16 (a-c)	0.46	0.29	0.25 - 0.83	BBF>FLU>PYR>BPE>CHR>INP>BKF>BAA>BAP>PHE>ANT>DBA
17 (a-c)	0.35	0.35	0.27 - 0.44	BKF>BBF>BPE>INP>PYR>CHR>BAP>FLU>ANT>BAA>PHE>DBA
18 (a-c)	0.02	0.03	0.02 - 0.03	ANT>PYR>BAA
19 (a-c)	0.11	0.08	0.06 - 0.18	BPE>ANT>BBF>PYR>PHE>FLU>CHR>BAP>BKF>BAA>ACE
20 (a-c)	0.16	0.09	0.07 - 0.32	BPE>ANT>PHE>CHR>FLU>BBF>PYR>INP>BAP>BKF>BAA

see Table 26 for key to PAH abbreviations used

Table 26 (cont.)

PAHs in Sediments from Apra Harbor

Site	<u>Σ₁₆PAH C</u>	oncentrati	on (µg/g dry wt.)	Overall Order of Abundance of Detectable PAH Congeners
	Mean	Median	Range	o to the office of the office
21 (a-c) 0.55	0.49	0.18 - 0.98	PYR>BPE>FLU>BBF>BAA>INP>CHR>BAP>PHE>BKF>ANT>DBA
22 (a-c) 0.16	0.15	0.10 - 0.24	PYR>FLU>CHR>BBF>BAA>BAP>ANT>BKF>INP>BPE>PHE
23 (a-c) 0.07	0.06	0.01 - 0.13	ACE>ANT>BPE>BBF>PYR
24 (a-c) 0.82	0.53	0.29 - 1.64	BBF>BAP>BPE>BKF>INP>CHR>FLU>PYR>BAA>DBA>ANT>ACE>ACY>PHE
25 (a-c) 2.47	0.82	0.75 - 5.85	FLU>PYR>BBF>BAP>BAA>BPE>CHR>INP>PHE>BKF>DBA>ACE
26 (a-c) 0.13	0.13	0.10 - 0.16	BPE>BBF>PHE>ANT>CHR>BAA>BKF>FLU>ACE
27 (a-c) 0.28	0.27	0.21 - 0.36	BBF>BPE>PHE>CHR>BKF>INP>PYR>FLU>BAA>BAP>ANT>DBA
28 (a-c) 0.12	0.15	0.06 - 0.16	BPE>CHR>ANT>BBF
29 (a-c) NC	BDL	BDL - 0.02	ANT
30 (a-c) 0.05	0.05	0.03 - 0.08	BPE>ANT

NC = not calculable; BDL = below detection limits

see Table 26 for key to PAH abbreviations used

PAHs in Sediments from Agat Marina

Site	<u>Σ₁₆PAH C</u>	Σ ₁₆ PAH Concentration (µg/g dry wt.)		Overall Order	of Abundance of Detectable PAH Congeners
	Mean	Median	Range		
1 (a-c)	0.01	0.01	0.01 - 0.02	ANT	
2 (a-c)	NC	BDL	BDL - 0.05	FLR>INP>ANT	
3 (a-c)	NC	BDL	BDL - 0.02	PYR>ANT	
4 (a-c)	NC	BDL	BDL - 0.03	PYR>ANT	
5 (a-c)	NC	BDL	BDL - 0.01	ANT>ACE	
6 (a-c)	NC	BDL	BDL - 0.02	PYR>ANT	
NC = not c	alculable	•.			
BDL = bell PAH Abbr	ow detection lim	nts ler of molecule	ar weight).		
1711171001	NAP	Naph	ithalene	BAA	Benzo(a)anthracene
	ACY	Acen	aphthylene	CHR	Chrysene
	ACE	Acen	aphthene	BBF	Benzo(b)fluoranthene
	FLR	Fluor	rene	BKF	Benzo(k)fluoranthene
	PHE	Phen	anthrene	BAP	Benzo(a)pyrene
	ANT	Anth	racene	BPE	Benzo(ghi)perylene
	FLU	Fluor	ranthene	INP	Indenol(1,2,3-cd)pyrene
	PYR	Pyrei	ne	DBA	Dibenzo(a,h)anthracene

PAHs in Sediments from Merizo Pier

Site	<u>Σ₁₆PAH C</u>	oncentrati	on (µg/g dry wt.)	Overall Ord	er of Abundance of Detectable PAH Congeners	
	Mean	Median	Range			
1 (a-c)	NC	BDL	BDL			
2 (a-c)	0.52	0.43	0.30 - 0.83	PYR>FLU>BB	F>CHR>BKF>BPE>BAA>BAP>INP>PHE>ANT>DBA	
3 (a-c)	0.08	0.06	0.06 - 0.11	BPE>CHR>FLU>ANT		
4 (a-c)	0.04	0.03	0.03 - 0.06	BPE>ANT>CHR>FLU		
5 (a-c)	0.36	0.35	0.26 - 0.48	BPE>CHR>BBF>BAP>BAA>BKF>INP>PYR>FLU>ANT>PHE		
NC = not c	calculable	nite				
PAH Abbr	reviations (in or	ler of molecula	ar weight):			
	NAP	Naph	thalene	BAA	Benzo(a)anthracene	
	ACY	Acen	aphthylene	CHR	Chrysene	
	ACE	Acen	aphthene	BBF	Benzo(b)fluoranthene	
	FLR	Fluor	rene	BKF	Benzo(k)fluoranthene	
	PHE	Phen	anthrene	BAP	Benzo(a)pyrene	
	ANT	Anth	racene	BPE	Benzo(ghi)perylene	
	FLU	Fluor	anthene	INP	Indenol(1,2,3-cd)pyrene	

Dibenzo(a,h)anthracene

DBA

PYR

Pyrene

recorded in Apra Harbor sediments from the Hotel Wharf (Site 1) and the Shell, Fox-1 Fuel Pier (Site 6) areas respectively. Relatively high levels of contamination were also found in sediments from Sites 8 (2.07 μ g/g) and 9 (1.12 μ g/g) in the Commercial Port area; Site 25 (2.47 μ g/g) adjacent to Dry Dock Island, and from Site 2 (1.90 μ g/g) in Agana Boat Basin. The PAH profiles determined at each of these sites by UV detection (254 nm) are shown in Figures 10-12.

 Σ PAH concentrations in harbor sediments from elsewhere in the world, though highly variable, generally lie between 1-50 µg/g although levels in excess of 2000 µg/g have been reported for grossly contaminated areas (McCarry 1997). Thus, the highest Σ_{16} PAH levels in sediments from Guam's harbors are towards the lower end of the range usually encountered in this type of location.

3.2 PAH Assemblages:

It is well known that the composition of environmental PAH mixtures vary according to their source. For example, 2- and 3-ring PAHs, (naphthalene to anthracene, see Table 4) are most likely related to petrogenic hydrocarbon spillages such as diesel and fuel oil, whilst 4- to 6-ring compounds, (fluoranthene to benzo(*ghi*)perylene, see Table 4) are primarily produced as a result of fossil fuel combustion (Prahl and Carpenter 1984, Prahl *et al.* 1984). One exception to this general rule is phenanthrene, a 3-ringed compound common to both petroleum and combustion sources of PAH (Rice *et al.* 1993).

While it is theoretically possible to differentiate between petrogenic and pyrogenic sources of PAH in sediments, based on the molecular weights of the dominant parent constituents, losses of the lighter PAHs due to volatilization, dissolution and dispersion, as well as biodegradation often makes this task difficult if not impossible. The crucial factor here of course is time. Fresh petroleum/oil spills leave a readily identifiable signature that becomes progressively more difficult to recognize in aged samples. In the latter instance, the low molecular weight PAHs generally tend to be more abundant in the water column whereas the underlying sediments usually show a predominance of the heavier compounds (Benlahcen *et al.* 1997).

Upon examination of the data in Tables 25-28, it is apparent that there are substantial differences in sedimentary PAH profiles between sites suggesting multiple source of both petrogenic and pyrogenic origin. However, there was a tendency for some of the lighter PAHs, particularly acenaphthylene and anthracene, to dominate in sediments from relatively clean sites (e.g. Agana Boat Basin: Sites 3-5; Apra Harbor: Sites 15, 18, 23 29; Agat Marina: Sites 1-5). We attribute this to the greater environmental mobility of these compounds rather than their source of origin, a function directly related to their relatively high water solubility and vapor pressure.

Some researchers have attempted to differentiate between petrogenic and pyrogenic sources of PAHs in sediments using ratios between certain individual components present in the extract. For example, Benlahcen *et al.* (1997) maintained that phenanthrene/anthracene ratios of less than ten, and/or fluoranthene/pyrene ratios greater than one, are indicative of combustion sources. We examined the ratios of these PAHs in our data and conclude from the

Figure 10: Polycyclic Aromatic Hydrocarbons in Sediments from Apra Harbor



Figure 11: Polycyclic Aromatic Hydrocarbons in Sediments from Apra Harbor



Figure 12: Polycyclic Aromatic Hydrocarbons in Sediments from Apra Harbor



fluoranthene/pyrene ratio (>1) that fossil fuel combustion was the primary source of PAHs in the majority of samples taken. The notable exceptions were in Apra Harbor at Site 1 (Hotel Wharf), Site 6 (Shell, Fox-1 Fuel Pier), and Site 21 (Cabras Power Plant), where fluoranthene/pyrene ratios of <1 were indicative of petrogenic hydrocarbon spillages. We also noted that the pyrene/benzo(*a*)pyrene ratios were less than one in sediments from the latter two sites. According to Buttini (1992), this is the signature of unburned petroleum, compared with ratios of 2-12 and 50-100 for gasoline and diesel exhausts respectively.

The notable absence of naphthalene in any of the samples deserves mention here. We attribute some of this to losses incurred during the analytical extraction and clean-up processes (see Table 2). Other factors suspected of contributing, are the relatively low affinity that this PAH has for sedimentary materials (Connell and Miller 1984) and the comparative ease with which microorganisms are capable of degrading it to simpler compounds (Cernglia and Heitkamp 1989).

CONCLUSIONS & RECOMMENDATIONS

1. CLASSIFICATION SCHEMES AND SEDIMENT QUALITY CRITERIA

In the following sections, an overall assessment of pollution levels in sediments from Guam's harbors is presented. To facilitate this, we have devised a series of classification schemes that categorize the data according to the degree of contamination determined at each site. Some consideration is also given to establishing numerical sediment quality criteria for the open water disposal of dredged spoil. Finally, some general recommendations are made for future investigations in these areas.

<u>1.1 Heavy Metals</u>:

The U.S. EPA, Region V, guidelines for classifying sediments according to their heavy metal content (Table 20) provides a useful starting point for evaluating the data gathered here. However, the elemental composition of unpolluted aquatic sediments varies in accordance with their source of origin. Thus, what may be considered normal background concentrations for one type of sediment may, in fact, reflect some degree of contamination in another. This is clearly shown by the examples listed in Table 29. Calcareous sediments, in particular, generally contain lower concentrations of trace elements than other major sediment types. Clearly then, the aforementioned standards will not suffice for all sediments.

Mindful of these limitations, we have formulated our own sediment pollution classification scheme, specifically for the calcareous sediments examined during the present study (Table 30). The contamination categories listed and their corresponding concentration ranges, though somewhat subjective in nature, take into account background levels, toxicity and pollution potential of the heavy metals listed. The fact that metals are relatively weakly sorbed to biogenic carbonates, and, as a consequence, tend to be more biologically available (Luoma and Jean 1977), was also taken into consideration.

Using this classification scheme, the data presented in Tables 16-19 can be quickly and conveniently assessed. Background or baseline values are those obtained from what we consider to be clean, uncontaminated sediments. The inclusion of the "light" degree of contamination category in Table 30 is of special significance insofar as serving as a cut-off point for the acceptance of dredged material for open water disposal³ (i.e., dredged materials may not be ocean dumped if they contain heavy metals at concentrations which exceed the upper limit of this category). For comparative purposes, we have listed these maximum acceptable values alongside established sediment quality criteria (SQG) from other areas, in Table 31. In addition, some critical values relating to adverse biological effects are included in Table 32.

Of course, the acceptability of sediments for open water disposal cannot be defined solely in terms of numerical limits. Nonetheless, the chemical analysis of dredged materials, in conjunction with realistic SQC, does provide a very useful platform from which decisions on the need for biological assessment studies can be made.

³ Although the ocean dumping of dredged sediments is not currently practiced on Guam, it is a possible option that may be adopted some time in the future.

Table	29
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Selected Heavy Metals Concentrations (µg/g dry wt.) in Various Unpolluted Sediment Types

Metal		Sedime	ent Type*_		Average Shallow	Baseline	
	Carbonate	Sandstone	Shales	Deep-Sea Clays	Water Sediment ^d	UK Estuaries ^f	This Study
Arsenic	1	1	13	13	-	4.8	1-3
Cadmium	0.035	0.02 ^a	0.3	0.43	0.17 ^e	0.13	< 0.1
Chromium	11	35	90	90	60	24	3-5
Copper	4	15 ^a	45	250	56	7	1-3
Lead	9	7	20	80	22	20	<1
Mercury	0.04	0.03	0.4	$0.001-0.4^{b}$	-	0.03	0.005-0.01
Nickel	20	2	68	225	35	14	1-3
Silver	0.19 ^a	0.12 ^a	0.27 ^a	0.11	-	0.07	<0.1
Tin	-	-	-	20°	4.6 ^e	0.4	< 0.1
Zinc	20	16	95	165	92	46	3-5

* after Turekian and Wedepole (1961); ^aHorn and Adams (1966); ^bBoström and Fisher (1969); ^cChester (1965); ^dWedepohl (1969/1978); ^euncited reference: U.S. Navy (1993); ^fBryan and Langston (1992). Dashes indicate no data.

Suggested Guidelines for Classifying Calcareous Sediments from Guam Harbors in Relation to Heavy Metal Content

Metal		Contamination.	<u>ination_(µg/g dry wt.)</u>		
	Clean	Light	Moderate	Heavy	Gross
Amonio	1.2	6 10	> 10.25	> 25 50	> 50
Arsenic	1-5	0-10	>10-23	>23-30	>30
Cadmium	< 0.1	0.1-0.5	>0.5-1	>1-10	>10
Chromium	3-5	10-25	>25-50	>50-100	>100
Copper	1-3	6-20	>20-50	>50-100	>100
Lead	<1	1-10	>10-50	>50-100	>100
Mercury ^a	0.005-0.01	0.02-0.1	>0.1-0.3	>0.3-1	>1
Nickel	1-3	6-20	>20-50	>50-100	>100
Silver	< 0.1	0.1-0.5	>0.5-1	>1-10	>10
Tin ^a	<0.1	0.1-5	>5-25	>25-50	>50
Zinc	3-5	10-50	>50-100	>100-300	>300

^a as total metal

Open Water Disposal of Dredged Material from Guam Harbors: Suggested Sediment Quality Criteria for Selected Contaminants Compared with Sediment Quality Criteria from Other Areas (all values as µg/g dry wt.)

Contaminant	Guam	Wisconsin ^a	Ontario ^b	Washington State ^c
Arsenic	10	10	8	70
Cadmium	0.5	1	1	0.96
Chromium	25	100	25	-
Copper	20	100	25	81
Lead	10	50	50	66
Mercury ^d	0.1	0.1	0.3	0.21
Nickel	20	100	25	-
Silver	0.5	-	0.5	1.2
Tin ^e	5	-	-	-
Zinc	50	100	100	160
Total PCBs	0.01	0.05	0.05	0.130
Total PAHs	0.5	-	-	-

^a Wisconsin Department of Natural Resources: Sullivan *et al.* (1985); ^b Ontario Ministry of Environment: Anon (1988); ^c Puget Sound Dredged Disposal Analysis (PSDDA) Program: (USACOE 1988); ^d as total mercury; ^e Tributyltin (TBT) not greater than 0.1% of the total tin (i.e. no more than 0.005 μg/g TBT). Dashes indicate no data

Proposed Numerical Sediment Quality Guidelines for Selected Contaminants from Other Areas
(all values as µg/g dry wt.)

Contaminant	Ontario Ministry	of Environment ^a	Florida Department of Environmental Protection ^b		
	No Effect Level (NEL)	Lowest Effect Level (LEL)	Threshold Effects Level (TEL)	Probable Effects Level (PEL)	
Arsenic	4.0	5.5	7.24 (2.7)	41.6 (46.8)	
Cadmium	0.6	1.0	0.68 (5.6)	4.21 (70.8)	
Chromium	22.0	31.0	52.3 (3.5)	160 (52.9)	
Copper	15.0	25.0	18.7 (9.0)	108 (55.9)	
Lead	23.0	31.0	30.2 (5.8)	112 (58.4)	
Mercury ^c	0.1	0.12	0.13 (7.8)	0.7 (36.7)	
Nickel	15.0	31.0	15.9 (3.3)	42.8 (9.4)	
Silver	-	-	0.73 (6.6)	1.77 (60.5)	
Tin	-	-	-	-	
Zinc	65.0	110	124 (3.8)	271 (60.5)	
Total PCBs	0.02	0.041	0.0216 (15.7)	0.189 (54.9)	
PCB A1016	-	0.007	-	-	
Total PAHs	-	-	1.684 (7.3)	16.77 (76.7)	

^a Persaud *et al.* (1989); ^b MacDonald *et al.*(1996), numbers in parenthesis are the frequencies at which adverse biological effects have been observed at \leq TEL and \geq PEL; ^c as total mercury.µg/g. Dashes indicate no data

The harbor sites that currently exceed the suggested numerical limits for one or more of the heavy metals looked at are listed in Table 33. It can be seen that, out of 46 sites, 20 were identified as "moderately" contaminated or worse. A site-specific classification analysis of these areas of enrichment is presented in Table 34. Major "hot-spots" included Site 1 at Apra Harbor (grossly contaminated with copper and zinc, and heavily contaminated with lead and mercury,); Sites 7 and 17 in Apra Harbor and Sites 2 in Agana Boat Basin (heavily contaminated with lead, copper and zinc); Site 27 at Apra Harbor and Site 5 at Merizo Pier (heavily contaminated with copper and zinc); Site 1 in Agana Boat Basin (heavily contaminated with copper); and Sites 8, 9 and 25 in Apra Harbor (heavily contaminated with copper); and Sites 8, 9 and 25 in Apra Harbor (heavily contaminated with copper); and Sites 8, 9 and 25 in Apra Harbor (heavily contaminated with copper); and Sites 8, 9 and 25 in Apra Harbor (heavily contaminated with copper); and Sites 8, 9 and 25 in Apra Harbor (heavily contaminated with copper); and Sites 8, 9 and 25 in Apra Harbor (heavily contaminated with copper); and Sites 8, 9 and 25 in Apra Harbor (heavily contaminated with copper); and Sites 8, 9 and 25 in Apra Harbor (heavily contaminated with copper); and Sites 8, 9 and 25 in Apra Harbor (heavily contaminated with copper); and Sites 8, 9 and 25 in Apra Harbor (heavily contaminated with copper); and Sites 8, 9 and 25 in Apra Harbor (heavily contaminated with copper); and Sites 8, 9 and 25 in Apra Harbor (heavily contaminated with copper); and Sites 8, 9 and 25 in Apra Harbor (heavily contaminated with copper); and Sites 8, 9 and 25 in Apra Harbor (heavily contaminated with copper); and Sites 8, 9 and 25 in Apra Harbor (heavily contaminated with copper); and Site 5 at Merizo Pier (heavily contaminated with copper); and Site 5 at Merizo Pier (heavily contaminated with copper); and Site 5 at Merizo Pier (heavily contaminated with copper); and Site 5 at Merizo

<u>1.2 Polychlorinated Biphenyls</u>

Although sedimentary PCB levels are, to some extent, related to certain physical and chemical characteristics of the sediments themselves, (e.g., grain size, organic matter), there is no such thing as a "normal" PCB concentration for the various sediment types in the same way as there is for heavy metals. PCBs are entirely man-made and any amounts in the environment, no matter how small, are exclusively derived from anthropogenic sources. In spite of this, we have to accept the fact that PCBs are ubiquitous contaminants that are now a part of every living and non-living component of our planet. Areas that we regard as totally unspoiled, even pristine, are all contaminated by PCBs, albeit at very low concentrations (<1 ng/ g).

Recognizing this, we have attempted to summarize the current findings by grouping the data into various pollution categories that describe the degree of PCB contamination determined (Table 35). This classification system adopts the same categories as described above for heavy metals. The concentration ranges within each category were based on the comments and opinions of many of the authors cited in Table 6. Once more, we recommend that the "light" degree of contamination be used as starting point to determine whether or not locally dredged sediments are acceptable for disposal at sea.

Thus, any sediment containing Σ PCBs in excess of 10 ng/g dry wt. would require remediation prior to open water disposal. This is somewhat lower than the SQC value of 50 ng/g used by the Ontario Ministry of Environment (OME) and the Wisconsin Department of Natural Resources (Table 31). However, in consideration of the fact that the lowest effect level reported by OME for the technical PCB mixture, Aroclor 1016, is 7 ng/g (Table 32), in addition to relatively recent findings that indicate certain "planar" or "co-planar" PCBs, present in technical PCB mixtures (i.e., congeners with no *ortho* substituents), are almost as potent as dioxin (Kannan *et al.* 1987, Tanabe 1988, Safe 1990, De Voogt *et al.* 1990), we feel a more conservative tolerance limit is justified.

1.3 Polycyclic Aromatic Hydrocarbons

In keeping with the strategy outlined for the other contaminant groups, we have also summarized the Σ PAH data obtained during the present study, according to the degree of contamination encountered (Table 36). The concentration ranges adopted within each category were decided upon following an extensive review of the available literature. According to our classification scheme, most of the sites visited had PAH levels in sediments that fell into the clean or lightly contaminated category. A total of seven sites were classified

Harbor Sites Exceeding Suggested Sediment Quality Criteria for Heavy Metals for Open Water Disposal of Dredged Material

Metal	Harbor Location				
	Agana Boat Basin	Apra Harbor	Agat Marina	Merizo Pier	
	site	site	site	site	
Arsenic	none	none	none	none	
Cadmium	none	none	none	none	
Chromium	2	none	5	2, 5	
Copper	1, 2	1, 6-9, 17, 25, 27	none	2-5	
Lead	1-3	1, 5-9, 17, 22, 24-27	none	2, 3, 5	
Mercury ^a	2	1, 4, 6, 7, 25, 27	none	none	
Nickel	none	none	1, 5	none	
Silver	none	none	none	none	
Tin ^a	2	1, 17	none	2	
Zinc	2	1, 6-9, 17, 25, 27	none	2, 3, 5	

^a as total metal

Metal	Degree of Contamination					
Wietai	Moderate	Heavy	Gross			
Arsenic	none	none	none			
Cadmium	none	none	none			
Chromium	ABB: 2; AM: 5	none	none			
Copper	AH: 6, 8, 9, 25; MP: 2-4	ABB: 1, 2; AH: 7, 17, 27; MP: 5	AH: 1			
Lead	ABB: 1, 3; AH: 5, 6, 8, 9, 22, 24-27; MP: 2, 3 5	ABB: 2; AH: 1, 7, 17	none			
Mercury	ABB: 2; AH: 4, 6, 7, 25, 27	AH: 1	none			
Nickel	AM: 1, 5; MP: 3, 4	MP: 2, 5	none			
Silver	none	none	none			
Tin	ABB: 2; AH: 1, 17; MP: 2	none	none			
Zinc	AH: 6, MP: 2, 3	ABB: 2; AH: 7-9, 17, 25, 27; MP: 5	AH: 1			

Classification of Heavy Metal Enriched Sites in Guam Harbors*

* ABB: Agana Boat Basin; AH: Apra Harbor; AM: Agat Marina; MP: Merizo Pier
Table 35

Evaluation of PCB Contamination* in Harbor Sediments from Guam

Degree of Contamination	PCB range (ng/g dry wt.)	Harbor Location				
		Agana Boat Basin	Apra Harbor	Agat Marina	Merizo Pier	
		site	site	site	site	
Clean	<1	4	15, 18, 19 23, 28, 29	1, 2, 3 4, 5, 6	1	
Light	1-10	3, 5	2, 3, 4, 5, 10, 11 12, 13, 14, 16, 20 21, 22, 24, 30	none	2, 3, 4, 5	
Moderate	>10-100	1, 2	1, 6, 8, 9, 17 25, 26, 27	none	none	
Heavy	>100-1000	none	7	none	none	
Gross	>1000	none	none	none	none	

*Based on average levels from subsites a-c at each site

Table 36.

Evaluation of PAH Contamination* in Harbor Sediments from Guam

Degree of Contamination	ΣPAH range (ng/g dry wt.)	Harbor Location				
		Agana Boat Basin	Apra Harbor	Agat Marina	Merizo Pier	
		site	site	site	site	
Clean	<50	3, 5	15, 18, 29	1-6	1,4	
Light	50-500	1, 4	2-5, 7, 10-14 16, 17, 19, 20, 22 23, 26-28, 30	none	3, 5	
Moderate	>500-5000	2	8, 9, 21, 24, 25	none	2	
Heavy	>5000-50000	none	1, 6,	none	none	
Gross	>50000	none	none	none	none	

*Based on average levels from subsites a-c at each site

as moderately contaminated and two others (Sites 1 and 6 in Apra Harbor) qualified as heavily contaminated.

The upper limit of the lightly contaminated category, again, serves as the cut-off point that distinguishes between acceptable and unacceptable sediments, from an ocean dumping standpoint. In other words, dredged sediments containing Σ PAH levels in excess of 0.5 µg/g would require further evaluation prior to any decisions being made on their immediate future. It can be seen, from Table 36, that sediments at nine sites exceeded this proposed SQC value. Seven of these sites were in Apra Harbor area adjacent to Hotel Wharf (Sites 1), Commercial Port (Sites 6, 8 and 9), Cabras Power Plant (Site 21), and Dry Dock Island (Sites 24 and 25). The remaining two sites were in the inner harbor area of Agana Boat Basin (Site 2) and off the public pier at Merizo (Site 2).

In formulating the proposed SQC for Σ PAHs, the following points were taken into consideration. Firstly, PAHs are natural components of the environment, and living organisms have evolved mechanisms for effectively metabolizing them at the levels normally encountered in the field. Secondly, several PAHs are known to be enzymatically transformed into active metabolites that exert mutagenic, toxic and carcinogenic effects in mammals and fish (James 1989). Of central importance here are the mixed function oxidases (MFOs), a group of enzymes that are induced by a wide range of aromatic hydrocarbons, including PAHs, at relatively low concentrations. Thirdly, there is now a strong body of evidence linking sedimentary levels of PAHs to liver cancer and other chronic diseases in benthic fish from polluted areas in the U.S. (Baumann *et al.* 1982, Black 1983, Malins *et al.* 1984, Malins *et al.* 1988, Varanasi *et al.* 1989). Fourthly, it has recently been demonstrated that Σ PAH levels as low as 1.0 µg/g have been shown to induce significant MFO activity in fish (Payne *et al.* 1988).

As a final consideration, we took into account the sediment quality guidelines (SQGs) for Florida coastal waters that were recently proposed by Macdonald *et al.* (1996). These authors, building on the previous work of Long and co-workers (Long and Morgan 1990, Long 1992, Long and MacDonald 1992, Long *et al.* 1995), estimated SQGs for a wide range of contaminants using existing biological effects data. From their extensive database, two SQGs were derived, a threshold effects level (TEL) and a probable effects level (PEL). These guidelines were formulated with the intention of delineating three ranges of contaminant concentrations that were rarely (\leq TEL), occasionally (> TEL to < PEL) and frequently (\geq PEL) associated with adverse biological effects.

The TEL and PEL estimates reported by MacDonald *et al.* (1996), for many of the contaminants examined during the present study, are listed in Table 32. It can be seen that the SQG for Σ PAH, below which minimal effects are anticipated (i.e., the TEL), is 1.684 µg/g. Based on this alone, it would appear that our proposed SQC value of 0.5 µg/g, for Σ PAH in Guam's harbor sediments, would afford adequate protection to sensitive biota inhabiting dredged spoil disposal sites at sea. However, the paucity of toxicity data relating to tropical marine species generally, coupled with likely differences in contaminant bioavailability

between different sediment types, warrants caution from an implementation stand point and highlights the urgent need for additional studies in these areas.

2. FUTURE DIRECTIONS

On the basis of the work already completed, the following recommendations are made for future work on the above trace contaminants:

- A need exists for investigations of greater geographical coverage, particularly in the Apra Harbor area. Such studies should include both previously unstudied areas, and more detailed sampling in those regions already sampled.
- An immediate assessment of tributyltin (TBT) levels in sediments from Inner Apra Harbor, and a thorough evaluation of its potential impact on the biota within the area, is particularly important.
- Emphasis should be placed on expanding the chemical database to include other organometallic compounds, dioxins, the persistent organochlorine pesticides, and the alkylated PAHs.
- Surveys should be undertaken to evaluate the bioaccumulation potential of the above contaminants in dominant components of the biota within each identified area of enrichment. This will provide valuable data from both a public health and ecological viewpoint. In addition, promising bio-indicators for future monitoring work will be identified.
- Studies are required to elucidate the possible interactive effects of multiple contaminant exposure upon organism living in, or close to, those sites already identified as excessively enriched with two or more contaminant groups.
- A more extensive and intensive effort needs to be directed towards formulating workable and effective sediment quality guidelines for dealing with the open water disposal of locally dredged materials.

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