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SOURCES AND AREAL DISTRIBUTION OF TRACE METALS IN RECENT SEDIMENTS  
OF MIDDLE LOCH, PEARL HARBOR (HAWAII)

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## EXECUTIVE SUMMARY

The primary objective of this project was to determine whether current operations of the Naval Inactive Ships Maintenance Facility contribute significant trace metal contamination to Middle Loch of Pearl Harbor. Secondary objectives were (1) to identify and quantify all major sources of trace metal contamination in Middle Loch and (2) to determine if trace metal concentrations in Middle Loch have declined following termination of direct discharges from the Pearl City Sewage Treatment Plant.

Middle Loch is a steep-sided basin with a shallow shoaling area along the west and north shorelines and deltas at the mouths of two streams. The relatively flat bottom of this basin is 7-8 m (22-25 ft) deep, except in the lower end of the loch, where depths reach 13 m (40 ft).

Sediment samples from ten locations within Middle Loch and from two locations in each of the two major streams entering the loch were analyzed for radioisotopes and metals. Major elements (aluminum and calcium) as well as organic and inorganic carbon were used to help characterize sediment composition and source. High aluminum-to-calcium ratios and high organic carbon concentrations are associated with terrigenous material carried into Middle Loch by the streams. This material is primarily deposited along the margins of the loch, especially on the deltas at the mouths of the two major streams. High inorganic carbon (i.e., carbonate) was found in the deeper areas of the loch, where shells of marine organisms are prevalent.

The presence of the natural, short-lived (53-d half-life) radioisotope  $^7\text{Be}$  was used to identify sites where the sedimentary material was recently deposited (i.e., within the past 3 months) and to identify patterns of recent sediment accumulation. Beryllium-7 was detected at eight of the ten sample sites within Middle Loch and in all stream samples. High  $^7\text{Be}$  inventories beneath the ships and at the mouths of the streams suggest that these are areas of rapid sediment accumulation, or sediment focusing. The concentrations of  $^7\text{Be}$  closely match the expected input based on rain-bucket data. This suggests that Middle Loch effectively traps all the  $^7\text{Be}$  through adsorption onto suspended matter and deposition to the sediments. If other particle-reactive contaminants are similarly trapped, as would be expected, then contamination in Middle Loch would not be exported to other areas of Pearl Harbor.

Average trace metal concentrations in old Middle Loch sediments (i.e., deposited ca. 1900 before construction of the Pearl Harbor Naval Shipyard) were: Cr, 300 mg/kg; Cu, 115 mg/kg; Ni, 193 mg/kg; Pb, 3 mg/kg; and Zn, 134 mg/kg. Average trace metal concentrations in recent sediments (i.e., those containing  $^7\text{Be}$ ) within Middle Loch are as follows: Cd 5.2 mg/kg; Cr 208 mg/kg; Cu 203 mg/kg; Ni 137 mg/kg; Pb 44 mg/kg; and Zn 253 mg/kg. Four sources of the increases in Cu, Pb, and Zn over historical levels were identified:

1. Inactive ship maintenance and mooring operations contribute Cu (232 kg/year), Pb (32 kg/year) and Zn (218 kg/year) contamination to the sediments of Middle Loch. Evidence suggests that only the sediments in the immediate vicinity of the inactive vessels are subject to this operation-dependent contamination. Moreover, paint debris and hydroblasting contribute only negligible amounts of these trace metals. Leaching of trace metals from paint below the waterline and sediment disturbances associated with mooring operations are the most likely sources of the contamination below the ships.
2. Freshwater streams carry sediment-bound trace metals into Middle Loch (Cd, 7.8 kg/year; Cr, 306 kg/year; Cu, 253 kg/year; Pb, 89 kg/year; Zn, 415 kg/year). As indicated by the major element and  $^7\text{Be}$  data, this material is primarily deposited along the loch margins, especially on deltas near the stream mouths, and probably does not have a large impact on sediments in the deeper areas. However,

these shallow margin areas appear to contain the greatest abundance of biota and are subject to public fishing from shore.

3. Sediment disturbances associated with ship movements can expose or resuspend and redeposit buried material from past contamination events. This source could potentially affect all areas of the loch.
4. Wind-blown material contributes relatively little trace metal contamination compared to the other sources (Cr, 4 kg/year; Cu, 2 kg/year; Pb, 2 kg/year; and Zn, 2 kg/year).

Average trace metal concentrations in recent Middle Loch sediments show no significant decline since the termination of direct sewage discharges in 1983 because (1) streams continue to discharge trace metal contamination into Middle Loch, and (2) sediment disturbances associated with mooring operations expose and/or resuspend buried sediments that contain high trace metal levels from past naval incidents and sewage discharges. As a result, contaminants once buried and removed from contact with benthic biota are now reintroduced into the water column and redeposited at the sediment surface.

## 1. INTRODUCTION

Several vessels of the U.S. Navy's Inactive Fleet are moored and maintained in Middle Loch of Pearl Harbor, Hawaii (and also at sites near Bremerton, Washington; Philadelphia, Pennsylvania; and Portsmouth, Virginia). Through natural weathering and some preservation activities, paint from these vessels may be introduced directly into the waters of the harbor. The primary trace metals in paints--i.e., Cr, Cu, Pb, and Zn (Appendix A)--are highly particle reactive; hence, most of the contamination associated with paint debris is likely to be confined to the sediments in the vicinity of the vessels.

Previous studies (Evans 1974, Ashwood et al. 1986) concluded that the primary source of trace metal contamination in Middle Loch sediments was the direct discharge of sludge from the Pearl City Sewage Treatment Plant. These discharges were terminated in 1983 (Ashwood et al. 1986).

The primary objective of this study was to determine if Inactive Fleet operations currently represent a significant source of trace metal contamination--a source which may have been masked by sewage discharges during previous studies. Secondary objectives were (1) identify and quantify major sources of trace metal contamination in Middle Loch and (2) ascertain whether reductions in trace metal contamination have occurred since termination of direct sewage discharges.

### 1.1 DESCRIPTION OF PEARL HARBOR

Pearl Harbor is a tropical (lat 21°N) coastal plain estuary composed of three major lochs and an entrance channel (Fig. 1). Together, these lochs drain an area of ~330 km<sup>2</sup> (Turner 1975). Most of this watershed is agricultural land; however, in the immediate vicinity of Pearl Harbor, there is considerable residential and industrial activity associated with Pearl Harbor Naval Shipyard (PHNS), Hickam Air Force Base, and Honolulu International Airport.

Wiesniewski (1981) indicates that a coral bar blocked the entrance of Pearl Harbor prior to 1902, when the bar was dredged to a depth of 11 m (35 ft). Construction of the PHNS began in 1909, and the first drydock was finally completed in 1919 (Wiesniewski 1981). Prior to World War II, Middle Loch was apparently used for mooring active ships. For example, on December 7, 1941, eight mine layers and mine sweepers were moored near the mouth of Middle Loch (Wiesniewski 1981). Inactive vessels were first moored and maintained in Middle Loch around 1946 (CDR J. E. Vroom, U.S. Navy, personal communication, 1986).

Middle Loch (Fig. 2) covers an area of approximately 3 km<sup>2</sup> [based on the Defense Mapping Agency (1984)]. Depth varies from less than 1 m near shore to 12 m where Middle Loch empties into East Loch [Fig. 3: depth contours based on U.S. Navy (1983)]. Most of the loch has been dredged to a minimum depth of 6.7 m (22 ft). The result of this dredging has been to form a large basin with steep sides and a relatively flat bottom. Cross sections of this basin are shown in Figs. 4 and 5. Shoaling areas, with a depth of approximately 1.5 m (5 ft), occur as deltas near the stream mouths and in a comparatively narrow band along the northern and western shorelines.

Three freshwater streams enter Middle Loch after passing through residential neighborhoods and commercial business districts (Fig. 2). Waiawa Stream drains the Pearl City Peninsula, which consists of residential and commercial areas. The stream that enters Middle Loch from the west is unnamed on local maps. We have dubbed it the Golf Course Stream because it borders the Ted Makalena Public Golf Course prior to discharging into Middle Loch. For some part of its length the Golf Course Stream is in a concrete-lined channel. It receives direct runoff and storm sewer discharge from residential and commercial areas in Waipahu. The third source of freshwater input to Middle Loch is a spring, which forms a small stream flowing through a low-lying, undeveloped area to the northeast of Middle Loch.

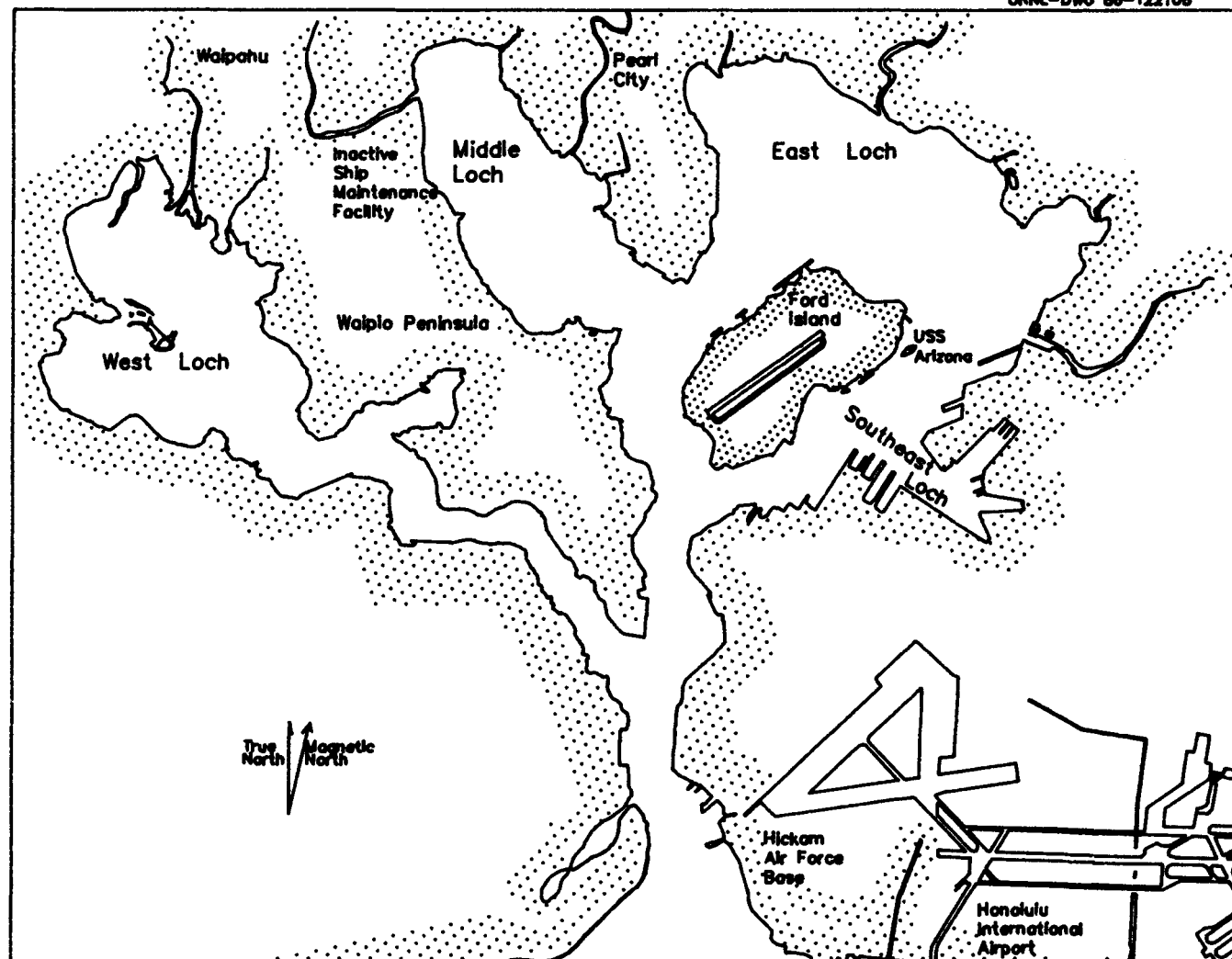


Fig. 1. Pearl Harbor, Hawaii

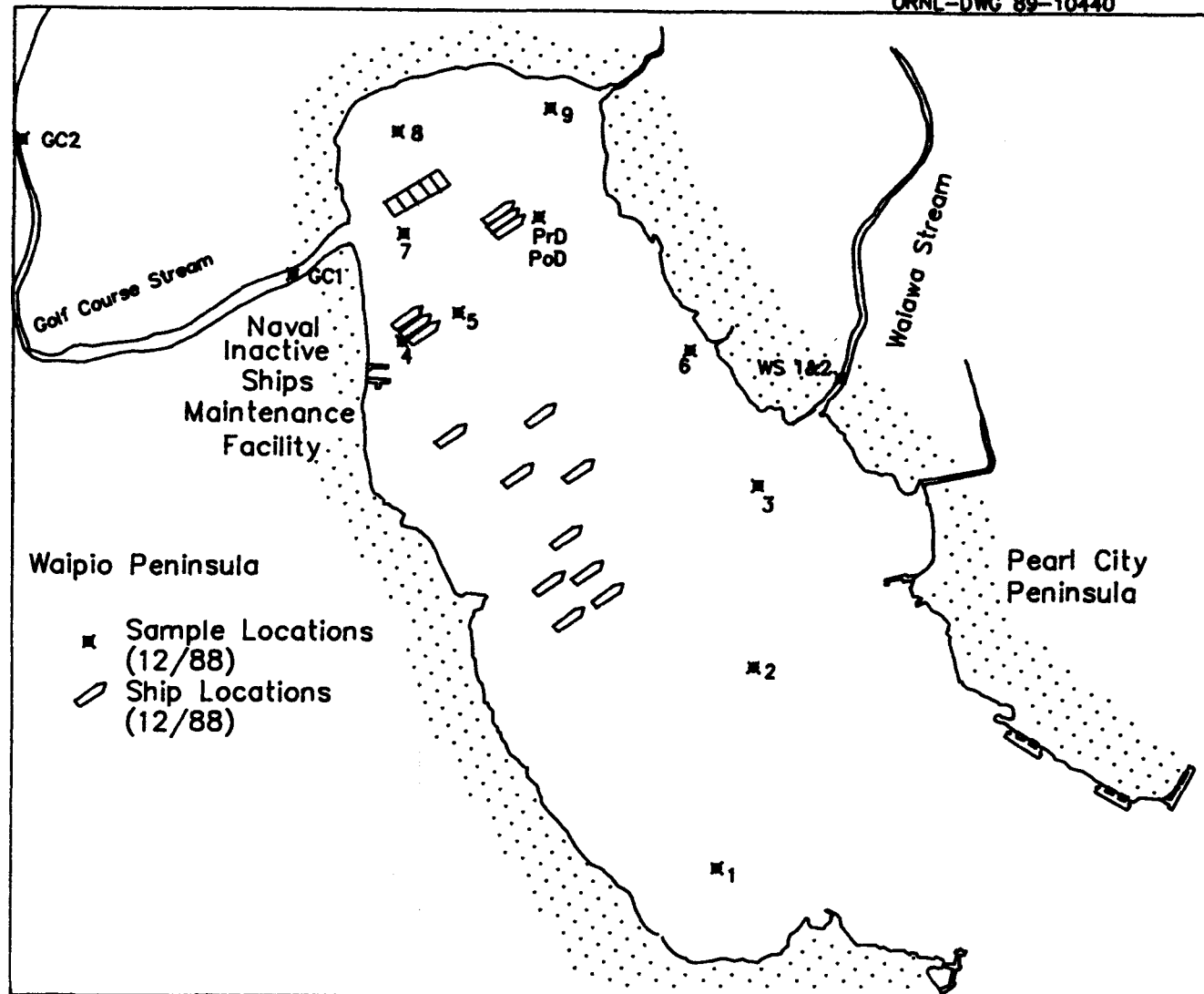


Fig. 2. Middle Loch of Pearl Harbor with locations of ships and sediment cores.

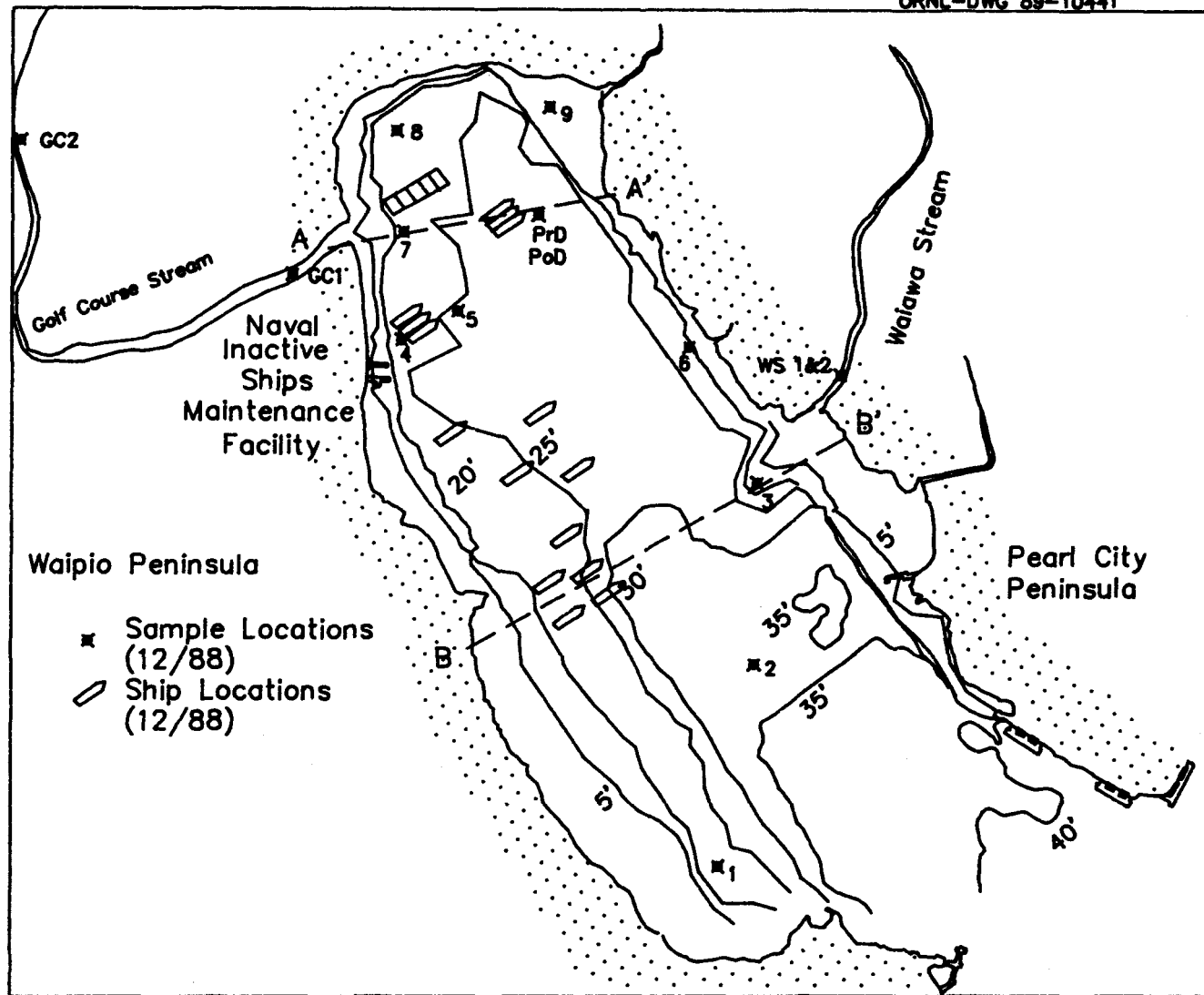


Fig. 3. Depth profile of Middle Loch and locations of cross sections.

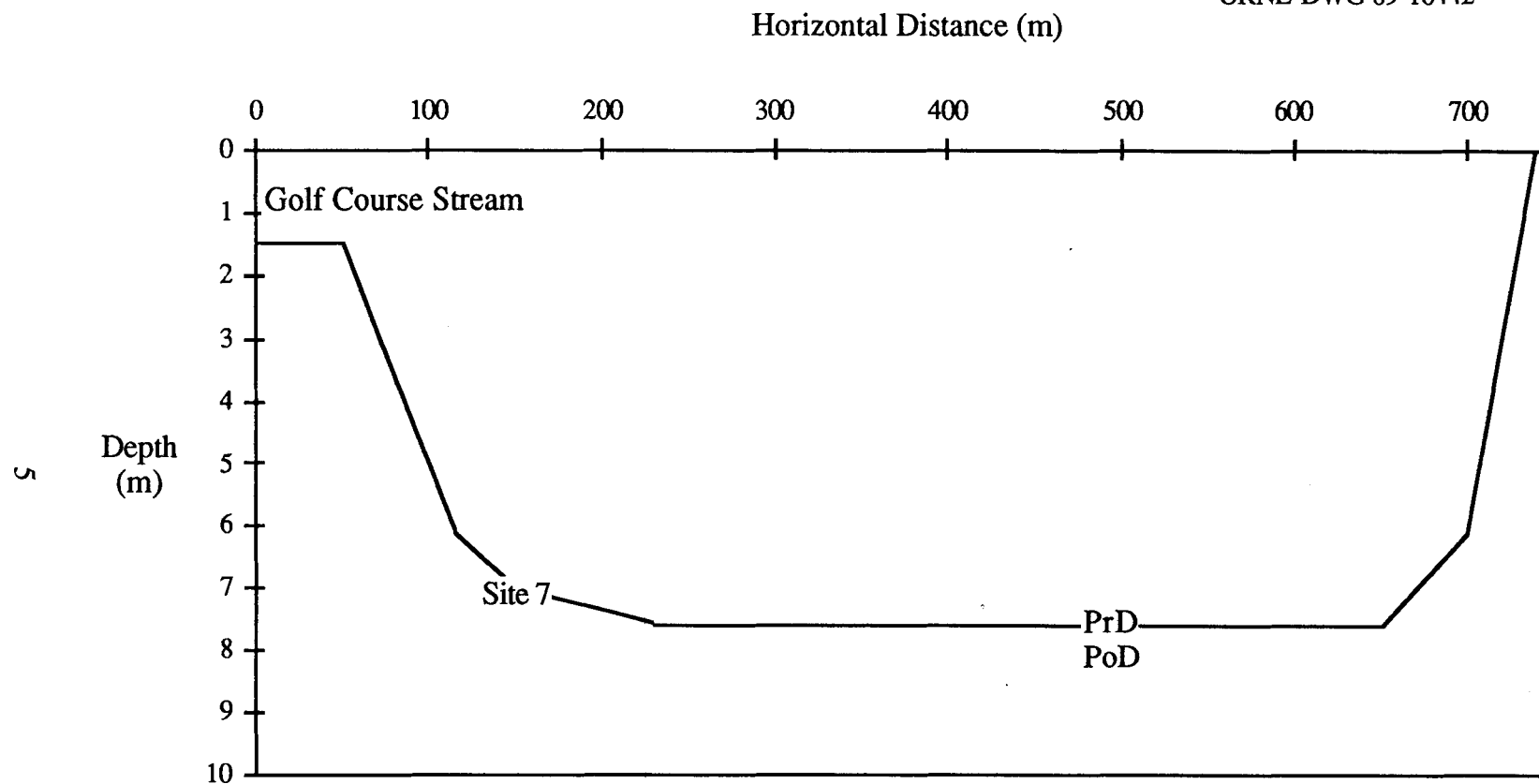


Fig. 4. Cross section A-A'.

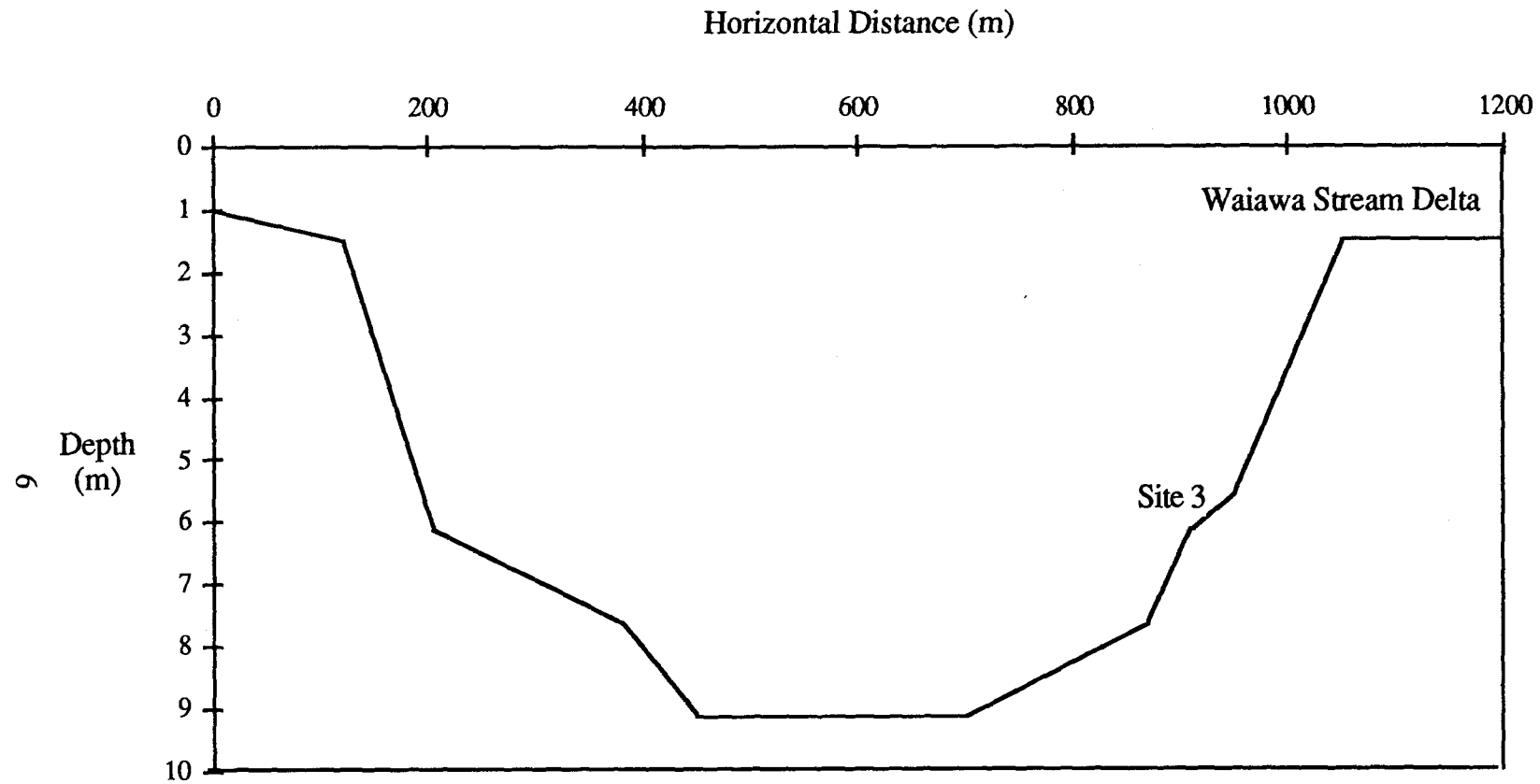


Fig. 5. Cross section B-B

Over 20 ships and craft, as well as sections of floating drydocks, are moored in the areas indicated in Fig. 2. These vessels have been released from "active" status and are maintained by staff and contractors of the U.S. Naval Sea Systems Command Detachment, Navy Inactive Fleet. Vessels are moved into mooring position with harbor tugs. Personnel and maintenance equipment (e.g., floating cranes and work barges) are transported between shore facilities and the ships using smaller "Mike Boats" and runabouts. Maintenance typically consists of dehumidification of the internal spaces on selected ships, active cathodic protection on all vessels, removal of blistered paint and repainting of exterior surfaces, and installation and monitoring of fire and flooding alarms.

## 1.2 PREVIOUS STUDIES

During the late 1960s and early 1970s, a number of environmentally relevant studies were conducted in Pearl Harbor by the U.S. Navy and its contractors (Cahill et al. 1972, Evans 1974, Fan 1976, Turner 1975, Youngberg 1973). Cahill et al. (1972) collected sediment, water, and biological samples from each of the lochs and analyzed those samples for radioisotopes. They concluded that  $^{60}\text{Co}$  released from nuclear submarines in Southeast Loch was confined to the sediments in the immediate vicinity of the submarine pens. Youngberg (1973) sampled sediments throughout Pearl Harbor and in the surrounding streams and analyzed the samples for several major and trace metals. He also analyzed soils from around the Pearl Harbor watershed. Youngberg's data is quoted by Turner (1975), who studied the mineralogy of Pearl Harbor sediments. The extensive Pearl Harbor biological survey (Evans 1974) also uses Youngberg's data to examine sources and biological effects of contamination in Pearl Harbor.

Subsequent to the mid-1970s, there were no published environmental studies on Pearl Harbor until the mid-1980s when Oak Ridge National Laboratory (ORNL) conducted a study of sediment contamination in Middle and West Lochs for the U.S. Navy Inactive Fleet (Ashwood et al. 1986, Ashwood and Olsen 1988). This study provided a pollution chronology for Middle Loch which indicated that trace metal contamination of Middle Loch began prior to the beginning of Inactive Fleet operations. Ashwood et al. (1986) also found that the trace metal signature (i.e., ratios of Cu, Pb, and Zn) in recent sediments were not consistent with the trace metal signature in paint. Both Evans (1974) and Ashwood et al. (1986) concluded that the primary source of trace metal contamination in Middle Loch was the direct discharge of sewage sludge from the Pearl City Sewage Treatment Plant. Ashwood and Olsen (1988) demonstrated that the Japanese bombing attack left a legacy of trace metal contamination in Middle Loch that was greater than all of the trace metal inputs in the 45 years subsequent to the attack.

Data from these earlier studies indicate that the highest concentrations of trace metals relevant to the current study are found in the sediments of Southeast Loch (Table 1). This loch is the site of the heaviest industrial activity associated with the PHNS. With the exception of cadmium, recent (i.e., 1972-1985) Middle Loch sediments contain higher levels of trace metals than do the recent sediments in either East or West Loch. Levels of Cu, Pb, and Zn have increased in Middle Loch sediments since the early 1900s when construction began on PHNS.

Table 1. Summary of trace metal data from previous studies.

Study Area	Period	No. of samples	Trace metal concentrations (mg/kg)					
			Cd	Cr	Cu	Ni	Pb	Zn
Middle Loch	1985 <sup>a</sup>	6	NR <sup>b</sup>	220 ± 28	178 ± 38	150 ± 17	49 ± 17	303 ± 89
	1972 <sup>c</sup>	11	0.2 ± 0.3	156 ± 32	105 ± 57	206 ± 162	32 ± 30	187 ± 85
	ca. 1900 <sup>d</sup>	4	NR <sup>b</sup>	300 ± 61	115 ± 24	193 ± 53	3 ± 2	134 ± 53
Upper West Loch	1985 <sup>e</sup>	1	NR <sup>b</sup>	NR <sup>b</sup>	125	NR <sup>b</sup>	38	157
	1972 <sup>c</sup>	10	0.5 ± 0.4	120 ± 39	72 ± 25	200 ± 120	20 ± 7	160 ± 43
Upper East Loch	1972 <sup>c</sup>	24	0.1 ± 0.2	100 ± 16	60 ± 27	130 ± 74	33 ± 24	120 ± 39
Southeast Loch	1972 <sup>c</sup>	39	1.7 ± 2.7	100 ± 62	240 ± 240	84 ± 43	210 ± 300	350 ± 400

<sup>a</sup> Based on 0- to 2-cm depth interval of cores CA, GD, GE, GG, and GH, and the 8- to 12-cm interval from core CX in Ashwood et al. (1986).

<sup>b</sup> NR = not reported.

<sup>c</sup> From Table 3.1-3 in Evans (1974).

<sup>d</sup> Based on the deepest sediment in cores CA, CX, GE, and GH in Ashwood et al. (1986).

<sup>e</sup> Based on the 0- to 2-cm depth interval of core WL-2 in Ashwood et al. (1986).

## 2. METHODOLOGY

In order to evaluate the impact, if any, of Inactive Fleet operations on Middle Loch sediments, sediment was collected from nine sites within Middle Loch and from two sites in the Golf Course Stream and two sites in the Waiawa Stream (Fig. 2). The sites were chosen to represent areas suspected to be impacted by Inactive Fleet operations (i.e., sites 4 and 5 immediately under or adjacent to ships) as well as areas suspected to be impacted by stream inputs (i.e., sites 3, 7 and 9) and areas removed from any external inputs (i.e., sites 1, 2, 6, and 8). A complete description of each site is included in Appendix B.

While we were in the field, an opportunity arose to obtain samples before and after a sediment disturbance. Specifically, the USS Davidson was brought into a mooring site in Middle Loch by harbor tugs. Harbor tugs have large propellers and powerful engines that can stir up bottom sediments even in 6 to 7 m of water. We sampled a location near the mooring site and in the path of the tugs (labeled PrD in Figs. 2 and 4) on the afternoon of December 7, 1988, before the ship arrived. We also sampled the same site (labeled PoD in Figs. 2 and 4 to distinguish the results from the PrD samples) on the morning of December 8, 1988, after the ship had been moored.

In order to assure that the evaluation of contamination sources was based on recent sediments and not on older sediments exposed by erosion or deposited more than a year ago,  $^7\text{Be}$  was used as a natural tracer. Beryllium-7 is a naturally occurring radioisotope produced in the atmosphere by cosmic-ray spallation of nitrogen atoms. Rainfall washes the  $^7\text{Be}$  from the atmosphere onto land and aquatic surfaces. Beryllium-7 is highly particle reactive at pH values above 5.5 ( $K_d^* = 10^5$ ) and rapidly adsorbs onto any particulate matter (Olsen et al. 1985). In aquatic systems,  $^7\text{Be}$  is removed from the water column (over a period of a few days) and deposited to the sediments. Due to its 53.3-d half-life,  $^7\text{Be}$  is found only in sediments which have recently been in the water column. Sediment samples from each site were analyzed for  $^7\text{Be}$ . In addition, rain-bucket samples and samples of water from Middle Loch were analyzed for  $^7\text{Be}$  in order to determine  $^7\text{Be}$  input to Middle Loch and how much remained in the water column.

The following sections describe the methodologies employed for sample collection and analyses.

### 2.1 SAMPLE COLLECTION

Sediment, rainwater, and water samples from Middle Loch and surrounding streams were collected by the authors, using SCUBA gear, during a period from December 7 through December 14, 1988. A special safety plan was developed for the SCUBA diving portion of the project and is included in Appendix C.

#### 2.1.1 Sediment Samples

All sediment samples were obtained by using plastic core barrels having an internal cross-sectional area of 17.4 cm<sup>2</sup>. At sites 1 through 9 (Fig. 2), the core barrels were pushed into the sediment by a diver. A detailed description of the SCUBA coring technique and descriptions of each of the nine cores is presented in Appendix B. Three separate cores were obtained within a

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\*  $K_d$  is a distribution coefficient which measures the affinity of a substance for suspended matter.

$$K_d = \frac{\left( \frac{\text{mg adsorbed } ^7\text{Be}}{\text{kg suspended matter}} \right)}{\left( \frac{\text{mg dissolved } ^7\text{Be}}{\text{L water}} \right)}$$

1-m radius at sites 3, 5, and 7. Marker buoys attached to heavy metal plates embedded in the sediments were left at these three sites to facilitate future sampling.

At the stream sites and the PrD/PoD site (Fig. 2), the core barrels were placed inside a brass gravity corer and lowered to the sediment from a small boat at the surface.

All core samples were extruded from the core barrels with a stainless steel washer attached to the end of a wooden rod. The sediment was sectioned into 0- to 2-cm, 2- to 5-cm and 5- to 10-cm segments as it was being extruded. Each segment was placed in a plastic-lined, 94 cm<sup>3</sup> aluminum can, which was then hermetically sealed and placed in a refrigerator. Each can was marked with a unique label and the date of sampling.

The process of extruding, sectioning, and canning samples was always completed <2 h after the cores were taken, and usually it was performed in the boat, immediately after the cores were obtained. The cans were kept refrigerated until the authors returned to ORNL.

### 2.1.2 Rainwater Samples

On June 27, 1988, two NOAA rain buckets (638-cm<sup>2</sup> area) were installed on top of two stationary work barges at the Naval Inactive Ships Maintenance Facility (NISMF) on Middle Loch. The buckets were placed at an elevation of approximately 6 m above the level of the loch and were approximately 100 m apart.

On December 12, 1988, the contents of each bucket were transferred to a separate 4-L plastic container. Each bucket was thoroughly rinsed with a small amount of muriatic acid (HCl) to remove any <sup>7</sup>Be adhering to the walls, and the rinseate was added to the plastic container with the rainwater. The plastic containers were returned to ORNL for analysis.

### 2.1.3 Water Column Samples

Also on December 12, 1988, two new 55-gal steel drums were filled with water from Middle Loch adjacent to the NISMF. The water in each drum was acidified by the addition of ~1.9 L (~0.5 gal) of muriatic acid. After mixing the acid and water, FeCl<sub>3</sub> and FeSO<sub>4</sub> were added and observed to thoroughly dissolve. Half of a 100-mL solution of stable Be (996 µg/mL × 100 mL = 99.6 mg of Be) in 2% HCl was added to each drum and thoroughly mixed.

In order to remove the dissolved metals (including any <sup>7</sup>Be and the stable beryllium spike) from the water sample, powdered NaOH was slowly added to each drum while the water was being stirred. Addition of the NaOH continued until the dissolved iron precipitated and flocculated from the dissolved phase as Fe(OH)<sub>3</sub>. During this flocculation process, dissolved metals are scavenged from the water column sample. The floc was allowed to settle, and the drums were decanted by siphoning off the water. The floc was transferred to two 4-L plastic containers, which were returned to ORNL for radionuclide and beryllium analysis.

## 2.2 RADIOISOTOPIC ANALYSIS

Radionuclide activities were measured in ORNL's Environmental Sciences Division by gamma-ray spectrometry with solid state detectors. Calibration of the detectors has been previously described by Larsen and Cutshall (1981).

Canned sediment samples were counted for a minimum of 24 h, using a Nuclear Data 9900 microprocessor system to acquire and store accumulated counts in 4096 channels. A Nuclear Data software program allows for an automated peak search routine to be performed, corrects for the presence of any background contributions, identifies radionuclides by their gamma-ray signature,

performs activity calculations, and corrects for decay based on the elapsed time interval between the sample collection and sample analysis dates.

Table 2 provides decay data and minimum detectable activities (MDAs) for the specific radionuclides of interest in this study.

Table 2. Radionuclide decay properties used in analysis.

Isotope	Photon energy (keV)	Photon abundance (%)	Half-life	Minimum detectable activity (MDA) (pCi)
$^7\text{Be}$	477.6	10.3	53.3 d	10
$^{137}\text{Cs}$	661.6	85.1	30.17 years	5
$^{40}\text{K}$	1460.7	10.7	$1.2 \times 10^9$ years	NA <sup>a</sup>

<sup>a</sup> NA = Not Applicable. Potassium-40 was detected in all samples.

MDA levels are based on Pasternak & Harley (1971). If such quantities of radioactive material were present in the samples when counted for 1000 min, then 95% of the time a value greater than zero would be reported. However, at the low activity levels represented by the MDAs, the relative analytical uncertainty may range from 40 to 100% of the value. The MDA depends upon the composition of the matrix (i.e., other radionuclides present and their amount), the sample size, counting time, detector efficiency, geometry, and any background contributions. Thus, the values reported in Table 2 should not be considered absolutes; they may range up or down by several factors. Their purpose is to provide the general level of sensitivity expected from a typical 1000-min counting interval.

Rainwater samples were evaporated to a volume of 90 mL and transferred to preweighed plastic jars. These jars were analyzed as described above for  $^7\text{Be}$ . Subsequent to gamma counting, the jars were oven evaporated at  $\sim 50^\circ\text{C}$  to dryness, placed in a desiccator overnight, and reweighed to determine the amount of particulate matter that was present in the rain samples.

The iron floc from the water column sample was centrifuged to remove free water and then dried at  $\sim 50^\circ\text{C}$  for  $>72$  h. The dried material was weighed (340.01 g) and then placed in a 0.5-L Marinelli beaker. The beaker was gamma counted similar to the sediment sample cans.

The 0- to 2-cm and 2- to 5-cm depth increments from sites within Middle Loch were initially counted separately as canned. However, only samples from the three sublocations at site 3 contained sufficient  $^7\text{Be}$  to permit detection in both depth increments. Accordingly, the two upper depth increments were combined to form a 0- to 5-cm sample at each of the other sites. Several samples that showed no  $^7\text{Be}$  in 24 h were counted for longer periods, ranging up to 5 d.

Early results from the gamma counting of core 5A showed little  $^7\text{Be}$ . Because the site 7 cores would provide an estimate of small-scale spatial variability in an area with comparatively little  $^7\text{Be}$ , duplication of the variability data at site 5 was deemed unnecessary. Accordingly, no attempt

was made to count the 0- to 5-cm depth increments of cores 5B and 5C. Similarly, these cores were not submitted for chemical analyses.

## 2.3 CHEMICAL ANALYSES

After the radioisotope data (Section 3.1) was reviewed, core 7C was dropped from further analysis. Potassium-40 concentrations for cores 7C and 7B indicated that the cores had similar sediment types, and the absence of  $^7\text{Be}$  in core 7C meant that the sediment in this core did not meet the criteria for consideration as recent material.

### 2.3.1 Analysis for Metals

The top 5 cm at each sediment sample site was air dried at  $\sim 50^\circ\text{C}$  for  $>72$  h and then ground to a fine powder, using an agate mortar and pestle which were thoroughly cleaned after each sample to avoid cross-contamination. The powder from each sample was divided between two plastic vials and sealed with a plastic cap. The vials were marked with the sample identifier and the date of sampling. One vial of material for each sample was submitted for metals analysis and the remaining vial was submitted for total carbon and inorganic carbon analysis.

Sediment samples were digested for metals analysis as follows. A measured quantity ( $\sim 250$  mg) of the fine powder was dissolved in a mixture of nitric acid ( $\text{HNO}_3$ ) and hydrogen fluoride ( $\text{HF}$ ). This solution was heated and evaporated until it was nearly dry and then redissolved in 8 N  $\text{HNO}_3$ . The new solution was again heated and evaporated until nearly dry and then made up to  $\sim 50$  ml with 2%  $\text{HNO}_3$ . After preparation, the solution was injected into an inductively coupled plasma spectrometer (ICP) to determine the concentrations of several metals. The boiling  $\text{HF-HNO}_3$  preparation was chosen in order to dissolve the entire sample matrix. Because the solutions are boiled to near dryness, this preparation does not yield accurate values for silicon and boron, but these are not elements of concern in this study.

Approximately 10 g of the dried material from the water column sample was ground to a powder by using an agate mortar and pestle. The powder was placed in a plastic vial similar to the sediment samples. One gram of the powder was dissolved in  $\text{HNO}_3$  and analyzed by flame emission atomic absorption spectrometry for beryllium.

### 2.3.2 Analyses for Carbon

Total carbon was measured on a LECO analyzer. Inorganic carbon was obtained by reacting the sample with phosphoric acid and measuring the  $\text{CO}_2$  produced with an Oceanography International Carbon Analyzer. This procedure is identical to that in U.S. Environmental Protection Agency (EPA) Method 9060. Total organic carbon was obtained by subtracting inorganic carbon from total carbon.

### 2.3.3 Quality Control

All chemical analyses were performed by the Analytical Chemistry Division of ORNL. This division has been certified as part of the EPA's Certified Laboratory Program. In addition to their standard internal QA/QC practices (e.g., duplicates, blank analyses, spikes, and comparison with various standard reference materials), we submitted a blind duplicate of the sample from site 9 and blind National Bureau of Standards (NBS) 1645 (River Sediment) and 1646 (Estuarine Sediment) standards. The laboratory also ran its own set of NBS 1645 and 1646 samples as well as a U.S. Geological Survey (USGS) MAG-1 sample. Results of the laboratory selected duplicates, standards, and the blind samples on metals of interest to the study are presented in Table 3.

Table 3. Analytical results for standards and duplicates on metals of interest

Standard/Sample	Major metals (%)					Trace metals (mg/kg)					
	Al	Ca	Fe	Na	Ti	Cd	Cr	Cu	Ni	Pb	Zn
NBS 1645 Certified	2.26	2.90	11.3	0.54	NR <sup>1</sup>	10.2	2.96 <sup>2</sup>	109	45.8	714	1720
NBS 1645 Observed (Blind)	2.31	2.39	8.96	<0.04	NR <sup>1</sup>	10.3	>0.15 <sup>2</sup>	111	35.8	591	>875
NBS 1645 Observed	2.16	2.72	8.74	0.48	NR <sup>1</sup>	10.4	2.60 <sup>2</sup>	105	33.6	718	1760
NBS 1646 Certified	6.25	0.83	3.35	2.00	0.51	0.4	76	18	32	28.2	138
NBS 1646 Observed (Blind)	6.12	0.80	3.01	1.9	0.33	3.3	67	15	29	31.5	136
NBS 1646 Observed	6.10	0.77	3.07	1.58	0.34	3.3	70	14	26	29.8	135
USGS MAG-1 Certified	8.66	0.98	4.75	2.84	0.45	0.2	97	30	53	24.0	130
USGS MAG-1 Observed	7.54	0.93	3.41	2.36	0.34	3.3	107	24	66	27.8	141
SCUBA-4	6.16	2.80	4.77	6.17	0.35	4.0	140	339	99	45.7	307
SCUBA-4 Duplicate	6.12	2.76	4.78	6.38	0.34	4.1	137	317	96	45.8	308
SCUBA-9	8.32	2.85	10.5	0.10	0.36	6.3	298	158	165	31.1	218
SCUBA-9 Duplicate (Blind)	8.62	3.06	10.8	0.28	0.39	5.9	314	175	178	35.1	176
Waiawa Stream-1	7.88	0.86	8.84	3.03	0.34	6.3	228	169	149	70.0	216
Waiawa Stream-2 Duplicate	8.54	0.94	9.44	2.91	0.39	6.5	251	190	167	67.6	233

<sup>a</sup> NR = Not Reported

<sup>b</sup> Values given in %

In general, there is reasonable agreement between the ICP results and the standards. Reproducibility between duplicates is also acceptable. However, two important points need to be considered:

1. Reported values for iron and titanium are lower than the standards (recovery is 65-75% for titanium and 72-90% for iron, per Table 3). Our earlier study indicated that iron and titanium were abundant in Middle Loch sediments (Ashwood et al. 1986). On the other hand, recovery of aluminum and calcium is reasonable (87-102% for aluminum; >93% for calcium, except blind 1645; Table 3). The aluminum and calcium results indicate that the HF-HNO<sub>3</sub> preparation effectively breaks down the sediment matrix and any associated carbonate materials. The earlier study used a LiBO<sub>2</sub> preparation method in addition to the HF-HNO<sub>3</sub> method used in this study and achieved adequate iron and titanium recovery (Ashwood et al. 1986). It appears that the HF-HNO<sub>3</sub> preparation does not fully recover these two elements, perhaps due to losses during the heating of the HF-HNO<sub>3</sub> solution. Recovery values for sodium are also low for the standards (Table 3). However, the predominant source of sodium in the Middle Loch samples is NaCl, which should be readily dissolved in the HF-HNO<sub>3</sub> preparation.

With the exception of nickel, trace metal recovery rates appear adequate (Table 3). Trace metals are typically adsorbed to the surface of sediment particles and should be dissolved by the HF-HNO<sub>3</sub> preparation.

2. At levels near 10 mg/kg, the ICP results for cadmium are quite accurate. However, when cadmium values are below 1 mg/kg, the ICP still reports a value of 3.3 mg/kg. Hence, ICP values between 3.3 and 10 mg/kg must be considered suspect. This finding will be discussed further in Sect. 3.

### 3. RESULTS

#### 3.1 RADIOISOTOPES

The analysis described in Sect. 2.2.1 provides data on the abundance of a number of radionuclides. For this study, only three radionuclides were of interest:  $^7\text{Be}$ ,  $^{40}\text{K}$ , and  $^{60}\text{Co}$ . Cobalt-60 is an activation product produced and discharged by some nuclear reactors. Previous studies (Cahill et al. 1972) documented the presence of  $^{60}\text{Co}$  in Pearl Harbor sediments. We found no evidence of  $^{60}\text{Co}$  in Middle Loch during this study. For completeness and possible future reference, data on the abundance of  $^{137}\text{Cs}$  are also included (Table 4). This study focuses on recent sediment; hence, the older and deeper sediments needed to utilize  $^{137}\text{Cs}$  for radio-dating were not sampled. Readers interested in a pollution chronology of Middle Loch are referred to Ashwood et al. (1986).

Table 4. Results of gamma-ray spectrometry for selected radioisotopes of interest

Core (Segment)	Wet weight (g)	Dry weight (g)	Total $^7\text{Be}$ (pCi)	$^7\text{Be}$ inventory (pCi/cm <sup>2</sup> )	Total $^{137}\text{Cs}$ (pCi)	Total $^{40}\text{K}$ (pCi)	$^{40}\text{K}$ concentration (pCi/g)
SCUBA-1 (0-5 cm)	102.52	15.28	11.2	0.6	2.8	60.1	3.9
SCUBA-1 (5-10 cm)	91.47	23.80	0.0	0.0	4.9	100.6	4.2
SCUBA-2 (0-5 cm)	95.65	19.00	8.8	0.5	3.7	120.0	6.3
SCUBA-2 (5-10 cm)	105.66	29.41	0.0	0.0	5.4	302.0	10.3
SCUBA-3A (0-2 cm)	29.21	3.80	9.1	0.5	1.3	67.0	17.6
SCUBA-3A (2-5 cm)	45.08	11.40	25.8	1.5	6.1	78.0	6.8
SCUBA-3A (5-10 cm)	108.82	29.75	69.8	4.0	15.2	199.0	6.7
SCUBA-3B (0-2 cm)	45.51	4.29	6.6	0.4	1.4	64.0	14.9
SCUBA-3B (2-5 cm)	52.18	12.99	30.2	1.7	5.6	81.2	6.3
SCUBA-3B (5-10 cm)	108.41	28.97	67.3	3.9	14.1	153.0	5.3
SCUBA-3C (0-2 cm)	33.77	3.19	7.9	0.5	1.2	60.0	18.8
SCUBA-3C (2-5 cm)	48.49	12.95	15.2	0.9	5.2	89.0	6.9
SCUBA-3C (5-10 cm)	101.05	30.00	52.9	3.0	18.5	132.0	4.4
Average SCUBA-3 (0-10 cm)				5.5			9.0
SCUBA-4 (0-5 cm)	74.44	12.68	11.6	0.7	1.1	33.9	2.7
SCUBA-4 (5-10 cm)	86.54	21.12	6.4	0.4	3.1	143.0	6.8
SCUBA-5A (0-5 cm)	74.82	8.33	8.4	0.5	1.6	50.1	6.0
SCUBA-5A (5-10 cm)	91.37	20.61	0.0	0.0	2.9	69.0	3.3
SCUBA-6 (0-5 cm)	77.00	15.25	7.0	0.4	2.5	215.0	14.1
SCUBA-6 (5-10 cm)	93.82	26.23	0.0	0.0	5.8	324.0	12.4

Table 4 (continued)

Core (Segment)	Wet weight (g)	Dry weight (g)	Total $^7\text{Be}$ (pCi)	$^7\text{Be}$ inventory (pCi/cm <sup>2</sup> )	Total $^{137}\text{Cs}$ (pCi)	Total $^{40}\text{K}$ (pCi)	$^{40}\text{K}$ concentration (pCi/g)
SCUBA-7A (0-5 cm)	90.69	15.68	4.9	0.3	2.8	261.0	16.6
SCUBA-7A (5-10 cm)	87.55	21.92	0.0	0.0	4.3	283.0	12.9
SCUBA-7B (0-5 cm)	78.51	15.70	0.0	0.0	2.8	74.3	4.7
SCUBA-7B (5-10 cm)	69.65	16.79	0.0	0.0	3.2	88.6	5.3
SCUBA-7C (0-5 cm)	70.36	16.39	0.0	0.0	2.7	136.0	8.3
SCUBA-7C (5-10 cm)	72.53	17.46	0.0	0.0	2.6	286.0	16.4
SCUBA-8 (0-5 cm)	78.76	25.06	0.0	0.0	3.8	143.0	5.7
SCUBA-8 (5-10 cm)	112.66	26.84	0.0	0.0	5.1	168.0	6.3
SCUBA-9 (0-5 cm)	97.58	33.63	8.1	0.5	1.1	141.0	4.2
SCUBA-9 (5-10 cm)	128.77	75.41	0.0	0.0	2.0	230.4	3.1
Waiawa Stream-1 (0-5 cm)	109.94	26.33	23.9	1.4	11.3	314.0	11.9
Waiawa Stream-2 (5-10 cm)	112.63	28.94	33.0	1.9	13.5	70.0	2.4
Average Waiawa Stream				1.6			7.2
Golf Course Stream-1 (0-5 cm)	118.55	41.55	18.9	1.1	4.1	211.0	5.1
Golf Course Stream-2 (5-10 cm)	114.78	37.74	80.3	4.6	4.4	132.9	3.5
Pre-Davidson (0-4 cm)	79.71	25.59	0.0	0.0	2.7	68.6	2.7
Post-Davidson (0-5 cm)	90.36	24.68	0.0	0.0	4.3	91.2	3.7

### 3.1.1 Beryllium-7

One rain bucket contained  $249 \pm 9.6$  pCi of  $^7\text{Be}$ . The second rain bucket contained  $256 \pm 9.0$  pCi of  $^7\text{Be}$ . Since each rain bucket sampled an area of  $638 \text{ cm}^2$ , the average inventory of  $^7\text{Be}$  supported by precipitation is  $0.40 \pm 0.01$  pCi/cm<sup>2</sup>. If this material were evenly deposited over the sediments in Middle Loch, one would expect to find an inventory of  $0.40 \text{ pCi/cm}^2$  at each sample site.

The area of Middle Loch [as measured from Defense Mapping Agency (1984)] is  $3.0 \text{ km}^2$  ( $3.0 \times 10^{10} \text{ cm}^2$ ). Hence, the total activity of naturally occurring  $^7\text{Be}$  deposited to the surface waters of Middle Loch, and still expected to be present, was  $1.2 \times 10^{10}$  pCi. This activity should be present in either the water or sediments of Middle Loch, unless  $^7\text{Be}$  has been transported into or out of the loch.

Atomic absorption analysis of water column material indicated that we recovered virtually all (98.9 mg recovered + 99.6 mg added = 99%: see Sect. 2.1.3) of the stable beryllium spike, indicating recovery of virtually all of the dissolved  $^7\text{Be}$  present in the water sample. The floc contained  $75 \pm 11$  pCi of  $^7\text{Be}$ , and the combined volume of two 55-gal drums is 425 L. Thus, the water in Middle Loch contained  $0.18 \pm 0.03$  pCi/L of  $^7\text{Be}$ . The estimated average depth of Middle Loch is  $\sim 7$  m (Fig. 3), which yields a total volume of  $21 \times 10^6$  m<sup>3</sup>, or  $2.1 \times 10^{10}$  L. At the average concentration indicated above, the Middle Loch water column still contained  $\sim 0.4 \times 10^{10}$  pCi of  $^7\text{Be}$ --33% of the total activity expected to be present.

It is not surprising that a third of the  $^7\text{Be}$  remained in the water column, as the Pearl Harbor area had received lower than usual rainfall prior to December (Walt Leonard, U.S. Naval Sea Systems Command Detachment, NISMF Pearl Harbor, personal communication, December 1988) and there was a steady rainfall for the two days immediately preceding the sample period (Walt Leonard, U.S. Naval Sea Systems Command Detachment, NISMF Pearl Harbor, personal communication, December 1988). It appears that a large fraction of the recent rain input of  $^7\text{Be}$  had not settled out of the water column prior to sampling.

The net result of the preceding analysis is that only 67% of the  $^7\text{Be}$  input could have reached the sediments--and that assumes that none was exported. Thus, the average sediment inventory should be about 0.27 pCi/cm<sup>2</sup>.

The experiment was planned based on  $^7\text{Be}$  inventories encountered in previous studies, where precipitation supports inventories that range from 1 to 2 pCi/cm<sup>2</sup> (Olsen et al. 1985). At these levels, a core area of 17.4 cm<sup>2</sup> would yield sufficient  $^7\text{Be}$  to be readily detected. However, with only 0.27 pCi/cm<sup>2</sup>, the same core would only be expected to contain  $\sim 5$  pCi--an activity very near the limit of detection (Table 2).

Notwithstanding the above discussion,  $^7\text{Be}$  was detected at all but two sites (Table 4 and Fig. 6). In general the precision of the data is not high due to the low activities present; but the values are in the range expected. The presence of  $^7\text{Be}$  indicates that sediment in the 0- to 5-cm depth increment at all sites, except at sites 8 and PrD/PoD, has recently been in the water column--and thus reflects recent contaminant inputs. Moreover, within the available precision, the sediments of Middle Loch appear to contain all of the  $^7\text{Be}$  predicted from the rain bucket and water sample data. This suggests that Middle Loch effectively traps all of the  $^7\text{Be}$  input. If this trapping extends to other particle-reactive contaminants, as would be expected, then contamination input to Middle Loch would not impact other areas of Pearl Harbor.

The similarity between the relatively high  $^7\text{Be}$  inventories in the top 5 cm of Waiawa Stream sites 1 and 2 and SCUBA site 3 suggests that the material at site 3 is primarily derived from Waiawa Stream. Because site 3 is on the edge of the Waiawa Stream delta (Fig. 5), material from this site would be expected to reflect stream input.

The elevated  $^7\text{Be}$  inventory at site 4 (1.1 pCi/cm<sup>2</sup>: Table 4 and Fig. 6) suggests that this site accumulates sediment at a greater rate than other locations in the deep areas of Middle Loch. This is an important result since it would mean that the presence of vessels (at least ships with relatively deep draft) may act to focus sediment deposition. The previous ORNL study also indicated that sediment accumulation rates under inactive vessels were higher than in other deep areas of the loch (1.5 cm/year in core CX versus  $0.7 \pm 0.4$  cm/year in cores GD, GE, and GG: Table 4 in Ashwood et al. 1986). The difference between the  $^7\text{Be}$  inventory at sites 4 and 5 (0.5 pCi/cm<sup>2</sup>: Table 4 and Fig. 6) suggests that sediment focusing occurs only immediately under the ships.

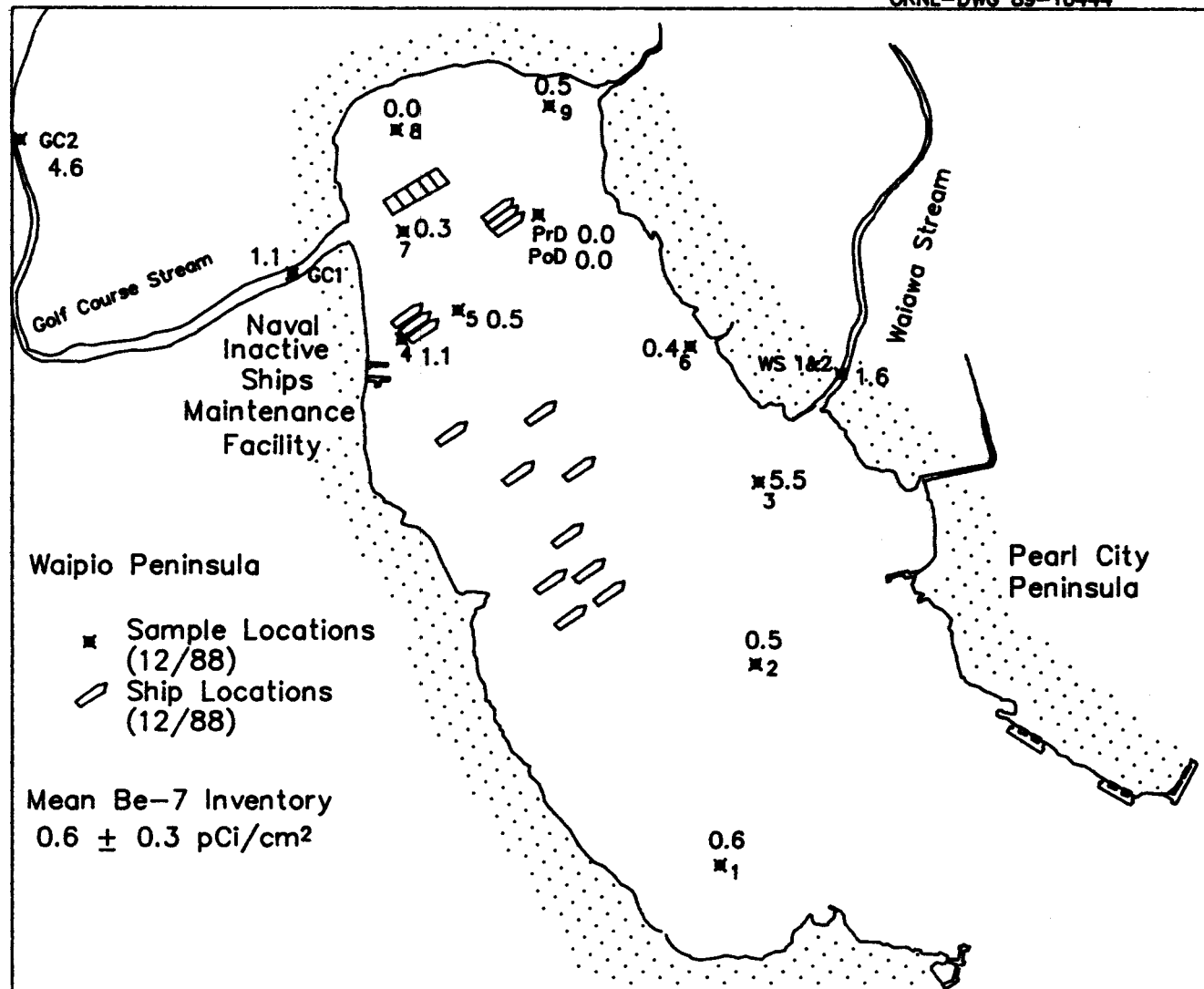


Fig. 6. Beryllium-7 inventories in Middle Loch sediments.

The elevated  $^7\text{Be}$  inventories in the Golf Course Stream (1.1 to 4.6 pCi/cm<sup>2</sup>; Table 4 and Fig. 6) are not reflected at site 7 (0.0 to 0.3 pCi/cm<sup>2</sup>; Table 4 and Fig. 6). This suggests that material derived from the Golf Course Stream accumulates along the shallow margin of the loch and does not influence the adjacent deeper areas such as site 7.

### 3.1.2 Potassium-40

Potassium-40 is a naturally occurring radionuclide that is a constituent of all substances containing potassium. In sediments, the abundance of  $^{40}\text{K}$  is correlated with the clay and silt fraction which is generally the fine-grained material. Hence,  $^{40}\text{K}$  is typically found at higher concentrations in sediments composed of silts and clays and at lower concentrations in sandy sediments.

The relatively high  $^{40}\text{K}$  concentrations in the 0- to 2-cm depth increments of the three cores from site 3 (Table 4) suggest that this material contains fine-grained material, probably of terrigenous origin. On the other hand, the relatively low  $^{40}\text{K}$  concentrations at sites 1 and 4 (Table 4) reflect less fine-grained material.

## 3.2 ORGANIC AND INORGANIC CARBON

High inorganic carbon concentrations at sites 1, 2, 4, and 5 (Table 5) probably reflect the presence of carbonate shell fragments. The presence of such shell fragments was apparent during core collection at sites 4 and 5. At these sites, the shell fragments may represent barnacles from nearby ships. Note that the inorganic carbon values for both cores 7A and 7B are virtually identical. This indicates that the source of variation in  $^{40}\text{K}$  and  $^7\text{Be}$  values between these two sites is not the differences in the levels of carbonate material.

Table 5. Key chemical parameters in Middle Loch

Sample location	Carbon (%)			Major Metals (%)					Trace Metals (mg/kg)						
	Total	Organic <sup>a</sup>	Inorganic	Al	Ca	Al/Ca	Fe	Na	Cd	Cr	Cu	Ni	Pb	Zn	
Site 1	3.7	2.7	1.0	7.3	2.9	2.5	7.3	4.4	4.8	198	173	133	31	263	
Site 2	3.8	2.4	1.5	7.6	3.0	2.5	6.9	3.7	5.1	187	140	124	41	199	
Site 3A	5.8	5.7	0.1	8.1	0.9	9.5	8.8	4.6	5.6	238	166	158	45	182	
Site 3B	5.2	5.1	0.1	7.4	0.9	8.6	8.2	4.9	5.3	218	152	142	53	177	
Site 3C	5.6	5.6	0.1	7.9	0.9	8.6	9.0	4.5	5.4	245	171	160	52	191	
Site 3 Mean	5.6	5.5	0.1	7.8	0.9	8.9	8.6	4.6	5.4	234	163	153	50	183	
Site 4	6.0	4.3	1.7	6.1	2.8	2.2	4.8	6.3	4.0	138	328	98	46	308	
Site 5	4.1	2.7	1.4	6.1	3.0	2.1	5.4	10.2	4.1	152	198	107	34	251	
Site 6	3.5	2.7	0.8	7.3	2.6	2.9	7.5	3.9	5.4	193	152	126	45	225	
Site 7A	3.3	2.7	0.7	7.6	2.3	3.3	7.7	4.4	5.4	205	179	142	55	263	
Site 7B	3.3	2.6	0.7	7.5	2.3	3.3	7.6	4.4	5.0	206	184	143	54	263	
Site 7 Mean	3.3	2.6	0.7	7.5	2.3	3.3	7.7	4.4	5.2	206	182	143	55	263	
Site 8	2.9	2.4	0.6	7.4	2.2	3.3	7.7	4.0	5.4	203	179	137	81	259	
Site 9	2.3	1.6	0.8	8.5	3.0	2.9	10.7	0.2	6.1	306	166	172	33	197	
Waiawa Stream-1	6.0	5.9	0.1	8.2	0.9	9.2	9.1	3.0	6.4	239	179	158	69	224	
Waiawa Stream-2	6.0	5.8	0.1	7.9	1.0	7.6	9.2	3.1	5.6	245	188	161	56	216	
Waiawa Stream Mean	6.0	5.9	0.1	8.1	1.0	8.3	9.2	3.0	6.0	242	184	160	62	220	
Golf Course Stream-1	3.8	3.3	0.6	7.6	2.1	3.6	9.1	1.5	6.3	227	168	158	119	318	
Golf Course Stream-2	5.4	5.2	0.3	8.1	1.4	5.8	9.0	1.4	6.6	238	193	183	179	384	
Pre-Davidson (PrD)	2.9	2.2	0.8	8.0	2.9	2.8	8.3	2.5	5.6	219	151	139	34	206	
Post-Davidson (PoD)	3.1	2.5	0.6	7.7	2.3	3.3	7.9	2.6	5.7	479	164	137	61	>907	

<sup>a</sup> Organic carbon determined by difference between total carbon and total inorganic carbon.

Organic carbon appears high (i.e., >4%) only in the streams, at site 3 on the Waiawa Stream delta, and at site 4 under the destroyers (Table 5). The similarity in organic carbon levels between the Waiawa Stream (6.0%) and site 3 (5.6%) suggests that site 3 material comes from the Waiawa Stream.

Jellyfish and planktivorous fish congregate in the calm space between ships, and parrotfish feed on the fouling organisms on ship hulls (personal observations). Detritus from these animals and the organic fraction of paint debris are the likely sources of organic matter at site 4. The contrast between organic carbon values at sites 4 (4.3%) and 5 (2.7%) suggests that either (1) the source at site 4 is not affecting site 5 or (2) material from the source at site 4 is substantially diluted at site 5 by material from another source.

### 3.3 METALS

The ICP analysis provides data on the abundance of over 40 elements. Of those elements only a few are germane to this study. Al, Ca, Fe, and Ti are major constituents of Hawaiian soils and sediments (Ashwood et al. 1986). Cd, Cr, Cu, Pb, and Zn are components of paints from Navy vessels (Appendix A). Nickel was implicated as a contaminant in Middle Loch in the early studies (Evans 1974, Youngberg 1973), although nickel was not a significant contaminant in our previous investigation (Ashwood et al. 1986), nor is it a major component of paints (Appendix A).

While measured values of metals other than aluminum and calcium yield a picture of contamination at a specific site, they also reflect the specific sedimentary composition at the site. In order to reduce the variability associated with differing amounts of carbonate and authigenic iron-hydroxides at different sites, we chose to normalize iron and all trace metal values to aluminum (Table 6). The normalization equation used is

$$E_i^* = E_i \times \left( \frac{Al_{avg}}{Al_i} \right) \quad (1)$$

where

$E_i$  = measured concentration of element E at site i,

$E_i^*$  = normalized value of  $E_i$ ,

$Al_{avg}$  = average concentration of aluminum at all sites (7.6%),

$Al_i$  = concentration of aluminum at site i.

For sites where duplicates were run (Table 3), the mean value of the duplicates was used in EQ 1. For site 3, the mean of all three cores is shown in Figs. 7-10. For site 7, only the value for core 7A was used in Figs. 7-10, since core 7B did not contain recent sediments (as indicated by the absence of detectable  $^7Be$ ). Statistical data (mean and standard deviation) in Figs. 8-10 are based only on those sites within Middle Loch that contained recent sediment (i.e., sites 1-7A and 9).

Table 6. Iron and trace metal concentrations normalized to average aluminum concentration

Sample location	Al <sup>a</sup>	Fe <sup>a</sup>	Cd <sup>a</sup>	Cr <sup>a</sup>	Cu <sup>a</sup>	Ni <sup>a</sup>	Pb <sup>a</sup>	Zn <sup>a</sup>
Site 1	7.3	7.6	5.0	206	180	139	33	274
Site 2	7.6	6.9	5.1	187	140	124	41	199
Site 3 Mean	7.8	8.4	5.3	228	159	149	49	179
Site 4	6.1	5.9	4.9	171	406	121	57	382
Site 5	6.1	6.7	5.1	189	246	133	42	311
Site 6	7.3	7.8	5.6	200	158	131	47	233
Site 7A <sup>b</sup>	7.6	7.7	5.4	206	180	143	55	266
Site 8	7.4	7.9	5.5	208	183	140	83	265
Site 9	8.5	9.6	5.5	275	149	154	30	177
Waiawa Stream Mean	8.1	8.6	5.7	228	173	150	59	207
Golf Course Stream-1	7.6	9.1	6.3	228	169	159	119	319
Golf Course Stream-2	8.1	8.5	6.3	224	182	172	169	362
Pre-Davidson (PrD)	8.0	7.9	5.3	209	144	133	33	197
Post-Davidson (PoD)	7.7	7.8	5.7	476	163	136	60	>900
Recent mean <sup>c</sup>	7.6	7.6	5.2	208	203	137	44	253
Recent standard deviation <sup>c</sup>		1.1	0.2	32	89	12	10	71

<sup>a</sup> Aluminum and iron concentrations given in %; trace metal concentrations given in mg/kg. Iron and trace metal concentrations normalized to aluminum concentration by multiplying the original trace metal concentration by the ratio of the average aluminum concentration (7.6%) to the aluminum concentration in a specific sample.

<sup>b</sup> Site 7A is used in this table and in the figures derived from it because site 7B did not contain <sup>7</sup>Be.

<sup>c</sup> Mean and standard deviation for iron and trace metals calculated only from those sites inside Middle Loch which contained recent sediments (i.e., sites 1-7A and 9). Aluminum mean is for samples at all locations inside and outside Middle Loch (see Table 5).

### 3.3.1 Major Metals

Aluminum is a major element in soils and should be an indicator of terrigenous material. Calcium is also associated with soils, but is more likely to be found as calcium carbonate (CaCO<sub>3</sub>) in the shells of marine organisms. Hence, the Al/Ca ratio should be a strong indicator of the source of sedimentary material. Comparatively high Al/Ca values in the Waiawa Stream samples (mean = 8.3: Table 5 and Fig. 7) and the upper reaches of the Golf Course Stream (5.8: Table 5 and Fig. 7) are indicative of aluminum-rich, terrigenous material. The presence of similarly high Al/Ca values at site 3 (8.6: Table 5 and Fig. 7) is another indication that site 3 material is derived from the Waiawa Stream. Low Al/Ca ratios at sites 1 (2.5), 2 (2.5), 4 (2.2), and 5 (2.1) probably reflect the high calcium carbonate content of sediment at these sites (Table 5 and Fig. 7).

The low recovery of titanium indicated in the QA samples (Table 3) resulted in titanium values for all samples that were much lower than previous data (Ashwood et al. 1986). Such low values are not representative of titanium concentrations in the sediment. For this reason, titanium is not included in this study.

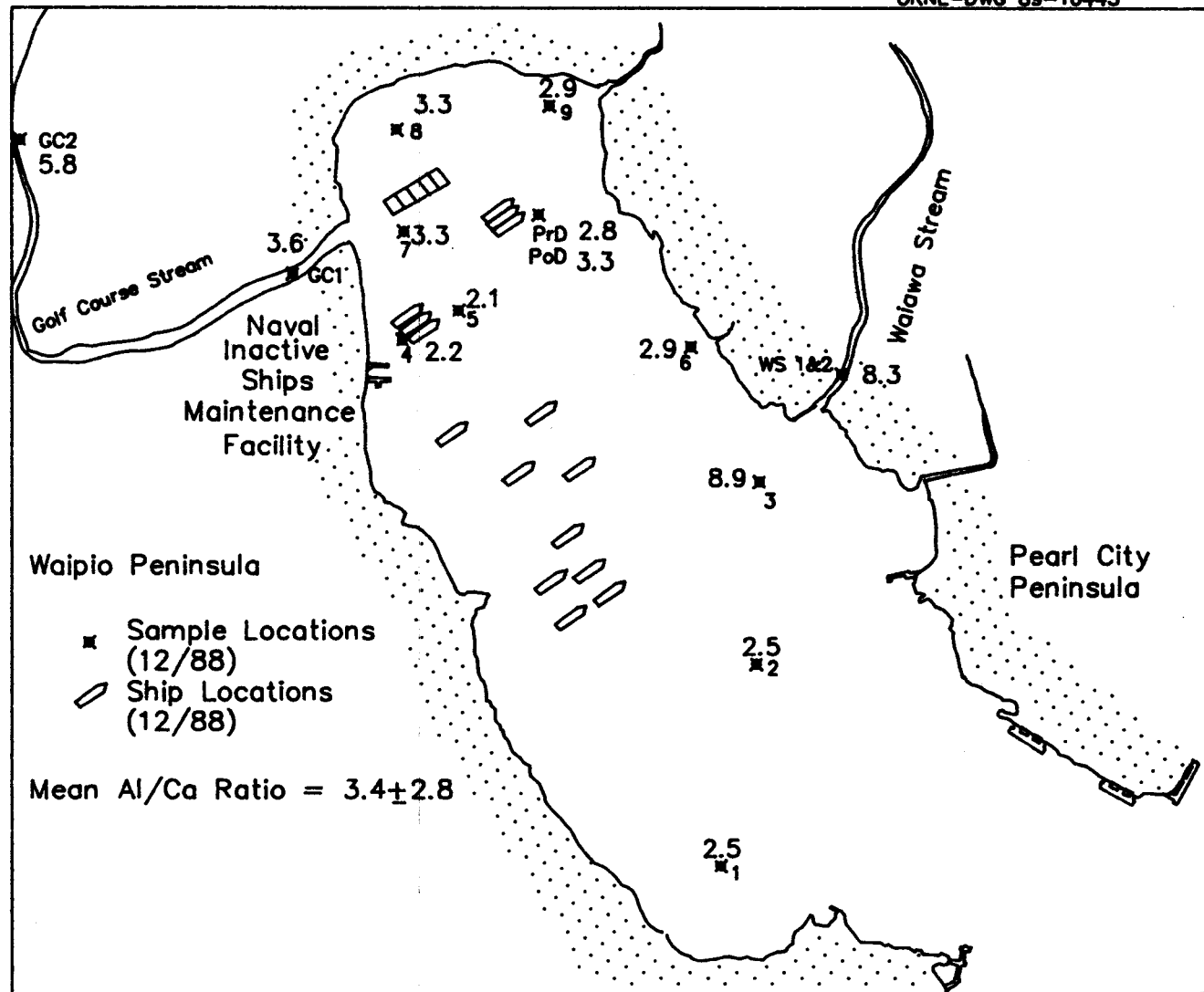


Fig. 7. Al/Ca ratios in Middle Loch sediments.

Both streams contain relatively high concentrations of Fe (Table 6). Once again, site 3 (mean = 8.4%: Table 6) reflects the Waiawa Stream input (8.6%: Table 6). Site 9 also contains elevated iron levels (9.6%: Table 6). Comparatively low iron concentrations at sites 4 (4.9%: Table 6) and 5 (5.4%: Table 6) are more difficult to explain because rust from the ships would be expected to contribute iron to the sediments. Because recovery values for iron were low and variable (Sect. 2.3.3), iron values at sites 4 and 5 may represent an analytical anomaly.

Sodium cannot be used as a direct measurement of salinity because it is a constituent of some minerals (e.g., montmorillonite) known to exist in Middle Loch sediments (Turner 1975). Nevertheless, the major source of sodium in our samples is probably NaCl. Hence, large variations in sodium probably represent variations in NaCl content, which could arise through differences in either the volume or salinity of pore water between samples. While small variations in pore water volume do occur (see differences between wet and dry weights in Table 4), they do not account for the anomalous Na values at sites 4, 5, and 9, and in the Golf Course Stream. Low sodium concentrations at site 9 (0.2%: Table 5) and in the Golf Course Stream samples (1.4-1.5%: Table 5) suggest that the salinity of the pore water at these sites was lower than at other sites in Middle Loch, probably reflecting the freshwater input of the spring (site 9) and stream. More moderate sodium concentrations at site 3 (4.6%: Table 5) and in the Waiawa Stream samples (3.1-3.2%: Table 5), suggest that the estuarine circulation pattern (i.e., marine salinity levels in bottom waters) extends into the Waiawa Stream at least as far as the sample sites. The comparatively high sodium concentrations at sites 4 and 5 are difficult to explain, unless there is another source of sodium at these sites or unless these sites have accumulated more montmorillonite than other areas.

### 3.3.2 Cadmium

While the absolute values of cadmium are suspect due to performance on standards (Sect. 2.4), the pattern in cadmium data appears consistent with the sediment contamination patterns indicated by other data. Moreover, cadmium is a constituent of paint (Appendix A) and an element of great environmental and human health concern. For these reasons, we have included cadmium in this report, and we suggest that the data are of the correct order of magnitude.

The general analytical accuracy for cadmium by ICP is 10-15%. Adding this analytical uncertainty to the standard deviation in Table 6 yields a total measurement uncertainty of  $\pm 0.8$ . When this total uncertainty is used as a measure of variability, none of the values in Table 6 are significantly different than the mean (i.e.,  $p > 0.05$  for all samples). However, certain patterns emerge from the data.

The Golf Course Stream (6.3 mg/kg: Table 6) appears to be a source of cadmium contamination. Cadmium levels in this stream are not reflected at site 7 (5.4 mg/kg: Table 6), indicating that material from the stream is deposited in the shallow area before reaching site 7.

Cadmium concentrations at sites 4 (4.9 mg/kg: Table 6) and 5 (5.1 mg/kg: Table 6) are relatively low, suggesting that either (1) the ships are not acting as sources of cadmium or (2) conditions under the ships are favorable for mobilization of cadmium.

### 3.3.3 Chromium

Chromium is a particularly difficult element to evaluate on the basis of ICP data alone. There are substantial differences in both chemical and biological mobility between the different oxidation states (III and VI). Without knowledge of the chromium species being analyzed and the oxidation potential at each site, interpretation of chromium data is qualitative at best. Nevertheless, chromium is a major constituent of paints (Appendix A) and has been measured in previous studies (see Table 1). For completeness, we have included the chromium data in this report.

Site 9 (275 mg/kg; Table 6) is the only location with recent sediments where chromium was found at >2 standard deviations above the mean ( $208 \pm 32$  mg/kg; Table 6). The post-Davidson sample contains 475 mg/kg (Table 6) of chromium. This is more than twice the pre-Davidson level. Previous studies (Ashwood et al. 1986, Ashwood and Olsen 1988) have documented the presence of chromium at levels exceeding 1000 mg/kg in buried layers. The post-Davidson data suggests that one of those layers may have been exposed or resuspended and redeposited as a result of the Davidson mooring operation (see Sect. 4.1.3).

### 3.3.4 Copper

In the previous ORNL study copper was considered to be an indicator of sewage input because our limited paint data (one sample from an aircraft carrier in Bremerton, Washington) suggested that copper was not a major constituent of paint debris (Ashwood et al. 1986). Subsequent to that study, several samples of paint from various inactive vessels in Middle Loch were analyzed (Appendix A). Data from these samples clearly indicated that copper was a significant component of paint on those vessels (>150,000 mg/kg for samples near a vessel's waterline; 371 mg/kg for samples above the waterline: Appendix A).

Site 4 (406 mg/kg; Table 6 and Fig 8) is the only location in Middle Loch or the adjacent streams where copper is found at levels >2 standard deviations higher than the mean in recent sediments. This strongly suggests that paint debris from inactive vessels is the only current source of copper contamination. The large difference between copper concentrations at site 4 and site 5 (246 mg/kg; Table 6 and Fig. 8) indicates that contamination from the paint debris is restricted to the immediate vicinity of the ships.

Copper concentrations at sites 1 (180 mg/kg; Table 6 and Fig. 8) and 2 (140 mg/kg; Table 6 and Fig. 8) are both below the mean ( $203 \pm 89$  mg/kg; Table 6 and Fig. 8) for recent Middle Loch sediments. This indicates that the lower portion of Middle Loch is unaffected by copper contamination from paint debris. Similarly, the relatively low concentrations at sites 6 (158 mg/kg; Table 6 and Fig. 8) and 7 (180 mg/kg; Table 6 and Fig. 8) suggest that paint-derived copper contamination is not reaching any of the adjacent areas of the loch.

The comparatively low copper value in the Post-Davidson sample (163 mg/kg; Table 6 and Fig. 8) indicates that the material exposed or resuspended and redeposited by the Davidson mooring operation was not rich in copper (see Sect. 4.1.3).

### 3.3.5 Nickel

Nickel is not a major component of paint (Appendix A), nor was it a significant contaminant in the previous ORNL study, where nickel concentrations in recent sediments were found to be no different than concentrations in sediments deposited around the turn of the century (Ashwood et al. 1986). Evans (1974), however, found significant Ni contamination in Middle Loch and attributed it to sewage input.

Only the Golf Course Stream 2 sample (172 mg/kg; Table 6) contains nickel at a concentration > 2 standard deviations different from the mean ( $137 \pm 12$  mg/kg; Table 6). The Golf Course Stream 2 sample is not significantly different ( $p > 0.05$ ) than the mean value for recent sediments ( $168 \pm 32$  mg/kg) in Ashwood et al. (1986). Hence, our data do not identify a source of Ni contamination in Middle Loch.

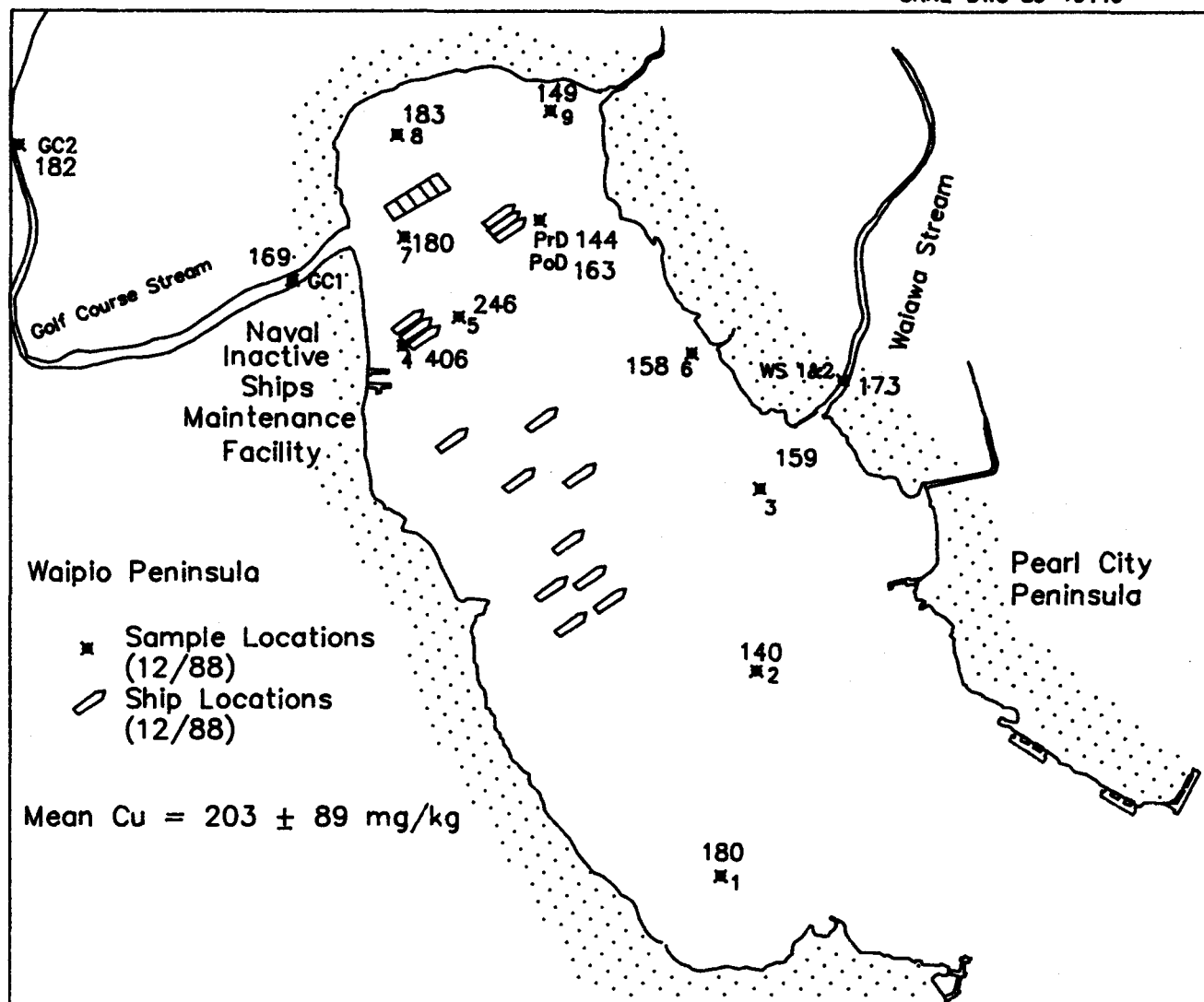


Fig. 8. Copper concentrations in Middle Loch sediments.

### 3.3.6 Lead and Zinc

Both lead and zinc are found at elevated levels in three areas: (1) the Golf Course Stream (lead 119-169 mg/kg; zinc 319-362 mg/kg: Table 6 and Figs. 9 and 10); (2) site 4 (lead 57 mg/kg; zinc 382 mg/kg: Table 6 and Figs. 9 and 10); and (3) the Post-Davidson sample (lead 60 mg/kg; zinc >900 mg/kg: Table 6 and Figs. 9 and 10).

The Golf Course Stream is clearly a source of both lead and zinc contamination to Middle Loch. However, the contamination from this stream does not appear to influence the sediment at site 7 (lead 55 mg/kg; zinc 266 mg/kg: Table 6 and Figs. 9 and 10).

Paint-derived lead and zinc contamination at site 4 does not appear to influence site 5 (lead 42 mg/kg; zinc 311 mg/kg: Table 6 and Figs. 9 and 10). This is consistent with other trace metal, organic carbon, and  $^7\text{Be}$  data, which indicate that sediment at site 5 has a different composition than that at site 4.

None of the sources of lead or zinc contamination appear to have affected sediments in the lower end or the eastern side of Middle Loch (see sites 1, 2, and 6 in Figs. 9 and 10).

### 3.4 EOLIAN INPUT

When the rain-bucket samples were collected, solid material was observed in the buckets. This eolian (windblown) material represents an additional source of sediment to Middle Loch. The rain buckets contained 0.62 and 0.53 g of material during the 6 months they were installed. This represents an eolian sediment input of  $27 \pm 2.8$  tonnes/year ( $30 \pm 3$  tons/year) to Middle Loch. This represents almost 3% of the sediment input from the Waiawa Stream (986 tonnes/year: Fan 1976).

Chemical analysis of the eolian material was beyond the scope of this study. However, some insight can be obtained from the soil data in Youngberg (1973). Youngberg provides this description of soils on most of the Waipio and Pearl City Peninsulas which border Middle Loch (Fig. 2): "Unconsolidated noncalcareous deposits of alluvium. Consist of black to brown coarse detritus only slightly weathered, or in some areas it consists of black sticky mud called 'taro patch clay'" (Youngberg 1973, p. 9).

Only one sample point appears to represent the soil in this area [sample SD03 in Youngberg (1973)]. Trace metal values for this sample are Cd, 0.25 mg/kg; Cr, 140 mg/kg; Cu, 62 mg/kg; Ni, 59 mg/kg; Pb, 63 mg/kg; and Zn, 110 mg/kg. Compared to the values in Table 6, soil in this area would appear to be a potential source only of lead (see Table 7).

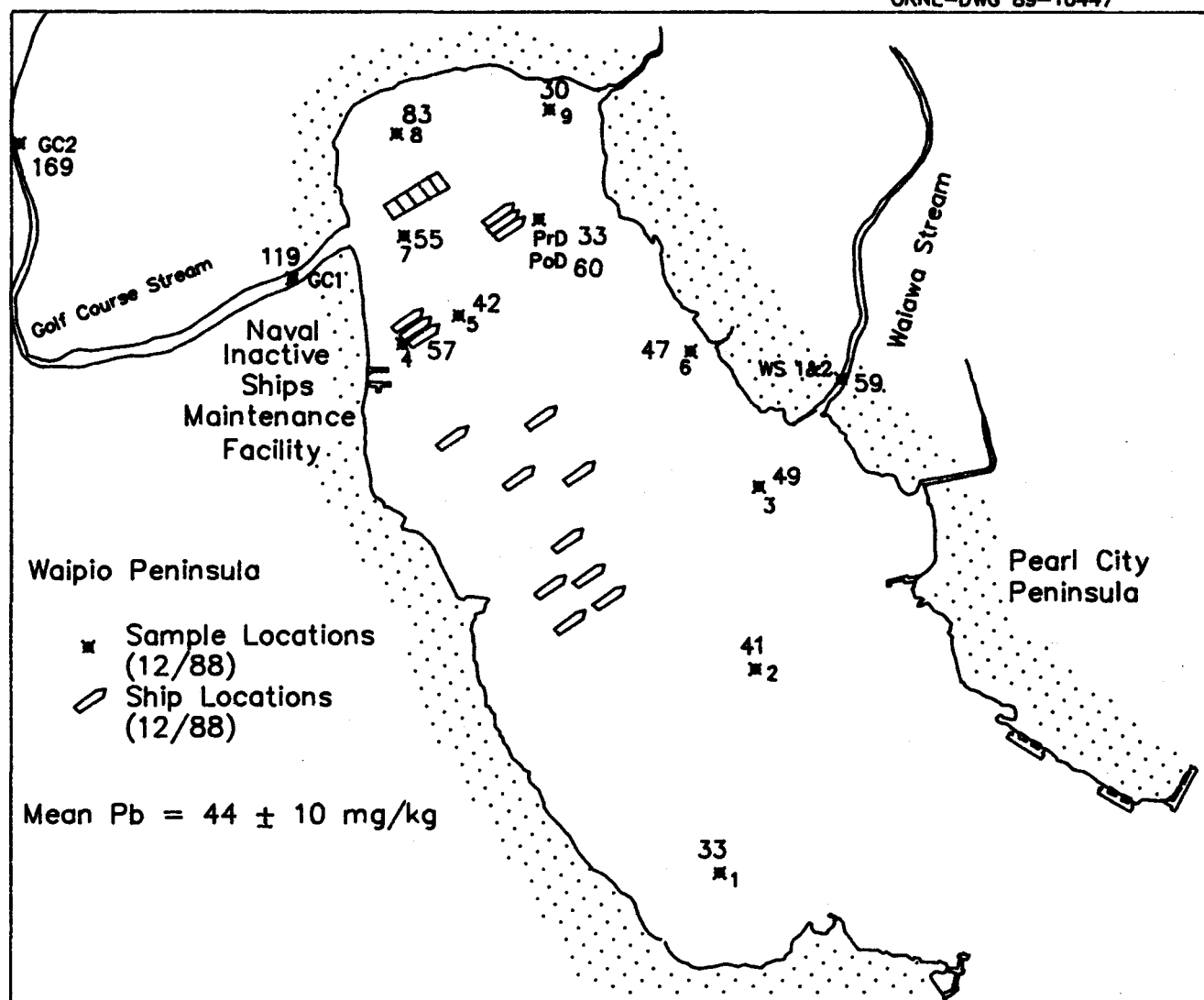


Fig. 9. Lead concentrations in Middle Loch sediments.

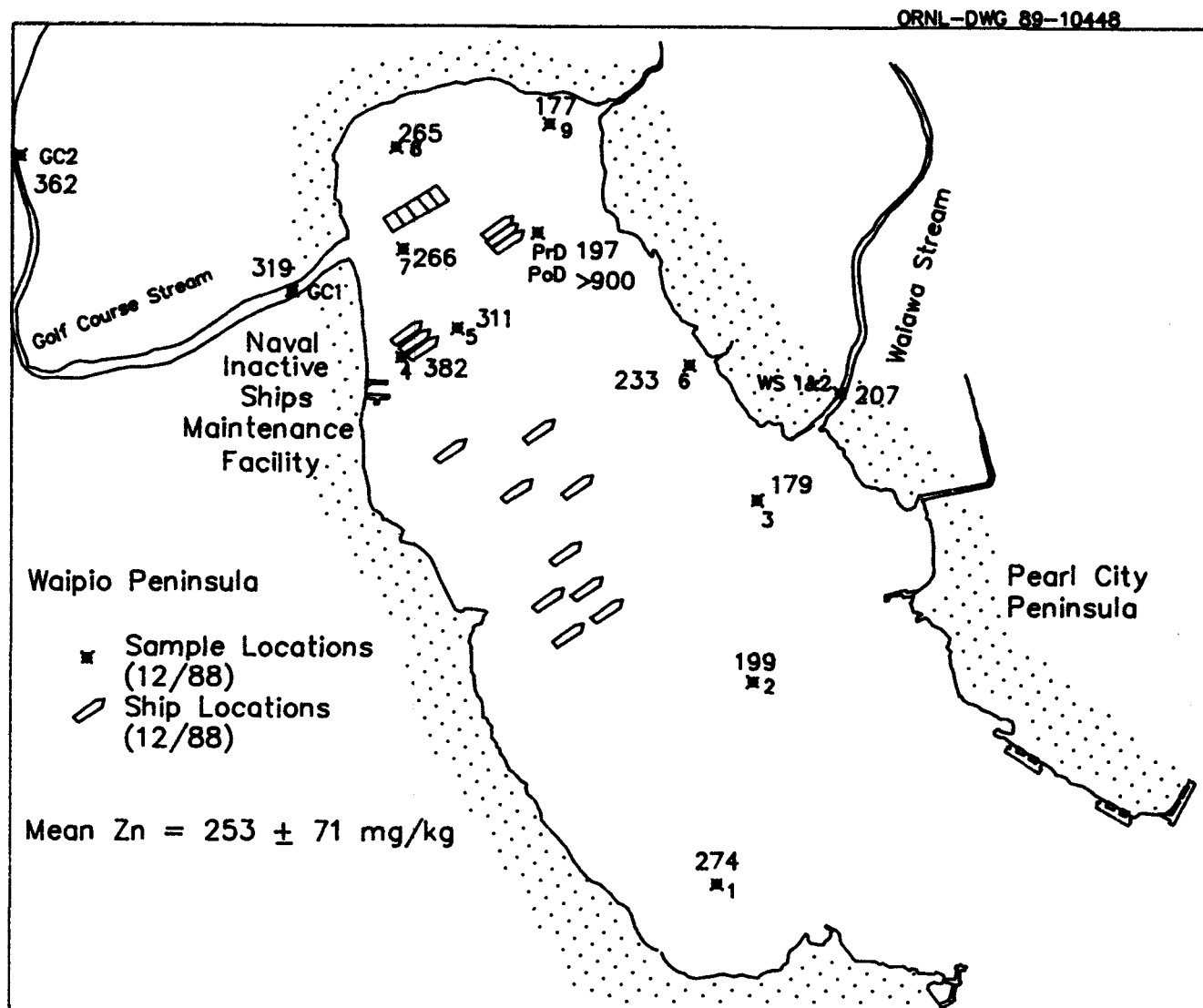


Fig. 10. Zinc concentrations in Middle Loch sediments.

## 4. DISCUSSION

### 4.1 SOURCES OF CONTAMINATION

There appear to be four generic sources of metal contamination in Middle Loch: (1) the freshwater streams entering the loch, (2) paint debris from inactive ships and craft, (3) eolian material, and (4) resuspension of buried sediments containing the legacies of past contamination events. Only the first three of these sources can be quantified with existing data (see Table 7).

Table 7. Sources of trace metal contamination in Middle Loch

Source	Sediment input (tonnes/year)	Trace metal input (kg/year) <sup>a</sup>					
		Cd	Cr	Cu	Ni	Pb	Zn
Waiawa Stream	986 <sup>b</sup>	4.7	195	171	131	31	259
Golf Course Stream	490 <sup>c</sup>	3.1	111	82	77	58	156
Inactive Ships Maintenance Operations	708 <sup>d</sup>	2.8	98	232	69	32	218
Eolian material	27 <sup>e</sup>	<0.1	4	2	2	2	3

<sup>a</sup> Trace metal values from Table 5 were multiplied by the sediment input to obtain the trace metal input values. For Waiawa Stream the average of both Waiawa Stream samples was used. For the Golf Course Stream, sample 1, near the mouth of the stream, was used. For paint debris, the trace metal concentrations for site 4 were used. Eolian material trace metal concentrations were taken from Sect. 3.4, which is based on Youngberg (1973).

<sup>b</sup> Calculated from Fan (1976, Fig. 3).

<sup>c</sup> No data are available on the input of sediment from the Golf Course Stream. Personal observation by the authors would suggest that the sediment input is less than that of Waiawa Stream. A value of half the Waiawa Stream input was used for these calculations.

<sup>d</sup> This value does not represent the amount of paint debris input to Middle Loch. Rather it represents the amount of sediment that accumulates under the vessels. The sediment accumulation rate from core CX (1.5 cm/year: Ashwood et al., 1986) was multiplied by the area calculated to be under moored ships and craft (~210,000 m<sup>2</sup>: from sketch supplied by Walt Leonard, Pearl Harbor NISMF, 1989). The sediment volume thus derived was multiplied by the dry sediment density calculated for the 5- to 10-cm depth increment at site 4 (21.12 g dry weight/94 cm<sup>3</sup> volume of a full can). The 5- to 10-cm depth increment was used because the 0- to 5-cm increment was not a full can.

<sup>e</sup> Value taken from Sect. 3.4.

#### 4.1.1 Stream Inputs

Clearly, the streams are the predominant source of trace metals other than copper. However, most of these contaminants are deposited in the shallow areas near the stream mouths.

The delta at the mouth of the Waiawa Stream is a zone of rapid sediment accumulation (>6 cm/year: Ashwood et al. 1986), and sediment on this delta appears to closely reflect input from Waiawa Stream. Recent sediments from Waiawa Stream contain elevated levels of Cd, Fe,

and Pb (Table 6). The Waiawa stream does not appear to contain elevated levels of Cr, Cu, Ni, or Zn (Table 6). However, the volume of sediment carried by this stream results in the input of large quantities of all trace metals to Middle Loch. Trace metals (possibly excluding cadmium), carbon, and radioisotope data suggest that contaminant inputs from Waiawa Stream do not significantly affect deep areas (i.e., sites 2 and 6 in Figs. 6-10).

The Golf Course Stream is the source of an unknown quantity of sediment. Its delta is much smaller than that of the Waiawa Stream (Fig. 3). Deeper sediments beyond the foot of the delta, as measured at site 7, do not tend to reflect input from the Golf Course Stream (Table 6), suggesting that this stream's area of influence is limited to the shallow areas around its mouth. A notable exception to this observation is lead (Table 6 and Fig. 9). The Golf Course Stream contains elevated levels of Cd, Fe, Pb, and Zn (Table 6) relative to the average for Middle Loch.

#### **4.1.2 Inputs From Inactive Fleet Operations**

Inactive Fleet maintenance operations appear to be the source of elevated Cu, Pb, and Zn concentrations at site 4 (Table 6). By extension, the other moored inactive vessels could also be similar sources of trace metal contamination. There are insufficient data to accurately identify the zone of influence of these vessels; however, the large reductions in contaminant levels between sites 4 and 5 suggest that the impact of paint debris is likely to be limited to the immediate vicinity of the vessels. Moreover, the relatively low levels of trace metal contamination at sites 1 and 2 suggest that sediments in the lower end of the loch are not significantly affected by paint debris from the inactive ships and craft.

The most obvious source of trace metal contamination associated with Inactive Fleet operations is the generation of paint debris. Paint debris would be expected to contain the trace metal concentrations indicated in Appendix A. These concentrations together with the data in Table 7 can be used to calculate the amount of paint debris actually generated as follows:

Assume that all of the 232 kg/year of copper input to Middle Loch from the ships and craft (Table 7) is derived from paint debris with an average copper concentration of 62,358 mg/kg (Appendix A). Then the quantity of paint required to provide 232 kg/year of copper is 3720 kg/year ( $232 \text{ kg/year} \div 0.062358 \text{ kg Cu/kg paint}$ ).

If paint debris is generated at the rate of 3720 kg/year, then the input rates for the other trace metals would be: Cd, 0.2 kg/year; Cr, 6 kg/year; Pb, 221 kg/year; and Zn, 102 kg/year. Two apparently contradictory observations emerge from this analysis:

1. Paint debris generation at 3720 kg/year would result in seven times more lead input (221 kg/year) than was calculated from the lead concentration at site 4 and the sediment accumulation rate beneath the moored vessels (32 kg/year: Table 7).
2. However, paint debris generation at 3720 kg/year would not produce sufficient Cd, Cr, or Zn to account for the input rates calculated for these trace metals (Cd, 2.8 kg/year; Cr, 98 kg/year; Zn, 218 kg/year: Table 7).

The apparent contradiction can be resolved if paint debris is generated at a rate much lower than 3720 kg/year and other sources account for the Cd, Cr, Cu, and Zn contamination. We suggest that the following three processes would, in some combination, explain the elevated trace metal concentrations at site 4.

1. Data from the pre- and post-Davidson samples strongly suggest that mooring operations can expose or resuspend and redeposit contaminated layers of buried sediment. Mooring operations took place near site 4 within the past year (personal

observation). Chromium, copper, lead, and zinc are all known to exist at levels in excess of 1000 mg/kg in buried layers in Middle Loch (Ashwood et al. 1986; Ashwood and Olsen 1988). This source is discussed further in Sect. 4.1.4.

2. Paint data in Appendix A indicate that copper is present at levels exceeding 20% in antifouling paint at or below the waterline and that cadmium concentrations in paint at or below the waterline are twice as high as in paint above the waterline. Leaching of this cadmium and copper could be a source of dissolved cadmium and copper, leading to increased cadmium and copper concentrations in sediments.
3. Some ships have sacrificial zinc anodes, which are designed to slowly erode away. While the destroyers at site 4 are currently under active electrical cathodic protection (personal observation), it is possible that relict zinc anodes still exist on these ships. Dissolved zinc from such anodes could ultimately represent a source of zinc to the sediments.

The relative importance of these processes cannot be thoroughly quantified with existing data. However, there is sufficient data to suggest that all three processes are operating to some extent. Furthermore, the relative contribution of paint debris input can be determined as follows:

Assume that all of the 32 kg/year of lead input to Middle Loch from the ships and craft (Table 7) is derived from paint debris with an average lead concentration of 59,624 mg/kg (Appendix A). Then the quantity of paint required to provide 32 kg/year of lead is 537 kg/year ( $32 \text{ kg/year} \div 0.059624 \text{ kg Pb/kg paint}$ ).

Generation of 537 kg/year of paint debris (equivalent to ~150 gal of paint) is probably not unreasonable and would result in the following trace metal inputs to Middle Loch: Cd, .03 kg/year; Cr, 0.8 kg/year; Cu, 33 kg/year; Zn, 15 kg/year. Comparing these inputs to the total input associated with ships and craft (Cd, 2.8 kg/year; Cr, 98 kg/year; Cu, 232 kg/year; Zn, 218 kg/year; Table 7) suggests that paint debris is a trivial source of the trace metal contamination in Middle Loch. This result is consistent with our earlier study (Ashwood et al. 1986).

Hydroblasting is another potential source of trace metal contamination from inactive ship maintenance operations. The 0- to 5-cm sample at site 4 probably represents sediment accumulated over the past 3-4 years (5 cm  $\div$  1.5 cm/year accumulation rate: core CX in Ashwood et al. 1986). Within that period, the only hydroblasting operation conducted on the ships moored at site 4 was a brief experiment in July, 1987 to test the toxicity of hydroblast rinse water (S. R. Thompson, Naval Sea Systems Command Detachment, Navy Inactive Fleet, personal communication, 1989). The measured trace metal concentrations in hydroblast rinse water were: Cd, <5  $\mu\text{g/L}$ ; Cr, 40  $\mu\text{g/L}$ ; Cu, 72  $\mu\text{g/L}$ ; Pb, <200  $\mu\text{g/L}$ ; and Zn, 58  $\mu\text{g/L}$  (A. J. Stewart, ORNL, personal communication, 1987). Of these, only the copper and zinc values were elevated above levels in hydroblasting feed water (A. J. Stewart, ORNL, personal communication, 1987).

The volume of water used in the hydroblast test was not measured, but was probably less than 1000 L because the experiment was run only long enough to allow collection of a 5-L sample (personal observation). Thus the maximum trace metal inputs which could have been due to hydroblasting were: Cu, 72 mg; Pb, <200 mg; and Zn, 58 mg. The total area beneath the ship being hydroblasted was  $\sim 25 \times 10^6 \text{ cm}^2$ . If the hydroblast trace metal input was focused entirely in the sediments beneath the ship, the hydroblast contribution to the contamination at site 4 (sample area = 17.4  $\text{cm}^2$ ) would be: Cu, 0.05  $\mu\text{g}$ ; Pb, <0.14  $\mu\text{g}$ ; and Zn, 0.03  $\mu\text{g}$ . The trace metal content of the 0- to 5-cm sample from site 4 were: Cu, 4159  $\mu\text{g}$ ; Pb, 583  $\mu\text{g}$ ; and Zn, 3905  $\mu\text{g}$  (based on concentrations in Table 5 and the sample dry weight in Table 4). Clearly, the hydroblasting contribution to the trace metal contamination at site 4 was trivial.

#### 4.1.3 Sediment Focusing Beneath Moored Vessels

As noted in Sect. 3.1.1, both the  $^7\text{Be}$  data from this study and the sediment cores from our previous study (Ashwood et al. 1986) indicate that sediment is accumulating at a faster rate beneath the inactive ships than in other deep areas of Middle Loch. Such focusing of sediment might result in higher contaminant concentrations at site 4 if sediment from another contamination source were accumulating under the ships.

Sediment from other sites in Middle Loch contains the following trace metal concentrations: Cd, 5.3 mg/kg; Cr, 213 mg/kg; Cu, 173 mg/kg; Pb, 42 mg/kg; and Zn, 234 mg/kg (averages for sites 1, 2, 3 mean, 5, 6, 7A, and 9: Table 6). With the exception of cadmium and chromium, these values are substantially lower than the trace metal levels at site 4 (Table 6). Thus, sediment focusing would not be expected to be a major cause of the increased Cu, Pb and Zn concentrations at site 4. This strongly suggests that Inactive Fleet operations are the major source of these three trace metals in the areas immediately under the moored vessels.

#### 4.1.4 Resuspension of Buried Contamination Layers

The differences in chromium and zinc levels between the pre- and post-Davidson samples are difficult to explain unless the mooring operation either exposed or resuspended a buried layer of high contamination. Such buried layers were observed by Ashwood et al. (1986) in cores CA and CX. Core CX also had elevated copper (5400 mg/kg) and zinc (910 mg/kg) in the 0-4-cm depth increment (Ashwood et al. 1986). However, this core was taken in the immediate vicinity of craft which had recently been part of an in situ repainting program. The frigates moored near the pre- and post Davidson site had not been painted in that location. Hence, there is no reason to expect a recent source of high trace metal contamination in that location.

Resuspension of a buried contamination layer might be expected to cause homogenation of that layer with other, less contaminated, sediment. The data from core CA taken by Ashwood et al. (1986) on the delta of the Golf Course Stream can be used to explore the effect of such sediment mixing due to resuspension and homogenation. The Japanese bombing attack in 1941 left a highly contaminated (Cr, 1500 mg/kg; Cu, 1000 mg/kg; Pb, 3700 mg/kg; and Zn, 5900 mg/kg) 4-cm thick layer of sediment buried under 1 m of sediment (Ashwood and Olsen 1988). The total mass of lead in that 4-cm layer was  $8.1 \text{ mg/cm}^2$ , whereas the mass of lead in the entire 102 cm above was only  $1.4 \text{ mg/cm}^2$  (Ashwood and Olsen 1988). Complete mixing of this material would result in a total lead mass of  $9.5 \text{ mg/cm}^2$ . Dividing this lead mass by the total mass of sediment ( $24 \text{ g/cm}^2$ ) yields an average lead concentration of 396 mg/kg--a substantial increase over the lead concentration in the surface layer of core CA (58 mg/kg: Ashwood and Olsen 1988). Hence, even homogenation of deeply buried contamination can result in trace metal concentrations that are much higher than recent levels.

#### 4.2 COMPARISON WITH HISTORICAL DATA

Direct comparisons with previous studies are not possible, because there is spatial variation in contaminant levels and our samples were not taken in exactly the same locations as previous cores and grab samples. Nevertheless, a comparison can be made between mean values from the top 5 cm of sediments in the earlier ORNL study [specifically cores GD, GE, GG, GH, CA, and CX in Ashwood et al. (1986)] and those samples from the current study where  $^7\text{Be}$  was detected (see Table 8). Due to different preparation techniques, the major metals (i.e., Al, Ca, Fe, and Ti) are not comparable from one study to the other. Also, the dilutions used in the 1986 study precluded detection of cadmium at levels as low as were detectable in this study; therefore no comparison of cadmium values is made.

While the concentrations for all trace metals except copper appear to have declined since the earlier study (Table 8), none of the differences are significant ( $p > 0.05$ ).

Table 8. Temporal comparison of mean values for trace metal concentrations in Middle Loch surface sediments (1985-1988)

Period of study	Mean concentration (mg/kg)					Total
	Cr	Cu	Ni	Pb	Zn	
11/84-3/85 (n=6) <sup>a</sup>	220±28	178±38	150±17	49±17	303±89	901±93
12/88 (n=7) <sup>b</sup>	202±52	187±59	132±24	42±9	236±43	799±76

<sup>a</sup> Data from Ashwood et al. (1986, Appendix B). The data for core CX in the 0- to 4-cm depth increment were anomalously high. Accordingly, the data for the 8- to 12-cm depth increment were used.

<sup>b</sup> Data from Table 5 of this report for sites 1, 2, 3 (mean), 4, 5, 6, 7A, and 9.

## **5. CONCLUSIONS**

### **5.1 TRACE METAL INPUTS FROM INACTIVE FLEET OPERATIONS**

Inactive Fleet maintenance operations add measurable amounts of Cu, Pb and Zn to the sediments in the immediate vicinity of the ships and craft. However, actual paint debris appears to contribute <15% of the Cu and <10% of the Zn added by these operations. Hydroblasting also contributed negligible amounts to the trace metal contamination beneath the moored ships. This is an important conclusion because it suggests that corrective actions aimed at reducing or eliminating paint debris or hydroblast rinse water will have little effect on trace metal contamination in Middle Loch.

The most likely sources of the trace metal contamination associated with inactive ships maintenance operations are leaching of trace metals from paint and sacrificial anodes below the waterline and resuspension of buried contamination through mooring operations and ship traffic. These sources are inherent to the maintenance of inactive vessels and are not amenable to abatement actions with existing technology.

### **5.2 TRACE METAL INPUTS FROM OTHER SOURCES**

Most of the Cd, Cr, Pb, and Zn enter Middle Loch from the Waiawa Stream and the Golf Course Stream. This contamination is primarily confined to the stream deltas, where we observed the highest density of biota, and where fishermen catch bottom-feeding fish and crabs. In terms of direct risk to man and the environment, the stream contamination cannot be overlooked.

Eolian inputs of trace metals are minor compared to other sources.

### **5.3 EFFECT OF SEWAGE DISCHARGE ELIMINATION**

Some reduction in trace metal contamination may have occurred since termination of direct sewage discharges. There are two reasons why trace metal contamination in the recent sediments has not declined in the 5 years since termination of direct sewage discharges: (1) in the shallow areas and on the deltas, where sediment is accumulating at 2-6+ cm/year, the streams continue to input contamination at elevated levels; and (2) ship traffic and other maintenance activities (e.g., moving anchor chains) continually disturb buried sediments, resulting in exposure or resuspension and redeposition of buried contamination.

## **6. ACKNOWLEDGMENTS**

Melvin W. F. Won and his staff (especially Walt Leonard) at the Naval Inactive Ship Maintenance Facility on Middle Loch, together with the staff of their contractor, Global Associates, provided valuable logistical support for the data collection efforts and information on the history of Inactive Fleet operations. The evaluation of hydroblasting effects on trace metal contamination levels relies heavily on data obtained by Art Stewart as part of a toxicity test. Karen Von Damm provided relevant insights throughout the project and reviewed a draft of the final report. Norm Cutshall was especially helpful during the preliminary planning phase and also reviewed a draft of the final report.

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## APPENDIX A: TRACE METAL CONCENTRATIONS IN PAINT SAMPLES

**OAK RIDGE NATIONAL LABORATORY**

OPERATED BY MARTIN MARIETTA ENERGY SYSTEMS, INC.

POST OFFICE BOX X  
OAK RIDGE, TENNESSEE 37831

September 19, 1986

Director,  
U.S. Navy Inactive Fleet (SEA 076)  
Building 8Y, St. Juliens Creek Annex  
Portsmouth, Virginia 23702-5002

Attention: CDR J. E. Vroom

Dear Jim:

As we discussed Wednesday (9-17-86), the analysis of paint samples from vessels at Pearl Harbor is complete. The attached table summarizes the results for the metals of interest in our sediment study. Also attached for your information are the data sheets containing the results for all elements covered by the analysis. Following is a brief description of the analytical procedure we used as well as a discussion of the results and their impact on the sediment study report<sup>1</sup> (five copies of which were express mailed to CAPT Berry yesterday).

Each of the paint samples obtained from Mel Won at Pearl Harbor was dried, ground to a fine powder, and homogenized. From each sample, three replicate batches (typically ~250 mg each) were weighed out and dissolved in strong nitric acid. The resulting solution was analyzed by Inductively Coupled Plasma spectroscopy (ICP).

As you can see from the table, the mean results vary significantly from the USS Hornet sample we included in our sediment study report<sup>1</sup>. The most striking variation is in the copper values. Based on the paint sample from the USS Hornet, the sediment study report<sup>1</sup> concludes that paint is not likely to be a potential source of copper contamination in the sediments. The extremely high copper values in some Pearl Harbor paint samples most likely results from inclusion of paint from the water line area of the ships that contains antifouling agent (primarily copper oxide). However, even ignoring the samples which contained antifouling paints (see "Mean W/O WL" in table) the mean copper concentration in the remaining samples is greater than the copper level in the sediments. This means that paint from inactive vessels may, in fact, be a potential source of copper to the sediments, contrary to what we observed in the sediment study report<sup>1</sup>.

There are two possible pathways by which copper from paints may reach the sediments. First, paint chips removed from the vessels may add copper directly to the sediments. Second, copper may leach out of the

September 19, 1986

antifouling paint and become associated with suspended solid particles in the water column which eventually settle out as sediment. Since copper-based antifouling paints used by the Navy are non-ablative<sup>2</sup>, this latter pathway is unlikely to be significant for more than a few years after initial paint application.

Lead and zinc values in the Pearl Harbor paint samples are also higher than corresponding values in the USS Hornet sample. On a gross basis, the lead:zinc ratio of the Pearl Harbor paint samples (~2.4:1) is similar to that of the USS Hornet sample (2.1:1). However, when the samples containing antifouling paint are removed from the average, the lead:zinc ratio of the Pearl Harbor paint samples drops to 0.7:1. The significance of this latter ratio is that it means paint removed from the vessels has very close to the same lead:zinc ratio as that in the sediments (0.2:1).

Notwithstanding the above differences, the primary conclusion of our sediment study report remains the same--paint from inactive vessels is probably not a significant source of trace metal contamination to the sediments of Middle Loch. The reasons for this are as follows: (1) our core data show that trace metal contamination began prior to inactive fleet activities in Middle Loch; (2) the copper:lead ratio of the Pearl Harbor paints (<1:1, with or without antifouling paint included) is quite different than that of the sediments (3.7:1); (3) the trace metal signature (i.e. ratios of copper, lead and zinc) in Middle Loch is very similar to that in an area of West Loch where there is little or no Navy activity; and (4) information in a previous Navy study<sup>3</sup> indicates that the Pearl City Sewage Treatment Plant discharged over 1.5 tons/day of suspended solids into Middle Loch (almost half as much as the stream input of ~3 tons/day), which is undoubtedly orders of magnitude greater than the input of paint chips.

After you have reviewed the attached data, we can discuss issuance of an addendum to the sediment study report. In the meantime, please call me if you have questions on this data.

Best regards,



Tom L. Ashwood  
Environmental Sciences Division

TLA:pab

Attachment(s)

cc: N. H. Cutshall  
C. R. Olsen  
M. F. Won

- <sup>1</sup>Ashwood, T. L., C. R. Olsen, I. L. Larsen, and T. Tamura. 1986.  
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- <sup>2</sup>U. S. Navy. 1984. Environmental assessment fleetwide use of  
organotin antifouling paint. U.S. Naval Sea Systems Command,  
Washington, D.C.
- <sup>3</sup>Evans, E. C., A. E. Murchison, T. J. Peeling, and Q. D. Stephen-Hassard.  
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# Pearl Harbor Paint Analysis

Sample ID	Cadmium (Cd)	Chromium (Cr)	Copper (Cu)	Nickel (Ni)	Lead (Pb)	Zinc (Zn)
USS HORNET	< 48	890	170		17000	8100
YTM-496 SW 1	35	1300	730	25	29000	30000
YTM-496 SW 2	35	1300	750		29000	30000
YTM-496 SW 3	35	1200	690		28000	29000
Mean YTM-496 SW	35	1267	723	25	28667	29667
YTM-496 TD 1	42	1900	140		44000	85000
YTM-496 TD 2	46	2100	280	29	47000	89000
YTM-496 TD 3	42	1900	240		44000	83000
Mean YTM-496 TD	43	1967	220	29	45000	85667
YTM-496 TWL 1	48	1900	520	75	41000	100000
YTM-496 TWL 2	48	1700	420		40000	100000
YTM-496 TWL 3	47	1700	360		39000	99000
Mean YTM-496 TWL	48	1767	433	75	40000	99667
YTM-496 WL 1	<77	940	190000	110	25000	1600
YTM-496 WL 2	<78	910	190000	110	24000	1500
YTM-496 WL 3	<77	930	190000	110	25000	1800
Mean YTM-496 WL	<77	927	190000	110	24667	1633
DD-948 MD 1	12	1100	370	120	1300	23000
DD-948 MD 2	10	1100	240	110	1300	22000
DD-948 MD 3	11	1100	240	120	1300	23000
Mean DD-948 MD	11	1100	283	117	1300	22667
DD-948 WL 1	<100	2100	230000	32	1400	9300
DD-948 WL 2	<100	2200	240000	32	1200	9300
DD-948 WL 3	<98	2200	230000	32	1100	9500
Mean DD-948 WL	<99	2167	233333	32	1233	9367
AFDB-2J SW 1	44	1800	650		43000	23000
AFDB-2J SW 2	49	1800	630		42000	24000
AFDB-2J SW 3	46	1700	690		42000	23000
Mean AFDB-2J SW	46	1767	657		42333	23333
AFDB-2J TW 1	33	2900	110		22000	17000
AFDB-2J TW 2	31	2900	110		22000	18000
AFDB-2J TW 3	37	3000	120		23000	18000
Mean AFDB-2J TW	34	2933	113		22333	17667
AFDB-2J TWL 1	110		140000	35	130000	1700
AFDB-2J TWL 2	110		150000	39	150000	1800
AFDB-2J TWL 3	110		140000	39	140000	1700
Mean AFDB-2J TWL	110		143333	38	140000	1733

# Pearl Harbor Paint Analysis

Sample ID	Cadmium (Cd)	Chromium (Cr)	Copper (Cu)	Nickel (Ni)	Lead (Pb)	Zinc (Zn)
AFDB-2J WL 1	110		130000	32	280000	2600
AFDB-2J WL 2	110		110000	27	300000	2200
AFDB-2J WL 3	98		110000	32	300000	2100
Mean AFDB-2J WL	106		116667	30	293333	2300
MEAN	54	1643	62358	57	59624	27436
STD. DEVIATION	35	670	90514	38	86126	33774
NUMBER OF POINTS	8	9	11	8	11	11
MEAN W/O WL	36	1670	371	61	24733	40967
STD. DEVIATION	14	683	240	43	17468	36149
NUMBER OF POINTS	6	7	7	4	8	7
- MEAN WL	108	1547	170833	53	152667	3758
STD. DEVIATION	3	877	51523	38	134780	3750
NUMBER OF POINTS	2	2	4	4	3	4

## APPENDIX B: DESCRIPTIONS OF SAMPLE SITES AND CORES

### Obtaining Sediment Cores Using SCUBA

The use of SCUBA to obtain sediment cores offers three significant advantages over surface-based methods (e.g., gravity cores and vibracoring): (1) precise control over the location from which the core is taken, (2) the ability to visually inspect the coring site, and (3) the ability to capture even the very fine sediment at the sediment/water interface. Because this study required that the sample contain all the  $^7\text{Be}$  at a given site, the first and third advantages were particularly important.

At each site the following steps were repeated:

1. Anchor the boat by using a heavy metal plate attached to a length of anchor line. (An estimate of water depth was obtained from the amount of anchor line that was let out before the anchor touched bottom.)
2. Both divers enter the water and descend to ~10-ft depth, where buoyancy was neutralized. (At shallow locations, the depth of equalization was reduced to ~5 ft.)
3. Using a head-down orientation, one diver led the way down the anchor line carrying the core barrel and one plastic cap, while the other diver followed carrying the other plastic cap.
4. Approximately 5 ft from the bottom, the trailing diver halted, while the lead diver continued down the anchor line to the bottom maintaining slightly positive buoyancy and pulling on the rope to descend.
5. At the bottom, the diver selected an undisturbed site near the anchor and pushed the core barrel into the sediment until only a few centimeters remained exposed.
6. The diver then capped the top of the core and allowed his buoyancy to lift him and the core barrel;
7. The second diver intercepted the first diver, and they ascended slowly together as the second diver capped the bottom of the core barrel.
8. At the surface, the core was inspected to be sure there were no cracks in the sediment caused by pulling the core barrel out of the mud and to be sure that there was a clear sediment/water interface with a minimum of suspended matter.
9. If necessary the process was repeated in a nearby location until a satisfactory core was obtained.

At the sites where three cores were obtained (3, 5, and 7), the above process was simply repeated; however, the marker buoy anchor was used rather than the boat anchor. All cores at such sites were taken from a 1-m circle around the marker buoy anchor.

Several points need to be noted about this procedure. First, it is absolutely essential that both divers practice the technique several times to be sure that they can maintain the head-down orientation and proper buoyancy control. Failure to maintain these two attributes invariably resulted in disturbance of the sample site. Second, the anchor lines were lowered very slowly to minimize disturbance of the sediment. The boat was allowed to come to a stop and begin drifting (drift was minimal due to negligible currents) before the anchor line was lowered. Third, we found it helpful for the same diver (Ashwood) to obtain all of the cores. This assured that consistent care was taken in the selection of undisturbed sites and the minimization of disturbances during the insertion

and capping of the core barrel. Finally, in the low visibility (~ 5 ft) environment from which these cores were taken, both divers must remain constantly aware of the other diver's position, since a diver could quickly disappear from view. It was also essential that the divers take their time and not rush the descent lest they settle into the bottom without seeing it.

### Sample Site Descriptions

**General:** Because of the rain preceding the sample period, the water in all of Middle Loch was quite turbid. Visibility in the upper 5 ft was less than 5 ft. Below this zone, there was little light, but the water was clearer, with visibility improving to 5-6 ft.

In general, the bottom of Middle Loch in the deeper areas is a very fine brown mud. There appears to be a pattern of pock marks, possibly caused by gas from decaying organic matter. The deeper areas are virtually devoid of benthic organisms large enough to be readily visible.

**Site 1:** This core was taken on 12/9/88 in approximately 18 ft of water at the location shown in Fig. 2. This location was chosen because it roughly corresponded to the area where core GH was taken in our earlier study (Ashwood et al., 1986). That core revealed that this area was relatively "pristine" with regard to trace metal contamination.

**Site 2:** The first core taken in this area (Fig. 2) on 12/9/88 was lost in the canning process. A second core was taken at this location on 12/13/88. The water depth was 30-35 ft. This location was selected because it represented the deep region near the mouth of the loch.

**Site 3:** In our earlier study, core CI was taken on the edge of this delta and exhibited exceptionally high sediment accumulation rates (> 6 cm/year in Ashwood et al., 1986). The three cores in this study were taken in 15-20 ft of water (Fig. 2). The bottom was littered with detritus such as tree limbs and leaves. The surface water at this site was cooler, probably reflecting the influence of the Waiawa Stream.

**Site 4:** This site (Fig. 2) was located in an area between two destroyers, approximately 30 ft from their sterns. In May, 1987, one author (Ashwood) observed maintenance activities on these destroyers as part of another study. At that time, paint removal work resulted in a layer of paint chips floating on the surface of the water at this location. The core at this location was taken in 20 ft of water. The bottom was a black, grainy substance. The core had an odor of decaying matter and contained several carbonate shell fragments.

**Site 5:** This site was located approximately 300 ft from site 4, off the bows of the two destroyers (Fig. 2). Depth of the bottom at this point was about 20 ft. The core also contained carbonate fragments.

**Site 6:** This core was taken in 25 ft of water near the eastern shore of the loch (Fig. 2). The site was selected to obtain an area not impacted by inactive vessels, but possibly impacted by activities on the Pearl City Peninsula (Fig. 1).

**Site 7:** The three cores at this site were taken in 20 ft of water on the edge of the Golf Course Stream delta (Fig. 2). This site is close to the location of core CA from our earlier study (Ashwood et al., 1986; Ashwood & Olsen, 1988). This area was selected because it is potentially affected by both the stream and activities on the nearby floating drydocks.

- Site 8: This core was taken in 22 ft of water near the north end of the loch (Fig. 2). It was chosen to represent an area not impacted by any external contaminant sources.
- Site 9: Near the mouth of the spring at the northeast corner of Middle Loch (Fig. 2), this core was taken in 6 ft of water. The water at this site was much cooler than adjacent areas, confirming that we were in the discharge zone of the spring.
- Site PrD/PoD: This site is located about 30 ft off the mooring buoy of the frigates (Fig. 2). The USS Davidson passed through this area as it was being moored. The PrD core was taken by gravity corer on the afternoon of 12/7/88 an hour before the USS Davidson arrived. The PoD core was taken by gravity corer on the following morning, several hours after mooring operations were completed.
- Site WS-1 & 2: Two gravity cores were obtained approximately 300 ft upstream from the mouth of the Waiawa Stream (Fig. 2). The cores were obtained within 3 m of each other in about 10 ft of water. The top 5 cm of each core were canned in the boat, and the remaining material was discarded.
- Site GS-1: This gravity core was obtained about 300 ft upstream from the mouth of the Golf Course Stream (Fig. 2). The water was 10-15 ft deep.
- Site GS-2: At this point (Fig. 2), the Golf Course Stream is in a concrete lined ditch. However, a small, unlined drainage ditch intersects the stream at this point. This gravity core was obtained in about 5-10 ft of water at the point of intersection.

## APPENDIX C: SAFETY PLAN

PROJECT SAFETY PLAN

PEARL HARBOR SEDIMENT STUDY

APPROVED BY

*Tom L. Ashwood*

*12/1/88*

Tom L. Ashwood, Principal Investigator

*Curtis R. Olsen*

*12/1/88*

Curtis R. Olsen, Co-Principal Investigator

*R. K. McConathy*

*12/2/88*

R. K. McConathy, Division Safety Officer

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## BRIEF PROJECT DESCRIPTION

The U. S. Navy Inactive Fleet has asked Oak Ridge National Laboratory to conduct an investigation of sediment contamination in Middle Loch of Pearl Harbor (Hawaii). The data collection activities will be conducted from December 6 - 15, 1988, by Tom L. Ashwood and Curtis R. Olsen, research staff members in the Environmental Sciences Division.

The objectives of this project are: (1) determine the levels of certain trace metals in recent sediments of Middle Loch and whether these levels have declined in response to cessation of sewage discharges; (2) determine the correlation between sediment inventories of  $^7\text{Be}$  and sediment concentrations of certain trace metals; (3) determine the small-scale spatial variation in sediment inventories of  $^7\text{Be}$ . The latter two objectives will provide confirmation that sediment inventories of  $^7\text{Be}$  can be used to measure the short-term dynamics of suspended matter and associated contaminants.

The experiment will consist of three data acquisition/analysis steps: (1) obtain short sediment cores from 9 sites in Middle Loch; (2) analyze the most recent sediment in each core by ICP for trace metals; (3) measure the  $^7\text{Be}$  inventory in each core by gamma-spectrometry. The cores will be obtained using SCUBA to minimize sediment disturbance during the coring process and to assure that cores are taken from a specific location.

## PRIMARY SAFETY CONCERNS

The use of SCUBA to obtain the sediment cores introduces special safety concerns. These concerns are discussed below, and plans to minimize the concerns are presented in the next section.

### Drowning

The most common cause of death among SCUBA divers is drowning. This is typically caused by running out of air at depth.

### Barotrauma

Several severe physical problems can arise from the changes in pressure that occur during SCUBA-diving. During descent, a set of phenomena collectively known as squeezes may occur. These typically occur because there are external, or internal, air spaces, where the air pressure does not increase as rapidly as the pressure in the surrounding water. The most common and most serious squeezes are: (1) middle ear squeeze caused by failure of the diver to adequately equalize the pressure in his ears as he descends; (2) facemask squeeze caused by failure of the diver to equalize the pressure in his mask during descent; (3) external ear squeeze caused by some obstruction (e.g., earplugs, wetsuit hood) covering the ear and preventing equalization of the outer ear canal with water.

During ascent, a set of problems associated with expansion of the air in the lungs can occur. Complications from these problems can vary from discomfort to death. All of the problems are caused by failure of the diver to breathe normally during ascent. During emergency ascent without air (free ascent), the pressure in the lungs can be relieved by exhaling constantly during the ascent.

### Nitrogen Narcosis

"Rapture of the Deep" is a phenomenon caused by breathing nitrogen at pressure. The diver becomes disoriented, similar to alcohol intoxication. The severity of the problem is strictly a function of depth.

### Decompression Sickness

The "bends" is caused by supersaturation of nitrogen in the blood and tissues of a diver caused by breathing compressed air during a dive. This supersaturated nitrogen can form gas bubbles as a diver ascends and the pressure of the blood and tissues is reduced. The primary symptom is pain, and the affliction is always serious and can be fatal. Nitrogen is absorbed by the blood and body tissues over a period of time and the extent of nitrogen adsorption is a function of depth. At depths less than one atmosphere (33 ft in seawater), decompression sickness is not a problem because the reduction of pressure during ascent is not sufficient to cause formation of gas bubbles. Tables that provide an indication of the amount of time that can be spent at depth have been developed and extensively tested.

### Bad Air

During the compression process any contaminants in the air become effectively concentrated. This can lead to sickness or death. The most frequently encountered contaminants are oil vapor from the compressor lubricating system and CO produced by gasoline driven compressors. CO may also be introduced if the air intake of a compressor is located in an area where automobile emissions raise the CO level.

### Hypothermia

The body loses heat rapidly in water--even in the tropics. While concentrating on work a diver may not be aware of becoming chilled. When on the surface after a dive, the wet body is subject to rapid cooling in the air. All of these problems may lead to hypothermia, where the body temperature drops below the level at which metabolic processes can maintain an adequate temperature. From this point on, the temperature drops rapidly and the victim loses consciousness and may die.

### Dangerous Organisms

Previous research has shown Pearl Harbor to be frequented by the following dangerous animals: hammerhead and black-tipped sharks, barracuda, sting rays, and jellyfish. Because the sediment cores will be collected in areas having muddy bottoms, species such as moray eels, sea urchins, and lion fish are not expected to be encountered.

### Physical Hazards

A problem in all diving situations is entanglement in various types of debris or plant growth. Middle Loch is relatively free of such hazards because only shore fishing is permitted, although there are numerous mooring chains in the area. Boats also pose a hazard to swimmers and divers. Again, Middle Loch is closed to commercial and private boats, so only Navy boats should be present.

## **Steps to Minimize Safety Problems**

### **Training**

Adequate training is the primary way to minimize the potential for all of the above hazards. Both divers involved in this project have received training leading to certification by recognized international SCUBA training organizations. Tom Ashwood is certified by the Professional Association of Diving Instructors (PADI) as an Advanced Open Water diver (Certificate #83270181, 9/5/83). Curtis Olsen is certified as an Open Water Diver (Temporary Certificate, 11/88) by the National Association of Underwater Instructors (NAUI).

Consistent with this training both divers will take the following steps to minimize the potential for safety problems:

- a) constantly equalize air pressure in ears and sinuses during descent to reduce the possibility of middle ear or sinus squeezes (if problems develop the descent will be stopped and both divers will return to the surface);
- b) exhale through the nose periodically to equalize pressure inside the facemask and reduce the likelihood of mask squeeze;
- c) regularly monitor air pressure remaining in the tank to reduce the risk of running out of air (the dive will be terminated immediately if either diver's tank reaches a pressure of 300 psi) (see also section on the Buddy System);
- d) breathe normally throughout the dive, especially during ascent, to avoid overpressuring the lungs and causing air to enter the blood stream (during any emergency free ascent, a diver will exhale continuously);
- e) stay well within the no-decompression limits on depth and time established by the U.S. Navy to avoid nitrogen supersaturation and decompression sickness (see section on Dive Planning);
- f) wear or carry the safety equipment described in the next section;
- g) stay alert for dangerous animals, obstacles or other physical hazards;
- h) maintain a first aid kit to treat minor cuts and neutralize stings;
- i) monitor the other diver for symptoms of problems (see section on the Buddy System).

In addition to the certification training, both divers will develop and practice a system of hand signals to maintain communication while submerged. Communication will be further enhanced by use of slates carried by each diver.

### **Safety Equipment**

The following safety equipment will be taken by each diver:

- (a) octopus regulator to facilitate buddy breathing if one diver loses air;
- (b) pressure gage on regulator to monitor air remaining in tank;

- (c) buoyancy compensator to regulate rate of ascent and descent and to provide for free ascent in an emergency;
- (d) depth gage to measure depth and help assure that dives do not exceed decompression limits;
- (e) underwater watch to monitor dive time and help assure that dives do not exceed decompression limits;
- (f) quick-release weight belt to aid in buoyancy control;
- (g) wetsuit to minimize loss of body heat;
- (h) sturdy gloves to prevent cuts to the hands;
- (i) knife to help free oneself from entanglements;
- (j) underwater light to facilitate visual inspection of the area for obstructions and dangerous animals.

The above gear will be provided by each diver or rented in good condition from a SCUBA shop certified by either the Professional Association of Dive Instructors (PADI) and/or the National Association of Underwater Instructors (NAUI). Each diver will also wear a facemask, snorkel and fins to facilitate vision, surface breathing, and movement, respectively.

Each diver will use a standard 80 ft<sup>3</sup> aluminum tank that has been inspected and hydrostatically tested in accordance with Department of Transportation standards. The tanks will be rented from a SCUBA shop certified by PADI and/or NAUI. In addition, each diver will inspect his tanks to be sure that they carry a current hydrostatic testing stamp and that the pressure in the tanks is within the limits specified on the tank.

Prior to each dive, each diver will check his equipment to be sure it is in good condition.

In addition to the above equipment, a first-aid kit will be maintained on the dive boat. This kit will contain necessary supplies to deal with minor injuries, especially cuts and jellyfish stings.

Sufficient towels will also be provided on the dive boat to allow each diver to fully dry after each dive. Between dives, each diver will wear adequate clothing to keep warm.

#### Buddy System

The buddy system (two divers in constant visual contact) will be employed at all times. Divers will stay within sight of each other at all times during a dive. If visual contact is broken, both divers will surface.

Each diver will watch the other diver for signs of any of the previously mentioned problems. At the first sign of a problem, appropriate first-aid will be given or medical attention will be sought.

Each diver will periodically check both his own and the other diver's pressure gage to assure that sufficient air remains. Any time either diver's pressure gage reads 300 psi or less, the dive will be terminated immediately.

If a diver loses his air supply during a dive, the other diver will provide air via his octopus regulator or by buddy breathing, as appropriate.

Each diver will maintain his own log of each dive. Both divers will maintain independent measurements of maximum depth and duration of each dive. The greatest depth and longest duration measured by either diver will be used in planning subsequent dives (see Section on Dive Planning).

#### Certified Source of Air

Air will be obtained from a PADI and/or NAUI certified supplier. The compressor inlet will be inspected by both divers to assure that it is not likely to be impacted by potentially toxic emissions. The divers will also verify that the compressor inlet is filtered to eliminate oil vapor.

#### Boat and Operator

The contractor who operates the Navy Inactive Ships Maintenance Facility on Middle Loch will provide a suitable boat and boat operator. The boat will be large enough to allow free movement for both divers as well as storage of equipment. It will also be large enough to provide a stable platform. The boat will be anchored at each dive site, and the boat operator will be present during the entire dive. While anchored at a dive site the boat will fly a dive flag to aid in keeping other boats away.

The operator will warn other boats away from the dive site and will also watch out for sharks. In case of emergency the boat, which is radio equipped, will provide rapid transportation to medical facilities.

### Medical Facilities

The divers will have access to medical facilities especially suited for diving accidents. This includes a decompression chamber and medical staff trained in diving medicine. Following is a list of facilities available and their respective phone numbers.

a) Diving Accident Network (DAN) (919) 684-8111

b) Decompression chambers are available at:

Hyperbaric Treatment Center (Look Lab)  
42 Ahui  
Kewalo Basin  
Honolulu, Hawaii 96813  
Phone: (808) 523-9155

and

Pearl Harbor Submarine Base  
MUDSU 1  
Pearl Harbor, Hawaii 96960  
Phone: (808) 471-3884 -- Available only if other chamber is unavailable

c) Emergency treatment for injuries not related to compression is available from:

Kaiser Punawai Clinic  
94-235 Leoku St.  
Waipahu, Hawaii 96797  
Phone: (808) 677-0711

or

Kaiser Hospital  
3288 Moanalua Rd.  
Honolulu, Hawaii 96818  
Phone: (808) 834-5333

This list will be kept with the first-aid kit and in the contractor's office so that the office can notify the facility of an emergency in advance.

### Dive Planning

All dives will be thoroughly planned in advance and in writing (see Dive Plan & Log). Topics to be included in each dive plan are expected depth, planned duration, maximum depth allowable, and tasks to be completed. Both divers will agree to the dive plan before the dive is undertaken.

The dives will be planned using U. S. Navy dive tables to avoid the need for decompression stops. Where two or more dives are planned for the same day, sufficient time will be allowed between dives to avoid compound decompression problems. To the maximum extent possible, all dives will be kept to a depth no greater than 30 feet.

No dives will be completed later than 24 hours prior to departure by airplane for home. This will allow sufficient time between the last dive and ascent to flight altitude. This is necessary because the lower air pressure in an aircraft cabin can be low enough to cause gas bubbles to form, depending upon the amount of residual nitrogen in the blood. Virtually all residual nitrogen is gone by the end of a 24-hour period.

No dives will be conducted during thunderstorms or other weather conditions that appear threatening. In addition, potential coring sites will be screened to assure that there is sufficient visibility (minimum of 5-10 ft) to avoid obstacles and maintain visual contact between divers.

Divers will get sufficient rest and will avoid medication, food and beverages that could interfere with safe diving.

## **DISTRIBUTION OF SAFETY PLAN**

Copies of this plan will be kept by each diver, by the Division Safety Officer, and by the contractor providing boat support for the dives.

## DIVE PLAN & LOG

DATE: \_\_\_\_\_ DIVE NO.: \_\_\_\_\_

SURFACE INTERVAL: \_\_\_\_\_ PRE-DIVE GROUP: \_\_\_\_\_

DIVE OBJECTIVE: \_\_\_\_\_  
\_\_\_\_\_

PLANNED MAXIMUM DEPTH (ft): \_\_\_\_\_

RESIDUAL NITROGEN TIME (min): \_\_\_\_\_

MAXIMUM DIVE DURATION (min): \_\_\_\_\_

ACTUAL MAXIMUM DEPTH (ft): \_\_\_\_\_

ACTUAL DURATION (min): \_\_\_\_\_

POST-DIVE GROUP: \_\_\_\_\_

COMMENTS: \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

### DIVERS SIGNATURES

\_\_\_\_\_  
Tom L. Ashwood

\_\_\_\_\_  
Curtis R. Olsen

**INTERNAL DISTRIBUTION**

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**EXTERNAL DISTRIBUTION**

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79. W. E. Cooper, Department of Zoology, College of Natural Sciences, Michigan State University, East Lansing, MI 48824
- 80 - 89. CDR D. G. Dickover, Naval Sea Systems Command Detachment, Navy Inactive Fleet, Building 8Y, St. Juliens Creek Annex, Portsmouth, VA 23702-5002
90. William O. Forster, Ecological Research Division, Office of Health and Environmental Research, Office of Energy Research, ER-75, U.S. Department of Energy, Washington, DC 20545
91. J. G. Grovhoug, Marine Sciences Division-Code 513, Naval Ocean Systems Center, Hawaii Laboratory, P. O. Box 997, Kailua, HI 96734
92. N. E. Korte, Oak Ridge National Laboratory-Grand Junction Office, U.S. Department of Energy, P. O. Box 2567, Grand Junction, CO 81502
93. G. E. Likens, Director, The New York Botanical Garden, Institute of Ecosystem Studies, The Mary Flagler Cary Arboretum, Box AB, Millbrook, NY 12545
94. C. J. Mankin, Director, Oklahoma Geological Survey, The University of Oklahoma, 830 Van Vleet Oval, Room 163, Norman, OK 73019
95. CAPT William F. Martin, Director, Naval Sea Systems Detachment, Navy Inactive Fleet, Building 8Y, St. Juliens Creek Annex, Portsmouth, VA 23702-5002
96. Helen McCammon, Director, Ecological Research Division, Office of Health and Environmental Research, Office of Energy Research, ER-75, U.S. Department of Energy, Washington, DC 20545
97. S. V. Smith, Hawaii Institute of Marine Biology, Department of Oceanography, University of Hawaii, Honolulu, HI 96822
- 98 - 99. M. W. F. Won, Site Director, Naval Sea Systems Command Detachment, NISMF, 93-051 Waipio Point Access Road, Waipahu, HI 96797-3272
100. Office of Assistant Manager for Energy Research and Development, Oak Ridge Operations, P. O. Box 2001, U.S. Department of Energy, Oak Ridge, TN 37831-8600
- 101-110. Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831