HAWAIʻI UNDERSEA MILITARY MUNITIONS ASSESSMENT

Final Investigation Report
HI-05
SOUTH OF PEARL HARBOR, OʻAHU, HAWAIʻI

June 2010

Prepared for:

The National Defense Center for Energy and Environment

Prepared by:

The University of Hawaiʻi at Manoa
1600 East West Road
Honolulu, HI 96822-3920

In association with:

Environet, Inc.
650 Iwilei Road, Suite 204
Honolulu, HI 96817-5318

Prepared under:

Contract Number W74V8H-04-005, Task Number 0496

HAWAI‘I UNDERSEA MILITARY MUNITIONS ASSESSMENT (HUMMA)

FINAL INVESTIGATION REPORT FOR HAWAII -05

SOUTH OF PEARL HARBOR, O‘AHU, HAWAI‘I

June 2010

Prepared for:

The National Defense Center for Energy and Environment

Prepared by:

The University of Hawai‘i at Manoa
1600 East West Road
Honolulu, HI 96822-3920

In association with:

Environet, Inc.
650 Iwilei Road, Suite 204
Honolulu, HI 96817-5318

Prepared under:

Contract Number W74V8H-04-005, Task Number 0496

FIGURES

TABLES

APPENDICES

ACRONYMS

ANOVA	analysis of variance
As	arsenic
ATSDR	Agency for Toxic Substances and Disease Registry
AUV	autonomous underwater vehicle
CA	chemical agent
CADD	Chronic Average Daily Dose
CCD	charge-coupled device
CDC	Centers for Disease Control and Prevention
CEC	cation exchange capacity
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
CSF	cancer slope factor
CTC	Concurrent Technologies Corporation
cm	centimeter
cm^2	square centimeter
COPCs	chemicals of potential concern
CSF	cancer slope factor
CVAA	2-chlorovinyl arsenous acid
CVAO	2-chlorovinyl arsenous oxide
CWM	chemical warfare material
DLNR	State of Hawai‘i Department of Land and Natural Resources
DMM	discarded military munitions
DMM-DS	discarded military munitions in a region dominated by dredge spoils
DNB	dinitrobenzene
DNT	dinitrotoluene
DoD	Department of Defense
DQO	data quality objective
DS	dredge spoils
DVS	Doppler Volume Sampler
ECBC	Edgewood Chemical Biological Center
ELCR	Excess Lifetime Cancer Risk
EPA	United States Environmental Protection Agency
EPC	exposure point concentration
ERA	ecological risk assessment
ESOH	Environment, Safety and Occupational Health
FRSR	Fisheries Research Services Report
ft	feet
GC	gas chromatograph
g/day	grams per day
g/L	grams per liter
g/mL	grams per milliliter
g/mol	grams per mole
GIS	Geographic Information System
GPS	Global Positioning System
HD	distilled mustard (2,2’-dichloroethyl sulfide)
HELCOM	Helsinki Commission
HHRA	Human Health Risk Assessment
HI	Hazard Index
HI-05	Hawai‘i-05
HMRG	Hawai‘i Mapping Research Group
HMX	high melting explosive (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine)

HOV	human occupied vehicle
HQ	Hazard Quotient
HUMMA	Hawai‘i Undersea Military Munitions Assessment
HURL	Hawai‘i Undersea Research Laboratory
IARC	International Agency for Research on Cancer
ID	identification
IDW	investigation-derived waste
IEUBK	Integrated Exposure Uptake Biokinetic
in	inches
IMI	Imaging and Mapping Instrument
IOP	Internal Operating Procedure
kg	kilogram
kHz	kilohertz
km	kilometer
km^2	square kilometer
K_{ow}	octanol-water partition coefficient
K_{oc}	organic carbon partitioning coefficient
kt	knots
L	liter
lb	pound
LADD	Lifetime Average Daily Dose
LCS	laboratory control sample
LCSD	laboratory control sample duplicate
LOAEL	lowest observed adverse effects level
L-I	lewisite I
L-II	lewisite II
MC	munitions constituents
m	meter
MMP	McLane Moored Profiler
MDL	method detection limit
mg/kg	milligram per kilogram
mg/kg-day	milligram per kilogram per day
mi	mile
mL	milliliter
mm	millimeter
mm Hg	millimeter of mercury
m/s	meters per second
MS	matrix spike
MSD	matrix spike duplicate
MW	molecular weight
μm	micrometer
μg/dL	microgram per deciliter
μg/kg	microgram per kilogram
μg/L	microgram per liter
NA	not applicable
ND	no data
NDAA	National Defense Authorization Act
NDCEE	National Defense Center for Energy and Environment
NOAA	National Oceanic and Atmospheric Administration
NOAEL	no observed adverse effect level
NT	nitrotoluene

NTP	National Toxicology Program
ODASA	Office of the Deputy Assistant Secretary of the Army
OSHA	United States Occupational Safety and Health Administration
P4	Pisces IV HOV
P5	Pisces V HOV
PARCC	Precision, Accuracy, Representativeness, Comparability, and Completeness
PCA	principal component analysis
PCB	polychlorinated biphenyl
PCS	Pacific Commercial Services
pH	hydrogen potential
ppb	parts per billion
PPE	personal protective equipment
ppt	parts per trillion
PQL	practical quantitation limit
PVC	polyvinyl chloride
QA/QC	quality assurance/quality control
RC	reference control
RCRA	Resource Conservation and Recovery Act
RDX	Royal Demolition Explosive (1,3,5-trinitroperhydro-1,3,5-triazine)
RfD	Reference Dose
ROV	remotely operated vehicle
RPD	relative percent differences
RL	reporting limit
RME	Reasonable Maximum Exposure
RSD	Relative Standard Deviation
R/V	Research Vessel
R/V KoK	R/V Ka`imikai-o-Kanaloa
S	water solubility
SAP	Sampling and Analysis Plan
SDG	Sample Delivery Group
SI	International System of Units
SONAR	sound navigation and ranging
SOP	standard operating procedure
SSS	sidescan SONAR
TAC	Sea Disposal Technical Advisory Committee
TDG	thiodiglycol
tetryl	methyl-2,4,6-trinitrophenylnitramine
TM	trace metal
TNT	trinitrotoluene
TSCA	Toxic Substances Control Act
UCL	Upper Confidence Limit
UH	University of Hawai‘i at Manoa
U.S.	United States
USACE	United States Army Corps of Engineers
USBL	Ultra-Short Baseline
USFDA	United States Food and Drug Administration
USGS	United States Geological Survey
UXO	unexploded ordnance
W	watt
WHO	World Health Organization
WRCC	Western Regional Climate Center

WW	World War
1,3,5-TNB	1,3,5-trinitrobenzene
2,6-DNT	2,6 dinitrotoluene
4-Am-DNT	4-amino-2,6-dinitrotoluene
2-Am-DNT	2-amino-4,6-dinitrotoluene
°C	degrees Celsius
%	percent

EXECUTIVE SUMMARY

The Department of Defense (DoD), through the National Defense Center for Energy and Environment (NDCEE) contracted Concurrent Technologies Corporation (CTC), which subcontracted the University of Hawai‘i at Manoa (UH) and the environmental consulting firm Environet to conduct the Hawai‘i Undersea Military Munitions Assessment (HUMMA). On a local scale, HUMMA’s objective was to assess (bound) and characterize a historic deep-water munitions sea disposal site to determine the potential impact of the ocean environment on sea disposed munitions and of sea disposed munitions on the ocean environment and those that use it. HUMMA also evaluated whether significant ecological differences existed between an area with discarded military munitions (DMM) and similar areas without DMM. From a broader perspective, HUMMA’s objective was to develop and demonstrate cost-efficient and effective methodologies for surveying and sampling other historic munitions sea disposal sites.

HUMMA is the most comprehensive deep-water investigation in the United States to look at both chemical and conventional munitions. HUMMA used innovative technologies to design a unique approach that is adaptable enough to be tailored to any sea disposed munitions site, each of which would be expected to pose its own set of logistical and environmental challenges. The collection of analytical data and observations of the site were necessary to evaluate the potential for human health and ecological risks; this was required due to the limited number of previous studies at sites in excess of 250 meters in depth. The approach described in this report was necessary even though at the water depths of the HUMMA Study Area (400-600 meters) the extremely low likelihood of explosive safety risk and the fact that there is limited human activity at the seafloor where DMM are located made the project team think that risk was likely to be low. The study was intended to collect data to allow risk to be evaluated so that the need for further actions (e.g., monitoring or removal) could be evaluated by decision makers. HUMMA was a special circumstance and the effort was not conducted within the DoD's Military Munitions Response Program (MMRP). Few, if any, other ocean sites would be likely to fall under the MMRP.

HUMMA specifically examined six factors in the HUMMA Study Area including: 1) the spatial extent and distribution of munitions; 2) the integrity of DMM; 3) whether munitions constituents (MC) could be detected in sediment, seawater or human food items near DMM; 4) whether MC levels at DMM sites differed significantly from levels at reference control (RC) sites; 5) whether statistically significant differences in ecological population metrics could be detected between DMM and RC sites; and 6) whether MC or their derivatives potentially posed an unacceptable risk to human health. Following are the conclusions for each factor studied.

Figure ES-1 depicts the approximate location of site Hawai‘i-05 (HI-05), the boundaries of the HUMMA Study Area and the Barber’s Point Study Area, the 19 study sites within the HUMMA Study Area, and the approximate location of the tentative mustard identification.

SPATIAL EXTENT AND DISTRIBUTION OF DMM

The backscatter data from a sidescan *sound navigation and ranging* (SONAR) (SSS) were extremely effective in detecting 1-2 meter-long reflective targets within, and extending to the southern boundary of, the HUMMA Study Area. Subsequent examination of these targets using video systems and visual observation identified them as DMM. With the exception of one broad circular field of DMM, all of the sea disposed DMM were distributed in narrow, nearly linear trails ranging from hundreds of meters to a few kilometers (km) in length. Munitions extended beyond the boundaries of the HUMMA Study Area and although munitions were readily detected within the area studied, the full spatial extent of DMM was not determined during the study.

Conclusion: Narrow, linear trails of reflective targets are readily recognized by near-bottom towed SSS, and suggest that most DMM in the HUMMA Study Area were disposed of by ships that were underway as munitions were cast overboard.

INTEGRITY OF MUNITIONS (DMM)

The integrity of DMM in the HUMMA Study Area ranged from nearly intact to almost completely disintegrated. The state of deterioration varied within similar munitions types located in the same general area, as well as between different types of munitions spread over a wide region. In general, munitions with thicker casings maintained their integrity better. Many of the DMM were imaged with "skirts" or columnar "pedestals" beneath them. This may be the result of rusting, possibly in combination with leakage of internal MC.

Conclusion: The integrity of DMM in the HUMMA area spans a broad spectrum, with even the best-preserved munitions casings deteriorating at a yet-to-be determined rate. Skirts and pedestals at the base of munitions may be the result of rusting, possibly in combination with leakage of MC.

MC IN COLLECTED SAMPLES

HUMMA participants collected 94 sediment samples, 30 water samples, 16 fish samples, and 19 shrimp samples (plus additional quality assurance/quality control (QA/QC) duplicate samples) from 19 separate study sites within the HUMMA Study Area. Samples were analyzed for chemical agent (CA), energetics (i.e., explosives), and metals. Of these samples, there were no confirmed detections of CA or energetics, although there was one tentative identification of the CA mustard in a single sediment sample. This identification could not be confirmed in two subsequent analyses. The unconfirmed identification of mustard could not have resulted from any surrogate or other source and thus is attributed to a specific DMM. There were elevated levels of arsenic and lead in several biota samples; however, the origin of these metals cannot be tied to a specific source.

Conclusion: The analytical methods used to detect MC during sampling were effective. Except for an unconfirmed mustard detection, neither CA nor energetics were detected in any of the samples.

COMPARATIVE STRATUM FOR MC

HUMMA's stratified sampling approach was designed to enable comparisons of DMM sites against "clean" RC sites. Comparison of data between DMM and RC sites did not show statistically significant differences in levels of MC, including CA. There was some variation in concentrations of metals detected in sediment, but principal component analysis (PCA) performed on the sediment metals data indicated that both DMM and RC samples have relatively little anthropogenic component, whereas selected sediment samples from the DS stratum display much greater influence from elements associated with anthropogenic activity.

Conclusion: Most COPCs were not detected in any stratum. Results of PCA analysis performed on metals data in sediment indicate that sediment samples from the DMM stratum displayed relatively little anthropogenic influence.

COMPARATIVE ECOLOGICAL HEALTH INDICATORS

Field observations did not identify any macrobiotic mid-water species that could be considered ecological health indicators or key sentinel species. An assessment of benthic infauna using push cores was conducted to look for differences in abundance or richness between study sites. Higher average abundances of benthic infauna were found in association with DMM located within dredge spoil (DS) sites, although the difference was not statistically significant.

Conclusion: Collection of push core samples for benthic infauna analysis was successful for gauging infauna abundance and diversity, although larger sample sizes would provide a more robust data set. The observations and data collected do not indicate any adverse impacts on ecological health in the HUMMA Study Area.

HUMAN HEALTH RISK ASSESSMENT

The Human Health Risk Assessment (HHRA) evaluated human health risks associated with the consumption of shrimp samples collected from the HUMMA Study Area and fish collected nearby. COPCs included various metals and munitions compounds. COPCs were initially screened against applicable Food and Drug Administration's screening levels for human consumption. Although not directly applicable, the screening level assessment was performed to provide a frame of reference to compare COPC concentrations in biota to previously accepted and available human health screening levels. Four out of 19 shrimp samples and one out of 16 fish samples exceeded the Food and Drug Administration screening levels for metals. There were no detections of CA or energetics in any of the biota samples collected. Consequently, CA and energetics were eliminated from further review and the project team conducted a quantitative HHRA using metals data only. The quantitative assessment evaluated risk assuming a recreational exposure scenario. The assessment determined that risks and hazards from the consumption of fish and shrimp collected from the study area were within United States Environmental Protection Agency (EPA) levels. If realistic consumption values for biota from the HUMMA Study Area are used, these risks and hazards are anticipated to be significantly reduced and almost certainly below the EPA point of departure risk level of 10^{-06} and the hazard index of 1.

Conclusion: The risk to human health from the consumption of fish and shrimp collected near the HUMMA Study Area were within EPA acceptable risk levels.

This page is intentionally left blank.

1. Introduction

The University of Hawai‘i at Manoa (UH), with assistance from the environmental consulting firm Environet conducted the Hawai‘i Undersea Military Munitions Assessment (HUMMA) Project. The UH was sub-contracted to perform the assessment by Concurrent Technologies Corporation (CTC), the primary contractor for the Department of Defense (DoD), through its National Defense Center for Energy and Environment (NDCEE). The work was performed under NDCEE Contract Number W74V8H-04-005, Task Number 0496.

1.1 LEGISLATIVE INITIATIVE

The HUMMA Project was designed to assess (bound) and characterize a historic deep-water munitions sea disposal site to determine the potential impact of the ocean environment on sea disposed munitions and of sea disposed munitions on the ocean environment and those that use it. To this end, HUMMA evaluated whether significant ecological differences existed between an area with discarded military munitions (DMM) and similar areas without DMM. A secondary objective was to develop and demonstrate cost-efficient and effective methodologies for surveying and sampling historic munitions sea disposal sites in waters in excess of 300 feet of depth.

HUMMA’s Sampling and Analysis Plan (SAP), as well as its overall design, provided the DoD with the option of using the data collected to address requirements in the John Warner National Defense Authorization Act (NDAA) for Fiscal Year 2007, Public Law 109-364, Section 314. The law requires that the DoD "conduct research on the effects on the ocean environment and those who use it of military munitions disposed in coastal waters." This specifically included the "sampling and analysis of ocean waters and sea beds at or adjacent to military munitions disposal sites to determine whether the disposed military munitions have caused or are causing contamination of such waters or sea beds; investigation into the long-term effects of seawater exposure on disposed military munitions, particularly effects on chemical munitions; and investigation into the impacts any such contamination may have on the ocean environment and those who use it, including public health risks. In conducting this research, Section 314 required DoD to select “at least two representative sites each in the areas of the Atlantic coast, the Pacific coast (including Alaska), and the Hawaiian Islands.”

1.2 OBJECTIVES AND SCOPE

The selected site for this study, which DoD designated as Hawai‘i-05 (HI-05), is located approximately 5 miles south of Pearl Harbor, Hawai‘i. HI-05 was suspected to contain both conventional and chemical DMM. Historical, but poorly documented, information indicated that 16,000 M47A2 100-pound (lb) mustard-filled bombs may have been sea disposed in this area following World War (WW) II. Although HUMMA was initially focused on characterizing suspected chemical warfare materials --a collective term DoD uses to address chemical munitions and chemical agent (CA) in other than munitions configurations-- DoD recognized that CA might not be encountered. DoD believed, regardless of whether CA was encountered, HUMMA would provide valuable information concerning the effect of the oceans on munitions and the effect of munitions on ocean environment and those who use it. For the purpose of this report all further reference to DMM includes both conventional and chemical munitions as well as related materials (e.g., munitions casings, packaging materials, etc.).

The HUMMA Project was designed to answer two overarching study questions:

1) Do the chemical warfare materials that were reportedly sea disposed south of Pearl Harbor present an unacceptable risk to human health?

2) Are there sufficient, statistically significant ecological differences between the disposal area and nearby, but otherwise similar areas to suggest the need for future research that would allow for the development of a valid ecological risk assessment (ERA) for this environment? The study authors note that statistically significant differences are not summarily interpreted to mean biologically significant differences.

The HUMMA team addressed these two overarching study questions by collecting samples at representative study sites within the overall HUMMA Study Area, and investigating the sites and their corresponding samples using six more definitive study questions:

1. What is the spatial extent and distribution of the historically disposed CA in the HUMMA Study Area? If CA cannot be distinguished, what is the spatial extent of historically disposed DMM?
2. What is the range of integrity (e.g., level of breaching or corrosion of items) of DMM within the HUMMA Study Area with special emphasis on areas densely populated with CA or other DMM?
3. Are munitions constituents (MC), particularly CA and their degradates, present at detectable levels in sediment, seawater, and human food items when using conventionally available methods of analysis?
4. Are levels of MC, particularly CA and their degradates, in sediment, seawater, and human food species in the HUMMA Study Area significantly different from those in a reference control (RC) site (e.g., similar habitat, but without DMM)?
5. Are there statistically significant differences in ecological health indicators, especially for key sentinel species, between DMM and RC sites?
6. If MC or their degradates are identified in subject media (e.g., sediment, seawater, and human food items), do the detected concentrations suggest a potentially unacceptable risk to human health using conventional Human Health Risk Assessment (HHRA) techniques?

(Note: During planning, it was taken as a given that there is no valid mechanism to assess ecological risks in the deep-water ecosystem without significant additional basic research (e.g., toxicological studies on species of interest, relevant and accurate benchmark values, site-specific fate and transport mechanisms for the deep water ecosystem, and appropriate endpoints). While the potential risks to human health were assessed by conducting a screening level HHRA, the potential impacts to the environment have been evaluated by comparing species richness and species composition and/or abundance between DMM sites and nearby RC sites.)

The collection of analytical data and observations in the HUMMA Study Area were necessary to evaluate the potential for human health and ecological risks that were required due to the limited number of previous studies at sites in excess of 250 meters in depth. The approach was necessary even though at the water depths of the HUMMA Study Area (400-600 meters) the extremely low likelihood of explosive safety risk and the limited human activity at the seafloor where DMM are located made the project team think that risk was likely to be low. The study was intended to collect data to allow risk to be evaluated so that the need for further actions could be evaluated by decision makers. HUMMA was a special circumstance and the effort was not conducted within the DoD's Military Munitions Response Program (MMRP). Additionally few, if any, other ocean sites would be likely to fall under the MMRP.

The first phase of the HUMMA Project employed sidescan *sound navigation and ranging* (SONAR) (SSS) technology to search the HUMMA Study Area for potential DMM. The second phase entailed visual inspection of suspected DMM identified in the SSS data using towed video cameras, remotely operated vehicles (ROVs) and deep-sea human-occupied vehicles (HOVs). Additionally, the HOVs collected sediment and water samples within 1-2 meters (m) of DMM to evaluate whether MC, including CA or CA degradation products, were detectable relative to nearby "clean" RC sites. Human food item biota (shrimp and snapper) were collected near several of the sampling sites investigated by the HOVs during the third phase of the HUMMA Project. The final phase of the project involved shore-based and laboratory analyses of all images and samples collected during the first three phases. End products of the data analysis include a baseline HHRA, a comparison of ecological indicators between DMM and RC sites, and a Geographic Information System (GIS) utility that includes maps of the DMM locations, images of individual DMM and associated results from sampling.

1.3 HISTORICAL INFORMATION

HI-05 (Figure 1-1), south of the entrance to Pearl Harbor, was selected as the primary site for the HUMMA Project based on the United States (U.S.) Army's comprehensive archival research of DoD's sea disposal operations that were conducted prior to 1970, but primarily between WW I and WW II. Additional reasons for its selection, included but were not limited to the following:

- The site is:
    - Where three DoD contractors were injured in 1976 aboard a commercial vessel conducting dredging operations after inadvertently recovering three cylindrical objects containing CA (mustard);
    - Located close to Pearl Harbor and logistical support functions;
    - Located in close proximity to Māmala Bay, which has been the subject of several environmental studies because it has been used for over 100 years for the disposal of dredge spoil (DS) materials from the Ala Wai Canal, Honolulu Harbor, and Pearl Harbor. As such, other data exist for the region that would benefit the HUMMA Project;
- The water depths in the region vary between 300 and 500 m, well within the operational range of the Hawai‘i Undersea Research Laboratory (HURL) HOVs and ROV;
- The area is known to contain human food items such as fish and shrimp, and it is not regularly used for commercial or recreational fishing so was unlikely to be depleted of biological resources.

Historical reports of munitions disposal south of Pearl Harbor specified distances in English units. To remain consistent with the archival information, distances are expressed in English units throughout this section of the report and in all figures referenced by this section. In subsequent sections of this report; however, we switch to the International System of Units (SI), which is considered standard for scientific reports (with an exception made for the nautical term knots (kt)).

The only documented disposal of chemical munitions at HI-05 was of approximately 16,000 M47A2 100-lb mustard bombs that took place in October-November of 1944. This operation occurred over a 21-day period during which the bombs were taken to sea by barge and disposed over the side of the vessel. The M47A2 bombs were taken out of service because they did not withstand tropical conditions well, and as a result, leakage had become a problem. Mustard bombs that began leaking prior to the disposal operation were over-packed in 240-millimeter (mm) howitzer powder casings prior to transport. Convoys of the containers were moved through the Honolulu area to a dock where they were loaded onto a barge, and then "dumping of the bombs took place approximately five (5) miles off Oahu" (Chemical Officer, 1944). A report on the disposal stated, "It is safe to say that over 40% of all the bombs leaked, in connection with the operations incident to their dumping" (Javits, 1944). Because of the known issues with the integrity of these bombs at the time of disposal and the exposure of the thin steel skin to the corrosive effects of seawater for over 60 years, it is likely that a release of mustard has occurred. Although documents from the time of the disposal directed that CA should be disposed "5 mi from shore," no specific latitudes and longitudes for this operation were reported. The exact location of sea disposed munitions would have depended on several other factors including, but not limited to: sea conditions at the time, the vessel's course and speed, multiple disposal operations within a given area, and the fact that individual munitions or cases of munitions were cast overboard rather than being consolidated and dropped all at once (Chemical Officer, 1944; MEDEA, 1997).

For safety in storage and handling**,** most munitions are not fuzed until just prior to use. Those disposed munitions that are fuzed would not have experienced the sequence (e.g., firing, flight) required to arm the fuze. Therefore, most sea disposed munitions are probably not fuzed, and if fuzed they would not be armed; however, either fuzed or unfuzed munitions potentially contain energetics (e.g., high explosive fills). As Hawaiʻi was a battleground during WWII, some unexploded ordnance (UXO) and emplaced sea mines have already been located in the waters south of Pearl Harbor (Kerby, 2009). In particular, anti-submarine munitions are present in the shipping channels.

1.3.1 Previous Investigations – HUMMA Study Area

1976 U.S. Army Corps of Engineers (USACE) Study

During a 1976 environmental study of a proposed deep-ocean disposal site for DS**,** ten to twelve canisters, which were tentatively identified as stokes mortars, were inadvertently dredged from the Pacific Ocean floor. This environmental study was conducted under the USACE Contract No. DACW84-76-C-0032, in the vicinity of Site 3, some 3.3 nautical miles from Pearl Harbor, off the south coast of Oʻahu, Hawaiʻi. The canisters were uniformly cylindrical, approximately two feet (ft) in length and five inches (in) in diameter, with a cap on one end. All were black in color, unmarked, and badly pitted and corroded. A brownish, foul-smelling liquid, which was later identified as mustard agent, leaked from two or three of the recovered canisters causing burns to three individuals on the vessel (USACE, 1977).

Of the 1976 USACE environmental study sites, two (Sites 3 and 3A) lie within the HUMMA Study Area (Figure 1-1). Site 3 was centered at approximately 21° 14.8'N, 157° 55.9'W while Site 3A was centered at approximately 21° 12.8'N, 157° 55.9'W. The 1976 study included collection of data on currents, bathymetry, geology, sediment chemistry, and ecology at these sites. Basic geological characterization at Site 3A found the sediments to be predominantly well sorted and typical of shelf sediments found in offshore areas. Carbonate content was 80 to 90 percent (%) for all samples. During the study, two species of deep-sea shrimp, *Heterocarpus ensifer* and *Heterocarpus laevigatus*, were collected in the vicinity of Site 3, while only *H. ensifer* was collected in the vicinity of 3A. Commercial shrimp trapping operations were reported in the vicinity of Site 3A. Heavy metal concentrations in sediment samples collected from Site 3A were analyzed and reported to fall within the normal range. The few exceptions to this were attributed to sampling methodology. Biological analysis found Site 3A to have a higher percentage of infaunal micromollusks (mollusks living within the sediment) than Site 3 which contained a higher percentage of epifaunal micromollusks (mollusks living attached to the outer surfaces of rocks, gravel, or other hard surfaces). The number and types of polychaetes (worms) at Site 3A were determined to be indicative of a plentiful food supply. The summary of biological data indicated that Site 3A could be expected to be more diverse than Site 3, due to the irregular topography of Site 3A. A more detailed description of the site is presented in Section 2.

1994-1995 Surveys

Several SONAR and video tows of the location where the “canisters” were recovered were conducted by UH for USACE in an attempt to determine the locations and types of munitions present. All surveys were conducted between September 1994 and December 1995 in the offshore waters of Honolulu, Hawai‘i (University of Hawai‘i Environmental Center, 1996a and 1996b).

During these surveys, Sites 3 and 3A were examined again. SSS and video camera surveys were conducted from the University of Hawai‘i *Research Vessel (R/V) Moana Wave* and the *R/V Kila*. Hi-8 videotape of the seabed identified 43 possible munitions for one set of surveys, but none matched the description of those retrieved in the 1976 incident (University of Hawai‘i Environmental Center, 1996b). Hi-8 videotape of the seabed identified 24 possible munitions during a second set of the surveys, but none of these match the description of those retrieved in the 1976 incident (University of Hawai‘i Environmental Center, 1996a). The SONAR survey was not effective at detecting munitions-sized manmade objects, but it was able to detect significant topographic features that were later confirmed with the video footage (Figure 1-1 shows the investigation locations).

1.3.2 Other Studies - Hawai‘i

A baseline study to select environmentally acceptable deep ocean disposal sites for dredge spoil materials from five Hawaiian harbors was conducted in 1977 (Neighbor Island Consultants, 1977). The five harbors were Hilo, Hawai‘i; Kahului, Maui; Honolulu, O‘ahu; Nawiliwili, Kaua‘i; and Port Allen, Kaua‘i. The study considered two alternative sites (inner and outer sites) that were located in close proximity to each harbor. The study assessed the effects of deposition of the DS materials on the benthic environment. The study included available historical data and primary data collected during the study. The study considered currents, water column stratification, geology, and benthic and demersal ecology of the alternative sites. Outer alternative sites were selected for three harbors (Kahului, Maui; Nawiliwili, Kaua‘i; and Port Allen, Kaua‘i) and inner alternative sites were selected for the remaining two harbors (Hilo, Hawai‘i and Honolulu, O‘ahu). Selected disposal sites that would have the least adverse environmental effects ranged from distances of 5.5 to 10.3 kilometers (km) offshore and water depths of 338 to 1,555 m.

As part of a study to locate an offshore site suitable for use as a control site for dredge spoils, sediment characterization was conducted in August 2000 (Environet and Little, 2001) at five locations off the southern coast of O‘ahu. The study design followed the USACE/United States Environmental Protection Agency (EPA) “Green Book” and “Inland Testing Manual” Guidelines for Tier III analysis. Sediment sampling was conducted at 27 stations within the five locations. Laboratory analyses for sediments included sediment grain size, total organic carbon, sulfides, ammonia, heavy metals, polynuclear aromatic hydrocarbons, pesticides, polychlorinated biphenyls (PCBs), phenols, and organic tin. Sediments were also subjected to three suspended-particulate phase toxicity tests, two solid-phase toxicity tests, and two 28-day bioaccumulation exposures. Study results suggested that each of the five sites possessed the qualities of an acceptable reference site. None of the five sites were rejected based on gross chemical contamination or extreme physical sediment characteristics.

1.3.3 Other Studies –Worldwide

Studies on aquatic disposal sites (oceans or lakes,) of chemical or conventional munitions have been conducted in parts of Europe including the United Kingdom, Germany, Denmark, Norway, Russia, and Sweden. These studies were carried out at depths of 30 to 400 m below the water surface, predominantly in northern Europe. Most of the studies showed that CA or energetics were not detected in the marine or lake sediment and water samples (Fisheries Research Services Report (FRSR), 1996; Tornes *et al.*, 2002; Helsinki Commission (HELCOM), 1994; Beddington and Kinloch, 2005; Defense Construction Service (Denmark), 2001).

For example, in 1995, a comprehensive survey was conducted in Beaufort's Dyke, UK for disposed munitions. Beaufort's Dyke is a deep trench that lies between Scotland and Northern Ireland. The depth of the trench is between 100 to 200 m, and in some areas up to 300 m. After the two world wars, over 1,000,000 tons of chemical and conventional munitions are estimated to have been disposed at Beaufort's Dyke. The trench is more than 50 km long and 3.5 km wide. An average density of munitions is about 5,700 tons per square km. The survey did not find detectable concentration of CA in surface seabed sediments (FRSR, 1996). The results of the explosives and propellant residue and heavy metal analyses indicated that munitions dumping operations after both world wars have not resulted in chemical contamination of the surface seabed sediments or the edible flesh of commercially exploited fish and shellfish species.

In a second example, a detailed survey was done in 2001 at the Lake of Mjøsa, Norway, where munitions were disposed from the early 1940s to 1971. Mjøsa is the largest lake in Norway and an important drinking water source for the surrounding Lillehammer region. The munitions dumped were mainly grenade components and ammunition remnants of explosives. Dumping depth varies from 160 to 400 m. No energetics were found in the water or the sediments (Defense Construction Service (Denmark), 2001). Subsequent monitoring of the disposal area showed only sporadic cases of detection of picric acid in the pore water of the sediments.

A few studies, however, have shown detectable levels of CA and energetics in some of the collected samples (HELCOM, 1994). A research project carried out at the munitions disposal site in the Baltic Sea in Denmark in 1992 (HELCOM, 1994; Darrach, *et al.*, 1998; Tørnes *et al.*, 2002) found mustard in one of the two sediment samples collected from the middle of the disposal field, and found its degradation product 1,4-dithiane in both sediment samples. The details of the research were not provided in the report.

Trace explosives were detected in marine sediments in Halifax Harbor, Canada, which was used as a storage area for live ordnance. In 1917, a huge explosion occurred in Halifax Harbor when a French cargo ship fully loaded with wartime explosives accidentally collided with a Norwegian ship. In 1945, a minor fire caused detonation of munitions and sent a large quantity of them into the water. In research conducted by Darrach, *et al.* (1998), trinitrotoluene (TNT) and dinitrotoluene (DNT) were detected in Halifax Harbor at levels of low parts per billion or high parts per trillion adjacent to the munitions that appeared to be intact. The sampling distance was 0.15 to 0.3 m around the munitions. No explosives were detected around the broken munitions in their research.

In 2002, the Norwegian Ministry of Defense undertook an extensive investigation of ships loaded with chemical munitions that had been sunk in an area of the Skagerrak Straight measuring approximately 14 km by 4 km (Tørnes et al., 2002). It is estimated that the sunken ships were loaded with 168,000 tons of chemical munitions. This investigation was conducted after a similar effort in 1989 in which none of the water or sediment samples collected close to the ship wrecks contained detectable concentrations of CA or their degradation products. However, in the 2002 investigation, one of the 33 sediment samples contained sulphur mustard at a concentration of 2.4 milligram per kilogram (mg/kg) of dry sediment. Arsenic and the degradation products of mustard were identified in many of the samples. However, only four sediment samples contained elevated concentration of arsenic compared to the background arsenic concentration. No CA or their degradation products were detected in the seawater samples.

Sampling distance may be a significant contributing factor to whether or not munitions constituents can be detected near leaking DMM. In a research project conducted by Darrach et al. (1998), TNT and DNT were detected at levels of low parts per billion or high parts per trillion adjacent to munitions that appeared to be intact. The sampling distance was 0.15 m to 0.3 m around the munitions. Compared to this research, the sampling distance of the HUMMA project may be too far to detect any CWA or energetics. However, due to the instrument operation limits and safety considerations, collecting samples directly adjacent to the munitions was determined not appropriate for this project.

An ecotoxicological research project was conducted in the southern area of the Adriatic (Mediterranean Sea) at a chemical ordnance dumping site, to evaluate the effects of released CA on marine ecosystems (Amato et.al., 2006). Mustard degradation products 1,4-thioxane and 1,4-dithiane were found in the sediment samples and the arsenic levels in fish tissue were found higher than those from reference site. However, neither CA nor their degradation products were detected in fish tissues.

The aforementioned research studies show that the CA and energetics have only been sporadically detected in the sediments or water in aquatic disposal sites even in some concentrated disposal areas. This suggests that any CA or energetics that may have been released from the disposed munitions have not produced a significant amount of pollution in the surrounding water, sediment, and fish tissues. Localized contamination may, however, be present.

1.4 HUMMA STUDY AREA

1.4.1 Study Area Selection

The location of the 1944 munitions sea disposal site, which DoD has designated HI-05, is approximately 8 km from the mouth of Pearl Harbor. The HUMMA Study Area was defined as the 69 square kilometer (km^2) region located between 5.6 and 14.5 km from the mouth of Pearl Harbor. It includes both the area where canisters tentatively identified as (mustard-filled) stokes mortars were reportedly recovered in 1976, as well as another area where conventional munitions were recovered (Figure 1-1).

The location of the 1944 disposal event was poorly documented, thus the study team took a conservative approach towards bounding the location of the HUMMA Study Area.

A comprehensive review of existing HURL video footage at the outset of the HUMMA Project identified 266 occurrences of suspect military munitions on the seafloor, which guided selection of the northern boundary for the HUMMA Study Area. Many of these HURL targets did not fit the description of chemical munitions, and they were found in locations considered too far inshore for the 1944 disposal event; thus the northern boundary of the HUMMA Study Area was chosen to nearly coincide with the southern boundary of the munitions identified in the HURL videos.

The southern boundary of the HUMMA Study Area was estimated on the basis of the archival disposal records discussed in Section 1.3, which stated that the M47A2 mustard containers were to be disposed 5 mi south of Pearl Harbor. To be conservative, this distance was doubled and the southern boundary for the HUMMA Study Area was established at ~10 mi (<15 km) from the mouth of Pearl Harbor.

The region to the west of the HUMMA Study Area is dominated by coral reef that was built and then drowned during historical changes in sea level around O‘ahu (Fletcher *et al.*, 2008). Because coral is highly reflective in SSS data, the likelihood of detecting DMM in this region is diminished; thus, for this first attempt at developing the methodology to detect DMM, the project team concentrated on soft-bottom sediment areas where the contrast between metal containers and muddy seafloor would maximize the probability of detecting targets. Consideration of the likelihood of detecting targets on various types of substrate determined the selection of the western boundary of the HUMMA Study Area.

The eastern boundary of the HUMMA Study Area was set to encompass some, but not all of the historic DS areas discussed previously. This was necessary because many of the HURL targets had been identified in areas of historic DS areas, and the project team wanted to ensure that the HUMMA Study Area incorporated areas of historic DS disposal without munitions that could be investigated for comparative purposes. DS areas also include numerous potential entanglement hazards for near-bottom instruments such as video sleds, ROVs and HOVs, so an effort was made to keep work in these areas to a minimum.

As explained above, the HUMMA Study Area has been used both for the disposal of DMM and for the disposal of miscellaneous materials (including mud, sand and refuse) dredged from the Ala Wai Canal, Honolulu Harbor, and Pearl Harbor. Due to the presence of dredged materials within portions of the HUMMA Study Area, the experiment design necessarily incorporated approaches intended to separate the influence of potential contamination attributable to DS material disposal and other anthropogenic contamination from potential contamination attributable to DMM. Specifically, the experiment compared DMM disposal areas against RC sites, including "clean" RC sites as well as sites that have been used for DS material disposal. In this way, certain study sites act as controls for other sites.

In order to clearly make this distinction, the following four strata were selected within the HUMMA Study Area, with multiple study sites within each stratum:

1. DMM Disposal Stratum (seven study sites);
2. RC Stratum with no dredged material (five study sites);
3. DMM Disposal in DS Stratum (DMM-DS) (three study sites); and
4. DS Stratum (four study sites).

Specifically, the stratified approach allowed the following comparisons:

- Clean RC sites act as a control for the DMM sites, and
- DS material disposal sites act as a control for the DMM-DS sites.

The possibility that no DMM would be found within the HUMMA Study Area led to a contingency plan that involved selecting an area due south of Barber's Point where chemical munitions had been observed previously during HURL HOV training dives (Figure 1-2). To support the contingency plan, one day of SSS mapping was dedicated to this area (the "Barber's Point Study Area"), which is located to the southwest of the HUMMA Study Area (Figure 1-3). Although the Barber's Point Study Area was known to contain chemical munitions, the plan to visit this region with the HOVs was established only as a last resort because the water depths are too great to use either the towed video camera or the ROV for pre-dive reconnaissance. Ultimately, DMM were found in the HUMMA Study Area and no work beyond the SSS survey was done in the Barber's Point Study Area.

1.4.2 Study Area Setting

Figure 1-3 shows the HUMMA Study Area and the Barber's Point Study Area, and indicates the location of the 2007 high-resolution SSS survey, the reported locations of the 1976 investigation that recovered DMM (i.e., both chemical and conventional munitions), the DoD-controlled Defensive Sea Area, as well as the water depths and substrate reflectivity.

The HUMMA Study Area terrain is gently sloping, with enough sediment cover to produce a generally low reflectivity background in the SSS data. There are two exceptions readily apparent:

the steeper and more reflective terrain to the west of the HUMMA Study Area, which has been previously identified as drowned coral outcrops (Fletcher *et al.*, 2008); and the flat area in the northeastern corner of the HUMMA Study Area, which stands out because of its mottled reflectivity. The latter seafloor texture results from an assemblage of individual DS material dumps in slightly different locations over time.

1.5 HUMMA'S TIMELINE

Various components of the HUMMA Project have been individually discussed in this introduction. Summarized below is the general timeline when each component took place to provide an overarching context for how the different aspects of the HUMMA effort blended together.

1. Beginning in 2006 and continuing as new information has come to light, DoD's historical review of sea disposal information, as well as simultaneous review of UH and EPA reports published in Hawaiʻi and HURL archival video tapes, led to the selection of the HUMMA Study Area. Even after the HUMMA Study Area was selected, new and important information continued to be discovered about the WW II sea disposal operations, including a former tugboat sailor (now an octogenarian retiree) who came forward with information about sea disposal operations conducted near Barber's Point upon hearing about the HUMMA program on local newscasts.

2. From August 23-30, 2007, the *R/V Kilo Moana* were used to create regional and high-resolution SSS maps of the selected HUMMA Study Area. The first two days focused on mapping most of the region south of Pearl Harbor and north of Penguin Banks using the hull-mounted echo sounder multibeam EM1002 SONAR system, which has an operating frequency of 95 kilohertz (kHz) and yielded backscatter maps with 2 m x 2 m grid cells. During the final five days of the *R/V Kilo Moana* survey, the Imaging and Mapping Instrument (IMI)-120 SONAR was towed 50-100 m above the seafloor to produce 0.5 m x 0.5 m grids of the HUMMA Study Area. Subsequent to the *R/V Kilo Moana* field program the IMI-120 data were analyzed to find targets for the video and sampling efforts. Analysis of the IMI-120 data analysis led to the decision to study the curvilinear trails of small reflective targets (a.k.a. "speckle trails") on the seafloor.

3. From November 2008 through February 2009 several surveys took place on the *R/V Klaus Wyrtki*, deploying a towed camera system to examine the speckle trails from a distance of 3-5 m above the seafloor.

4. From March 3-18, 2009, the *R/V Ka`imikai-o-Kanaloa (R/V KoK)*, with two Pisces HOVs and the RCV-150 ROV onboard, completed video reconnaissance plus water and sediment sampling around several of the speckle trails that had been identified during the 2007 mapping field program aboard the *R/V Kilo Moana*. A total of 94 sediment and 30 water samples were collected within 1 and 2 m of high-interest DMM as well as RC sites (Appendix A – Study Site Descriptions). The Edgewood Chemical and Biological Center (ECBC) supported field operations to ensure shipboard personnel were not exposed to CA that the HOVs or ROV might encounter during operations and bring to the surface. ECBC's actions also ensured that the *R/V KoK* did not become contaminated by such CA. ECBC's primary function was to process samples on board to determine if any CA were present. Samples processed and cleared by ECBC were then packaged and shipped to various shore-based laboratories to evaluate the presence of energetics and metals.

5. From late April through early May 2009, sampling of fish and shrimp in or near the HUMMA Study Area took place. The samples were packaged and shipped to ECBC for CA analysis and Columbia Analytical Services for metals and energetics analysis.

6. From March through September 2009, shore-based analyses of the physical samples, maps, and videos were completed for inclusion in this report.

1.6 PROJECT TEAM

A number of key personnel and subcontracted firms were instrumental in designing and conducting the HUMMA Project. The Army was the proponent for HUMMA and had overall oversight of the project. CTC served as the prime contractor, and in turn subcontracted UH as the prime technical subcontractor. UH was assisted by the environmental consulting firm Environet. ECBC provided support and technical expertise related to CA safety and sample analysis. The Sea Disposal Technical Advisory Committee (TAC) provided input to the planning process and was instrumental in providing reviews and comments during the 10-month planning process, which culminated in the creation of the HUMMA SAP.

1.7 ORGANIZATION OF THE REPORT

This report addresses both objectives of the HUMMA Project, assessing the potential risk to human health posed by the DMM and developing cost-efficient and effective methodologies for use at DMM sea disposal sites.

Section 2 provides a detailed description of the HUMMA Study Area and the Barber’s Point Study Area, although only the HUMMA Study Area was investigated during the last three phases of the project.

Section 3 describes the approaches used for all aspects of the project, including detailed descriptions of field methodologies employed and analytical methods used.

Section 4 reports the results from the imaging and sampling programs.

Section 5 describes the data quality assessment conducted on laboratory analytical results generated from the field-sampling program.

Section 6 evaluates the fate and transport of the project-specific chemicals of potential concern (COPCs).

Section 7 presents the HHRA that the project team conducted to assess potential impacts of shrimp and fish consumption to human health as a result of the initial screening level HHRA addressed by Section 4.

Section 8 provides the project team’s overarching conclusions for the project as well as the smaller, more pragmatic aspects of this study.

2. Physical Characteristics of the HUMMA Study Area

Because the global ocean has only been marginally explored, there is a common misconception that ocean environments are analogous in most places. This is an oversimplification. In addition to changes in the physical oceanographic parameters as a function of latitude, proximity to land, plus prevailing atmospheric conditions, chemical oceanographic parameters vary throughout the global ocean as do the biological and geological settings. It is thus more accurate to state that DMM disposal sites are unique, as opposed to similar, with each having a specific set of environmental conditions that must be understood in order to assess how the ocean environment could affect DMM and conversely, how DMM could affect the local ocean environment. As the most comprehensively studied deep-water site for both chemical and conventional munitions, the HUMMA Study Area is as different from nearby Ordnance Reef, a nearshore coastal reef environment on the west side of O‘ahu, as it is from Puerto Rico or the Baltic Sea. HUMMA used innovative technologies to design a unique approach that is adaptable enough to be tailored to any sea disposed munitions site, each of which would be expected to pose its own set of logistical and environmental challenges.

To support the overall objectives of the HUMMA Project, the physical characteristics of the HUMMA Study Area needed to be well defined prior to the start of the field program. These characteristics, particularly the oceanographic conditions at the seafloor, ultimately aid the project team in understanding whether any releases from DMM are likely to have occurred and what might be happening to COPCs that might have been released from DMM. Bottom currents and seafloor topography also serve as an important consideration in planning sampling since the neutrally buoyant HOVs and ROV have to adjust their approach to munitions based on environmental conditions.

2.1 CLIMATE

Temperatures at the surface of the HUMMA Study Area are generally mild and fluctuate very little throughout the year. The mean annual air temperature is approximately 25 degrees Celsius (°C); temperature extremes range from 12 °C to 35 °C. The mean daily air temperature during the winter is 23 °C, while the mean daily air temperature in the hottest summer month (August) is 27 °C (WRCC, 2004). Temperatures at the depths of the HUMMA Study Area (328 to 545 m) have been reported as 5-6 °C (Kelley, 2007).

2.2 OCEANOGRAPHY

Understanding the stratification of the ocean in the vicinity of the HUMMA Study Area is important because a highly stratified water column will not allow mixing of deep water with surface waters. If the water column above a DMM disposal area is highly stratified, any contaminants dissolved in seawater near the seafloor would be unlikely to rise through the water column from deep water to surface waters by normal mixing processes. Stratification of the ocean is influenced by temperature, pressure and salinity, with temperature exerting the primary influence in the water column of the HUMMA Study Area. Typical profiles of salinity, temperature (Neighbor Island Consultants, 1977) and hydrogen potential (pH)(Shitashima *et al.*, 2002) were reviewed prior to the launch of fieldwork. A mixed layer of approximately 50 m thickness is generally formed through a combination of wave- and wind-drive processes, and thus varies seasonally. Below this layer, temperature decreases rapidly and density increases, both as a function of depth. Salinity increases with depth between the base of the mixed layer and a depth of 180 m and then decreases in concert with temperature. The pH profile, typical of marine waters, is characterized by slightly basic conditions throughout the water column, although conditions at depth approach neutral. Generalized profiles of the HUMMA Study Area, which has a maximum water depth of 600 m, were generated at the SAP stage, and indicated that the upper 600 m of the water column is highly stratified. However, the HUMMA Project included a plan to collect additional data within the HUMMA Study Area to support this generalization. The physical oceanographic research component of the HUMMA Study Area is discussed in further detail in Sections 3 and 4.

2.3 BATHYMETRY AND SEDIMENT DISTRIBUTIONS

A shallow shelf with depths ranging from 50 to 75 m extends south of the entrance to Pearl Harbor for approximately 3.2 km. South of the 3.2-km mark there is an abrupt drop-off to approximately 300 m, the northern boundary of a gently sloping saddle between O‘ahu to the north and the Penguin Banks of Maui to the southeast. Water depths on the western half of this saddle rarely exceed 600 m. A few tens of km south of the mouth of Pearl Harbor, the seafloor falls away rapidly, reaching depths of thousands of m over distances of 16-32 km. The seafloor is relatively smooth in the primary HUMMA Study Area and has been characterized as a “flat silty plain with no significant topographic features” (University of Hawai‘i Environmental Center, 1996a). In contrast, in the southwestern part of the HUMMA Study Area, the morphology changes to include drowned Pleistocene shorelines (Fletcher *et al.*, 2008) with irregularly shaped mounds abruptly rising 10 to 20 m above the adjacent seafloor and channels a few meters deep running roughly north to south. These submerged reef platforms have a thin sediment cover (Kelley, 2007).

The morphology and surface texture of the Barber’s Point Study Area are considerably steeper and rougher. The greater slope in this region, in combination with sediments derived from erosional processes, have produced a series of narrow, sub-parallel gullies that channel debris from near shore to the deep seafloor over distance of tens of km. Coarse material tends to be deposited in the base of these narrow canyons, and the flanks of these features are therefore dominated by fine sediments similar to those in the lower slope HUMMA Study Area. Toward the western edge of the Barber’s Point Study Area blocks of the material have eroded away from their source, which results in rapid changes in topographic relief on the order of tens of m.

Seafloor material likely to be encountered in the HUMMA Study Area and the Barber’s Point Study Area can be classified into three general categories: carbonate sand/silt, reef platform carbonate, and DS material. Grain sizes of the natural carbonate sands are variable, ranging from 0.1 mm to 2 mm and generally grading coarser to finer from north to south. Samples are composed of 80 to 90 % reef fragments, with foraminifera, basaltic grains, and volcanic clay constituting most of the remaining 10 to 20 %. The clay minerals present are poorly crystallized montmorillonite and halloysite/kaolinite. Sedimentation rates at the site average 1 mm per year (Fletcher *et al.*, 2008). Thus the total amount of sedimentation in the site after 60 years would be approximately 60 mm.

DS material is on average coarser and more poorly sorted than the carbonate sand/silt. Grain sizes range in size from clay grains to boulders. DS material also contains a significant fraction of volcanic clay and basaltic fragments. Large chunks of carbonate and basalt as well as considerable trash were incorporated into the DS material. Cores taken by the U.S. Geological Survey (USGS) suggest that the maximum thickness of the DS deposits is on the order of 0.5 m (Hampton *et al.*, 1997).

The drowned reef platform in the southwest corner of the HUMMA Study Area is a hard bottom composed mainly of solid carbonate. Over their lifetime coral reefs develop depressions at many scales ranging from centimeter-wide gaps between individual coral heads to ten’s of meters wide sink holes (if the reef has been subaerially exposed for a period of time) and runoff channels. These depressions may or may not be filled by subsequent sedimentation. Both the USGS and USACE surveys reported other isolated occurrences of carbonate reef exposure throughout the HUMMA Study Area, particularly in the deeper water of Site 3A (USACE, 1977; Hampton *et al.*, 1997).

Chemical analysis of sediment samples from Sites 3 and 3A were done as part of the 1976 USACE survey (USACE, 1977). Amounts of mercury, lead, manganese, zinc, nickel, chromium, cadmium, and copper were all within a range expected for deep Pacific Ocean sediments.

2.4 ECOLOGY

The major factor affecting biota in the HUMMA Study Area is the fact that it lies too deep for the penetration of light, which typically only extends to depths of 150 to 200 m below the ocean surface. Without light from the surface, photosynthesis is not possible and the macrobiotic benthic community is reduced to scavengers living off detritus, filter feeders, and the occasional mid-water predator.

Foraminifera (forams) are sand grain sized unicellular animals that form calcium carbonate shells (tests) and are common components of seafloor sediments in tropical oceans less than a few thousand meters deep. Forams can be both pelagic and benthic, with the tests of dead pelagic forms generally being more abundant contributors to seafloor sediments than the benthic forms. In 1976, investigators found between 2,000 and 4,000 specimens present per milliliter (mL) of sediment (USACE, 1977). The benthic varieties, which can be assumed to be, or have been, alive at the bottom were represented by 60 species, approximately 30 of which were only reported as trace occurrences. The USACE study reported that both total benthics and living benthics were more abundant at the shallower Site 3 than at 3A.

Micromollusks are the most abundant fauna at depths between 400 and 550 m, represented primarily by 12 species. Epifaunal browsers that live off a detrital organic film on sediment particles make up most of the mollusks, although holes in many of the mollusk shells suggest an active predator presence. Bivalves are also common. The 1976 study found that at the shallower Site 3 there was a higher proportion of epifaunal browsers than infaunal burrowers while the opposite case was true at Site 3A. Site 3A also exhibited a greater number of carnivores versus suspension or deposit feeders (USACE, 1977).

Polychaetes (worms) present in the sediments can be separated into predators, detritivores, and suspension feeders, with detritivores predominant in the HUMMA Study Area. The USACE survey identified 33 species, the majority of which were detritivores. The abundance of detritivores is indicative of a plentiful food supply for infaunal biota. Many of the polychaetes were tube worms, which play a major role in the mixing of bottom sediments near the seafloor while they process detritus internally.

Other invertebrates found in the area include Cnidaria (corals, jellyfish, anemones), Sipuncula (worms), Echinoidea (specifically starfish), and various Crustacea.

The State of Hawaiʻi Department of Land and Natural Resources (DLNR) prohibits bottom trawling (fishing nets) in the HUMMA Study Area and all coastal areas of Hawaiʻi. The water column above the HUMMA Study Area is not heavily fished, but there are some deep sea shrimp (known locally as *ama ebi*) that have been commercially harvested in the area in the past. Ahi, mahi mahi, *onaga* and other deep water or open ocean (pelagic) fish are sometimes taken by trolling (fishing hooks), but they are not present in numbers to warrant a commercial fishery (Kelley, 2007).

This page is intentionally left blank.

3. HUMMA Investigation Activities

3.1 MAPPING EFFORTS

3.1.1 *R/V Kilo Moana* SONAR Mapping

R/V Kilo Moana cruise 0716 departed from the UH Marine Facility at 08:00 on August 23, 2007. The ship spent seven days at sea and returned to port at 08:00 on August 30, 2007. The first two days were devoted to completing a wide-area reconnaissance survey of the area south of Pearl Harbor. The Kongsberg Simrad EM1002 hull-mounted multibeam, which operates at a frequency of 95 kHz yielding an optimal spatial resolution of 2 m, simultaneously collected bathymetry and backscatter data for the region. The data were Global Positioning System (GPS)-navigated and collected at the relatively low speed of 6 kt to provide along-track resolution that was comparable to the across-track resolution with the ultimate goal of producing a well-navigated base map for the towed IMI-120 survey to follow. Although the resolution of the hull-mounted system was recognized as being insufficient to locate 1-2 m munitions on the seafloor in these water depths, it was necessary to collect these data to map broad geological provinces (i.e., coral outcrops versus sandy plains) and identify those regions where the towed SONAR would be most effective at detecting reflective targets. In addition, the base map derived from the hull-mounted system includes seafloor shape and roughness allowing the towed IMI-120 system to be piloted 50-100 m above the seabed with reduced risk of collision. The EM1002 multibeam mapping effort covered an area of approximately 650 km^2, which extended from just below the entrance to Pearl Harbor to the northern edge of Penguin Bank. Track lines for both the EM1002 and IMI-120 surveys are illustrated in Figure 1-3.

On the morning of August 25, 2007 the *R/V Kilo Moana* picked up the Hawai‘i Mapping Research Group (HMRG) engineers, who finalized preparations for the IMI-120 SONAR survey. The instrument was deployed approximately 18 hours later (See Appendix G – Photo Log). The IMI-120 operates at a frequency of 120 kHz yielding an optimal spatial resolution of 0.5 m at altitudes less than 100 m above the seafloor and a swath width of approximately ten times the altitude above bottom. In selecting the system to use for the towed mapping effort, emphasis was placed on balancing the trade-off between resolution and the amount of seafloor that could be mapped based on usable swath width. The IMI-120 was ultimately selected because its resolving capabilities would detect 1-2 m objects on the seafloor from average altitudes of 75 m, allowing 2.7 km^2 to be mapped per hour. Previous experience searching for wrecks with HMRG’s towed systems revealed that the angle of incidence of sound waves directly affects what a SONAR system can image; therefore, the region around Site 3 (Figure 1-3) was surveyed with overlapping tracks in both east-west and north-south directions to maximize the ability to detect DMM where historical reports said CA had been recovered (University of Hawai‘i Environmental Center 1996a; 1996b). The north-south trending lines were completed first, followed by much longer east-west lines that crossed over then north-south tracks and covered most of the sedimented area south of O‘ahu, including the HUMMA Study Area.

After the initial survey south of Pearl Harbor the *R/V Kilo Moana* diverted to the Barber’s Point Study Area, where HURL HOVs had imaged objects on the seafloor that Army personnel identified as likely chemical munitions. The project team decided to collect data for the Barber’s Point Study Area as a contingency plan in the event that no DMM were detected in the HUMMA Study Area. There was a high probability that the field team would be able to return to previously detected munitions in the Barber’s Point Study Area and sample near them as the HOV pilots have repeatedly returned to this area to perform deep-water trials of the HOVs. After less than 24 hours of surveying the Barber’s Point Study Area, *R/V Kilo Moana* returned to the HUMMA Study Area and surveyed more east-west lines to extend the boundaries of the HUMMA Study Area to the south, close to the base of Site 3A.

Within the HUMMA Study Area, the IMI-120 was towed 50-75 m above the seafloor producing a backscatter swath width of 400 m on both the port and starboard sides of the towfish. In the Barber's Point Study Area to the southwest, because the terrain was more undulating, the towfish was towed at altitudes of 75-100 m. Backscatter data were gridded onboard the ship at a resolution of 2.0 m, which was later improved to 0.5 m, twice the across-track sampling rate. The IMI-120 towfish was navigated at sea using a layback correction, which assumes that the towfish is traveling exactly in the ship's track and uses depth below water plus the length of wire between the ship and the towfish to calculate the distance of the towfish behind the ship. After the cruise was completed, the IMI-120 data were re-navigated by correlating features observed in those data with features in the EM1002 backscatter data and shifting individual east-west and north-south swaths to align small-scale features evident in adjacent IMI-120 backscatter swaths.

The collected IMI-120 SSS data provided the basis for all subsequent investigations. The anomalous small, reflective targets observed in curvilinear trails in the backscatter data had the correct size and distribution to make them likely DMM that were cast overboard according to the procedures described in the historical reports from the end of WWII.

3.1.2 *R/V Klaus Wyrtki* Camera Tows

The UH towed camera system consists of a color charge-coupled device (CCD) camera, a video-to-fiber converter, power supply, and two 500 watt (W) underwater lights. The entire system is rated to full ocean (6,000 m) depths. It is deployed on a wire using a non-conductive strength member clipped to a fiber-optic line. The camera is towed 3 m above the seafloor at an optimal speed of 1-2 kt, which produces a swath width of approximately 5 m.

Beginning on November 20, 2008 and continuing until February 20, 2009 the *R/V Klaus Wyrtki* was used for several camera tows of the UH camera system (see Appendix G – Photo Log). Tows in November and December took place within 4.8 km of Honolulu Harbor in fairly shallow water depths to test various components of the camera system. An Ultra-Short Baseline (USBL) navigation system was incorporated into the camera sled to provide navigation with approximately 5 m accuracy for the instrument during its HUMMA deployments.

On January 27, 2009, the seabed was successfully surveyed for about 30 minutes in water depths of approximately 150 m. This was an operational test of the system at depth, and the video data were not recorded or interpreted. Images from the real-time video and navigational displays were captured and presented to DoD personnel on Friday, January 30, 2009 to demonstrate that the camera system was functioning as expected.

After the successful January test, the length of the fiber-optic cable connected to the camera sled was doubled, and two more surveys took place in February 2009. The first test, on February 6, 2009 was aborted shortly after the camera sled entered the water when the fiber-optic telemetry system failed. The problem was quickly traced to the connector at the camera-sled termination. On February 20, 2009 the camera sled succeeded in capturing several hours of video data over one of the speckle trails. Figure 3-1 shows the track lines for this experiment, which completed four oblique passes relative to the speckle trail. For all transects the UH camera sled was towed 1 to 4 m above the seafloor yielding video imagery with a field of view from 3 to 10 m. Navigational data were excellent, with an accuracy of approximately 5 m as estimated by comparing the video results with the re-navigated IMI-120 backscatter data. Unfortunately, wave and wind conditions were such during the deployment that it was difficult for the *R/V Klaus Wyrtki* to maneuver along a parallel course to the speckle trail at a constant speed. As a result few munitions were identified. Use of a larger vessel would have overcome the issues with deployment and maintaining course.

3.1.3 *R/V KoK* HOV and ROV Surveys

3.1.3.1 HOV RECONNAISSANCE FIELD PROCEDURES

The Pisces IV and V HOVs are each equipped with one forward-looking and one down-looking video camera system and sufficient lighting to capture imagery during every dive. On the Pisces V the forward-looking camera is a high-definition (HD) mini-Zeus built by Insite Pacific, which provides imagery and zoom capability; all other video cameras are standard format. Video is recorded on digital media inside the HOVs during the dive operations, and subsequently transferred to DVDs for analysis and interpretation. During reconnaissance surveys, the HOVs typically hover between 1 and 3 m above the seabed resulting in a minimum field of view (near the HOV) of 2 m and approximately 10 m in the far-field when the lights are set to maximum illumination. Speed of the HOVs during the video transects ranged from 0 to 2 kts. Navigation for the HOVs was acquired using an identical USBL system to the unit mounted on the UH camera tow sled. As such, the navigational accuracy of an HOV track when only one HOV was in the water was identical to that for the towed camera sled, about 5 m. During dives with both HOVs in the water, the *R/V KoK*, and thus the USBL receiver, had to be located between Pisces IV and Pisces V in order to communicate with both of them as acoustic communications are distance limited. This resulted in slightly poorer navigational accuracy (about 10 m) during dives with both HOVs in the water, a problem likely exacerbated because each HOV introduces more sound in the water that interferes with the USBL tracking signal for the other HOV.

During the March 2009 field program on the *R/V KoK*, reconnaissance surveys were accomplished by the HOVs on each of the 16 dives. Sampling dives during the reconnaissance surveys would typically last less than one hour, while on dives with no sampling the video surveys could last up to eight hours. If sampling was a priority for a dive, the reconnaissance was usually accomplished along a straight-line path from one waypoint to the next. When the primary goal was to image a speckle trail, the survey paths tended to "connect the dots" by traveling from object to object along a line of DMM, frequently stopping to examine a feature of interest at closer proximity.

Sample site selection was accomplished using the HOVs as opposed to the original plan of using towed video camera. During HOV investigation of a particular speckle trail when munitions of interest, typically those that potentially could contain CA, were identified by the pilot and on-board scientists, and the munitions' location was designated as a site for sampling. Usually sampling occurred as soon as munitions of interest were identified, but on a few occasions the location and description of munitions were noted and one of the HOVs would return to sample the site on a subsequent dive. The latter course of action was necessary because HOVs were limited in the number of sediment and water samplers that could be carried on any one dive – discovery of potential CA munitions casings after sample containers had already been filled meant a return to the location to sample on another day.

Dredge materials appeared visually different from the undisturbed sediment in the HUMMA Study Area in that the DS substrate was consistently covered with coarser material than in the sediment fields and random debris including dinnerware, soda and beer cans, plastic sheeting, coral and basalt cobbles and boulders, etc. were present. DS regions were therefore readily distinguished and allowed the rapid identification of the different strata for sampling.

Sampling at a "clean" RC site was accomplished during the first HOV dive to estimate the time necessary for the pilots to collect a full suite of samples and to evaluate the efficacy of the samplers. Subsequent RC sites were chosen after a full morning of visual reconnaissance from the HOV had not identified any munitions that potentially contained CA. For every "clean" RC site, the internal

SONAR display was used to ascertain that no targets were located within a circle with a 100 m radius, and then sampling would proceed. For RC sites in DS areas, the HOV SONAR always showed targets, so the HOV occupants would wait until they hadn't seen any munitions for 10-15 minutes (corresponding to a distance of 200-400 m at typical HOV speeds of 1 kt), and then the HOV would position itself so that sampling could proceed. White, positively buoyant bucket lids with labels were deployed at each sampling site so that HOVs could return to the site if necessary.

Bottom currents significantly influenced the survey strategy for the HOVs. As the diurnal currents changed direction in the midst of each dive, the survey plan developed prior to launch frequently had to be revised mid-dive to save power or improve data quality and quantity. As neutrally buoyant platforms, HOVs must expend more power to head into a current than to be pushed along with it. If an HOV uses too much power fighting the current it must return to the surface, shortening its bottom time. Thus, to maximize the amount of reconnaissance data collected, it is best to have HOVs move in the same direction as the current. However, when sampling and acquiring high-resolution imagery in proximity to DMM, it is safest for the HOV to face into the current, minimizing the risk of contact with munitions. In addition, bottom currents can stir up sediments, noticeably reducing both the visibility of the pilot driving the HOV, the quality of the imagery being collected, and affecting samples being collected.

The HUMMA project team established two facts in advance of the March 2009 *R/V KoK* program. The first was that Pisces V had superior video capability because of its high-resolution camera. The other was that Pisces V had newer batteries that would provide more on-the-bottom time than the Pisces' IV batteries. In addition, HURL standard operating procedure (SOP) is that when only one HOV is diving, assuming there are not mechanical problems, the one sub that dives is the Pisces V. When two HOVs are deployed on the same day, the Pisces V is deployed first and recovered last, so it always has more time on the bottom than Pisces IV. For all of these reasons, the project team decided in advance of the project to have Pisces V undertake the bulk of the reconnaissance work, while the Pisces IV would concentrate on collecting samples near DMM that had been identified during previous HOV or ROV operations.

3.1.3.2 ROV RECONNAISSANCE FIELD PROCEDURES

During the March 2009 field program on the *R/V KoK*, the plan was to initiate nighttime surveys using the ROV, after HOV activities had been completed for the day. The goal of these surveys was to assess the likelihood of finding chemical munitions in speckle trails or fields that had been identified in the SSS data but had not been previously imaged by the HOVs. In actuality, the ROV program results proved to be similar to the camera tows aboard the *R/V Klaus Wyrtki*. Although the *R/V KoK* is much larger than the *R/V Klaus Wyrtki*, it is still subject to wind, wave, and current conditions, especially when it is towing over-the-side gear that could get entangled in the propellers. To account for this limitation, ROV survey tracks were not planned until just before each system deployment after consultation with the bridge crew about which directions were best suited for that evening's tow based on the conditions observed during the day.

Once the *R/V KoK* reached an appropriate site for the survey given the surface conditions, the RCV-150 System was launched using the *R/V KoK's* specialized over-the-side handling system. On the first two RCV-150's deployments, mechanical failure of various components led to recovery of the system without any data acquisition; however, the RCV-150 was successfully deployed during its third attempt on March 7, 2009 and it completed five additional nighttime tows before the field program ended on March 18, 2009. Towing speed for the ship was typically 1 to 2 kts, although the configuration of the ROV allowed the operator some flexibility to vary that rate. Navigation was accomplished using the same USBL system that acquired navigation for the HOVs although it was recorded at less frequent intervals due to the straight-line nature of the survey plans.

When the RCV-150 system reached an altitude of approximately 10 m above bottom, the ROV was released from the RCV-150 system's cage. The ROV remained tethered to the RCV-150's cage throughout its deployment. This two-body tow approach had two distinct advantages. First, it effectively decoupled the ROV from the motion of the ship; second, it allowed the ROV to wander within an 8-10 m diameter circle where it would investigate items for several seconds before moving to maintain pace with the ship. Using a scanning SONAR plus a down-looking camera mounted on the RCV-150 system's cage, the pilot sent the ROV to investigate objects on the seafloor, approaching each target from the downstream side to minimize the chance of collisions.

The six ROV reconnaissance surveys had an average duration of two hours each, beginning at approximately 1900 and typically ending before 2200. Limiting ROV surveys to this interval allowed the pilot and engineer sufficient time to rest as they were required members of the early-morning HOV pre-launch team. Furthermore, almost all of the speckle trails investigated were less than 4 km in length and were adequately covered during a 2-hour deployment. In practice the project team was able to approach DMM more closely and from more angles using the ROV than the HOVs, although the HOVs were far less constrained in their ability to move around the seafloor because they weren't tethered to the *R/V KoK.*

3.2 SAMPLE COLLECTION ACTIVITIES

Sample collection activities were presented in the draft SAP and heavily reviewed and modified based on input from the TAC as well as the experts from the Office of the Deputy Assistant Secretary of the Army (ODASA), ECBC, UH, HURL, and Environet. This extensive planning and review process was necessary due to the unique challenges posed by the HUMMA Study Area depths, the types of DMM - specifically CA - anticipated to be encountered, potential safety hazards posed by the possibility of operating HOVs in close proximity to CA, and the time and weight limitations of the HOVs.

The initial selection of COPCs for the HUMMA Project was based on historic disposal records. The COPCs are specific munitions constituents and associated munitions constituent degradation products related to the M47A2 100-lb mustard bombs and the other DMM historically reported for the area. Individual COPCs from these sources include a variety of chemicals in the following groups: CA and their degradation products from bomb fill materials; energetic materials from bursters and conventional munitions; and metals from munitions casings.

The mustard fill [1,1'-thiobis(2-chloroethane), i.e., HD] weight of the M47A2 100-lb mustard bomb ranged from 29.5 to 33.9 kg depending on fill level and the purity of the mustard. The bombs were not fuzed at the time of disposal, but a burster (an explosive charge designed to rupture the bomb casing and permit release of the CA) would be present. The burster for these bombs had one of three possible fills: 1) 0.68 kg of TNT; 2) a 50/50 mix of black powder (a mixture of sulfur, charcoal, and potassium nitrate) and magnesium; and, 3) TNT and methyl-2,4,6-trinitrophenylnitramine (tetryl) pellets. The bomb body was constructed of 0.15 cm thick sheet steel (estimated as 8.4 kg). The gross weight of the bombs was 42.9 to 45 kg. Mustard and lewisite are the only chemical warfare material (CWM) COPCs. Mustard is a COPC because documentation indicated disposal of mustard in the area. Although lewisite is not believed to have been disposed in the area, the persistence of lewisite's degradation products could present a concern and Lewisite was retained as a COPC in case it had been disposed in the area. The degradation products of mustard retained as COPCs are thiodiglycol (TDG), 1,4-dithiane, and 1,4-thioxane. The degradation products of lewisite retained as COPCs are 2-chlorovinyl arsenous acid (CVAA) and 2-chlorovinyl arsenous oxide (CVAO).

Typical munitions high explosive fills from the WWII era include Composition B (a mixture of cyclotrimethylenetrinitramine (i.e., Royal Demolition Explosive (RDX)) and TNT); torpex (a mixture of RDX, TNT, and aluminum, used in torpedos); amatol (a mixture of TNT and ammonium nitrate); ammonium picrate (Explosive D); and TNT. The corrosion of the metal casings of conventional munitions and consequential leakage can release energetics and their degradation products to the environment. Because the specific fills are not known, and based on the M47A2 bursters that contained TNT or tetryl, the energetic compound COPCs are TNT, DNT, RDX, and tetryl.

Explosive D, ammonium picrate, was initially considered as a candidate COPC for this study. This compound is an ammonium salt of picric acid and under normal aqueous conditions will dissociate to ammonium and picrate ions. In sediment slurry tests, picric acid was found to remain in the aqueous phase with little partitioning to the sediments. Transformation to picramic acid was limited (Yost *et al.*, 2007). It is likely that the ions would transform further depending on the redox conditions. Ammonium picrate is highly soluble and dilution and dispersion are expected to be predominant factors in its environmental fate and transport. Because of its high solubility and low probability of partitioning to sediment, ammonium picrate was not anticipated to be sufficiently persistent in the environment to justify looking for it in sediment or water samples. It was thus dropped from consideration as a COPC for the project.

The study was also designed to evaluate the potential effect of munitions casings on the composition of sediment, seawater, and human food item biota by analyzing for heavy metals specifically associated with munitions casings; and in order to distinguish certain CA degradation products from study sites influenced by anthropogenic sources such dredge material input. Metals are released to the surrounding environment due to the corrosion of the munitions bodies. Due to the amount of shipping traffic, dredged material disposal activities, and DMM in dredge material areas, there may be other sources of metals present in these locations. Assigning attribution is easiest where samples are collected very close to munitions. Metals typically associated with large munitions include iron and copper, although small amounts of lead may also be present. Iron is a nutrient and as such does not present a significant hazard to human health and the environment; it is not included therefore as a COPC. Other metals are associated with munitions but typically in much lower quantities. Lewisite breaks down to inorganic forms of arsenic, which can persist indefinitely in the environment.

Although the study initially called for analysis of metals in seawater, subsequent review of fate and transport information indicated that the environmental conditions at the study sites would not be conducive to finding metals in seawater. The pH range, likely adsorption to sediments, and dilution with seawater at the study sites (discussed in greater details in Section 4.5) were the major factors considered. Seawater samples were thus analyzed for CA and energetics only.

Metal COPCs for sediment and biota samples of HUMMA Project are the following:

- arsenic (total),
- copper, and
- lead.

Samples were also screened for a suite of major elements (aluminum, calcium, iron, magnesium, and strontium), selected minor constituents (barium, manganese and titanium) and a group of trace elements (cobalt, chromium, cadmium, uranium, vanadium, and zinc) that were selected based on their potential to distinguish individual concentrations of munitions constituents from terrigenous (volcanic) materials, and anthropogenic sources (National Oceanic and Atmospheric Administration (NOAA), 2007).

COPCs selected for the HUMMA Project and the analytical methods used for each COPC are presented in Table 3-1. Many COPCs lacked applicable or appropriate screening criteria; valid screening levels are presented in Section 7 and Appendix H (HHRA Calculations).

The HUMMA Project culminated in the collection of samples from 19 sites, distributed amongst four strata: DMM sites, DMM-DS sites, DS sites, and RC sites (Table 3-2). Media types sampled included seawater (30 samples), sediment (94 samples), shrimp (19 samples), fish (16 samples), and infauna (18 samples), plus associated quality assurance/quality control (QA/QC) duplicates. The following sections describe the process of selecting locations at each sample site where sediments or water were collected, collecting the samples, handling and processing the samples, and delivering samples to the various subcontract labs for chemical analysis.

3.2.1 Sediment Sample Collection

3.2.1.1 RANDOMIZED LOCATIONS

Sediment samples were collected following at stratified random sampling sites that fell into four categories: DMM sites in "clean" sedimented terrain (DMM), DMM sites in DS terrain (DMM-DS), control sites in DS terrain (DS), and reference control sites in "clean" sedimented terrain (RC). A minimum of six sediment samples were targeted for collection from each of the 19 sites, although this was not always possible due to equipment and time constraints (See Table 3-2 for the actual collection summary). As described in the SAP, sample collection at each site was randomized by designing a semicircular sampling area divided by ten radial lines every 20 degrees. For sediment sampling, each radial line was bisected at the 1 m and 2 m marks creating two semi-circles along which sampling would occur (see Appendix C – HUMMA Sample Collection Sheets). Using the random number generating function of Microsoft Excel® or an equivalent randomization technique, three locations along the 1 m arc were chosen as were three locations along the 2 m arc. Sediment collection from a neutrally buoyant HOV is somewhat problematic in that thrusting of the sample bottles into the substrate can cause an inverse reaction that sends the HOV moving backward. To combat this force, HOV pilots would modify submersible buoyancy. They were assisted in this effort by the sediments themselves, which were "sticky" enough to retain small troughs where the scooping first occurred; this provided a reference point so that the pilots could adjust HOV position as necessary to keep sampling within a few centimeters (cm) of the initial location. In order to meet laboratory QA/QC requirements, several sites included collection of matrix spike (MS)/matrix spike duplicates (MSD) or field duplicate samples. MS/MSD samples consisted of extra sampling containers collected at one of the six randomly selected sites to achieve the volume required by the laboratory. Upon return to the ship, the material was homogenized and split into the various sampling containers. Field duplicates were also collocated with one of the six randomly selected samples, but were treated as an individual sample, assigned a unique identifier, and submitted "blind" to the laboratory for analysis (i.e., the lab would have no way of telling whether any sample was a primary sample or a field duplicate based on the information presented on the sample label and the chain of custody).

3.2.1.2 SEDIMENT SAMPLE COLLECTION

Sediment samples for laboratory analysis for COPCs (i.e., energetics, metals, CA) were collected using clear polyvinyl chloride (PVC) sediments scoops designed and built by the HURL team (see Appendix G – Photo Log). Each scoop was labeled with a unique identifier number. The contents of a single scoop corresponded to one discrete sample (e.g., contents of multiple scoops were not combined or homogenized for samples undergoing chemical analysis). At the beginning of each dive day, two crates were secured to the front of the HOV. One crate would be filled with approximately nine pre-cleaned sediment scoops (sediment scoops were decontaminated after each use by washing with an alconox and freshwater mix using scrub brushes followed by a triple rinse using freshwater). The second was either a duplicate, also containing sediment scoops, or it was a lidded crate, designed to carry up to six water-sampling containers. When the HOV reached a sampling site, the pilot would verify with the on-board scientist the planned locations for sediment samples, then would remove a sediment scoop, collect a sample by scooping a shallow (0 to 20 cm) swath of sediment in the predetermined location, repeating as necessary to fill the scoop, and then close the ball valve near the terminal end of the scoop. The on-board scientist noted the unique number of the sediment scoop on the field form and radioed it to the *R/V KoK* control room. This process was repeated throughout the sampling site until all sediment samples had been collected, until all sediment scoops were filled, or until sampling became impractical due to time or equipment constraints.

3.2.1.3 SEDIMENT SAMPLE HANDLING, PROCESSING, AND ANALYSIS

When the HOV returned to the *R/V KoK*, it was flushed with water to remove any CA that may have inadvertently been captured in the HOV's struts or other areas. The HOV was then brought on deck and secured to the deck. ECBC personnel then screened the exterior of the HOV and the sample containers for the presence of CA using a portable gas chromatograph (GC) and removed the sample containers from the HOV. ECBC packaged the sample containers into 6 mil plastic bags, and transferred them to ECBC's on-board wet lab. ECBC personnel opened each sample container inside a glove box, conducted head-space monitoring (vapor screening for CA that may have entered the airborne phase from the sediment), and collected an aliquot of sediment for analysis for CA. ECBC personnel then removed all sediment from the scoop container and transferred it to a 5-gallon Ziplock bag that was then stored in the wet lab refrigerator at 4 °C. Once ECBC personnel reviewed the results of their analysis to ensure both that CA was not present and the safety of personnel handling the samples, the UH team assumed custody of the samples from ECBC.

Sediment samples from the scoops contained a large volume of seawater. A vacuum pump filtration array using Whatman 47 mm filters was used to remove the majority of the seawater from each sediment sample. Seawater and any sediment suspended therein was poured from the 5-gallon Ziplock bag through the filtration array. Once all seawater had been poured off and filtered out, sediment trapped in/on the filter was transferred back into the 5-gallon Ziplock bag using a dedicated plastic spoon. The 5-gallon bag was then homogenized by kneading the bag to ensure sediments were well-mixed. Sediment samples were not homogenized from multiple scoops; rather the contents of one scoop equated to one discrete sample. Following filtration and mixing, sediments were transferred using a dedicated plastic spoon from the 5-gallon bag into 4 ounce pre-cleaned, laboratory supplied sample jars for energetics analysis, and Ziplock bags for metals analysis. Sample containers were labeled with a unique identifier, which was then entered on the chain-of-custody form. Sample containers were stored in the wet lab refrigerator, and upon return to port they were delivered to the appropriate laboratories for chemical analysis.

Sediment samples were analyzed for CA using ECBC Internal Operating Procedure (IOP) MT-08, energetics using EPA method 8330, and metals using a UH proprietary method analogous to EPA method 6020A.

3.2.1.4 SEDIMENT QUALITY ASSURANCE/ QUALITY CONTROL SAMPLES AND FREQUENCY

QA/QC samples consisted of field duplicates and MS/MSD samples (consisting of an extra volume of sediment collected from a randomly selected sampling location). Because the COPCs for this study did not include volatile compounds, trip blanks were neither appropriate nor required. Duplicate samples were collected at a frequency of 10 % of the primary samples, and MS/MSD samples were collected at a frequency of 5 % of the primary samples.

3.2.1.5 PUSH CORES FOR BENTHIC INFAUNA COUNTS

In addition to the sediment samples collected for chemical analysis, sediment samples for benthic infauna counts were also collected. The SAP called for collecting one sample from each site for benthic infauna counts using a mini-PONAR grab sampler, to ensure that a consistent surface area was sampled. As the project moved forward, however, the field team realized that carrying a mini-PONAR sampler or box corer to a sample site would limit the HOV's capacity to carry sediment or seawater samplers. Because of the limited number of field days, it would have been impossible to collect the targeted number of sediment and seawater samples if the mini-PONAR were used. The steps required to trigger the device were also anticipated to pose difficulties for the HOVs' robotic arms. Alternatively, HURL had designed a small (6.5 cm interior diameter, 42.3 square centimeter (cm^2) surface area) push core device that required no more room than the sediment samplers, and was easily maneuvered by the HOV's robotic arms (see Appendix G – Photo Log). The push core device was inserted straight into the sediment and then extracted. A rim of inverted, unidirectional stiff plastic material at the terminal end of the push core reduced sediment leakage once the push core was retracted from the sediments. These push cores were successfully used to obtain samples at 10 of the sites. Push cores were unsuccessful at some of the sites where there was a thin layer of sediment overlying a solid coral substrate. In these locations, the push core device broke when the HOV's robotic arm pushed through the sediment and the corer contacted the solid substrate. The breakage occurred at the handled end of the unit, where the cap with the T-bar handle had been attached to a plastic cylinder using a hose clamp. During the field program the HURL engineers improved the durability of the push cores by tightening the hose clamp and gluing the exterior parts of the push core handle together. Future improvements to the design will include using a wider cylinder that had been manufactured to have a solid end cap on one side rather than attaching a discrete cap to a cylinder that was opened at both ends.

The project team wanted to submit at least one sample for benthic infauna counts from each site where a full suite of sediment and water samples were collected, so for those sites where a push core was not collected, the following modification was instituted. All sediments remaining from samples collected at any one site, after the appropriate amounts were extracted for laboratory analyses of 1 and 2 m mark scoops, were combined into a single container and preserved for benthic infauna counts. This collection of sediment was called "a composite sample" rather than a push core, and was used to provide qualitative rather than quantitative data. It is not possible to assign a surface area to the composite samples, and consideration must be given to the fact that these samples were filtered by the field team to remove excess water before partitioning into the sample jars for chemical analysis. A total of eight composite samples were collected. In order to have some basis of comparison between the push core samples and the composite samples, the field team prepared composite samples at three of the sites that had successful push cores.

ECBC screened the sediment samples from the push core devices for the presence of CA. Once ECBC cleared the samples, they were transferred to gallon-size Ziplock bags and stored in the wet lab refrigerator at 4 °C overnight. Once ECBC personnel were certain that CA was not present and that onboard personnel could handle the samples safely, the UH team assumed custody of the benthic infauna samples. Benthic infauna sediment samples were transferred to laboratory-supplied containers, to which magnesium chloride was added to relax any benthic organisms present in the sediment. The amount of magnesium chloride added to each container was determined by the volume of sediment; magnesium chloride was added until the sediment was sufficiently covered to enable saturation of all pore spaces. The containers then sat undisturbed for a period of 20 minutes, after which time the remaining volume of the container was filled with 10 % formalin to preserve any soft-bodied tissues. Unique sample identifiers were written on laboratory-supplied labels which were placed on the interior and exterior of each container. The containers were then sealed with tape, and could be stored at room temperature awaiting benthic infauna count analysis. Upon return to port, the benthic infauna samples were shipped to Cove Corporation and identified to the species level if possible, or to the genus level.

3.2.2 Seawater Sample Collection

3.2.2.1 RANDOMIZED LOCATIONS

Seawater samples were collected following the same stratified random sampling strategy used throughout the project: DMM sites, DMM-DS sites, DS sites, and RC sites. A minimum of two seawater samples were prioritized for collection near the seafloor at each site, from two randomly selected locations, although this was not always possible due to time and equipment limitations (See Table 3-2 for the actual collection summary). As described in the SAP, ten segments of the semicircle sampling area were consecutively numbered from 1 to 10. As explained previously, the HOVs approached and sampled each DMM from the down-current direction in order to minimize the risk of contact caused by currents pushing on the neutrally buoyant HOVs. As such, all samples, including seawater, were acquired down current from DMM. The random number generating function of Microsoft Excel® or an equivalent method was used to select two locations for obtaining seawater samples at each of the sample sites. The HOV collected the seawater samples from the randomly selected locations approximately one m from the central point of the semicircle, and at a height above the sediment of approximately 1 to 1.5 m. This height was dictated by position of the sampling arms on the HOVs above the sample basket. As both arms were necessary to hold and close the bottles during seawater sampling, collection could not have taken place any closer to the sediment.

3.2.2.2 SEAWATER SAMPLE COLLECTION

Seawater samples from each site were collected in sampling containers designed and built by HURL. Seawater sample containers were constructed of clear PVC pipe with a ball valve on each end and a handle that could be manipulated by the HOV operator (see Appendix G – Photo Log). Containers were pre-cleaned and soaked in a mild (10 %) hydrochloric acid solution prior to being loaded onto the HOV. A total of six water samplers could be loaded into a lidded crate mounted on to the front of the HOV. A second, open container on each HOV was dedicated to carrying sediment sample scoops and push core devices. Due to the volume of seawater required by the laboratories to complete the requested analyses, two containers were required for each sample. Any given HOV trip could thus collect a maximum of three seawater samples.

Seawater sample containers were loaded onto the HOV in the “open” position, allowing seawater to freely flow through the container during the descent and transit to the sample site. Once the HOV reached a site, the on-board scientist would relay the randomized location for collection of a seawater sample and direct the HOV pilot to collect the seawater samples before collecting any other sample type (sediment or push core). This minimized the amount of sediment that was suspended in the water column due to HOV activity, and thereby ensured a minimum of sediment introduced into the water sample. The pilot would select an empty container, call out the unique identifier label on the container, move it through the water column a few times to ensure water within the tube was representative of the water present at the site vice water that may have been trapped during transport, then position the sampler directly over the substrate. The HOV pilot would close both ball valves and store the container back in the lidded crate mounted to the front of the HOV. The on-board scientist would note the sample container identifier tag and the location from which it was collected, as well as the date, time, and any relevant comments. This process would be repeated with an additional sample container at the same location (to achieve the volume required for laboratory analysis). If sufficient empty containers remained on-board, the HOV pilot would collect additional seawater samples from the other randomly selected locations.

3.2.2.3 SEAWATER SAMPLE HANDLING AND PROCESSING

Once the HOV had returned to the *R/V KoK* and was secured on the deck, the exterior of the HOV and the sample containers were screened by ECBC for the presence of CA using a portable GC. ECBC personnel then removed all sample containers from the HOV, packaged the sample containers in 6 mil plastic bags, and transferred them to ECBC's on-board wet lab. ECBC personnel opened each seawater sample container inside a glove box, conducted head-space monitoring (vapor screening for CA that may have entered the airborne phase from the seawater), and collected an aliquot for analysis for CA. For the seawater samplers, the ECBC personnel closed the ball valves after collecting an aliquot of seawater, and stored all samplers in the on-board sample refrigerator. Once ECBC personnel reviewed the results of the CA analysis to ensure both that CA was not present and the safety of personnel handling the samples, the UH team assumed custody of the samples from ECBC.

Seawater samples were partitioned into containers with a specific procedure in place to minimize the potential introduction of contamination into the sample. A UH scientist donned a pair of class 10 trace metal (TM) clean gloves to keep the environment free of contamination. The field sample container was opened by an assistant and then handed to the scientist. The UH scientist would then pour the seawater from the sampling container into two laboratory-supplied, pre-cleaned 1-liter (L) plastic amber bottles. Although the field-sampling plan specified the use of glass containers for analysis of energetics in seawater, the laboratory subsequently requested that plastic amber bottles be used instead. These bottles were labeled, sample numbers and sample details entered onto a chain of custody, and the bottles were stored in the on-board sample refrigerator. Upon return to land, the samples were immediately shipped to the relevant laboratory for subsequent analysis for energetics.

Seawater samples were analyzed for CAs using ECBC IOP MT-08, and energetics using EPA method 8330.

3.2.2.4 SEAWATER QUALITY ASSURANCE/QUALITY CONTROL SAMPLES AND FREQUENCY

QA/QC samples consisted of field duplicates and MS/MSD samples. Because the COPCs for this study did not include volatile compounds, trip blanks were neither appropriate nor required. Duplicate samples were collected at a frequency of 10 % of the primary samples, and MS/MSD samples were collected at a frequency of 5 % of the primary samples.

3.3 HUMAN FOOD ITEM BIOTA SAMPLING

3.3.1 Human Food Item Biota Sampling Rationale/Design

Human food item biota sampling was conducted subsequent to the sediment, water and infauna sampling that took place aboard the *R/V KoK*. A separate, commercial fishing vessel was used for this later effort, with sample collection targeting food items likely to be consumed by humans. The two targeted species selected were a highly prized finfish *Etelis coruscan* (known locally as *onaga)* and a commonly eaten shrimp *Heterocarpus laevigatus* (*ama ebi)*. Because the two types of biota are collected and consumed by humans, the project team conducted sampling using the same methods that commercial and recreational fishermen use (i.e., rod and reel for fish and traps for shrimp).

3.3.1.1 HUMAN FOOD ITEM BIOTA SAMPLE LOCATIONS

Human food item biota was collected following the stratified random sampling strategy used throughout the project with four distinct strata: DMM strata, DMM-DS strata, DS strata, and RC strata. The specific strategy for collecting the human food items was to fish and trap near sample sites where sediment and water had been collected using HOVs. The SAP established target collection goals for *onaga* and *ama ebi*, and specifically addressed the need for flexibility based on actual field conditions. The collection goal for the shrimp was readily achieved. *Ama ebi* traps were deployed at multiple sites within each of the four strata (four RC sites, seven DMM sites, two DS sites, and three DMM-DS sites), although the exact distance between each trap and any DMM could not be determined due to the lack of visual information from the seabed. GPS readings were taken at the location where each shrimp trap was dropped, and the biota field team made every attempt to drop the traps in proximity to the selected study area sites based on the USBL information provided from the HOV operations, but in practice it was not possible to obtain an exact position of where the trap was deployed on the seafloor.

It was not possible to meet the collection goal for *onaga* due to the relative shortage of fish in the vicinity of the sample sites. Some reasons for the absence of *onaga* included the depth of the sample sites as well as the lack of suitable habitat – these fish prefer habitats near rocky outcrops, which we avoided in order to improve the chances of locating highly reflective munitions in the sandy regions of the HUMMA Study Area. The fish collection goals were reduced from the initial intention of catching a total of 36 fish to catching a minimum of six *onaga*, or a total of six days of fishing, whichever came first. Additionally, the sampling strategy for fish was expanded to cover the overall HUMMA Study Area, as opposed to the discrete sampling sites, which was justified due to the highly transient and far-ranging habits of *onaga*.

3.3.1.2 HUMAN FOOD ITEM BIOTA SAMPLE COLLECTION AND FIELD AND LABORATORY ANALYSIS

All fishing activities were conducted from a 35 ft surface vessel (see Appendix G – Photo Log). The vessel was equipped with two bottom-fishing rigs to target the *onaga* and one pinch puller to assist with the retrieval of the shrimp strings. Bottom-fishing rigs consisted of a rod and an electric reel. The main line of the reel was attached to a leader containing a baited hook that ended with a three-lb weight. Shrimp strings consisted of a 3/8-in nylon line with an individual shrimp trap spaced every 50 ft. A total of five shrimp traps were attached to each string. To assist in locating the shrimp strings and to prevent possible entanglement with other boaters, large orange surface floats with flags were used.

Shrimp collection activities began and ended each day the fishing vessel was at sea to allow both a day soak and a night soak. A total of two strings were used and each was deployed at a separate sample site. The shrimp string was deployed as close to the sample site as possible. The shrimp string was deployed by first dropping a large weight followed by five evenly spaced weighted traps. GPS coordinates were collected once the last trap entered the water. Day soaked strings were deployed at the start of each day. The strings were then hauled at the end of the day emptied, re-baited and redeployed to allow an overnight soak.

Once all the traps were on deck, the shrimp were sorted by species and transferred into uniquely labeled bags. The bags were labeled with the date, time, and trap number and then placed into a cooler with ice for preservation.

Fishing efforts took place after the morning shrimp haul and set had been completed. Using the boat's GPS, baited fishing lines were dropped to the bottom of the ocean. GPS coordinates were collected as soon as the weighted line made contact with the bottom. The fishing lines were fished for five minutes at which point they were retrieved. Once the five minutes had passed GPS coordinates were again collected to mark the bottom fishing drift. Lines would then be re-baited and dropped again. Multiple drops were attempted at each location. Due to the depths in the HUMMA

Study Area each bottom fish drop took approximately 30 minutes from deployment to retrieval. On average, four drops were made at each site before moving on to another location. If fish were caught at a location more drops were made before moving on.

In the event that a fish was hooked within the five-minute window, the line was immediately retrieved and GPS coordinates were collected. As fish were landed on the fishing vessel, they were removed from the hook and immediately euthanized by placing them on ice. Fish were subsequently identified and tagged with a unique tag number. It should be noted that the process of reeling *onaga* to the surface from depth frequently resulted in their swim bladders protruding from their mouths caused by the change in pressure from approximately 36 atmospheres of pressure to 1 atmosphere of pressure. When this occurred, the fish were photographed “as is” and treated like any other sample.

Once fishing efforts finished for the day, samples were prepared to be sent to the laboratory. Photographs and measurements were taken of all specimens, which were then inventoried and transferred into Ziplock bags. Fish and shrimp were examined for deformities, eroded fins, lesions, and tumors. Each sample bag was labeled with a unique identifier and transferred to a freezer to await shipment to the mainland laboratory. To preserve sample integrity and preparation consistency, the laboratory was responsible for the preparation and analysis of the fish tissue.

Fish and shrimp were analyzed for CA, energetics, and metals. Fish tissues to be analyzed included fillets only, while shrimp tissues analyzed included tails only, to be reflective of local consumption habits. Fish fillets were of sufficient mass to represent a unique sample, however in some cases two or more shrimp tails were combined in order to achieve the minimum sample mass required. In these instances, shrimp of roughly the same size and from the same shrimp trap were combined. Samples were sent directly to Columbia Analytical Services, where they were processed and analyzed for energetics and metals. Columbia Analytical Services also prepared a subset of extract that was sent to ECBC to be analyzed for CA and degradation products including dithiane and thioxane.

3.3.1.3 HUMAN FOOD ITEM BIOTA QA/QC SAMPLES AND FREQUENCY

QA/QC samples consisted of laboratory duplicate samples and MS/MSD samples. Because the COPCs for this study did not include volatile compounds, trip blanks were neither appropriate nor required. Duplicates were collected at a frequency of 10 % of the primary fish and shrimp samples, and the laboratory was instructed to prepare MS/MSD samples of 5 % of the fish and shrimp samples.

3.4 PHYSICAL OCEANOGRAPHY INVESTIGATION

An oceanographic mooring was deployed in approximately 500 m depth at 21.2181° N, 157.9381°W from November 13, 2008 to February 13, 2009. It was recovered on February 14, 2009, the data it collected were cataloged on shore, and on February 28, 2009 it was redeployed at 21.2186° N, 157.9329°W. Unfortunately, at some point between the redeployment and August 1, 2009 the mooring broke loose and efforts to recover it and analyze data collected during the March 2009 *R/V KoK* field program were unsuccessful. However, the data from the November 2008 to February 2009 time period were consistent with observations made during the HOV dives, and no significant events that might alter oceanographic conditions south of Pearl Harbor (e.g., a hurricane) occurred that were likely to alter the physical oceanographic findings of the first deployment.

The purpose of the mooring deployment was to measure current speeds near the seafloor that might lead to turbulent mixing and re-suspension of sediments, and to characterize the stratification of the water column above the study area. The mooring’s instrumentation included a down-looking

Teledyne RDI Doppler Volume Sampler (DVS) mounted approximately 10 m above the seafloor and a McLane Moored Profiler (MMP) mounted above the DVS (Figure 3-2). The DVS recorded 5 minute averaged currents and temperature throughout its deployment. The MMP literally crawled up and down the mooring line every day, providing a vertical profile of current, temperature, salinity, and pressure every 20 minutes. The profiler data presented in this report represent data collected between 326 m and 488 m water depth. A Seabird SBE39 temperature sensor was located near the upper stopper of the profiler as a calibration check.

3.5 POST ACQUISITION VIDEO ANALYSIS

The video systems deployed on the UH camera system, the HOVs and ROV are similar in the type and resolution of the information that they capture. This being the case, all video analyses were accomplished in the same way, reviewing the imagery for objects of interest (Appendix B – Glossary of Select Munitions Types).

A fundamental goal of the video analysis was to document the total number, type and orientation of DMM depicted in video footage for each camera survey. A second goal was to qualitatively describe the integrity of munitions casings. When an object was detected, its size was estimated based on the lasers in the field of view, which were 5.1 cm apart for the UH towed camera system and 15.25 cm apart for the HURL HOVs and ROV. Because the HURL video data included an overlay with time, water depth and HOV/ROV heading, this information was also listed for each object of interest, as was the orientation of the object with respect to the video frame. General comments were made on the condition of each DMM observed, classifying the condition of munitions in qualitative categories ranging from “intact” to “very deteriorated.” Many DMM were imaged with “skirts” or columnar “pedestals” beneath them. One component of the post-acquisition video analysis was devoted to reviewing images of DMM and describing the characteristics of any pedestals with as much detail as possible (Appendix D – Pedestal Analysis). In addition, distinctive aspects of each target were described in general terms for subsequent co-registration with the backscatter imagery. For example, where groups of munitions were found, their distribution relative to each other (e.g., “tight grouping” or “triangular distribution”) would be described. Similarly, if some aspect of a particular DMM made it distinctive so that it would be recognized in a subsequent video survey (e.g., “wrapped in plastic” or “there’s a Coca-Cola can adjacent to it”), these characteristics would also be noted. This latter notation was useful for correlating objects seen in multiple video passes over the same piece of seafloor. These descriptions are also included in Appendix D.

After the video analyses were completed, still frames for each object of interest were captured. The time when each object was encountered was combined with the navigation for the corresponding video reconnaissance survey track to determine a geo-referenced location for every still image. The latitude and longitude for a particular picture was then used to hyperlink the image into the HUMMA GIS to visually document trails of munitions (Figure 3-3).

HOV videotapes were also reviewed to compile an inventory of the macrobiota observed while on station at the sampling sites during the *R/V KoK* field program. The HOV dives were reviewed in real time to ensure that all mobile macrobiota were inventoried. An inventory sheet was completed for every HOV dive at which sampling occurred. The inventory sheets included the dive number, site name, date, time, common name, scientific name (if known) number of that particular organism, substrate, depth, activity of animal, and any comments. These sheets have been assembled into one table in Appendix F (Biota Assessment Table).

Dr. Christopher Kelley of UH assisted with the identification of the species documented in the video assessment of macrobiota. Because of the nature of the video systems’ resolution and field of view, many organisms could not be definitively identified. Lack of identification could be attributed to one or a combination of the following reasons: the organisms were not in focus, either from being too close or too far from the camera, a sediment cloud impeded line of sight, the animal moved by the camera too fast, the lighting was insufficient to illuminate the animal, or the animal was too small. In some cases it was difficult to discern whether an organism type viewed more than once represented different animals or the same animal swimming in and out of view. The inventory in these cases reflected the best judgment of Dr. Kelley.

Another problem encountered during the video assessment of macrobiota was that some animals were either attracted to or scared away by the lights, size or movement of the HOVs. To combat this problem, five minutes of video collected before the sampling start and after the sampling stop time were included in the review for presence of macrobiota. The animals documented before and after the sampling period are delineated with a “pre-” and “post-” respectively in the sampling sheets (Appendix F – Biota Assessment Table).

3.6 INVESTIGATION-DERIVED WASTE

Miscellaneous investigation-derived wastes (IDW) were generated during the HUMMA Project, consisting of personal protective equipment (PPE) generated by the ECBC personnel, Environet and UH scientists. No CAs or their degradates exceeding laboratory reporting limits were encountered during the on-board screening by ECBC personnel, head-space monitoring, or on-board CA laboratory analysis. IDW were handled, stored, and labeled accordingly. IDW were stored on-board temporarily, within a 55-gallon drum that met the criteria for performance-oriented packaging, located in an on-board equipment staging area. The drum was labeled with:

- the date of generation,
- contents,
- point of contact,
- telephone number, and
- unique drum identification (ID) number.

The contents of the drum were inventoried daily while on-board. Upon completion of field activities, a final inventory of the drum was conducted to ensure that it had been labeled correctly, and it was removed from the ship to a staging area to await disposal.

Resource Conservation and Recovery Act (RCRA) regulations were used to evaluate constituents associated with the IDW. Under RCRA, a waste that is not excluded from regulation is defined as hazardous if it is any of the following:

- listed as a hazardous waste under Title 40 Code of Federal Regulations (CFR) Part 261;
- fits any of the four RCRA hazardous characteristics; or
- subject to listed mixed waste rules.

After the completion of field activities, the IDW drum was staged in a secure location temporarily at Snug Harbor during data assessment and IDW characterization. IDW materials generated during the HUMMA Project were characterized according to the analytical results obtained from the samples collected.

Based on the sample results and regulatory waste classification requirements, all of the IDW generated during the field operations were characterized as non-hazardous waste (Non-Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), Non-RCRA and Non-Toxic Substances Control Act (TSCA) regulated). Based on site data and observations, there was no evidence that the IDW contained listed RCRA hazardous wastes or exhibited RCRA hazardous waste characteristics. Pacific Commercial Services (PCS) was subcontracted to pick up, transport, and dispose of the IDW drum contents. The non-hazardous waste manifest is included in Appendix I (IDW Manifest).

4. Results

4.1 SONAR MAPPING

4.1.1 EM1002 Hull-Mounted Multibeam

The two-day survey using the Kongsberg Simrad EM1002 multibeam mapping system covered an area of approximately 650 km^2, which extended from just below the entrance to Pearl Harbor to the northern edge of Penguin Bank (Figure 1-3). The EM1002 reconnaissance survey covered a much larger region than the proposed IMI-120 survey site in case no targets of interest were detected during the high-resolution survey, a contingency plan that fortunately was never implemented as potential munitions targets were recognized early in the real-time displays of the high-resolution (IMI-120) SSS data. The results gleaned from the hull-mounted multibeam data thus focus solely on the data within the HUMMA Study Area. The swath width of the EM1002 data system is 1-2 km in these water depths, and because the track lines were spaced to accommodate the 600-800 m swath-width of the deep-towed IMI-120 prior to the beginning of the survey, overlapping coverage of the EM1002 backscatter data ranged from 100-300 %.

The EM1002 bathymetry data depict the HUMMA Study Area as predominantly gently sloping terrain with a minimum water depth of 300 m near shore and a maximum water depth of 550 m in the southeastern corner of the HUMMA Study Area. The co-registered backscatter data from the EM1002 survey were gridded at a resolution of 2 m x 2 m to produce a map of general surface type that delineates major provinces. The largest province encompasses the majority of the HUMMA Study Area. It consists of poorly reflective (low backscatter strength) SSS returns, which are interpreted to represent seafloor covered by sediments tens of cm to m thick. To the north and east of the HUMMA Study Area the backscatter return strength increases and the seafloor takes on a mottled appearance. This region corresponds to the EPA-established site for dredged deposits from Pearl and Honolulu Harbors as well as the Ala Wai Canal. Finally, there are several highly reflective features with 10 or more m of relief near the west-central and southern portions of the HUMMA Study Area that are notable for their non-uniform surface reflectance. These are drowned reef fragments that formed during lower sea-level stands around O‘ahu; they are composed of irregularly shaped coral outcrops.

Acquisition of EM1002 SONAR data occurred at the beginning of the *R/V Kilo Moana* seven-day HUMMA program to provide a basemap of seafloor shape and roughness that would allow the IMI-120 system to be safely towed 50 to 75 m above the seabed without risk of collision. In particular, many of the coral outcrops have nearly vertical relief, and course changes when the towfish is close to these features represent a threat because the towed platforms typically lose altitude during large course changes. The other reason for acquiring the lower resolution hull-mounted data was to use this information to re-navigate the higher resolution IMI-120 backscatter data. Because the *R/V Kilo Moana* has sophisticated motion sensors and is GPS-navigated, the location of features depicted in maps produced by the EM1002 system is typically accurate to within a few m. Contrastingly, at sea the IMI-120 position is determined by assuming the towfish is following directly along the ship’s track at some variable distance behind the vessel. Post-cruise processing has repeatedly demonstrated that towfish positioning data is less accurate than that from the EM1002 because mid-water currents push the towfish to one side or the other of the ship’s track; thus considerable effort is spent registering the backscatter swaths acquired by the IMI-120 system to align it with features that are also observed in the EM1002 backscatter data.

4.1.2 IMI-120 Towed Sidescan

The last five days of the *R/V Kilo Moana* survey were devoted to near-bottom surveys of the HUMMA Study Area and the Barber's Point Study Area using the IMI-120 SSS. Over approximately four days the IMI-120 comprehensively mapped the 69 km^2 HUMMA Study Area, and spent an additional 24 hours mapping the 12 km^2 Barber's Point Study Area (Figure 1-3). The survey tracks were designed to provide greater than 100 % backscatter coverage of both survey sites to allow potential targets to be examined from multiple sound-wave incidence angles. In particular, both east-west and north-south survey track lines were run near Site 3 to maximize the chances of detecting munitions within regions dominated by DS.

The difference between the hull-mounted 95 kHz EM1002 backscatter images and the 120 kHz IMI-120 backscatter images, even when gridded at the same 2 m x 2 m resolution, are striking. The predominantly sediment-covered terrain that encompasses most of the HUMMA Study Area in the EM1002 data is revealed to be crisscrossed by dozens of lines of reflective features. The differences between the two datasets result from the variable response of the seafloor to slightly different wavelengths of sound as well as stronger echoes recorded by the IMI-120 system, which acquires data 100's of m closer to the seafloor. Most of the reflective trails in the IMI-120 data are far too large to correspond to munitions, but the smaller linear trails of targets were intriguing, and quickly caused the HUMMA Project team to rethink the approach for detecting DMM.

At the outset of the HUMMA Project, prior to any of the mapping efforts, the historical research suggested that munitions disposal was a systematic effort with ships repeatedly venturing to a given location and discarding munitions into what would eventually become a dense accumulation on the seafloor. In retrospect this scenario was not consistent with the navigational capabilities of ships at the time, nor is it likely that off-shore conditions would lend themselves to rolling munitions off the side of an idling barge. The linear trails of small (1 to 2 m) highly reflective targets detected by the IMI-120 instead led the HUMMA team to consider another scenario, one in which tugs led barges in the directions that produced the most stable conditions for those handling the munitions. As more and more narrow linear trails of targets were discovered during the high-resolution, near-bottom mapping, the project team became convinced that the latter scenario was correct, and the post-cruise processing focused on improving the location and depiction of these features in the backscatter data for subsequent investigation using optical systems including the towed camera, HOVs and ROV. Multiple trails and one broader field of small reflective targets were identified; examples are shown in Figure 3-3.

4.2 VIDEO RECONNAISSANCE

4.2.1 *R/V Klaus Wyrtki* Camera Tows

On February 20, 2009, the UH towed camera sled collected approximately two hours of video data near one of the trails of reflective targets. Because of the prevailing ocean and atmospheric conditions, all four passes of the camera system over the "speckle" trail intersected the trail at a high angle. Analysis of the resulting video showed only a handful of objects of interest including 55-gallon drums and other debris.

4.2.2 *R/V Ka`imikai-o-Kanaloa* HOV and ROV Surveys

The *R/V KoK* field program included sixteen HOV dives and six ROV tows covering the most pronounced trails and fields of reflective targets in the IMI-120 backscatter data. During the HOV dives, sediment and water samples were collected from 19 different sites (Figure 4-1; Appendix C – HUMMA Sample Collection Sheets). The *R/V KoK* field program successfully accomplished the majority of its goals demonstrating that:

- Lines and fields of reflective targets observed in the IMI-120 backscatter data were trails of DMM;
- HOVs can acquire samples within 1-2 m of DMM;
- HOVs can return to a specific DMM even when several days have passed between visits;
- The sediment and water samplers were mostly effective for collecting discrete samples and bringing them to the surface intact;
- The ROV nighttime dives are useful for evaluating DMM trails prior to daytime HOV operations and increase the efficiency of the HOV operations;
- On-board screening of samples for the presence of CAs is well-suited for protecting personnel safety; and
- The UH team's method of on-ground sample coordination and tracking with shore-based laboratories ensured that all samples were delivered to the laboratories within holding times.

The HOV dives were extremely successful in their ability to follow munitions trails thanks to the HOVs' internal SONAR displays and the ability of the pilots to follow a trail visually once it had been detected. The HOV video reconnaissance clearly demonstrated that an individual trail was composed primarily of one type of DMM, a result that is borne out in the GIS maps (Figure 3-3). Because of their ability to move freely except in the vicinity of dangerous entanglements, the HOVs could follow trails even when they deviated from the original dive plan; as such they were able to document the intersection of several munitions trails. Furthermore, visual observations could distinguish small areas of DS that neither the hull-mounted nor the towed SSS could resolve, and for that reason some of the sites marked as being DS or DMM-DS are based on HOV observations and not the broader SONAR interpretations.

Because it remains tethered to the ship throughout a survey, the ROV was not as successful at exploring munitions trails as the HOVs, but this shortcoming was compensated for by the ROV's ability to get very close to a DMM that it encountered and view the object from several different angles. Efforts to use the ROV to survey narrow munitions trails improved when the survey strategy was changed to slalom along these trails instead of trying to follow them directly. Because of bottom currents near the ROV and surface conditions affecting the ship, the latter approach was as likely to have the ROV running parallel to, but slightly too far away from, a munitions trail.

Details of the March 2009 field program on the *R/V KoK*, including track maps for the HOVs and ROV, are reported in Appendix J (*R/V KoK* Final Shipboard Report). Here the accomplishments of each video reconnaissance survey and types of samples collected are briefly summarized.

- ***HOV Dive Pisces V (P5)-717 (03MAR09):*** Visual confirmation that targets along the most prominent speckle trail in the backscatter data were DMM. Sediment samples collected in RC strata.
- ***HOV Dive P5-718 (04MAR09):*** Video reconnaissance of three distinct munitions trails, all identified in the backscatter data, including the trail imaged on P5-717. No samples collected.
- ***HOV Dive P5-719 (05MAR09):*** Numerous video transects across Site 3 to look for canisters similar to those involved in the 1976 incident. None were located. Water samples collected at the Pisces IV sample site.
- ***HOV Dive Pisces IV (P4)-212 (05MAR09):*** Limited reconnaissance while moving from one sample site to another, both within the DS material area. Water and sediment samples collected for DS strata.

- ***HOV Dive P5-720 (07MAR09):*** Video surveying following backscatter-identified debris trails when they were detected. One wreck and additional types of DMM were imaged. Water and sediment samples were collected near one potential chemical DMM located in DS strata. Two push cores were attempted, but both corers broke as they were inserted into the sediment.
- ***ROV Tow R-425 (07MAR09):*** The ROV surveyed one broad, scattered field of targets and crossed over two additional speckle trails.
- ***HOV Dive P5-721 (08MAR09):*** Completed reconnaissance surveys of most of the remaining speckle fields near Site 3A. A full suite of samples were collected in RC strata.
- ***HOV Dive P4-213 (08MAR09):*** Video reconnaissance and re-location of potential chemical munitions identified during P5-718. Water and sediment samples plus one push core were successfully acquired.
- ***HOV Dive P5-722 (10MAR09):*** Video reconnaissance of a trail of several meter-wide highly reflective targets in the backscatter data, which were revealed to be large balls of steel cable that represent significant entanglement hazards. The HOV also encountered a broad field of depth charges in the vicinity of a large coral head and a trail of disposed torpedo warheads. A full sample suite for DS strata was collected.
- ***ROV Tow R-426 (10MAR09):*** Video survey of a broad speckle field near the western edge of the backscatter data. Most of what was observed was either depth charges or ammunition boxes, thus the HOV did not return to this area.
- ***HOV Dive P4-214 (11MAR09):*** Video reconnaissance of the northern half of the speckle trail determined that the “speckles” are valved cylinders. Water and sediment samples were collected, but the push core failed because of the hard coral substrate at the site.
- ***HOV Dive P5-723 (11MAR09):*** Video survey of a number of speckle trails in the backscatter data including the southern portion of the trail Pisces IV imaged. A full sample suite was collected.
- ***ROV Tow R-427 (11MAR09):*** Reconnaissance confirming the presence of small DMM along a speckle trail that will not be investigated with the HOVs.
- ***HOV Dive P5-724 (13MAR09):*** Video survey of three wrecks plus one trail of 1000-lb bombs. Another DS sample suite collected.
- ***ROV Tow R-428 (13MAR09):*** Video transect across a broad region with no readily identifiable targets in the backscatter data. With the exception of a few small depth charges, no DMM were detected along this transect. Conducted to confirm the absence of DMM in areas with no suspected DMM based on SONAR data interpretation.
- ***HOV Dive P5-725 (14MAR09):*** Video reconnaissance throughout Site 3 despite very strong currents. No samples were collected.
- ***HOV Dive P5-726 (16MAR09):*** Video survey of several speckle trails plus collection of a complete suite of samples.
- ***ROV Tow R-429 (16MAR09):*** A video transect of one of the speckle trails that documented many DMM, none of which were assessed likely to have CA constituents.
- ***HOV Dive P4-215 (17MAR09):*** Video reconnaissance between the site where Pisces V was sampling and a region to the west along a speckle trail.

A set of water samples was collected by Pisces IV at the Pisces V site, plus another full suite of samples was acquired for DMM strata.

- ***HOV Dive P5-727 (17MAR09):*** Video surveys completed between two complete sampling sites and one partial sampling site. Pisces IV assisted by collecting water samples at the first Pisces V sampling site, but Pisces V collected 2 full sets of sediment samples and one set of water samples.
- ***ROV Tow R-430 (17MAR09):*** Video reconnaissance within the Defensive Sea Area in advance of the final dives.
- ***HOV Dive P5-728 (18MAR09):*** Video survey within the Defensive Sea Area covering speckle trails that had, and had not, been previously imaged. A full sample suite was collected for DS strata.

Table 4-1 contains a count of munitions identified in the videos from each HOV or ROV tow.

As discussed in Section 3, HOV and ROV video footage was reviewed to analyze the integrity of munitions in the HUMMA Study Area. The video shows that DMM integrity ranged from nearly intact to almost completely disintegrated. The state of deterioration varied within similar types of munitions located in the same general area, as well as between different types of munitions spread over a wide region. In general, munitions with thicker casings were better preserved. However, noticeable differences in the amount of deterioration within populations made up of one type of munitions suggests that either variations in localized processes (e.g., currents, sediment volumes) resulted in different amounts of weathering or that some munitions may have been in worse condition than others when originally sea disposed. Many DMM were imaged with “skirts” or columnar “pedestals” beneath them. This may be the result of rusting, possibly in combination with leakage of the internal MC. The DMM pedestal analysis is included as Appendix D (Pedestal Analysis). Also included in Appendix D is a video interpretation summary that catalogues munitions observed, and notes the size and condition of each object, the time at which it was observed, estimated depth, and a link to any photographs taken of the object.

4.3 BENTHIC INFAUNA ANALYSIS

Soft-bottom communities are composed of the benthic infauna made up of an assemblage of invertebrate organisms. Benthic infauna are sedentary creatures that live under the surface of the ocean floor in the sediment layer. Because they are sedentary, they respond to pollution stress and are an important indicator group (Nieland and McMahon, 1999). The distribution of the benthic infauna may depend on several environmental factors such as temperature, salinity, character of the substrate, and seasonal changes. Between March 3 and 18, 2009 a total of 18 sediment samples for benthic infauna analysis were collected from 15 of the 19 study sites within the HUMMA Study Area (Figure 4-2). The objective of the benthic infauna survey was to determine benthic infauna species richness and abundance.

Samples were collected from an HOV by one of two sediment-sampling methods (i.e., push core or composite). The surface area sampled using the push core was known. However, because the composite samples were taken from multiple sediment samples that were not of a uniform diameter, it is impossible to determine how much surface area was sampled for any given composite sample. For that reason, composite samples cannot be used to calculate infauna density, and instead serve as a qualitative piece of information rather than a quantitative one. Push core sample data were analyzed to determine the relative abundance and richness of benthic infauna at each site and within each stratum, while composite sample data were analyzed to determine species richness.

Abundance is measured by the actual number of individuals found per sample, while richness is the number of different taxa in a given sample. There were a total of 101 different organisms identified to the species level and three organisms identified to the genus level across all samples for a total of 104 different taxa identified. A total of 266 animals were identified across the sample sites. Of the ten push core samples collected, the abundance ranged from 0 to 10 organisms while richness ranged from 0 to nine taxa (Tables 4-2 and 4-3). The highest occurrence of abundance and richness occurred in the push core sample collected from site DMM-DS3 (Table 4-2). Composite samples were analyzed and contained an abundance ranging from nine organisms (DMM5) to 65 organisms (RC2). As discussed previously, these data are not comparable to push core data due to the unknown surface area sampled.

The sample sites were grouped by stratum to calculate and compare average abundance and average richness. As shown in Table 4-4, the average abundance and richness did not appear to vary widely amongst the four strata. Because of the small sample sizes for the RC and DS strata (n=1 and n=2, respectively), the data were not sufficiently robust to allow for meaningful statistical analyses. The average density calculated for the four strata, also presented in Table 4-4, indicate that the DMM in DS material stratum had the highest density of organisms followed by the DMM stratum, but this is merely an observation having no statistical significance due to the aforementioned sample size.

There were three sites where both composite and push core samples were taken. Table 4-5 compares the number of organisms per sample and number of taxa represented per sample for sites where both push core and composite samples were collected. As shown in Table 4-5, there was a marked difference in both the number of organisms and the number of taxa identified in a composite sample compared to a push core sample, with both indices being higher for composite samples in all three instances.

While the benthic infauna datasets were not sufficiently robust to allow statistical comparisons of abundance or richness, the comparison of push core versus composite samples does have some practical applications. The marked difference in the number of animals and number of taxa identified in the composite samples compared to the push core samples indicates that the size of the push core device should be increased to obtain a good representation of the benthic infauna at any given site. The push core design was a clear success, as the device was able to be carried to the site, manipulated by the HOV pilot, and retrieved mostly intact by the UH scientists on-board the *R/V KoK*. Subsequent investigations should modify the design to allow a greater surface area to be sampled, and attempt to collect a more robust set of data upon which to confidently run statistical comparisons.

4.4 MACROBIOTA ANALYSIS

The average abundance of macrobiota was calculated and compared by stratum (e.g., RC, DMM). As shown in Table 4-6, the average abundance ranged from seven to seventeen animals, with no significant differences between groups. Richness could not be calculated because many of the species could not be identified to a discrete taxonomic level. Approximately 50 % of the species documented in the assessment could be identified to family or genus level, and the definition of richness as noted in the benthic infauna section precludes the use of unidentified species.

There was a difference in the number of organisms observed during periods of time when the HOV was actively moving along the bottom versus when stationary at a site and conducting sampling. It is likely that some animals are scared by the HOVs, while others are attracted by them; shrimp, in particular, appeared to be attracted to the HOVs during sampling activities.

One of the goals of the macrobiota assessment was to look for the presence or absence of key sentinel species (species which can provide information on ecological changes and give early warning signals regarding ecosystem processes in site-specific conditions due to their sensitive reactions to them) at all study sites, to assess whether there were significant ecological differences between DMM sites and non-DMM sites. None of the species observed were considered to be a key sentinel species. Some organisms appeared to be more abundant at the DMM sites, primarily due to the availability of hard substrate (the DMM) upon which they could rest. Common examples of this included sea stars and urchins (Appendix F – Biota Assessment Table), although they appeared just as likely to rest upon non-DMM objects of anthropogenic origin.

4.5 NATURE AND EXTENT OF CONTAMINATION

This section describes the sources and types of environmental contamination to the marine environment of the HUMMA Study Area and identifies COPCs. Physical and chemical properties of the MC adopted as COPCs are shown in Table 4-7.

4.5.1 Source Data

Data for the HUMMA Project were primarily from the field program conducted in March and April 2009, specifically results of sediment, seawater, and biota analysis. HUMMA used four separate laboratories (Calscience Analytical Laboratories, ECBC, Cove Corporation, and Dr. DeCarlo's UH Laboratory) to generate the data. Other sources of information include previous investigations discussed in Section 1.3. Description of the data and sampling locations are presented below.

4.5.2 Water Column Data

None of the CA COPCs, the energetics (explosives) COPCs, or their degradation products analyzed in seawater samples were detected at concentrations exceeding their corresponding method detection limits (MDL) (Table 4-8). For the CA and their degradation products, the MDLs were 5 micrograms per liter (µg/L) for mustard, 15 µg/L for Lewsite, and 25 µg/L for 1,4-dithiane and 1,4-thioxane. For the energetics and their degradation products, the MDLs were in the range of 0.14 to 0.43 µg/L. The project screening levels for these COPCs have not been established except for TNT whose screening level is 100 µg/L (EPA Marine Screening Benchmarks for Seawater, 2004).

The metal analysis in seawater was not carried out because the concentration of metal COPCs is expected to be much less in the seawater than in the sediments. At the pH range in the HUMMA Study Area (7.4 to 7.65), arsenic, copper, and lead will very likely exist as precipitation (World Health Organization (WHO), 2003; Agency for Toxic Substances and Disease Registry (ATSDR), 1997). Adsorption to the sediments will further reduce the concentration of metal COPCs in seawater. The small amount of dissolved metal ions will be quite diluted with large volumes of seawater.

4.5.3 Sediment Data

None of the CA COPCs, the energetic COPCs, or their degradation products analyzed in sediment samples were detected at concentrations exceeding their corresponding MDLs except for a tentative identification of mustard in one sample (Table 4-9; Figure 4-1). For the CA COPCs and their degradation products the MDLs are 23 to 24 micrograms per kilogram of dry weight (µg/kg) except for mustard whose MDL is 5 µg/kg. For the explosives and their degradation products the MDLs are in the range of 25 to 110 µg/kg. No screening criteria for CA, energetics, or their degradation products in sediments are available for this project.

This single tentative detection of mustard is of interest to the project team, not only because it represents an indication that mustard was present in the vicinity of one of the munitions, but also because of the sequence of events that occurred prior to collection of the sample having the detection. HOV pilots took extreme care to ensure that the HOVs did not come close enough to munitions to establish contact. The HOVs do disturb the area as they maneuver, primarily because of the twin thrusters mounted on either side of the HOV. Although these thrusters provide the sole means of an HOV's propulsion and maneuverability, they also create localized currents that can be significant. For the site where the tentative identification occurred, there were only two sediment samples collected due to the limited number of empty sampling containers remaining on the HOV at the time the DMM was encountered. The first sediment sample was collected from a distance of 1 m from the DMM. As the HOV pilot adjusted the position of the HOV to collect the second sample, the turbulence generated by the thrusters created sufficient force to push the DMM off the very narrow pedestal that was supporting it (see Section 4.2.2 for a description of pedestals) causing the DMM to fall onto its side. A second sediment sample was collected immediately following this accidental dislodgement, also at a distance of approximately 1m from the DMM but 2m from the previous sample collection location, and it is the only sample of the entire program that resulted in a tentative identification of CA.

Some heavy metals were detected in most of the sediment samples (Table 4-10). The screening guidelines established for metal COPCs (arsenic, copper, and lead) are 7.24 mg/kg, 18.70 mg/kg and 30.20 mg/kg respectively (EPA Region 3 BTAG, 2004). Sediments from the HUMMA Study Area generally display low trace element concentrations, as would be expected from their predominantly marine origin (Table 4-10). A few samples, however, display enrichments of selected elements (copper, zinc, lead) that appear to be anomalously high relative to typical deep-sea marine sediments. In all cases these samples derive from the DS sites, suggesting that the origin of the trace metal enrichment, while most likely anthropogenic, is not associated with DMM, but rather derives from materials dredged from Oʻahu harbors. Prior work (e.g., De Carlo and Spencer, 1995; De Carlo and Anthony, 2002; and De Carlo *et al.*, 2004; 2005) has shown that estuarine and coastal sediments from Oʻahu can be highly enriched in trace elements through land runoff of non-point source pollution. Probably of greater note, however, is the remarkable enrichment of arsenic (As) observed in all samples of sites DS3, DMM-DS2 and DMM2, which average 34 mg/kg) (range 22-40 mg/kg), and to a lesser extent those from Site DMM-DS3, which average nearly 20 mg/kg As. These values compare to a range of 4 to 8 mg/kg As at other DMM sites and 12 to 14 mg/kg As in sediments from DS1, DS2 and DS4. It is highly likely that the As in these materials is of anthropogenic origin because uncontaminated sediments around Hawaiʻi typically contain less than 10 mg/kg As (e.g., De Carlo and Anthony, 2002; De Carlo *et al.*, 2004; 2005). Because the sediments that contain higher As concentrations than expected for marine materials occur primarily in the DS sites and because the As enrichment is comparable to concentrations reported by De Carlo and Anthony (2002) in sediments from the Ala Wai Canal in Honolulu, it is quite possible that the As enrichment is owed to the ocean disposal of material dredged from the Ala Wai Canal in 2003 (also see the principal component analysis discussed in Section 4.5.3.1 below).

In evaluating the sediment results, it must be remembered that the samples were taken at distances of 1 m and 2 m from the munitions and except for the detection of mustard, no contaminants attributable to the munitions were detected. Sampling distance may be a significant contributing factor to the results. In a research project conducted by Darrach, et al. (1998), TNT and DNT were detected at levels of low parts per billion or high parts per trillion adjacent to munitions that appeared to be intact. The sampling distance was 0.15 m to 0.3 m around the munitions. Compared to this research, the sampling distance of the HUMMA project may be too far to detect any CWA or energetics. However, due to the instrument operation limits and safety considerations, collecting samples directly adjacent to the munitions was determined not appropriate for this project. In conclusion, based on the 1 m and 2 m sampling distances from DMM, sediments from the HUMMA

Study Area do not display any evidence of significant contamination from DMM. If present in sediment, the COPCs are within 1 m of the munitions indicating the area of influence is quite small.

4.5.3.1 PRINCIPAL COMPONENT ANALYSIS

Factor analysis, specifically principal components analysis (PCA) with varimax rotation was applied to analytical data to determine relationships between elemental components of the HUMMA sediment samples. All tables and figures generated as part of the PCA are included in Appendix K (Principal Component Analysis Tables and Figures). The derived linear correlations shown in Appendix K: Table 1 allow the establishment of relationships between interrelated elemental concentrations. PCA is particularly useful because it reduces a large number of variables, such as the elemental abundances in the current data set, to a smaller number of components (or factors) that represent some linear combination of the original variables. These variables are grouped into several factors, which account for a significant portion of variance (i.e., eigenvalues) of the original variables. Extracted factors can, in turn, be interpreted based on the meaning of variables clumped within. Thus, through the application of PCA, a large number of quantitative variables can be condensed into a few factors. The first component represents the best linear combination of the variables, the second component, the next best linear combination, and so on (Li, 2000). There are, however, problems with and restrictions to using PCA, especially if it is going to be used to explain geochemical processes (Reimann et al., 2002). Nevertheless, these authors do concede and a number of other authors (Grande et al., 2000; Helena et al., 2000; Li, 2000; Ruiz-Fernandez et al., 2001; Haag and Westrich, 2002; Townend, 2002) concur, that using PCA to look for patterns in data can be useful.

PCA of elemental data in HUMMA sediments extracted 4 component factors for the samples (Appendix K: Table 2). The four factors explained more than 80% of the variance of the samples (Appendix K: Table 3). The first component (Factor 1) grouped aluminum, iron, titanium, manganese, vanadium, chromium, cobalt, nickel, copper, arsenic, and silver (Appendix K: Figures 1 and 2). This factor is interpreted to represent metals whose concentrations likely derive from terrigenous sources (volcanic minerals and their weathering products) and which do not appear to have significant anthropogenic contributions. Factor 2 grouped zinc, cadmium, barium, and lead. The elements with high Factor 2 loadings are interpreted to represent elements with anthropogenic enrichment, likely from non-point source pollution, as previously reported by De Carlo et al. (2004, 2005). Factor 3, which grouped calcium, strontium and to a lesser extent magnesium, is interpreted to represent the contributions from marine carbonate minerals to the sediment composition. Magnesium also trends towards Factor 1, indicating that its provenance is likely from multiple sources (i.e., terrigenous and marine carbonates). Factor 4 only contained uranium. The correlation matrix shown in Appendix K: Table 1 reveals that uranium does not correlate significantly with any element. The original source of this element therefore remains unclear, but uranium may be derived in part from marine carbonates as is often observed in the marine environment. Interestingly, no factor arises that groups elements such as copper and lead, that might be expected to covary in munitions casings and projectiles. This observation is consistent with the individual analytical concentration data, which suggest that little, if any, contamination of the HUMMA sediment samples can be attributed to disposed military munitions.

Finally, factor scores for each sediment sample are derived from the statistical weight of each element following a pattern within that sample (Appendix K: Figure 3). Each element is weighted proportionally to its involvement in a pattern; the more involved a variable, the higher the weight. Variables not at all related to a given pattern would be weighted near zero. Appendix K: Figure 3 shows that samples from DMM, RC and DS sites generally clump together as would be expected for samples from a given “stratum”. It is also apparent, however, that significant overlap exists between both DMM and RC samples and also between DMM and DS samples, although a number of the latter do not show a strong relationship to other sediment samples. The sample scores also clearly indicate that both DMM and RC samples have relatively little anthropogenic component (i.e., Factor 2), whereas selected sediment samples from the DS stratum display much greater influence from elements associated with anthropogenic activity. The latter is not surprising as it has been previously reported that harbor and other urban sediments, the most likely materials to be found at the DS sites, typically contain relatively high concentrations of elements associated with terrigenous material or non-point source pollution.

4.5.4 Tissue Data

Shrimp and fish tissue samples were examined for CA, energetics, the degradation products, and heavy metals. The shrimp samples were collected in the HUMMA Study Area (Figure 4-3), however, the fish samples were caught from Barbers Point (approximately 9.25 km west of the HUMMA Study Area) after the intention of catching them from the HUMMA Study Area failed (Figure 4-4). Although consultation with local fishing experts during the planning phase of HUMMA indicated that *onaga* were the benthic food-fish most likely to be present within the HUMMA Study Area, the dearth of *onaga* in the HUMMA Study Area did not come as a complete surprise to the project team given the lack of benthic relief (e.g., pinnacles or other features that tend to aggregate fish populations) observed during the HOV operations that took place in the HUMMA Study Area prior to the fishing effort. The scientists aboard HOVs noted only a few occurrences of *onaga* during the entire set of dives within the HUMMA Study Area. The fishing program proceeded with the understanding that *onaga* were not likely to be present in large numbers in the HUMMA Study Area, reasoning that it was of use to attempt and fail to catch *onaga* rather than assume they would not be caught. Additionally, as mentioned in Section 3, because of the free-ranging nature of *onaga*, specimens caught within a few km of the HUMMA Study Area may have transited through, or fed within, the HUMMA Study Area at some point in their life histories, and are thus still considered valid samples for risk assessment.

No CA, energetics, or their degradation products were detected in shrimp or fish tissue samples (Table 4-11). However, due to matrix interference (See Section 5.1), the concentrations of energetics and their degradation products were underestimated for all 16 fish tissue samples and 10 of the 19 shrimp tissue samples. The MDL for the CA and their degradation products are in the range of 5-30 μg/kg dry tissue. For the explosives and their degradation products the MDLs are in the range of 0.22-0.79 mg/kg dry tissue. The tissue results do not indicate any bioaccumulation of CA or their degradation products in the shrimp or fish collected. While concentrations of energetics and their degradation products were underestimated in all 16 fish tissue samples, they were only underestimated in 10 of 19 of the shrimp samples, and the remainder of the samples (analyzed under normal analytical conditions) were found to be free of energetics and their degradation products. Further, no energetics or their degradation products were detected in any of the sediment or samples, from which the biota would acquire the contaminants. Thus the conclusion that tissue results do not indicate any bioaccumulation of CA, energetics, or their degradation projects is justified.

Heavy metals were analyzed for in the tissue samples (Table 4-12). The COPCs selected for the project were limited to arsenic, copper, and lead. Concentrations of these three COPCs were compared by stratum (i.e., DMM, DS, RC, and DMM-DS). An analysis of variance (ANOVA) statistical analysis (single factor, size of the shrimp is not considered) run on the data grouped by stratum showed that the mean concentrations of arsenic and lead were the same among all four groups while the mean concentrations of copper were not all the same among the four groups. An F-test (testing whether the variance from two groups are the same) and a student's T-test (testing if the mean values from two groups are the same) performed on the same data following the ANOVA analysis (Appendix M – Statistical Analysis for Biota Arsenic, Copper, and Lead) found that the mean concentration of copper in the RC group (62.9 mg/kg) is significantly higher than that in the other three groups (29.0-42.6 mg/kg). These results suggest that the disposed munitions have not introduced a significantly higher accumulation of heavy metals to the shrimp than the RC or DS sites. As discussed in section 4.5.3 above, elevated levels of arsenic and lead in sediments are most likely attributable to dredge spoils disposal as opposed to the presence of DMM. Also as discussed above, PCA performed on the sediment metals data indicated that DMM and RC samples have relatively little anthropogenic component, whereas selected sediment samples from the DS stratum display much greater influence from elements associated with anthropogenic activity. This is most likely also the case with biota tissues: metal accumulation in biota tissues is most likely a result of a combination of the other activities taking place within the HUMMA Study Area, including ship transportation and DS disposal.

The only COPC metals possessing screening levels for edible tissue (U.S. Food and Drug Administration (USFDA) Action Levels: Tolerance and Guidance Levels for Poisonous or Deleterious Substances in Seafood (USFDA, 2005)), are arsenic and lead, which are 76 mg/kg and 1.5 mg/kg respectively (note that while the title refers to these as action levels, for purposes of this project they are applicable only as screening levels). During the study, two shrimp samples contained arsenic concentrations that exceeded their screening levels. These two samples came from DMM2 and DMM-DS1 (Figure 4-4). Additionally, three shrimp samples contained concentrations of lead that exceeded their screening levels. These samples came from DMM2, DMM-DS2, and DS2. The initial HUMMA scope included a screening level HHRA. Because these two COPCs exceeded FDA screening levels and because the frequency of detections exceeded 5 %, the project team decided to supplement the study by conducting a baseline HHRA (refer to Section 7.1.3 for the selection process for determining whether a COPC is carried forward for risk assessment using quantitative analysis). This HHRA has been completed and is presented in Section 7.

For the fish tissue, the concentrations of the three heavy metal COPCs are generally lower than those in the shrimp tissue. The concentrations of copper and lead in the fish tissue are generally one order of magnitude lower while the concentration of arsenic in the fish tissue is generally two to three orders of magnitude lower. Only one of 16 fish samples had a lead concentration (4.05 mg/kg) higher than the screening levels. The generally higher metal concentration in the shrimp than in the fish can be a result of the differences in the evolution strategies adopted by the two phyla (Phillips and Rainbow, 1993) or shrimp's more frequent contact with the sediment (Attar *et al.*, 1992).

Fish and shrimp specimens were examined for deformities, eroded fins, lesions, and tumors. None were observed. Some shrimp specimens were missing partial or entire appendages, and some exhibited small patches of discoloration on their carapaces. Multiple shrimp were retrieved in each shrimp trap (See Appendix G – Photo Log), and the traps were being retrieved through over 1,000 ft of water column. Once retrieved, the traps were emptied straight onto the deck. Any or all of these activities could have contributed to the broken appendages and carapace discoloration instances observed.

4.6 PHYSICAL OCEANOGRAPHY

The bottom current, from the seafloor to 10 m above the seafloor, has a weak mean flow and is dominated by tides as seen in Figure 4-5. The tidal current is semidiurnal (twice per day) with peak amplitudes of <0.5 meters per second (m/s) during spring tides. Temperatures near the seafloor ranged from 6-8.5 °C and showed a dominant semidiurnal variation. The predominance of semidiurnal fluctuations, particularly in the temperature record, indicates the importance of internal tides, or internal waves at tidal frequency, at the HUMMA Study Area. Semidiurnal internal tides have been documented in Māmala Bay previously (Hamilton *et al.*, 1995; Eich *et al.*, 2004; Alford *et al.*, 2006; Martini *et al.*, 2007), so the results of the HUMMA physical oceanographic study are consistent with earlier findings.

The water column is stably stratified with mean temperatures increasing from 7 °C near the bottom to 11 °C near 325 m depth. Mean temperature and salinity profiles from the MMP are shown in Figure 4-6. Based on these results, the expectation is that slow vertical mixing is accomplished via shear and strain associated with the semidiurnal internal tide.

4.7 GIS UTILITY

Following the completion of field activities and continuing through various data analysis efforts, the GIS developed using HURL and other historical and background data prior to the HUMMA field programs were augmented by datasets derived from the various cruises. These supplemental datasets include the HOV/ROV track data, SSS re-navigated backscatter, images culled from the video reconnaissance surveys, physical oceanography data, the sampling locations, analytical results from laboratory analysis, etc. This collection of geo-referenced data will accompany the final report in the form of a GIS-containing DVD that can be operated from any personal computer. The enhanced HUMMA GIS will allow users to view and integrate all aspects of the Project deliverables in a geographic reference frame so that analyses can continue even after the HUMMA Project has been concluded. The GIS utility has been created using ArcReader 9.2, which is available for free download from Environmental Systems Research Institute, Inc. (http://www.esri.com).

5. Data Quality Assessment

This section presents details on the QA/QC samples collected and tested for the HUMMA Project, but does not address the sampling procedure or associated QA objectives of the field screening conducted by ECBC personnel (described in the SAP).

QA/QC samples consisted of field duplicates and MS/MSD samples. Because the COPCs for this study did not include volatile compounds, trip blanks were neither appropriate nor required. Duplicate samples were collected at a frequency of 10 % of the primary samples, and MS/MSD samples were collected at a frequency of 5 % of the primary samples.

The validation reports present the Precision, Accuracy, Representativeness, Comparability, and Completeness (PARCC) results for all Sample Delivery Groups (SDGs). Each PARCC criterion is discussed in detail in the following sections. The laboratory analytical results and the data validation reports are provided in Appendix E.

5.1 PRECISION AND ACCURACY

Precision and accuracy were evaluated using data quality indicators such as MS/MSD, laboratory control samples (LCS), and surrogates. The precision and accuracy of the data set were considered acceptable after integration of qualification of estimated results as specifically noted in the data validation reports.

For the CA results, three of 30 water samples and one of 35 biota samples were flagged as non-detect with estimated detection limits for 1,4-thioxane or L due to the slightly low recovery of MS/MSD, indicating that the matrix of these samples contribute a low bias to the analytical result. Additionally, twelve of thirty water samples were flagged as non-detect with estimated detection limits for 1,4-thioxane or distilled mustard; 2,2'-dichloroethyl sulfide (HD) due to the slightly low recovery of LCS, LCS duplicate (LCSD), or high relative percent differences (RPD) between LCS and LCSD, indicating that the instruments or analysis procedure did not function properly at certain points. One of the 10 benthic infauna samples was flagged as non-detect with estimated detection limit for all four chemical agents due to the low internal standard area, indicating that the instrument or analysis procedure did not perform normally and a low bias resulted for that sample.

For the explosive results, no abnormal conditions were found in sediment and seawater samples. Low surrogate recovery was found in all 16 fish samples and ten of the 19 shrimp samples. This suggests that the analysis method for the biological tissue tend to give a low bias to the results. However, the LCS analysis showed that all LCS recoveries were within QC limits except for only two compounds with slightly low recoveries. It suggests that the analytical method is able to give a sound analysis to the target analytes in a clean matrix. Low recovery for MS/MSD in both fish and shrimp samples indicates that the tissue matrix might interfere with the analysis including surrogate recovery and give a low bias to the results. As a result, all fish samples and the ten shrimp samples were flagged as non-detect with estimated detection limits.

For the metal results of sediment samples, approximately 15 % of the data were obtained under normal condition. The rest of the data are mainly estimated results due to several protocol or technical reasons. The protocol deviations affected most of the samples are that analysis not carried out within the holding time, and that calibration verification not within the control limit. As a result, all the associated data were flagged as estimates. The technical reasons mainly include that the reported results for some metals were subtracted from the negative blank, and that some of the sample results were out of calibration range. Similarly, the associated data were flagged as estimates (j-flagged). Therefore, the precision and accuracy for sediment metal analysis are relatively low, although these data are still usable.

For the metal results of biota samples, MS recoveries were out of the control limits for two metals in the shrimp samples and four metals in the fish samples. The high MS recovery will result in high bias and the low MS recovery will result in low bias to the results. Therefore, the detections associated with high MS or low MS recovery are flagged. The non-detects associated with low MS recovery are flagged. For titanium in fish samples, because both fish MS recoveries are significantly lower than the lower control limits, all the detects of fish samples are flagged and all the non-detects are rejected. Titanium results for 15 fish samples were rejected due to the above reason.

In general, the precision and accuracy for CA, explosives, and their degradation byproducts are acceptable. The metals analysis, due to several protocol and technical difficulties, obtained lower precision and accuracy. Despite the fact that many of the metals data for sediments were assigned j-flags, the data are still usable. In addition, the metals data for tissues can be used for statistical analysis because only the three metals COPCs were considered (arsenic, copper, and lead) which have good data quality: only one of these data were flagged.

5.2 REPRESENTATIVENESS

All samples for each method and matrix were evaluated for holding time compliance. All samples were associated with method blanks in each individual SDG. The representativeness of the project data is considered acceptable after qualification for blank contamination.

The technical holding times for all samples were met except some sediment metal samples. Although the holding time for most of these samples were only slightly exceeded (a few days), this tends to give a low bias to the final results.

For the CAs and explosives, no contamination was detected in any of the method blanks for sediment, water, or biota samples.

For the CAs and explosives, no contamination was detected in any of the method blanks for sediment, water, and biota samples. For the metal analysis of sediment samples, three metals were detected in the method blanks. For the metal analysis of biota samples, seven metals were detected in the method blanks for the shrimp and nine metals were detected in the method blanks for the fish samples. The contaminations in the method blanks tend to give a high bias to the analytical results. After comparing the sample concentrations to the method blank concentrations for these metals, the ones that have been detected but have a concentration less than five times of the blank contaminants were flagged as U.

5.3 COMPARABILITY

Sampling frequency requirements were met in obtaining field duplicates. The laboratory used the same preparation and analytical methods for their analyses. The analytical results were reported in correct standard units. Holding times for most of the samples, sample preservation, and sample integrity were within QC criteria.

For the CAs and explosives, no difference is observed for the field duplicates because all the analytical results are non-detectable. It indicates that the difference between the primary and duplicate samples is less than the corresponding method detection limit.

For the metal results of sediment samples, all the duplicate concentrations are within RPD limits except for uranium in two duplicates. This indicates a very good comparability for sediment metal data.

For the metal results of biota samples, most duplicates have the concentrations the same order as the primary samples. However for one fish duplicate, the concentrations of calcium, lead, and strontium are two orders lower than the primary sample. Since the instruments and analysis procedures were in compliance, the significant difference could be a result of highly heterogeneous nature of the metal distribution in that fish .

Considering all of the above facts, the overall comparability is considered acceptable.

5.4 COMPLETENESS

Of the approximate 5,300 total analytes reported, 15 of the sample results were rejected. The completeness percentage based on rejected data met the 90 % data quality objective (DQO) goal. About 70 % of the data were obtained under correct and normal conditions. About 14 % of the data were obtained under low bias condition (including the rejected data) and about 2 % of the data were obtained under high bias condition.

All data quality assessment tables are included as Appendix L (The completeness for all SDGs is shown in Table 5-1, while individual summaries of QA/QC data for all analytes and all matrices are presented in Tables 5-2 through 5-6).

This page is intentionally left blank.

6. Fate and Transport of Contaminants

This section describes the fate and transport of COPCs detected in samples collected during the HUMMA Project. During the planning process, the fate and transport characteristics of CA and energetics were studied and used to guide the development of the sampling strategy. Although only metals were detected during the HUMMA field program, this section discusses the fate and transport of all COPCs (CA, energetics, and metals).

6.1 GENERAL DESCRIPTION OF FACTORS

Primary factors affecting transport of COPCs include ambient temperature, solubility (in seawater), density, and available transport methods within a given medium once COPCs are dissolved, suspended, or deposited. Bottom temperatures at the HUMMA Study Area are in the range of 6.0 to 8.5 °C, which affects the solubility, rate of CA reactions, and the physical state (e.g., HD freezes at 14 °C). The primary factors affecting fate are CA degradation mechanics, biouptake, transport through the food chain, or sequestration by natural means. Table 4-7 provides a summary of COPCs along with parameters important to their transport and fate in the marine ecosystem. The octanol-water partition coefficient (K_{ow}) and organic carbon partitioning coefficient (K_{oc}) give indications of the potential for bioaccumulation and the subsequent biomagnification of constituents in an ecosystem.

Bioaccumulation is the process where chemicals of any type, regardless of source, are taken up by an organism either from the direct exposure to a contaminated medium or through consumption of food containing the chemical. Bioaccumulation occurs when a chemical is taken up and stored faster than it is eliminated (i.e., metabolized, transformed, and/or excreted) (Corl, 2001).

Among the more important aspects of bioaccumulation is the process of biomagnification. Biomagnification occurs when the concentration of a chemical of any type increases at each successive level in the food chain. Because an organism at each higher trophic level theoretically consumes many organisms in the level below it, the consumer effectively becomes exposed to the amount of a chemical from all trophic levels below it (Corl, 2001).

The once-released CA COPCs may be deposited on the seafloor as free product (e.g., mustard as globules), dissolved in the water column, or sorbed to sediment particles. COPCs sorbed to suspended particles may settle from the water column and accumulate in sediment. Therefore, sediment can act as the ultimate sink for COPCs from munitions and other sources. The behavior and effect of chemicals of any type in the marine environment depends on their chemical and physical properties as well as external factors. The properties include water solubility (S), tendency to transform or degrade (e.g., a compound's half-life), and chemical affinity for solids or organic matter (partition coefficient).

Predictions regarding the fate and transport of CA and any breakdown products require detailed information about the integrity of the munitions or containers (relates to rate and duration of release), impurities present, temperature, pH, degree of burial in sediment, currents at the disposal site, and on the physical and chemical nature of the CA themselves (HELCOM, 1994).

Density is a determining factor as to whether a compound will sink or rise to the surface when released (Stock, 1996; U.S. Army, 2005). Seawater has a density of approximately 1.03 grams per milliliter (g/mL). Because all of the CA COPCs are denser than seawater, they are anticipated to sink. However, when dissolved in seawater, the CA COPCs will diffuse and disperse throughout the water column.

The K_{ow} is the ratio of the concentration of a chemical in octanol and in water at equilibrium and at a specified temperature. This measure indicates the affinity of the compound to accumulate in fatty tissue and is used to help determine the fate of chemicals in the environment. The greater the partitioning to octanol (i.e., the greater the K_{ow}), the greater the potential for bioaccumulation. A compound with a K_{ow} greater than 1,000 would be expected to accumulate in the food chain in fatty tissue, while a compound with a K_{ow} of less than 500 is less likely to bioaccumulate (Daugherty, 1998). The K_{oc} is also a measure of the degree to which a contaminant in water will be adsorbed to organic carbon in the environment. Often this leads to sequestration of the contaminant in sediments.

K_{ow} is typically determined at a temperature of 20 or 25 ^{o}C and at standard atmospheric pressure. The HUMMA Study Area is approximately 300 to 550 m deep, resulting in pressures of approximately 36 atmospheres or more and temperatures of approximately 6.0 to 8.5 °C. It is not known how temperature and pressure at the HUMMA Study Area alter the effective K_{ow} and hence bioaccumulation. None of the MC adopted as COPCs, however, have a log K_{ow} greater than 2.5 at standard temperature and pressure. In shallow conditions, none of the constituents are anticipated to significantly bioaccumulate or biomagnify in living tissue. As mentioned above, the conditions of the HUMMA Study Area are extreme in relation to methods which determine K_{ow}, and thus this study considers the possibility of bioaccumulation or biomagnification.

The degree of risk associated with leaking MC that leach into seawater depends on numerous factors. Potential for harm then, is a function of the rates of release, degradation or sequestration, the extent to which a constituent is diluted, toxicity, dose and the duration of exposure.

6.2 CHEMICAL WARFARE MATERIALS

The CA COPCs are mustard, lewisite, and the degradation products of these. CA are reactive (i.e., tend to readily change through interaction with other chemicals) and thus tend to be unstable (Lisichkin, 1996). Chemical reactions may occur within munitions through chemical interaction between the active ingredient and impurities in the product, and even with the storage vessel itself (Stock and Lohs, 1997). CA are particularly unstable in an aqueous environment and tend to rapidly degrade into generally less toxic constituents due to physical (e.g., transport, immobilization, dilution), biological (e.g., biodegradation by microorganisms), or chemical (e.g., oxidation, reduction, hydrolysis) processes (Lisichkin, 1996; Stock and Lohs, 1997).

In virtually every case, the breakdown products of CA in the marine environment are far less toxic than their original form. Therefore the stability or persistence of CA in the marine environment is the critical parameter in assessing long-term risk. The stability of a chemical compound (CA in this case) is generally expressed in terms of its “half-life,” the time required for half the mass to be degraded or otherwise removed. For example, the time necessary to environmentally transform completely one-half of an arbitrary unit mass of CA varies from a few minutes for phosgene to several hours for mustard (Stock and Lohs, 1997). Other factors (e.g., droplet size, water current, and presence of hydrolysis products on the surface of the CA) affect whether the predicted half-life matches actual behavior in the environment.

On exposure to water, CA-related COPCs for this study tend to rapidly degrade through hydrolysis. Thus another important factor in gauging the persistence of CA is the rate at which CA is released in an accessible form to the environment, including the rate at which the released CA is dissolved (HELCOM, 1994; Stock, 1996). Significant adsorption of CA by sediments, particularly claylike types, may occur. Dissolved solids may also affect hydrolysis rates (Donnelly, 1990). The dissolved solids can affect the rate by participation in the chemical reactions. While hydrolysis is not the only process by which mustard and lewisite degrade in the environment, it is the primary contributor to the process in the ocean.

The aqueous solubility of CA varies. Poor solubility limits the rate of dissolution and thus retards the process of degradation by reducing the exposure of the individual chemical molecules to water. Solubility is temperature-dependent. Table 4-7 lists the solubility at given temperatures. Generally, the solubility of solids and liquids is greater at higher temperatures (HELCOM, 1994). Although it may be possible to reach a compound's solubility limit in the laboratory, under actual conditions in a water body with a large dilution capacity, even a maximum concentration of less than 10 % of the theoretical solubility limit is only reached for a short period. The processes of dilution and degradation (e.g., hydrolysis, reactions with materials in the water column and biotransformation) make the maintenance of a high concentration of CA in seawater over a long period a remote possibility (Stock, 1996).

The physical state of a CA is an important factor when evaluating its behavior in the environment. The melting points provided in Table 4-7 show that the CA disposed in the waters off Hawai‘i are liquid or solid at 10 °C. The physical state of the material also bears on the dissolution process by varying the amount of material exposed to the solvent (in this case seawater) at a given time (Stock, 1996). The dissolution of the surface materials reveals more of the mass for dissolution until the entire mass is dissolved, assuming the capacity of the solvent (water) for the solute (CA) in a given unit volume is not exhausted or that the solvent is continuously replenished, as is the case under most circumstances in the open ocean.

6.2.1 Mustard

Mustard has a relatively high melting point and will usually form a solid mass at normal ocean temperatures at depth. Mustard is heavier than seawater and has only slight solubility (U.S. Army, 2005). Refer to Table 4-7 for more details.

Mustard continuously dissolves from an exposed surface into the water, but at a slow rate. Mustard can remain stable for years in underwater zones where there is little current or turbulence. The relatively low solubility of mustard in water results in slow dissolution and a relatively low overall rate of hydrolysis. In most circumstances, the rate of destruction by hydrolysis is assumed to be nearly the same as the rate of dissolution. As a result, no more than a few parts per million of the unhydrolyzed mustard will be present in the overlying water at any given time (Epstein *et al.*, 1973; Stock, 1996; McNaughton *et al.*, 1994). It is estimated that it would take about 36 days for a one-centimeter droplet of HD in 18 °C still, fresh water to decrease by half. It is estimated that the dissolution rate in flowing seawater would be approximately ten times as high as in quiet seawater. Anything that increases the solution rate will increase the apparent hydrolysis rate (McNaughton *et al.*, 1994). It is assumed that there will be some water flow over any solid mass of mustard on the seafloor.

Hydrolysis occurs at the mustard/water interface. However, under conditions where there is little or no current, a hard oligomeric/polymer layer can form on the surface and shield the bulk of the mass from hydrolysis (Stock and Lohs, 1997). Thus, mustard could persist as a solid in the environment under such conditions, unavailable to further hydrolyze. In such a way, releases of mustard could remain stable underwater for years in zones where there is little current or turbulence. Nonetheless, under normal marine conditions of flow and turbulence and temperatures as low as 5 °C, dissolved mustard can be reduced to one-thousandth of its original mass in about 30 hours and to one-millionth of its original mass in about 12.5 days (Epstein *et al.*, 1973). For example, when a cylinder of solid mustard with a surface area of 4×10^4 cm^2 was placed in a 0.15 kt current the mustard concentration dropped to 0.3 mg/kg within a one-foot distance (Bizzigotti *et al.*, 2009). Conditions at the

HUMMA Study Area, including temperature, are such that mustard can remain unhydrolized for quite a long time.

The major products of mustard hydrolysis are thiodiglycol (TDG), which is far less toxic than mustard, and hydrochloric acid, which is completely neutralized by seawater. TDG is not a unique product of mustard degradation; it has been used as a solvent in antifreeze solutions, in dyestuffs for printing, and in the production of polyvinyl chloride (Munro *et al.*, 1999). Munro *et al.* (1999) suggests that since mustard agents are somewhat persistent, sites involving potential mustard contamination should include an evaluation of both the agent and the degradation product TDG. According to Munro *et al.*, 1999: “1,4-dithiane and 1,4-oxathiane [1,4-thioxane] are referred to as thermal degradation products but are present as impurities in ton containers of mustard; 1,4-oxathiane is also a hydrolytic degradation product.” Mustard also can biodegrade in sediment by numerous microorganisms (Lisichkin, 1996; Paka and Spiridonov, 2002) more than 100 microorganisms including two *Pseudomonades spp*, capable of decomposing mustard agent have been identified. These organisms are capable of degrading mustard under a variety of environmental conditions, including low temperatures (4 °C or 39 ºF) (Lisichkin, 1996; Paka and Spiridonov, 2002).

Mustard is directly toxic to aquatic organisms, but its action is limited by its low solubility and its rapid hydrolysis to relatively innocuous end products, primarily TDG and two thianes. These degradation byproducts show little potential for bioaccumulation due to their generally low octanol/water partitioning coefficients. Some of the intermediates between mustard and the end products (TDG and 1,4-dithiane) may be toxic to some species (Munro *et al.*, 1999). Mustard may pose some limited risks to ecological receptors. The determining factor was the relative rate of release and dissolution in relation to the hydrolysis rate. This in turn will be governed primarily by turbulence in the water column. It is reasonable to expect that the rate of dissolution and the rate of hydrolysis will be roughly the same and that any ecological impact will be limited to the immediate vicinity of the disposal point.

6.2.2 Lewisite

In its common form, lewisite consists of a mixture of several arsenic isomers: lewisite I (L-I), β chlorovinyl dichloroarsine; lewisite II (L-II), bis-β chlorovinyl chloroarsine; and tris (2-chlorovinyl) arsine. The L-I form is always the predominant form (Epstein *et al.*, 1973; McNaughton and Brewer, 1994). Lewisite has a significantly lower melting point than HD and will generally be found as a liquid at temperatures normal to ocean depths. Lewisite is somewhat denser than HD. The solubility of lewisite is not a significant factor in its fate and transport as hydrolysis is virtually instantaneous in water (Munro *et al.*, 1999).

Hydrolysis of lewisite is rapid and results in the formation of the water-soluble CVAA. Although the hydrolysis may be complex with a number of intermediate reversible reactions, it results in the formation of lewisite oxide and 2-chlorovinyl arsenous acid (Munro *et al.*, 1999; McNaughton and Brewer, 1994). The first stage of hydrolysis is rapid formation of the water-soluble dihydroxy arsine (McNaughton and Brewer, 1994). Although CVAO is a modestly potent vesicant, it too is subject to further decomposition such that, ultimately, the greater long-term exposure risk is to the arsenic residuals. Arsenic trichloride, which is reportedly present in some lewisite mixtures, hydrolyzes instantaneously in seawater to form arsenous and hydrochloric acids. The trivalent arsenous acid is gradually oxidized to the pentavalent state to produce the less toxic arsenic acid (Epstein *et al.*, 1973). The dichloroarsine group and the vinyl double bond contribute to the instability of lewisite. It hydrolyzes rapidly to form chlorovinylarsine oxide (a blood toxin) and hydrochloric acid. The oxide can further react, with the final product of hydrolysis being a polymerized arsenic oxide. Lewisite is 36% arsenic (McNaughton and Brewer, 1994).

Lewisite decomposes into arsenic oxides that remain in the environment. The danger from the original CA is neutralized, but the hazard from the heavy metal remains (Munro *et al.*, 1999; Garnaga and Stankevicius, 2005). The chlorovinyl arsenic oxides and acids of lewisite decomposition have toxic properties comparable to the parent compound. The oxides are relatively insoluble, while the acid is quite soluble. However, under ambient conditions in the marine environment, the compounds are expected to degrade further into less toxic pentavalent arsenic forms (Munro *et al.*, 1999).

In an evaluation of potential impacts of arsenicals disposed in the Baltic Sea, it was determined that local enrichment of arsenic in the sediments was possible. However, bioaccumulation of arsenic in marine organisms or enrichment in adjacent sediments above the background level was not detected. There have been no reports of bioaccumulation of toxic agents in marine organisms in the Baltic Sea or of poisoning of fish due to the presence of CA (Beddington and Kinloch, 2005; Glasby, 1997).

Arsenic in an organic form, such as in the lewisite, is likely to undergo reactions to inorganic forms and enter the natural cycle of arsenic once released to the environment of the region. Arsenic is an exception among the CA degradation products in Hawaiian waters, as it has a modest potential to bioaccumulate in the trophic level most closely associated with contaminated sediments.

Some increase would occur in higher trophic levels but biomagnifications would not occur, nor would there be significant effects on the ecosystem due to bioaccumulation (MEDEA, 1997). Degradation of lewisite results in a net increase in arsenic concentrations either in sediments (in the case of insoluble end products) or in solution. Bioaccumulation of the arsenic is possible. No data are reported with regard to carcinogenicity, genotoxicity, reproductive or systemic toxicity (Munro *et al.*, 1999).

6.3 ENERGETICS

The HUMMA Project evaluated the potential effect of conventional munitions on the composition of sediment, seawater, and human food item biota by analyzing for energetics (or explosives) and their degradation products. The corrosion of the metal casings of conventional munitions and consequential leakage of the MC can release energetics and their degradation products to the environment. The fate and transport processes believed most applicable to energetics in sediment and deep water environments are biotic transformation, oxidation/reduction, covalent bonding, and sorption to sediment substrates. Most conventional munitions energetics are relatively polar but have low solubility in water and low vapor pressure.

Commonly occurring conventional munitions chemical compounds include explosives, propellants, impurities, and degradation compounds. As a group, military explosives have relatively low water solubilities and are relatively immobile in water. The degradation and dissolution of these materials may be slowed by the physical structure and composition of blended explosives (e.g., in Composition B, the dissolution rate of RDX controls the dissolution rate of TNT).

TNT transforms via a sequential reduction of its nitro groups (Yost, et al, 2007). It has been noted that dissolution rates of TNT are somewhat slower in saline water than in fresh water. TNT is rapidly removed from solution in sediment slurries with half-lives ranging from 2.8 to 7.3 hours in both fresh and saline solutions. Formation of the TNT transformation products 2-amino-4,6-dinitrotoluene (2-Am-DNT) and 4-amino-2,6-dinitrotoluene (4-Am-DNT) was noted in the sediments tested (Brannon *et al.*, 2005). The rapid drop in aqueous concentration appears related to the sorption of the compounds to sediment. The rate is related to the cation exchange capacity (CEC), organic carbon content, and particle size (Brannon *et al.*, 2005). Relevant literature was silent on basic transformation, fate, and transport of tetryl as it pertains to this study.

6.4 METALS

The MC that are metals adopted as COPCs have relatively poor solubility and are likely to accumulate in sediment and due to their elemental nature; they may oxidize or react with other materials but will not break down. Regardless of source, metal concentrations in sediments vary in relation to grain size. The sediment fraction under 2 µm is a major sink for contaminants introduced into natural waters, largely due to the presence of clay minerals, and the associated coatings of organic material and iron and manganese (oxy-) hydroxide precipitates. These substances scavenge dissolved trace metals from the water column and deposit them with the sediments (Garnaga and Stankevicius, 2005).

6.4.1 Arsenic

The sediment characteristics, namely pH, organic matter content, clay content, iron oxide content, aluminum oxide content, and CEC, have an effect on the adsorption of arsenic. Arsenic may be adsorbed from water onto sediments or soils, especially clays, iron oxides, aluminum hydroxides, manganese compounds, and organic material. Iron content has a significant influence on arsenic adsorption. However, arsenic that is adsorbed to iron and manganese oxides may be released under reducing conditions (Smieja and Puls, 2002). Transport and partitioning of arsenic in water depends upon the chemical form (oxidation state and counter ion) of the arsenic and on interactions with other materials present. Under the study area conditions arsenic is mostly expected to attach to the sediment. One source of arsenic in the water column can be resuspended sediment. Although some fish and shellfish take in arsenic, most of this arsenic is in the less toxic organic form, and biomagnification in aquatic food chains does not appear to be significant.

6.4.2 Copper

In sediment, copper is generally associated with mineral matter or is tightly bound to organic material. Copper is usually associated with fine- as opposed to coarse-grained sediment. The fate of copper in the aquatic environment is determined by the formation of complexes, sorption to hydrous metal oxides and organic matter. The formation of complexes with organic ligands modifies the solubility and precipitation behavior of copper. Between a pH 5 and 6, adsorption is the primary process for removing copper from the water column; above pH 6, precipitation becomes dominant (WHO, 2003). The HUMMA Study Area is anticipated to have pH falling between 7.4 to 7.65, and thus the expectation is that copper will be present in the form of precipitates (Section 2.6.5).

6.4.3 Lead

Sorption sequesters the concentration of soluble lead in water. The tendency for lead to form complexes with organic matter increases its adsorptive affinity for clays and mineral surfaces. Benthic microbes can methylate lead to a volatile and more toxic form. Lead in its inorganic form does not tend to biomagnify (EPA, 2010).

6.5 FATE AND TRANSPORT SUMMARY AND CONCLUSIONS

Transport mechanisms for COPCs to the HUMMA Study Area can be associated with natural and anthropogenic activities including point source (e.g., DS disposal) and nonpoint source discharges (e.g., discharge from vessels in transit), as well as aerial fallout or deposition. The diversity of point and nonpoint sources can result in inputs of complex mixtures of not only parent COPCs but also degradation products and metabolites. Additionally, metals COPCs in sediments can reflect inputs from present-day (e.g., DS disposal) as well as historical sources.

6.5.1 Seawater

The absence of CA and their degradation products, and energetics and their degradation products in seawater samples collected during HUMMA is not surprising., given the attenuation processes and the fact that the closest sampling distance to a DMM was 1m. COPCs released from DMM in this environment could be attenuated by a number of processes, including as a result of deposition of these COPCs into the sediments, dilution into the surrounding water column, or chemical degradation or transformation processes. These processes are largely controlled by the physical and chemical characteristics of the COPCs as well as existing environmental conditions. All of the COPCs have a greater density than the ambient seawater. Therefore, deposition in the sediment would likely occur if they were released from the munitions. Solubility of these analytes varies greatly, from 42 milligrams per liter (mg/L) for RDX to 3.99E+004 mg/L for 1,4-thioxane, a degradation product of mustard. For any COPCs released from the DMM and dissolved into the surrounding seawater, dilution and dispersion would be expected to rapidly attenuate the concentrations in seawater. Ocean currents could immediately disperse the dissolved chemicals and lower their concentration in the water column.

Mustard and lewisite can undergo hydrolysis once dissolved into the water. In a review written by Nancy Munro *et al.* (1999), the half life of dissolved mustard was reported as 158 minutes at a low temperature of 0.6 ºC (33 ºF), and the rate did not vary appreciably in the typical environmental pH range. However, in seawater having a high concentration of chloride ions, the hydrolysis process could be inhibited and result in a lower hydrolysis rate. In addition, the dissolution rate could also be a limiting factor for the hydrolysis. Furthermore, the intermediate hydrolysis products that coat the droplets of mustard may retard the hydrolysis too. As a result of both slow dissolution and formation of intermediate hydrolysis products, bulk amounts of mustard may persist under water for some time. This is a reason that mustard is considered fairly persistent in nature.. It is also reported that the lewisite undergoes hydrolysis rapidly to form water soluble 2-chlorovinyl arsenous acid. Since this hydrolysis product is extremely water soluble, it would be readily diluted in seawater. However, the arsenic does not degrade and will persist.

Hydrolysis of the energetics studied here is generally slow. For example, the half life for TNT hydrolysis is more than 50 years and for RDX is about 1.7 years (Gorontzy *et al.*, 1994). Although some of the energetics such as TNT, RDX and high melting explosive (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) (HMX) can undergo photolysis (Gorontzy *et al.*, 1994), this is unlikely due to depth and barriers to mixing.

The degradation products of mustard, 1,4-dithiane and 1,4-oxathiane are reported as persistent in the environment (Munro *et al.*, 1999). 1,4-dithiane is a thermal reaction product formed by dechlorination. This reaction can occur slowly under ambient temperature. 1,4-oxathiane is formed by dehydrohalogenation of partially hydrolyzed mustard. Due to their relatively high solubility (Table 4-7), 1,4-dithiane and 1,4-oxathiane are assumed to be diluted by seawater upon formation.

Biodegradation occurs to the hydrolysis products of mustard. Several researchers (Yang *et al.,* 1992; Harvey and DeFrank, 1993; and Beaudry *et al.*, 1995) have shown that thiodiglycol can be degraded by two strains of the bacterial species *Pseudomonas pickettii* and *Alcaligenes xylosoxidans*. It is not known if these bacterial are present in the study area. However, biodegradation could occur and help to transform mustard to a less toxic product.

Biodegradation of energetics may also occur in the study area. There are a few studies on energetics biodegradation in the marine environment (Nipper *et al.*, 2004; Bhatt, *et al.*, 2005; Zhao *et al.*, 2004). The research showed that 2,6-dinitrotoluene (2,6-DNT), RDX, and HMX can be biodegraded in marine sediment or water. One type of sulfate-reducing bacteria (*Desulfvibrio*) isolated from

Hawaiian tropical marine sediments (Bhatt *et al.*, 2005) was also reported capable of degrading 1,3,5-trinitrobenzene (1,3,5-TNB) (Boopathy *et al.*, 1998). However, these studies were conducted in a laboratory environment using sediments or seawater collected from shallow ocean areas. Whether or not these bacteria are present at the depths of the study area is not known. Similar biodegradation mechanism studies (Crocker *et al.*, 2006; Jing *et al.*, 2004) show that most of the energetics analyzed for the HUMMA Project act as electron acceptors in the decomposition process. Therefore, any areas having anoxic/anaerobic conditions within the study area could experience an enhanced level of biodegradation.

6.5.2 Sediments

Sediments were collected where the CA and energetics are most likely to be detected in the event that releases from the DMM have occurred. The sorption behavior of these COPC compounds to the marine sediments may vary greatly. Soil sorption studies for TNT, RDX and HMX (Haderlein *et al.*, 1996; Townsend *et al.*, 1996; and Price *et al.*, 1998) have shown that TNT is more adsorbed to soils than RDX and HMX. TNT and its degradation products, 4-Am-DNT and 2-Am-DNT can thus associate with soil organic matter. The two TNT degradation products were found to form covalent bonds with soil organic matter and irreversibly adsorb to the soil. However, the sediment composition at the study area (mainly carbonate sand/silt), particle size (mainly 0.1-2mm [0.0039 to 0.078 in]) and organic matter content can be very different from the soils used in the above referenced studies, thus the sorption behavior of the energetics can be quite different. The lack of detections of CA and energetics in the sediment samples suggests any one of the below factors.

Very small amounts of these COPCs have been adsorbed to the sediment, such that concentrations are below detection limits, that the ocean current has redistributed any contaminated sediments, or that biodegradation had occurred and transformed the original chemicals and their abiotic degradation products.

7. Human Health Baseline Risk Assessment

A baseline HHRA was performed to evaluate baseline risks associated with the consumption of fish and shrimp caught in the HUMMA Study Area. Section 4 of this report has reported exceedences of screening levels for metals in biota. The basic approach to the risk assessment follows HHRA guidance provided in EPA's Risk Assessment Guidance for Superfund, Volume I Part A - Human Health Evaluation Manual (EPA, 1989). The approach follows the four-step process of hazard identification, exposure assessment, toxicity assessment, and risk characterization defined by the National Academy of Sciences (NRC, 1983). This section summarizes the methodologies used in the current assessment and provides results of the risk evaluation.

7.1 HAZARD IDENTIFICATION

In the Hazard Identification step, analytical data are evaluated and relevant constituents are selected for quantitative risk assessment. Past and current uses of the site are analyzed to determine historic use. The following section, Section 7.1.1, describes the specific historical use of CA at the HUMMA Study Area. Section 7.1.2 describes the data collected and assessed in the study. Section 7.1.3 describes the selection of constituents quantitatively evaluated in the risk assessment.

7.1.1 Historical Use of CA COPC at the HUMMA Study Area

Site-specific COPC selection for quantitative risk assessment requires the thorough examination of historical records. There was no historical use of chemicals at the site per se, but disposal of military munitions as well as other materials did occur in the general area. The MC adopted as COPCs relate to the use of the area for disposal of military munitions. Available documentation indicates that approximately 16,000 M47A2 100-lb mustard bombs were disposed in the area. Therefore, the CA adopted as COPCs and their associated degradation products related to these CA (mustard) filled bombs and the other MC COPCs (e.g., energetics, metals) to these bombs, as well as any conventional munitions sea disposed in the study area may be present. Potential COPCs from these sources include a variety of constituents originating from CA and their degradation products from any chemical munitions present; energetic materials from bursters and conventional munitions that may be present; and metals from any munitions casings or packaging that may be present.

The CA (mustard) may be present based on documentation indicating disposal of mustard filled bombs in the area. Although archival records reviewed did not indicate that chemical munitions that contained lewisite were sea disposed in the study area, the persistence of arsenic from its degradation would be a concern if present and it was therefore included in the investigation. Additionally, corrosion may have released energetics and their degradation products to the environment from the munitions present. Because the specific fills are not known, a comprehensive sampling plan was developed that included the MC (energetics): TNT, DNT, RDX, and tetryl. Because of its high solubility and low probability of partitioning to sediment, ammonium picrate was not anticipated to be sufficiently persistent in the environment and was excluded from evaluation in sediment and water samples.

Heavy metals are specifically associated with munitions casings and some packaging. Metals are released to the surrounding environment via corrosion. Heavy metals directly related to munitions casings include copper and lead.

Lewisite may also break down to inorganic forms of arsenic, which can then persist indefinitely in the environment. Other hazardous metals may also be associated with munitions, but are typically found in much lower quantities.

Non-munitions related metals may also be present at the site due to shipping traffic, DS disposal activities, and DMM-DS sites. Samples were therefore screened for a suite of major elements (aluminum, calcium, iron, magnesium, and strontium), selected minor constituents (barium, manganese and titanium) and a group of trace elements (cobalt, chromium, cadmium, uranium, vanadium, and zinc), with the intent that PCA would be run to aid in identifying the source of these metals (e.g. land-based, marine origin, anthropogenic). These other non-COPC metals were used to aid in the PCA evaluation.

The identified COPCs, including some of the degradation products from the primary compounds and other information regarding known munitions disposals in the area and observations from previous oceanographic investigations, are discussed in Section 3. Details on the analytical methods used for each COPC are contained in Table 3-1. Fate and transport information for COPCs is presented in Section 6.

7.1.2 Summary of Available Site Data

Water column, sediment, and animal tissue samples were collected and analyzed for the MC adopted as COPCs from March through May 2009. Benthic infauna samples were screened to ensure they did not contain detectable concentrations of CA, then packaged and sent to Cove Corporation for infauna counts (but not to be analyzed for energetics or metals). A site map of the HUMMA Study Area displaying all of the sampling locations from the environmental investigations can be found on Figure 4-1.

Samples were analyzed for CA, energetics, degradation products, heavy metals, as well as a suite of major elements (aluminum, calcium, iron, magnesium, and strontium), selected minor constituents (barium, manganese and titanium) and a group of trace elements (cobalt, chromium, cadmium, uranium, vanadium, and zinc).

A total of 30 primary water column samples were collected and analyzed for CA (mustard, lewisite and selected degradation products, using ECBC IOP MT-08), and the standard list of energetics (using EPA Method 8330).

A total of 94 primary sediment samples were collected and analyzed for CA (using ECBC IOP MT-08), energetics (using EPA Method 8330), and metals (using a UH proprietary method analogous to EPA Method 6020A).

A total of 39 animal tissue samples were collected and included 16 fish and 19 shrimp samples (plus four additional field duplicate samples). These samples were analyzed for CA (using ECBC IOP MT-08), energetics (using EPA Method 8330), and metals (using several methods including EPA Method 200.8, 6010B, and 7742). Additionally, five shrimp samples were collected and analyzed exclusively to evaluate for the fraction of inorganic arsenic present. The current toxicological database for arsenic indicates that organic forms of arsenic are significantly less toxic and more easily eliminated from the body. The percent inorganic arsenic was calculated for the five additional samples taken and averaged to obtain an average percentage of inorganic arsenic that was applied to the shrimp samples taken from the HUMMA Study Area. The percent inorganic arsenic determined in this study was 0.11% of total arsenic. The calculations of the percent inorganic arsenic are provided in Table 7-8.

In the absence of arsenic speciation data, specifically for the fish samples taken, the EPA generally recommends that risk assessors assume that biota samples contain 10 % inorganic arsenic. The calculated inorganic fraction (0.11 %) is used in lieu of total arsenic concentrations in the evaluation of risk

7.1.3 Selection of COPCs Quantitatively Evaluated in the Human Health Risk Assessment

The selection process for determining if a COPC is carried forward for quantitative analysis included consideration of the following criteria:

- COPC must be detected using validated laboratory analyses.
- COPC must occur above a 5 % detection frequency and/or were historically used at the site.
- COPC must be present in excess of the MDL with a "J" qualifier or are above their practical quantitation limit (PQL).

Based on these criteria, in the animal tissue samples a total of 17 MC, including heavy metals, as well as major and minor elements detected in the laboratory analysis were carried forward into the quantitative HHRA. No CA, energetics, and their degradation products were detected in shrimp or fish tissue samples. CA and energetics were therefore eliminated from further consideration. It should be noted that finfish were not observed in large numbers in the immediate study area. Fish samples evaluated in this assessment were caught approximately five nautical miles west of the HUMMA Study Area, and were considered representative of the types of fish caught south of Pearl Harbor and eaten by O‘ahu residents.

In the water column samples, none of the CA, the energetics (explosives), and their degradation products were detected above their corresponding reporting limits (RLs). Seawater was therefore eliminated as an exposure media in this assessment.

Similarly in the sediment samples, there was only a single tentative detection of CA (mustard) in one sample. Other than this single detection, which could not be confirmed in two subsequent laboratory analyses, none of the CA, the energetics, and their degradation products analyzed were detected above their corresponding RL. Some metals were detected in sediment samples, but because contact with contaminated sediment was ruled out as a potential exposure route (See Section 7.2.2.2), all COPCs in sediment were eliminated from the quantitative analysis.

The complete list of constituents quantitatively evaluated in this HHRA are provided in Table 7-1. MDLs for CA, energetic, and metals in different matrix are provided in Tables 7-9 to 7-13. In addition, the numbers and concentration ranges of the detected compounds are summarized in Table 7-14.

7.2 EXPOSURE ASSESSMENT

The risk assessment process requires the creation of exposure scenarios to assess the potential for adverse health effects from MC at or near the HUMMA Study Area. While these scenarios only represent hypothetical people and activities, they reflect the physical description of the HUMMA Study Area and the surrounding industrial and commercial areas, as well as the activities that may typically occur in these areas. Both current and reasonably foreseeable future potential exposures are evaluated.

This section is divided into six subsections. Section 7.2.1 and 7.2.2 describes the potential exposure scenarios and pathways. Section 7.2.3 describes the methods used to estimate potential exposure doses. Section 7.2.4 describes the statistical methods used to estimate exposure-point concentrations. Section 7.2.5 describes exposure factors used in the risk assessment. Section 7.2.6 discusses the method to calculate an Average Daily Dose.

7.2.1 Identification of Potential Exposure Pathways

As described in the Superfund Public Health Evaluation Manual (EPA, 1986), four elements must be present for a potential human exposure pathway to be complete:

1. a source and mechanism of constituent release to the environment;

2. an environmental transport medium (e.g., soil, water or soil vapor);

3. an exposure point, or point of potential contact with the potentially affected medium; and

4. a receptor (e.g., human) with a route of exposure at the point of contact.

Potential exposure pathways are the mechanisms by which potential receptors may be exposed to constituents. The potential exposure pathways included in this assessment were selected based on the most likely mechanisms of exposure and observations at the HUMMA Study Area.

7.2.2 Potential Exposure Scenarios

In creating potential exposure scenarios for evaluation in the risk assessment, the likelihood of potential exposure to HUMMA Study Area-related COPCs via many pathways was considered. Based on study area's history, bathymetry, and current conditions, current and future exposure scenarios were developed for the HUMMA Study Area (Figure 7-1). Some pathways were excluded from further analysis because the route of exposure was physically impossible or highly unlikely given the conditions of the HUMMA Study Area. However, all exposure pathway scenarios, as well as the rationale behind their inclusion or exclusion from the baseline HHRA, are presented in the following sections. For the purposes of this assessment, only ingestion of fish and shrimp by recreational fishermen was found to be a potentially complete route of exposure.

7.2.2.1 DERMAL CONTACT, INHALATION, AND INGESTION FROM RECOVERY OF FREE PRODUCT

As previously stated, canisters, which were tentatively identified as stokes mortars (mustard-filled), were inadvertently retrieved from the seafloor in 1976 during an environmental study of the general area (USACE, 1977). A brownish, foul-smelling liquid, which was later identified as a mustard agent, leaked from two or three of the recovered canisters causing burns to three individuals on the vessel (USACE, 1977).

Human exposure via inhalation, although unlikely, could possibly occur if CA, including free product CA, or CA-contaminated media, is brought to the surface and undergo volatilization upon contact with the air. If CA or CA-contaminated media were to reach the surface through recovery of CA or CA-contaminated media, volatilization and the potential for exposure to the vapors through inhalation or absorption through the skin could be a concern. However, the potential for volatilization resulting in human exposure is considered remote because it would involve the recovery of CA or CA-contaminated media from depths of about or in excess of 1,000 ft. Because trawling, as a fishing method, is not permitted in the area the likelihood of retrieving CA or CA-contaminated media by fishing unlikely. The only activities in the area that might result in the retrieval of CA or CA-contaminated media is exploration or scientific investigations. It is highly unlikely that persons involved in scientific exploration within the HUMMA Study Area would be exposed to free product CA (e.g., dermal contact, inhalation, and ingestion) because protective measures (e.g., training, augmentation by technically qualified personnel) would be implemented when explorations or investigation are planned for that area.

In addition, although ocean currents can disperse substances along the seafloor, it is unlikely that concentrations of CA at levels of concern would remain either over a wide area or for a long duration. Due to the depth, hydrolysis, dilution, and dispersion that would occur during migration through the water column, volatilization from surface water is highly unlikely to present a hazard to human or ecological receptors at the surface. Also, CA is denser than water (e.g., mustard and lewisite) and will not typically rise. Therefore, CA is not expected to pose a hazard at the ocean surface (Stock, 1996). As a result, dermal contact, inhalation, and ingestion exposure routes to contaminants from free product have been eliminated as potential pathways to human health receptors.

7.2.2.2 DERMAL CONTACT WITH, INHALATION FROM, AND INGESTION OF CONTAMINATED SEDIMENT OR WATER

Dermal contact with, inhalation from, and ingestion of MC-contaminated media (sediment or water) is highly unlikely. Through dispersion and diffusion, released COPCs potentially could be transported through the water column. However, given the height of the water column, the low probability of shallow and deep water mixing (Section 4.6) and the chemical and physical characteristics (e.g., solubility limit, rate of hydrolysis) of the MC, contact with or ingestion of MC-contaminated water at the surface will not be at a level of concern for either human or ecological receptors. In addition, due to the depth to sediment and the low probability of MC-contaminants reaching the surface, the potential for dermal contact to the sediment has also been eliminated as a pathway in this assessment. The only activities in the area that might result in the retrieval of MC-contaminated media (sediment or water) relate to exploration or scientific investigations. However, it is highly unlikely that persons involved in scientific exploration of the HUMMA Study Area would have significant dermal contact, inhalation, and ingestion of sediment or water because protective measures (e.g., training, augmentation by technically qualified personnel) would be implemented when explorations or investigation are planned for that area. Therefore, ingestion or inhalation exposure to and dermal contact with MC-contaminated sediment or water are not evaluated in this risk assessment.

7.2.2.3 INGESTION OF CONTAMINATED BIOTA

Human exposure to the MC adopted as COPCs via ingestion could occur if MC-contaminated fish, shellfish, or other marine organisms are consumed. Recreational fishermen have been observed to occasionally fish in the area. *Ama ebi* (Heterocarpus laevigatus) live on or in the sediment, but may spend some time in the water column above the sediment. These habits could allow the shrimp to contact and uptake any COPCs present in the sediment or water column. *Ama ebi* are trapped at depths of 1,200 ft and greater and were observed and caught in the HUMMA Study area.

Ama ebi are also a prime food source for *onaga*, and tuna. *Onaga* are reportedly occasionally caught in the HUMMA Study Area by recreational fishermen by deploying baited lines at depths of 244 to 305 m (800 to 1,000 ft). Thus COPCs have several potential routes for ingestion: directly into *ama ebi* caught by humans, directly into *onaga* caught by humans, and directly into *ama ebi*, eaten by *onaga* which are in turn caught by humans. The ingestion of contaminated biota by current and future recreational human receptors is possible. Therefore, ingestion of fish and shrimp by current and future recreational fishermen is evaluated in this risk assessment.

7.2.3 Methodology for Estimating Exposure Point Concentrations

Exposure point concentrations (EPCs) for MC constituents detected in the biota at the HUMMA Study Area were estimated using all relevant analytical data collected (as representative of current conditions) from field investigations conducted at the HUMMA Study Area. As noted in Section 7.1.2 of this report, the assessment evaluated data from investigations conducted between March and May 2009.

Appendix H (Human Health Risk Assessment Calculations) presents the analytical results for each constituent detected in fish and shrimp samples collected from the HUMMA Study Area. Table 7-2 presents the estimated exposure point concentrations used in the quantitative risk assessment. The methodology for estimating exposure point concentrations is presented in Section 7.2.4.

In this HHRA, ingestion intake from contaminated biota is considered to be the only complete pathway and only exposure scenario analyzed in this assessment.

7.2.4 Statistical Methodology

The EPA has determined that the 95 % Upper Confidence Limit (UCL) of a COPC represents a reasonable estimate of the concentration in an environmental medium that a receptor may potentially contact when that contact occurs at random over an extended period of time (EPA, 2002b). For estimating exposures to COPCs in environmental media, EPA has proposed various ways of estimating the exposure point concentration to account for the uncertainty due to incomplete sampling and/or analytical data variability (EPA, 2002b). These range from using the maximum concentration when few samples have been collected from a potential exposure area to various methods of estimating a 95 % UCL on the mean concentration.

For exposure areas with fewer than ten samples, EPCs are often based on the maximum detected concentration. For exposure areas with ten or more samples, EPA recommends calculating the 95% UCL on the mean value differently depending on the distribution of the data. For data with a normal distribution, the 95 % UCL of the mean is calculated using the t-distribution (Student's t-statistic) in the following algorithm:

$$95\%\quad UCL\ (ppm) = x + \frac{s\,t}{\sqrt{n}}$$

where:

x = arithmetic mean concentration (mg/kg)

s = standard deviation (mg/kg)

t = Student’s t distribution statistic

n = number of data points

For data that are log-normally distributed, EPA (2002b) recommends the use of the Land method based on the H-statistic for determining the 95 % UCL of the mean. The algorithm supplied by EPA for determining the 95 % UCL when data are log-normally distributed is:

$$UCL = e^{\left(x + 0.5s^{2} + \frac{sH}{\sqrt{n-1}}\right)}$$

where:

x = arithmetic mean concentration (mg/kg)

s = standard deviation of log transformed data (mg/kg)

H = Land distribution statistic

n = number of data points

The H-statistic frequently estimates a 95 % UCL of the mean that is greater than the maximum concentration observed at a site when the input data are highly variable (i.e., when the relative standard deviation (RSD) exceeds 100 %) and, in some cases, estimates concentrations in excess of one part per part. In these cases, the biased estimates of the "average" concentration are likely reflecting datasets that include many samples collected from areas of higher concentrations and fewer samples collected from areas of lower concentrations. This is the case at most sites where sampling efforts have intentionally been focused in areas of expected contamination and their immediate vicinity, but often not in other portions of a site where concentrations are likely to be lower but where potential exposure may occur at equal or even higher frequency. In this case, the data distribution is controlled by the sampling strategy rather than any distribution in nature. That is, areas of high concentration are more frequently represented than areas of lower concentration, even though both may be equally likely to represent a contact point by a hypothetical receptor. Therefore, the estimated exposure point concentration is biased high and does not represent the actual concentration that the receptor "encounters." The "distribution" observed in the biased dataset similarly does not represent the actual distribution of concentrations across the entire site or exposure area. Furthermore, a large part of the error in applying the H statistic lies in the inability of the algorithm to properly calculate the arithmetic mean when the data are not lognormally distributed.

If the data were non-parametric in distribution (i.e., not normal or lognormal in distribution), the data were further evaluated to determine if the sample results represent highly skewed distributions (see Appendix H – Human Health Risk Assessment Calculations). For datasets that are neither normal nor lognormal or are highly skewed in distribution, the 95 % UCL on the mean was based on the higher of the values from the percentile or standard bootstrapping techniques (EPA, 2002). In cases where sufficient data to calculate a 95 % UCL of the mean were not available, the exposure point concentration was based on the maximum detected concentration. In accordance with EPA (1989) and EPA's Guidance for Data Usability in Risk Assessment (EPA, 1992), such sample results for individual analytes were omitted if the surrogate value exceeded the maximum detected level for the medium of interest.

Derivation of EPCs

Using the collected data, EPCs were generated for receptors that consume fish only, both fish and shrimp, and shrimp only. For exposure point concentrations for these receptors a 95 % UCL on the mean was derived for the entire HUMMA Study Area, as noted above, and per EPA’s guidance (EPA, 2002b) using EPA’s ProUCL software (EPA, 2009a). Statistical results and ProUCL outputs are presented in Appendix H (Human Health Risk Assessment Calculations). All biota data representing current site conditions was used in deriving the exposure point. In calculating exposure point concentrations, a value equal to one-half the sample quantitation limit reported by the laboratory was used as a surrogate concentration for those constituents that were not detected in a particular sample as specified by EPA (1989).

Shrimp data were further evaluated by dividing the HUMMA Study Area into four distinct strata or decision units to match the stratified sampling approach utilized for the rest of the project. These decision units consisted of DMM sites, RC sites, DS sites, and DMM-DS sites (Table 7-6). For the exposure point concentration used in the decision units assessment, a maximum concentration was used as a surrogate for each decision unit to conservatively estimate the concentration in shrimp as not enough representative samples were taken from each decision unit to accurately calculate a 95 % UCL.

7.2.5 Exposure Factors

The exposure factors used in the quantitative risk assessment are summarized in Table 7-3. Individual exposure factors are discussed below.

7.2.5.1 BODY WEIGHT

Body weights were taken from the EPA Exposure Factors Handbook (EPA 1997a). The average adult body weight used in this risk assessment was 70 kilograms (kg). The average child body weight used in this risk assessment was 15 kg.

7.2.5.2 DURATION OF EXPOSURE

Exposure durations were taken from the Human Health Evaluation Manual: Supplemental Guidance: Standard Default Exposure Factors (EPA, 1991) and Exposure Factors Handbook (EPA, 1997a). The recreational scenario in this assessment is split, assuming six years as a child and 24 years as an adult totaling a 30 year residential tenure.

7.2.5.3 EXPOSURE FREQUENCY

The exposure frequency for the recreational receptor assumes seafood caught from the HUMMA Study Area is consumed once a week totaling 52 days per year (assumption based on interviews with recreational fishermen who frequent the area). These assumptions are very conservative as the HUMMA Study Area is only occasionally fished.

7.2.5.4 INGESTION RATE

Commercial fishing is not expected to occur in the HUMMA Study Area in the foreseeable future. According to research and interviews conducted for the HUMMA Study Area, there are no current commercial fishing operations in the area. The HUMMA Study Area is used as an active shipping lane and the probability of having a trap or string of traps lost due to snagging on passing vessels is extremely high. Consumption in this study is therefore assumed for recreational fishermen only (see Telephone Memorandum in Appendix H).

The current assessment makes the extremely conservative assumption that all seafood consumed originates from the HUMMA Study Area. Ingestion rate for the seafood assessed in this study was derived from the EPA Fish Advisories Estimated Per Capita Fish Consumption in the United States (2002a). The consumption estimates were based on the 95th percentile of a survey conducted by the USFDA. Consumption rates used in this risk assessment were based on male and female consumption of marine finfish and shellfish. The child ingestion rate was conservatively estimated using the 95th percentile of the 14 years and younger age group. The adult ingestion rate was based on the more conservative 45 years and older age group. The consumption estimates used in this risk assessment are 40 grams per day (g/day) for the child receptor and 83 g/day for the adult receptor.

7.2.5.5 LIFETIME

For the carcinogenic risk assessment, the Lifetime Average Daily Dose (LADD) must be calculated. This assessment uses EPA's default value of 70 years (EPA, 1997a).

7.2.6 Method to Estimate Average Daily Dose

Reasonable Maximum Exposure (RME) scenarios evaluated in this risk assessment are based upon conservative exposure assumptions. Most individuals will not be subject to all the conditions that comprise the RME scenario. Individuals who do not meet all conditions in the RME scenario have lower potential exposures to constituents, and therefore, lower potential risks associated with those exposures.

The Chronic Average Daily Dose (CADD) is an estimate of a receptor's potential daily intake from exposure to constituents with potential noncarcinogenic effects. Note that Average Daily Dose is a term used in risk assessment and does not represent a true average because the assumptions used to derive it do not represent "averages". According to EPA (1989), the exposure dose should be calculated by averaging over the period of time for which the receptor is assumed to be exposed. The CADD for each constituent via each route of exposure is compared to the Reference Dose (RfD) for that constituent to estimate the potential hazard index due to exposure to that constituent via that route of exposure. Hazard indices are presented and discussed in Section 7.3.1.

For constituents with potential carcinogenic effects, LADD is an estimate of potential daily intake over the course of a lifetime. In accordance with EPA (1989), the LADD is calculated by averaging the assumed exposure over the receptor's entire lifetime (assumed to be 70 years). The LADD for each constituent via each route of exposure is combined with the cancer slope factor (CSF) for that constituent in order to estimate the excess lifetime cancer risk due to exposure to that constituent via that route of exposure. Excess lifetime cancer risks are presented and discussed in Section 7.3.2.

The equations for estimating a receptor's potential average daily dose (both lifetime and chronic) and the exposure parameters used are discussed in the following paragraphs. The calculations for all receptors evaluated in this risk assessment are presented in Appendix H (Human Health Risk Assessment Calculations).

Biota Ingestion:

$$A = \frac{B \times C \times D \times E \times F \times G}{H \times I}$$

where:

A = Chronic Daily Intake (mg of constituent per kg of body weight per day (mg/kg-day))
B = Constituent Concentration in Biota (mg/kg wet tissue weight)
C = Unit Conversion Factor ($1\text{x}10^{-3}$ kg/g)
D = Ingestion Rate (g/day)
E = Exposure Frequency (days/year)
F = Exposure Duration (years)
G = Fraction Ingested from Source (unitless)
H = Body Weight (kg)
I = Averaging Time (days)

7.3 TOXICITY ASSESSMENT

The purpose of the Toxicity Assessment is to identify the types of adverse health effects that the MC that were adopted as COPC may potentially cause, as well as the relationship between the amount of a COPC to which receptors may be exposed (dose) and the likelihood of an adverse health effect (response). The EPA characterizes adverse health effects as either carcinogenic or noncarcinogenic. Additionally, EPA defines dose-response relationships for oral and inhalation routes of exposure. The results of the toxicity assessment, when combined with the results of the exposure assessment (Section 7.2), provide an estimate of potential risk.

This section provides dose-response information for the COPCs evaluated in the risk assessment for the HUMMA Study Area. Section 7.3.1. describes the EPA approach for developing noncarcinogenic dose-response values. The carcinogenic dose-response relationships developed by EPA are discussed in Section 7.3.2. Toxicity criteria are presented in Table 7-4. Dose-response information used in this risk assessment was obtained from the following sources, in order of priority:

- EPA Integrated Risk Information System (EPA 2009c);
- EPA Provisional Peer Reviewed Toxicity Values Database (EPA, 2009d); and
- Health Effects Assessment Summary Tables (EPA, 1997b).

7.3.1 Noncarcinogenic Dose-Response

Constituents with known or potential noncarcinogenic effects are assumed to have a dose below which no adverse effect occurs or, conversely, above which an effect may be seen. This dose is called the “threshold dose”. In laboratory experiments, this dose is known as the “no observed adverse effects level” (NOAEL). The lowest dose at which an adverse effect is seen is called the lowest observed adverse effects level (LOAEL). By applying uncertainty factors to the NOAEL or the LOAEL, EPA developed RfDs for chronic exposures to constituents with potential noncarcinogenic effects (EPA, 2009c).

Uncertainty factors account for unknowns associated with the dose-response value, such as the effect of using an animal study to derive a human dose-response value, extrapolating from the high doses used in the laboratory experiment to the low doses typically encountered in environmental settings, and evaluating sensitive subpopulations. For constituents with potential noncarcinogenic effects, the RfD provides reasonable certainty that if the specified exposure dose is below the RfD, then no noncarcinogenic health effects are expected to occur even if daily exposure were to occur for a lifetime. RfDs are expressed in terms of mg/kg-day.

7.3.2 Carcinogenic Dose-Response

The underlying assumption of regulatory risk assessment for constituents with known or assumed potential carcinogenic effects is that no threshold dose exists. In other words, it is assumed that a finite level of risk is associated with any dose above zero. For carcinogenic effects, EPA uses a two-step evaluation in which the constituent is assigned a weight-of-evidence classification, and then a CSF is calculated.

The weight-of-evidence classification summarizes the evidence about the likelihood of the constituent being a human carcinogen. Group A constituents are classified as human carcinogens, Group B constituents are probable human carcinogens, Group C constituents are possible human carcinogens, Group D constituents are not classifiable as to human carcinogenicity, and, for Group E constituents, there is evidence of noncarcinogenicity for humans.

In the second part of the evaluation, CSFs are calculated for constituents that are known or probable human carcinogens. The EPA has developed computerized models that extrapolate observed responses at high doses used in animal studies to predicted responses in humans at the low doses encountered in environmental situations. The models developed by the EPA assume no threshold and use animal or human data to develop an estimate of the carcinogenic potency of a constituent. The EPA refers to this numerical estimate as the CSF. The computerized models used by EPA assume that carcinogenic dose-response is linear at low doses.

7.4 RISK CHARACTERIZATION

Risk characterization is the step in the risk assessment process that combines the results of the exposure assessment and the toxicity assessment for each COPC evaluated in this assessment to estimate the potential for carcinogenic and noncarcinogenic human health effects from chronic exposure to that constituent. This section summarizes the results of the risk characterization.

7.4.1 Noncarcinogenic Hazard Characterization

The potential for exposures to COPCs at or near the HUMMA Study Area to result in adverse noncarcinogenic health effects is estimated by comparing the CADD for each MC with the RfD for that MC. The resulting ratio, which is unitless, is known as the Hazard Quotient (HQ) for that MC. The HQ is calculated using the following formula:

$$A = B \div C$$

where:

A = Hazard Quotient (unitless);
B = Chronic Average Daily Dose (mg/kg-day); and
C = RfD (mg/kg-day).

When the HQ for a given constituent and pathway does not exceed 1, the RfD has not been exceeded, and no adverse noncarcinogenic health effects are expected to occur as a result of exposure to that MC via that pathway. The HQs for each MC are summed to yield the Hazard Index (HI) for that pathway. A Total HI is then calculated for each exposure medium by summing the pathway-specific HIs. A Total HI that does not exceed 1 indicates that no adverse noncarcinogenic health effects are expected to occur as a result of that receptor's potential exposure to the environmental medium evaluated.

7.4.2 Carcinogenic Risk Characterization

The purpose of carcinogenic risk characterization is to estimate the potential likelihood, over and above the background cancer rate, that a receptor will develop cancer in a receptor’s lifetime as a result of potential study area-related exposures to COPCs. This likelihood is a function of the dose of a MC and the CSF for that MC. The relationship between the Excess Lifetime Cancer Risk (ELCR) and the estimated LADD of a constituent may be expressed as an exponential equation:

$$A = 1 - e^{-B \times C}$$

where:

A = Excess Lifetime Cancer Risk (unitless);
B = CSF (1/(mg/kg-day)); and
C = Lifetime Average Daily Dose (mg/kg-day).

This is the general form of the equation, and may be used in all cases to estimate potential risk, regardless of the magnitude of the potential estimated risk. In particular, this equation should be used when the product of the dose and potency slope is greater than 10^{-02}. This practice prevents calculation of potential risks that are greater than one.

When the product of the dose and potency slope is less than 10^{-02}, the exponential equation can be simplified to a linear equation, which will closely approximate the results of the exponential equation. The simplified linear form of the equation is expressed as:

$$A = B \times C$$

where:

A = Potential Excess Lifetime Cancer Risk (unitless);
B = CSF (1/(mg/kg-day)); and
C = Lifetime Average Daily Dose (mg/kg-day).

For all potential risks estimated in this study, the product of the dose and potency slope is less than 10^{-02}. Therefore, the simplified linear equation was used in all risk calculations.

The product of the CSF and the LADD is unitless, and provides an estimate of the potential carcinogenic risk associated with a receptor's exposure to that MC via that pathway. ELCRs are calculated for each potentially carcinogenic MC. The ELCRs for each pathway by which the receptor is assumed to be exposed are calculated by summing the potential risks derived for each MC. A Total ELCR is then calculated for each exposure medium by summing the pathway-specific ELCRs. Under baseline conditions, regulatory level of concern for the total potential carcinogenic risk associated with the consumption of biota from the site in the recreational scenario is a range between 10^{-06} and 10^{-04} (i.e., one in one million to one in ten thousand).

7.4.3 Results

The results of the Risk Characterization are presented as lifetime carcinogenic risks for a recreational receptor (child and adult exposures combined) and acute noncarcinogenic hazards to child and adult recreational receptors. The lifetime carcinogenic risks and noncarcinogenic hazards were calculated across the entire site and for the individual strata. Noncarcinogenic hazards were calculated for both child and adult receptors. The results of the risk characterization are presented in Table 7-15.

Further analyses conducted divided the shrimp data into 4 distinct decision units (Table 7-6). These decision units consisted of RC sites acting as controls for DMM sites, and DS sites acting as controls for DMM-DS sites. Risks were calculated for each set of shrimp samples taken from each decision unit.

Appendix H (Human Health Risk Assessment Calculations) and the Section 7 tables present the PELCRs and HIs associated with the site-specific potential exposures to contaminated biota, as well as a summary the risks and hazards associated with all seafood ingestion and a summary of the risks associated with the four decision units used to characterize the shrimp samples taken at the site. The derivations of all calculation can be found in Appendix H (Human Health Risk Assessment Calculations).

7.4.4 Lead Risk Characterization

Lead has been included as a site-specific COPC in this risk assessment. Lead risk assessment is addressed separately from other COPCs as risks from lead are specifically assessed based on blood lead concentrations. In this assessment, lead has been evaluated using the EPA's Integrated Exposure Uptake Biokinetic (IEUBK) model. As the interaction of lead with the body is well understood, the IEUBK model is able to estimate the blood lead concentration in children based on potential exposure pathways. To assess risks using this model default values were used for all potential pathways to the receptor other than dietary intake. Dietary intake exposure parameters assumed that 100% of the meat consumption consisted of fish and shrimp from the Study Area. Site-specific EPCs for lead were calculated in the exposure assessment step and used in this model. The Centers for Disease Control and Prevention (CDC) has identified a blood lead concentration level of 10 microgram per deciliter (µg/dL) as the level of concern above which significant health risks occur.

The lead risk assessment resulted in no exceedences above the regulatory limit of 10 µg/dL. The highest lead risk calculated was at decision unit DMM for the discarded munition sites. Blood lead concentration for children ages three and four assumed to ingest shrimp from this area was 8.9 µg/dL. Table 7-7 presents all of the results of the lead risk assessment using the EPA's IEUBK model.

7.5 UNCERTAINTY ANALYSIS

Within any of the four steps of the risk assessment process, assumptions must be made due to a lack of absolute scientific knowledge. Some of these assumptions are supported by considerable scientific evidence, while others have less support. Every assumption introduces some degree of uncertainty into the risk assessment process. Conservative assumptions were made throughout this risk assessment to ensure that public health is protected. Therefore, when all of the assumptions are combined, actual risks may be overestimated.

The assumptions that introduce the greatest amount of uncertainty in this risk assessment are discussed in this section. Uncertainty is typically discussed in general terms, because, for most assumptions, there is usually not enough information to assign a numerical value that can be factored into the calculation of risk. However, this analysis also presents uncertainty via a quantitative assessment. As is evidenced by this quantitative analysis, significant health conservative measures have been considered when evaluating the potential risk from seafood caught near the Study Area, as well as the totality of HUMMA Study Area.

7.5.1 Hazard Identification

During the Hazard Identification step, constituents are selected for inclusion in the quantitative risk assessment. Of the MC adopted as COPCs, only arsenic, copper, and lead were determined to be directly associated with the DMM, however all detected metals were carried forward in the risk assessment. The remaining constituents included in this assessment also contribute to overall human health, even if they may originate from a variety of other sources. As a result, uncertainty may be introduced by the Hazard Identification step because all detected contaminants were included in the risk assessment instead of just those associated with underwater munitions. All other analytes, including CA and degradation products, were not detected in the biota samples and eliminated for further analysis in the human health risk assessment.

7.5.2 Exposure Assessment

During the exposure assessment, average daily doses of COPCs to which receptors are potentially exposed are estimated. The estimation of dose involves a host of assumptions including but not limited to assumptions about the amount of recreational fishing that occurs in the area, accessibility of the fishing resource, how often seafood is consumed and the types of seafood consumed. As many of these assumptions as possible are defined in this risk assessment. In general, the potential intake rates, exposure frequencies and durations and other exposure assumptions used in the risk assessment were conservative and health protective. For example, the recreational fisherman was assumed to ingest seafood caught from within the Study Area 52 days/year for 30 years. Significant uncertainty was also introduced by assuming that all fish consumed by a recreational fisherman was caught from the Study Area. Other exposure assumptions such as assuming that fish are not prepared in ways that reduce any MC contaminant concentration are also extremely health protective. This risk evaluation did not incorporate assumptions about how a fish is cleaned or cooked. Cleaning and cooking may significantly alter the quantities of certain contaminants in seafood. Such assumptions may overestimate actual exposures. If more realistic and reasonable potential exposure assumptions had been employed in the risk assessment, the estimated risks may have been lower.

Uncertainty was also introduced by using “J” qualified analytical data. “J” qualified data indicates that the quantity identified was estimated. As is standard in risk assessment practice and for risk assessments conducted for CERCLA sites, “J” qualified data are not discarded or rejected, but are used in estimating site risk. Values may be “J” qualified for a variety of reasons including extrapolation of values that may be outside a specific chemical’s calibration curve, matrix interference or detection of a compound but below typical reporting limits. In addition, sample analytical results may be considered estimates if variability between split samples or duplicates are of significant difference.

7.5.3 Toxicity Assessment

Dose-response values are usually based on limited toxicological data. For this reason, a margin of safety is built into estimates of both carcinogenic and noncarcinogenic hazards, and actual risks are lower than those estimated. The two major areas of uncertainty introduced in the dose-response assessment are: (a) animal to human extrapolation; and (b) high to low dose extrapolation. These are discussed below.

Human dose-response values are often extrapolated, or estimated, using the results of animal studies. Extrapolation from animals to humans introduces a great deal of uncertainty in the risk assessment because in most instances, it is not known how differently a human may react to the constituent compared to the animal species used to test the constituent. The procedures used to extrapolate from animals to humans involve conservative assumptions and incorporate several uncertainty factors that overestimate the adverse effects associated with a specific dose. As a result, overestimation of the potential for adverse effects to humans is more likely than underestimation.

Predicting potential health effects from the exposure to media within a HUMMA Study Site requires the use of models to extrapolate the observed health effects from the high doses used in laboratory studies to the anticipated human health effects from low doses experienced in the environment. The models contain conservative assumptions to account for the large degree of uncertainty associated with this extrapolation (especially for potential carcinogens) and therefore, tend to be more likely to overestimate than underestimate the risks.

7.5.4 Risk Characterization

The risk of adverse human health effects depends on estimated levels of exposure and on dose-response relationships. Once exposure to and risk and hazard from each of the selected constituents evaluated in this assessment is calculated, the total risk posed by exposure to Study Area-related COPCs is determined by combining the health risk contributed by each of the MC evaluated. Where these constituents do not interact, do not affect the same target organ or do not have the same mechanism of action, summing the risks for multiple constituents results in an overestimate of risk posed by DMM in the Study Area. However, in order not to understate the risk, it was initially assumed that the effects of the different MC evaluated in this assessment may be added together.

7.6 HHRA SUMMARY AND CONCLUSIONS

This report presents the results of a site-specific risk assessment at the Study Area. The HHRA evaluated risks to child and adult recreational fishermen who may consume potentially contaminated biota. The cumulative hazard indices and potential carcinogenic risks for Study Area site-specific receptors are presented in the Section 7 tables and Appendix H (Human Health Risk Assessment Calculations).

The potential recreational fisherman was assumed to ingest biota obtained from the Study Area once a week for 30 years, six years as a child and 24 years as an adult. The specific risk estimates are described below. Carcinogenic risks are summed for the child and adult scenarios to create a chronic lifetime carcinogenic risk. Noncarcinogenic hazards are presented separately for the child and adult receptors. The risk characterization is summarized in Table 7-15.

The lead risk assessment using the EPA's IEUBK model resulted in no exceedences above the regulatory limit of 10 µg/dL. The highest lead risk calculated was at the DMM sites. Blood lead concentration for children ages 3 and 4 assumed to ingest shrimp from this area was 8.9 µg/dL.

The Study Area is highly isolated and in reality very little if any biota will be consumed from the Study Area. This assessment assumed very conservative exposure assumptions in determining a RME scenario. Risks calculated assuming the RME scenario were all below or within the EPA acceptable risk range.

- Carcinogenic risks were above the point of departure risk threshold of 10^{-06} for the receptors that ingested fish, but were within the EPA acceptable risk range of 10^{-06} to 10^{-04}. Additional arsenic speciation analysis on the fish tissue samples would be able to provide a more accurate determination of carcinogenic risks from the fish ingestion pathway.

- Noncarcinogenic hazards were also approaching the regulatory limit, but none exceeded the applicable limit.

If more accurate consumption data could be retrieved based on actual recreational fishing in the area these results would almost certainly be lower. Risks were also calculated on all detected potential contaminants from the laboratory analysis, many of which may be from non-munition sources. The largest contributors to the non-carcinogenic hazards were mercury in the fish samples, and cadmium and mercury in the shrimp samples. Neither of these contaminants were determined to be directly related to the DMM located at the Study Area. If human heath risks were evaluated just on site-specific COPCs these results would in all probability be much lower. Under current and potential future uses of the HUMMA Study Area, health risks to likely receptors are within EPA acceptable levels.

8. Conclusions

The major conclusions for the HUMMA are presented in the Executive Summary of this report. In addition to those overarching conclusions, this section focuses on the more pragmatic conclusions for the various aspects of the HUMMA Project.

8.1 PRIMARY PROJECT RESULTS

The primary scientific goal of the HUMMA Project was to assess the effect of the ocean environment on DMM and DMM on the ocean environment. To this end, HUMMA scientists examined six factors in the HUMMA Study Area including: 1) the spatial extent and distribution of DMM; 2) the integrity of DMM; 3) whether MC could be detected in sediment, seawater or human food items near DMM; 4) whether MC levels at DMM sites differed significantly from levels at RC sites; 5) whether statistically significant differences in ecological population metrics could be detected between DMM and RC sites; and 6) whether MC or their derivatives potentially posed an unacceptable risk to human health. Following are the conclusions for each factor studied.

1) The spatial extent and distribution of DMM

Backscatter data from the SSS were extremely effective in detecting 1-2 m-long reflective targets within, and extending to the southern boundary of, the HUMMA Study Area. Subsequent examination of these targets using video systems and visual observation verified that these targets were usually DMM. With the exception of one broad circular field of DMM in the HUMMA Study Area, all of the DMM were distributed in narrow curvilinear trails ranging from hundreds of m to a few km in length. This distribution pattern suggests that most DMM in the HUMMA Study Area were disposed by ships that were underway as munitions were cast overboard. Munitions extended beyond the boundaries of the HUMMA Study Area and although munitions were readily detected within the area studied, the full spatial extent of DMM was not determined during the study.

2) The integrity of DMM

The integrity of DMM in the HUMMA Study Area spans a broad spectrum, with even the best-preserved munitions casings deteriorating at a yet-to-be determined rate. The deterioration level of DMM casings ranged from almost pristine to virtually disintegrated. The state of deterioration varied within similar munitions types located in the same general area, as well as between different types of munitions spread over a wide region. In general, munitions with thicker casings were better preserved. Most of the munitions casings visually studied were not obviously breached, although many DMM were imaged with “skirts” or columnar “pedestals” beneath them that may be the result of rusting, possibly in combination with leakage of internal MC.

3) MC detection in sediment, seawater or human food items near DMM

Analytical methods used to detect MC during sampling were effective. During the HUMMA Project a total of 94 sediment samples, 30 water samples, 16 fish samples, and 19 shrimp samples were collected. Of these samples, there were no confirmed detections of CA or energetics, although there was one tentative identification of mustard in a single sediment sample. This identification could not be confirmed in two subsequent analyses. The unconfirmed identification of mustard could not have resulted from any surrogate or other source and can thus be attributed to a specific DMM that was knocked over by one of the HOV’s thrusters during maneuvers when sampling. It seems likely that the CA detected was released when the pedestal supporting this DMM broke. For this reason, particular attention should be paid to pedestals and skirts at the base of DMM during any future efforts. There were detections of high arsenic and lead concentrations in several biota samples;

however, these metals detections could not be definitively linked to MC and as indicated in item 6 below, risks were within acceptable levels..

4) Differences in MC levels within different strata

HUMMA's stratified sampling approach was designed to facilitate comparisons of RC, DS, DMM and DMM-DS sites. Comparison of data collected in these different strata did not show statistically significant differences in levels of MC, including CA. Most of the MC adopted as COPCs for the HUMMA Project, lack established standards for MC present in a marine environment, however, particularly in deep-water environments. There were differences in concentrations of metals detected, but these differences were not statistically significant and thus cannot be interpreted as attributable to the presence or absence of DMM.

5) Differences in ecological population metrics within different strata

Collection of push core samples for benthic infauna analysis was successful for gauging infauna abundance and diversity, while composite samples from residual sediment samples were useful for gauging infauna diversity but not relative abundance. Higher average abundances of benthic infauna were found in association with DMM located within DS sites, although the difference was not statistically significant. Field observations did not identify any macrobiotic mid-water species that could be considered ecological health indicators or key sentinel species. Although the data set for this study was limited, no statistically significant differences in ecological population metrics were found within the four strata.

6) Risks and hazards to human health

The Human Health Risk Assessment (HHRA) evaluated human health risks associated with the consumption of fish and shrimp samples collected from the HUMMA Study Area. Four shrimp and one fish sample exceeded the Food and Drug Administration screening levels for metals. There were no detections of CA or energetics in any of the biota samples collected. Consequently, CA and energetics were eliminated from further analysis and the project team conducted a quantitative HHRA using metals data only. The quantitative assessment evaluated risk assuming a recreational exposure scenario. The assessment determined that risks and hazards from the consumption of fish and shrimp collected from the study area were within EPA acceptable levels. If realistic consumption values for biota from the Study Area are used, these risks and hazards are anticipated to be significantly reduced and almost certainly below the EPA point of departure risk level of $10^{-06}$and the hazard index of 1. This assessment found that the risk to human health from the consumption of fish and shrimp collected near the HUMMA Study Area were within EPA acceptable risk levels. .

8.2 HISTORICAL REVIEW

The historical review of documents prior to the HUMMA field programs, in combination with pre-cruise analyses of extant HURL video tapes, provided indispensible information for selecting the HUMMA Study Area, as well as the approach that would be used to search for, and sample near, specific DMM. Yet, despite this important information, no large accumulation or long-debris trail of the approximately 16,000 100-lb M47A2 bombs that were both believed to have been sea-disposed at HUMMA Study Area and the primary DMM of interest were located. Thanks to publicity that occurred during the HUMMA, new information continues to come to light regarding disposal of munitions off O‘ahu.

During HUMMA, the project team found the near-bottom towed SONAR to be efficient at detecting munitions trails. Investing sufficient time in SONAR surveys to bound the disposal area allows

ROV and HOV work to be focused on target rich areas. The IMI-120 survey of the HUMMA area included redundancy that can be reduced, and still managed to cover an approximately 100 km^2 area in under five days of dedicated surveying (the area covered included both the HUMMA Study Area as well as the area south of Barber's Point, as depicted on Figure 1-3).

8.3 SONAR SURVEYS

SONAR surveys of the Study Area were critical to the success of this program. Significantly, these surveys led to reconsideration of the scenario describing how munitions had been disposed at the end of WWII. Prior to the SONAR surveys, the project team's expectation was that large concentrations of munitions would be located at discrete sites in the field area. The SONAR results indicated that munitions were instead disposed along linear trails, and it was this insight that allowed the project team to image thousands of discrete DMMs during video surveillance.

The hull-mounted SONAR survey of the region south of Pearl Harbor was necessary at the outset of the HUMMA. First, the hull-mounted data enabled the IMI-120 team to safely tow the SONAR within 50 to 75 m of the seabed. Secondly, the GPS-navigated hull-mounted data provided a valuable basemap for co-registration of the towed SONAR, which has poorer quality navigation. Since almost the entire region between Pearl Harbor and Penguin Bank has now been mapped, any future efforts in this area should limit or forego dedicated reconnaissance surveys with hull-mounted systems and instead focus on acquiring as much towed near-bottom SONAR data as possible.

An interesting question is whether even higher resolution SONAR systems mounted on autonomous underwater vehicles (AUV) might further increase the likelihood of locating DMM in the Study Area. There are two points that argue against an AUV-based approach. The amount of area mapped by a given SONAR system decreases as altitude above bottom decreases (and resolution increases). Also, given the number of entanglement hazards discovered during the HUMMA, the possibility of an AUV being snared during a systematic survey seems high. One strength of an ROV and HOV approach is that its redundant HOV adds a measure of safety to any operation near entanglements.

8.4 VIDEO RECONNAISSANCE

The towed camera operations to evaluate speckle trails for munitions were the least successful part of the HUMMA. There were problems with the camera system itself that led to repeated delays in deploying the system. However, once the system was proven to be working the primary problem was determined to be the small platform (*R/V Klaus Wyrtki*) from which the system was deployed.

The *R/V Klaus Wyrtki* is a reasonable platform for camera surveys in terms of over-the-side handling capabilities and deck space, but it is just too small to make headway in the types of seas that are typical for the region south of O‘ahu. Subsequent to the HUMMA the UH camera system was deployed from the *R/V KoK* for a cable route survey and captured excellent images of the seafloor all along the proposed route. At a cost of $30,000 per day, use of the *R/V KoK* is reasonable only if the camera effort is conducted in support of and during the same field program as other types of mapping and imaging. If the need for video reconnaissance arises for future investigations, a more stable platform for deploying the camera system is necessary.

The ROV video surveys were extremely effective for imaging suspected DMM sites, although it was necessary in one instance to modify the survey approach. During operation, five of the six ROV nighttime surveys intersected DMM trails in enough locations for the project team to determine that those trails were dominated by munitions (e.g., smaller caliber, boxed munitions) that were obviously not M47A2 bombs or the type that should be sampled by the HOV. One of these five tows could have been improved had the trackline for the survey been developed to slalom down the debris trail instead of trying to follow it directly. The sixth ROV tow accomplished the important task of the "negative experiment," towing across a broad expanse where no targets were observed in the backscatter data and confirming that no DMM could be imaged along the video transect. ROV nighttime operations were valuable as they represented a time-saving aspect of the HUMMA Project.

The HOV video surveys produced the most comprehensive image records of the munitions trails and contributed significantly to the HUMMA scientific analyses. Video records were considered in almost all aspects of HUMMA including consideration of how DMM are deteriorating, what sort of biota are found near DMM, what affect physical oceanographic processes in the region are having around the DMM, etc. The ability of the HOVs to operate independently of the ship was another component in the successful HUMMA operation – frequently the HOV observers made judgment calls about directions to investigate that deviated from the pre-launch dive plan. In every instance this adaptability helped the HOVs locate new findings such as DMM that had not been previously detected or subtle branches of major trails that had not been initially targeted for investigation.

The question of the applicability of AUVs for projects like HUMMA must be considered when evaluating the performance of the HOVs. An AUV, because it is programmed, will carry out a very systematic survey of a site. This systematic approach will maximize information when the site was well selected, but it will minimize information if some aspect of the site makes it unsuitable. Contrastingly, a human operator relies on visual queues that will likely not lead to a systematic survey, but humans more likely to recognize when there is a dearth of information at the present location or when important information is just beyond the bounds of the specified site. If an AUV is entangled or contacts a dangerous object, there is no need to worry that a human life will be lost; however, humans are probably more likely to avoid problems in the first place and to come up with creative solutions for extricating themselves if difficult conditions are encountered. Based on HUMMA's success and the still-in-development aspects of many deep-water AUVs, the present approach using HOVs has merit. A careful review of the required tasks and a cost-benefit analysis should be conducted to determine whether HOV, ROV, or AUV should be used for a given investigation.

8.5 SEDIMENT AND WATER SAMPLING

The sediment and water samplers used during the March 2009 program on the *R/V KoK* were very effective tools for bringing collected materials to the surface for subsequent analysis. The handles were easy for the HOV manipulator arms to open and close and with the exception of one broken handle, every sampler was readily evacuated and cleaned so that it could make a return trip to the seafloor. The push corers took a few iterations to perfect and they never succeeded in completely preserving all of the material that originally captured, but they were able to preserve a stratified sample of known surface area that could be used for benthic infauna analysis. The maximum surface area of the push core devices, however, was less than ideal, and better infauna data would be collected if the push core devices were able to sample at least double their existing surface area capacity.

8.6 BIOTA

The biota sampling team was able to accurately return to selected HUMMA Study Area sites and drop shrimp traps to collect *ama ebi*. The field team did not have any difficulty trapping sufficient numbers of *ama ebi* to meet the volume requirements of the subcontract laboratories. However, the deployment method was from the ocean surface, a distance of approximately 500 m. It is difficult to say exactly how close to a target the shrimp traps were deployed. Future studies should try to deploy and recover shrimp traps adjacent to targets of interest using HOVs or ROVs.

Onaga, on the other hand, were not caught within the HUMMA Study Area despite several days of attempts. The biota sampling team eventually moved to the west of the HUMMA Study Area, to a region having more optimal bottom depths and bottom type to support *onaga*, and they were able to catch several specimens for analysis. Although the *onaga* were not caught from within the HUMMA Study Area, because of their free-ranging life history, any *onaga* caught within several km of the area could have either transited through or fed within the HUMMA Study Area. Similarly, the *onaga* may also have picked up contamination from a remote site and brought it to proximity of the HUMMA Study Area. These samples are still considered useful for the HUMMA Project, however subsequent investigations should select a target species that has a smaller range, preferably one that is limited to the specific study area.

A few of the biota samples contained concentrations of metals that exceeded the HUMMA Project's screening levels, and thus a baseline HHRA was conducted. This HHRA evaluated risks to child and adult recreational fishing receptors that might consume potentially contaminated biota from within the study area and found that risks are all within the range considered acceptable by the EPA.

8.7 GIS

Encapsulating the results of the various HUMMA analyses into a GIS has two advantages. First, it allows for easy comparison of information, for example the distribution of all depth charges seen in all video analyses with the high-resolution backscatter data. Secondly, it provides a means for non-HUMMA Project team members to evaluate the data without the filter of the research team. This ultimately contributes to the efficacy of the HUMMA by allowing non-participants to ask questions about the data that may not have been previously considered. Significant time has gone into the preparation of the HUMMA GIS, and it is an important part of the Final Project deliverable.

8.8 PHYSICAL OCEANOGRAPHY

The physical oceanography program provided few surprises during the HUMMA Project as the results were very consistent with prior, analogous studies in the same general area. It was disappointing that the mooring was lost before it could be recovered for the second time and that as a result, data acquired simultaneously with the March 2009 *R/V KoK* field program could not be included in the HUMMA GIS, but it seems highly unlikely that these data would have changed the overall results of this aspect of the HUMMA Project.

One unanticipated result of the physical oceanography program was the realization that the mooring was deployed in a field of speckles, many of which were subsequently determined to be DMM. UH (and other) researchers frequently place instruments on the seabed south of Pearl Harbor, and one completely unanticipated but useful legacy of the HUMMA Project will be publishing the general locations of DMM trails to minimize the risk of instrument packages interacting with DMM.

This page is intentionally left blank.

9. References

ATSDR (Agency for Toxic Substances & Disease Registry), 1997. Toxicological Profile for Lead. U.S. Department of Health and Human Services, Public Health Service, Atlanta, Georgia.

_____, 2003a. Blister Agents Sulfur Mustard Agent H or HD (C H Cl S), CAS 505-60-2, UN 2927; and Sulfur Mustard Agent HT CAS 6392-89-8.

_____, 2003b. Blister Agents Lewisite (L) (C H AsCl) CAS 541-25-3, UN 1556; and 2 2 3 Mustard-Lewisite Mixture (HL) CAS Number not available, UN 2810.

_____, 2007. Public Health Statement Arsenic. Division of Toxicology and Environmental Medicine. http://www.atsdr.cdc.gov/toxprofiles/tp2-c1-b.pdf Site visited January 27, 2010

_____, 2008. “Toxicological Profile for Sulfur Mustard (update)”. Accessed online at: http://www.atsdr.cdc.gov/toxprofiles/tp49.pdf Site Visited February 14, 2008.

Alford, M.H., M.C. Gregg, and M.A. Merrifield, 2006. Structure, propagation, and mixing of energetic baroclinic tides in Māmala Bay, O‘ahu, Hawai‘i, J. Phys. Oceanogr., 36, 997–1018.

Amato, E., L. Alcaro, I. Corsi, C. Della Torre, C. Farchi, S. Focardi, G. Marino, and A. Tursi, 2006. An Integradted Ecotoxicological Approach to Assess the Effects of Pollutants Released by unexploded Chemical Ordnance Dumped in the Southern Adriatic (Mediterranean Sea), Marine Biology, 149: 17-23, 2006.

Attar, M.A., M.Z. El-faer, T.N. Rawadah., and B.S. Twabini, 1992. Levels of Arsenic in Fish from the Arabian Gulf, Mar. Pollut. Bull., 24, 94-97, 1992.

Beaudry, W.T., P.C. Bossie, S.P. Harvey, J.E. Kolakowski, L.R. Prgcell, D.K. Rchrbaugh, D.C. Sorrick, A.N. Stroup, L.L. Szafraniec, and Y.C. Yang, 1995. Neutralization/biodegradation of HD. In: Analytical Methods for Environmental Sampling of Chemical Warfare Agents and Their Degradation Products (Watson AP, Kistner SL, eds) ORNL/M-4315. Oak Ridge, TN:Oak Ridge National Laboratory, 1995.

Beddington, J. and A.J. Kinloch, 2005. Munitions Dumped at Sea: A Literature Review, Imperial College London Consultants, June 2005.

Bhatt, M., J-S. Zhao, F. Monteil-Rivera, and J. Hawari, 2005. Biodegradation of Cyclic Nitramines by Tropical Marine Sediment Bacteria, J. Ind. Microbiol Biotechnol. 32: 261-267, 2005.

Bizzigotti, O.G., Castelly, H., Hafez, M.A., Smith, H.B. W., and Whitmire, T.M., 2009. Parameters for Evaluation of the Fate, Transport, and Environmental Impacts of Chemical Agents in Marine Environments, Chemical Review 109: 236-256, 2009.

Boopathy, R., M. Gurgas, J. Ullian, and J.F. Manning, 1998. Metabolism of Explosive Compounds by Sulfate-Reducing Bacteria, Current Microbiology 37: 127-131, 1998.

Brannon, J.M., Price, C.B., Yost, S.L., Hayes, C., and Porter, B., 2005. Comparison of Environmental Fate and Transport Process Descriptors of Explosives in Saline and Freshwaer Systems. Marine Pollution Bulletion, 50: 247-251.

Crocker, F.H., K.J. Indest, and H.L. Fredrickson, 2006. Biodegradation of the Cyclic Nitramine Exploisives RDX, HMX, and CL-20, Appl. Microbiol Biotechnol., 73: 274-290, 2006.

Chemical Officer, 1944. Memorandum from Chemical Officer, 7th Air Force, to Brigadier General Alden H. Waitt. Subject: Disposal of M47A2 H-Filled Bombs. November 12, 1944.

Corl, E., 2001. Bioaccumulation in the Ecological Risk Assessment (ERA) Process. Atlantic Division, Naval Facilities Engineering Command.

Darrach, M.R., A. Chutjian, and G.A. Plett, 1998. Trace Explosives Signatures from World War II Unexploded Undersea Ordnance, Environ. Sci., Technol., 32, 1354-1358, 1998.

Daugherty, J., 1998. Assessment of Chemical Exposures: Calculation Methods for Environmental Professionals. Lewis Publishers, New York. Pg. 117.

De Carlo, E.H., Spencer, K.J., 1995. Records of lead and other heavy metal inputs to sediments of the Ala Wai Canal, O‘ahu, Hawai‘i.Pacific Sci.49, 471–491.

De Carlo, E.H., Anthony, S.A., 2002. Spatial and temporalbvariability of trace element concentrations in an urban subtropical watershed, Honolulu, Hawai‘i.App. Geochem 17, 475–492.

De Carlo, E.H., Beltran, V.L., Tomlinson, M.S. 2004. Composition of water and suspended sediment in streams of urbanized subtropical watersheds in Hawai’i. App. Geochem. 19(7):1011-1037.

De Carlo, E.H., Tomlinson, M.S., Anthony, S.A. 2005. Trace elements in streambed sediments of small subtropical streams on O’ahu, Hawai’i: Results of the USGS Hawai’i NAWQA study. Appl Geochem. 20(12):2157-2188.

Defense Construction Service (Denmark), 2001. Dumped Ammunition in Mjøsa, Sediment Survey and Assessment of Spreading of Dumped Ammunition in Mjøsa, DNV report 2001-0478.

Donnelly, LTC. P.J., 1990. Environmental Fate of Chemical Agents in Deep Seawater: Literature Review. 3 August.

Eich, M. L., M. A. Merrifield, and M. H. Alford, 2004. Structure and variability of semidiurnal internal tides in Māmala Bay, Hawai‘i, J. Geophys. Res., 109(C5), C05010, doi:10.1029/2003JC002049.

Environet, Inc. and A. D. Little, 2001. Special Study for a Reference Site to Serve the South O‘ahu Disposal Site. Prepared for USACE under contract DACA83-00-C-0014. August, 2001.

Epstein, J., D. H. Rosenblatt, A. Gallacio, and W.F. McTeague, 1973. Summary report on a data base for predicting consequences of chemical disposal operations, EASP 1200-12, January 1973, DTIC accession no. AD-B955399.

EPA, Region 9 (EPA Region 9). 2004. EPA Region 9 PRGs [Preliminary Remediation Goals] Tables. October. San Francisco.

EPA, 1986. Superfund Public Health Evaluation Manual. Office of Emergency and Remedial Response. EPA 540/1-86/060.

_____, 1989. Risk Assessment Guidance for Superfund. Volume I: Human Health Evaluation Manual. Part A. Interim Final. Office of Emergency and Remedial Response.

_____, 1991. Human Health Evaluation Manual, Supplemental Guidance: "Standard Default Exposure Factors." OSWER Directive 9285.6-03. March 25, 1991.

_____, 1992. Supplemental Guidance to RAGS: Calculating the concentration term. May.

_____, 1997a. Exposure Factors Handbook, Volumes I-III. EPA/600/p-95/002Fb. August.

_____, 1997b. Health Effects Assessment Summary Tables. Fiscal Year 1997. Office of Health and Environmental Assessment. EPA 540/R-97/036.

_____, 2002a. Fish Advisories Estimated Per Capita Fish Consumption in the United States. EPA 821-C-02-003. August.

_____, 2002b. Calculating Upper Confidence Limits for Exposure Point Concentrations at Hazardous Waste Sites. OSWER 9285.6-10. December.

_____, 2004. EPA Region III BTAG Marine Sediment Screening Benchmarks.

_____, 2009a. ProUCL Version 4.00.04. EPA Technical Support Center. Las Vegas, Nevada.

_____, 2009b. Integrated Exposure Uptake Biokinetic Model for Lead in Children (IEUBKwin v1.1 build 9). June.

_____, 2009c. Integrated Risk Information System (IRIS). Office of Health and Environmental Assessment, Environmental Criteria and Assessment Office, U.S. EPA. Cincinnati, OH.

_____, 2009d. EPA’s Provisional Peer Reviewed Toxicity Values (PPRTVs), by EPA Office of Research and Development/National Center for Environmental Assessment/Superfund Health Risk Technical Support Center (STSC).

Fletcher, C.H., C. Bochicchio, C.L. Conger, M.S. Engels, E.J. Feirstein, N. Frazer, *et al.*, 2008 Geology of Hawai‘i Reefs. Chapter 11 in “Coral Reefs of the U.S.A.”, Springer, p. 435-488.

FRSR (Fisheries Research Services Report), 1996. Surveys of the Beaufort’s Dyke Explosives Disposal Site, Final Report, No. 15/96, November 1996.

Garnaga, G. and A. Stankevicius, 2005. "Arsenic and Other Environmental Parameters at the Chemical Munitions Dumpsite in the Lithuanian Economic Zone of the Baltic Sea." Environmental Research, Engineering and Management No. 3(33): 24-31.

Glasby G.P., 1997. Disposal of chemical weapons in the Baltic Sea. Science of the Total Environment, 206(2-3): 267-273.

Gorontzy, T., O. Drzyzga, M.W. Kahl, D. Bruns-nagel, J. Breitung, E. von Loew, and K.-H. Blotevogel, 1994. Microbial Degradation of Explosives and Related Compounds, Critical reviews in Microbiology, 20 (4): 265-284, 1994.

Grande J.A., Borrego J., Morales J.A., 2000. A study of heavy metal pollution in the Tinto-Odiel estuary in southwestern Spain using factor analysis. Environ. Geol. 39, 1095-1101.

Haag I., Westrich, B., 2002. Processes governing river water quality identified by principal component analysis. Hydrol. Proc. 16, 3113-3130.

Haderlein, S.B., K.W. Weissmahr, and R.P. Schwaraenbach, 1996. Specific Adsorption of Nitroaromatioc Explosives and Pesticides to Clay Minerals, Environ. Sci. Technol. 30, 612-622, 1996.

Hamilton, P. J., J. Singer, and E. Waddell, 1995: Māmala Bay study, Ocean current measurements: A report to the Māmala Bay Commission, HI. Technical report, Sci. Appl. Int’l. Corp., Raleigh, NC.

Hampton, M.A., Torresan, M.E. and J.H. Barber, 1997, Sea-floor geology of a part of Mamala Bay, Hawaii, Pacific Science, 51, 54-75.

Harvey, S.P. and J.J. DeFrank, 1993. Biodegradation of Chemical Warfare Agents: Demilitarization Application, in: Army Science: The New Frontiers, Military and Civilian Application (Kamely D, Sasmore R, eds), Woodlands, TX:Borg Biomedical Services, 1993.

HELCOM (Helsinki Commission), 1994. Report on Chemical Munitions Dumped in the Baltic Sea, Report to the 15th Meeting of Helsinki Commission from the Ad Hoc Working Group on Dumped Chemical Munition, Danish Environmental Protection Agency, January 1994.

Helena B., Pardo R., Vega M., Barrado E., Fernandez J.M., Fernandez L., 2000. Temporal evolution of groundwater composition in an alluvial aquifer (Pisuerga River, Spain) by principal component analysis. Water Res. 34, 807-816.

Javits, J., 1944. Report on Trip of Brigadier General A.H. Waitt and Lt. Col. J.K. Javits to POA and SWPA, 24 September 1944 to 21 November 1944, Report dated 15 December 1944. Pages 8-9.

Jing, Y., A. Singh, and O.P. Ward, 2004. Biodegradation of Nitroaromatics and Other Nitrogen-containing Xenobiotics, World Journal of Microbiology & Biotechnology 20: 117-135, 2004.

Kelley, C., 2007. Personal communication. University of Hawai‘i, Department of Oceanography, Associate Professor. September.

Kerby, T., 2009. Personal communication. Hawai‘i Undersea Research Laboratory, Director of facilities and submersible operations, March.

Li Y.-H. 2000. A compendium of geochemistry: from solar nebula to the human brain. Princeton University Press, Princeton, N.J.

Lisichkin, G.V., 1996. “Chemical Weapons on the Seabed,” in Sea-Dumped Chemical Weapons: Aspects, Problems and Solutions, Ed. A.V. Kaffka, Kluwer Academic Publishers, Dordrecht, pp. 121-127.

Martini, K. I., M. H. Alford, J. D. Nash, E. Kunze, and M. A. Merrifield, 2007. Diagnosing a partly standing internal wave in Māmala Bay, O‘ahu, Geophys. Res. Lett., 34, L17604, doi:10.1029/2007GL029749.

McNaughton, M. and J. Brewer, 1994. Environmental Chemistry and Fate of Chemical Warfare Agents, Final Report, SwRI Project 01-5864. Prepared by Southwest Research Institute for Department of the Army, Corps of Engineers, Huntsville Division. 3 March.

MEDEA, 1997. Ocean Dumping of Chemical Munitions: Environmental Effects in Arctic Seas. McLean, VA, 235 pp.

Munro, N.B., S.S. Talmage, G.D. Griffin, L.C. Waters, A.P. Watson, J.F. King, and V. Hauschild, 1999. The Sources, Fate, and Toxicity of Chemical Warfare Agent Degradation Products, Environmental Health Perspectives, 107 (12) 933-974, 1999.

NRC, 1983. Risk Assessment in the Federal Government: Managing the Process. Committee on the Institutional Means for assessment of Risks to Public Health. National Research Council. National Academy Press. Washington, D.C.

Nipper, M., Y. Qian, R.S. Carr , and K. Miller, 2004. Degradation of Picric Acid and 2.6-DNT in Marine Sediments and Waters: the Role of Microbial Activity and Ultra-violet Exposure, 2004. Chemosphere 56: 519-530, 2004.

Nieland, S. and T. McMahon, 1999. A Benthic Survey of Inner Bantry Bay. In: Marine Institute, Fisheries Research Center, Fisheries Bulletin. 18, 1999.

Neighbor Island Consultants, 1977. Environmental surveys of deep ocean dredged spoil deposits in Hawai‘i. Report prepared for USACE, Honolulu. Contract # DACW84-76-C-0032.

NOAA (National Oceanic and Atmospheric Administration), 2007. Remote Sensing Survey and Sampling at a Discarded Military Munitions Sea Disposal Site, Ordnance Reef, Wai’anae, Hawai‘i, Final Report, NMSP-07-01, March 2007.

Paka, V. and M. Spiridonov, 2002. “Research of Dumped Chemical Weapons made by R/V Professor Shtokman in the Gotland, Bornholm and Skagerrak Dump Sites,” Eds. T Missiaen, and JP Henriet, Chemical Munition Dump Sites in Coastal Environments, pp. 27-42.

Phillips, D.J.H. and P.S. Rainbow, 1993. Biomonitoring of Trace Aquatic Contaminants. Elsevier Science Publications, Barking UK.

Price, C.B., J.M. Brannon, and S.L. Yost, 1998. Transformation of RDX and HMX Under Controlled Eh/pH Conditions. Technical Report IRRP-98-2 US Army Engineer Waterways Experiment Station, Vicksburg, MS, 1998.

Reimann C., Filzmoser P., Garrett R.G., 2002. Factor analysis applied to regional geochemical data: problems and possibilities. Appl. Geochem. 17, 185-206.

Ruiz-Fernandez A.C., Paez-Osuna F., Hillaire-Marcel C., Soto-Jimenez, Ghaleb B., 2001. Principal component analysis applied to the assessment of metal pollution from urban wastes in the Culiacan River Estuary. Bull. Environ. Contam. Toxicol. 67, 741-748.

Shitashima, K., M. Kyo, Y. Koike, and H. Henmi, 2002. Development of in situ pH sensor using ISFET, Proc. 2002 Int. Symp. on Underwater Tech., 106-108.

Smieja, A.J., and R. Puls, 2002. Arsenate Reduction by Organic Molecules. Symposia Papers Presented Before the Division of Environmental Chemistry American Chemical Society, Orlando, FL April 7-11, 2002.

Stock, T., 1996. “Sea-dumped Chemical Weapons and the Chemical Weapons Convention” in Sea-Dumped Chemical Weapons: Aspects, Problems and Solutions. Ed. A.V. Kaffka, Kluwer Academic Publishers, Dordrecht, pp. 49-66.

Stock, T. and K. Lohs, 1997. “Old Chemical Munitions and Warfare Agents: Detoxification and Degradation,” in The Challenge of Old Chemical Munitions and Toxic Armament Wastes. Ed. T Stock, and K Lohs, Sipri Chemical & Biological Warfare Studies, Volume 16, Stockholm International Peace Research Institute/Oxford University Press, pp 35 – 52.

Tørnes, J. A., Ø.A. Voie, M. Ljønes, A.M. Opstad, L.H. Bjerkeseth, and F. Hussain, 2002. Investigation and Risk Assessment of Ships Loaded with Chemical Ammunition Scuttled in Skagerrak, TA-1907/2002.

Townend J., 2002. Practical statistics for environmental and biological scientists. Chichester, England, John Wiley & Sons, Ltd.

Townsend, D.M. and T.E. Myers, 1996. RDX and HMX Sorption in Thin Disk Soil Columns, Technical Report IRRP-96-1 US Army Engineer Waterways Experiment Station, Vicksburg, MS, 1996.

USACE (United States Army Corps of Engineers), 1977. Report of Proceedings of Contract DACW84-76-C-0032, Environmental Surveys of the Deep Ocean Dredging Soil Disposal Sites in Hawai‘i.

U.S. Army, 2005. Potential Military Chemical/Biological Agents And Compounds, released as FM 3-11.9, MCRP 3-37.1B, NTRP 3-11.32, and AFTTP(I) 3-2.55. January.

University of Hawai‘i Environmental Center, 1977. Baseline Studies and Evaluation of the Physical, Chemical, and Biological Characteristics of Nearshore Dredge Spoil Disposal, Pearl Harbor, Hawai‘i: Part A, Baseline Studies, Investigation and Selection of a Suitable Dredge Spoil Site, Final Report. May.

_____, 1996a. DERP – FUDS Inventory Project Report, Offshore Waters, Honolulu, Hawai‘i, Island of O‘ahu, Hawai‘i, Site 3 No. H09HI0466, Prepared for U.S. Army Engineer District, Pacific Ocean Division, Fort Shafter, Hawai‘i. February 28.

_____, 1996b. DERP – FUDS Inventory Project Report, Offshore Waters, Honolulu, Hawai‘i, Island of O‘ahu , Hawai‘i, Site 3a No. H09HI0467, Prepared for U.S. Army Engineer District, Pacific Ocean Division, Fort Shafter, Hawai‘i. February 28.

USFDA, 2005. FDA Action Levels, Tolerances And Guidance levels for Poisonous or Deleterious Substances in Seafood (FDA, 2005).

WRCC (Western Regional Climate Center). 2004. Climate of Hawai’i. http://www.wrcc.dri.edu/narratives/HAWAI‘I.htm.

WHO (World Health Organization), 2003. Guidelines for Drinking-Water Quality, Third Edition. Accessed via http://www.fsc.go.jp/senmon/tenkabutu/t-dai5/ten5-siryou2-3-4.pdf.

Yang, Y.C., J.A. Baker, and J.R. Ward, 1992. Decontamination of chemical warfare agents, Chem Rev, 92 (8) 1729-1743, 1992.

Yost, S.L., J.C. Pennington, J.M. Brannon, and C.A. Hayes, 2007. Environmental process descriptors for TNT, TNT-related compounds and picric acid in marine sediment slurries, Marine Pollution Bulletin 54(2007): 1262-1266.

Zhao, J-S., C.W. Greer, S. Thiboutot, G. Ampleman, and J. Hawari, 2004. Biodegradation of the Nitramine Explosives Hexahydro-1,3,5-trinitro-1,3,5-triazine and Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine in Cold Marine Sediment under Anaerobic and Oligotrophic Conditions, Can. J. Microbiol, 50: 91-96, 2004.

This page is intentionally left blank.

Figures

Tables