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Chemical Sensing in the Marine Environment
Final Report

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1.0 SUMMARY

The objective of the Chemical Sensing in the Marine Environment (CSME) program is the detection of trace levels of explosives and their degradation products in marine littoral environments. This involves developing an understanding of the influence of biological organisms on their distribution and fate, and the development of sampling techniques and strategies for studying these analytes in the near shore environment.

During the CSME program, new methods for sampling and detecting trace levels of explosives from unexploded ordinance in seawater were developed and demonstrated. This included the development of a large manifold pumping system to allow sampling and solid phase extraction of up to 100 liters of seawater in 15-30 minutes. This system allows detection to parts-per-trillion levels, and can be monitored by underwater video and current meters to select preferred sampling stations. Diver manipulated "wands" for the collection of large seawater samples were also demonstrated. This may have application for the study of other types of trace organic compounds in seawater.

The role of RVM Scientific in the first phase of the CSME program has been to provide support in the areas of experimental design for sample collection, test site selection, coordination of CSME meetings and field tests, to participate in sample collection, documentation of results, and to provide help with trouble-shooting and the development backup approaches during field testing. The present report focuses on the sampling approaches and configurations used in the CSME field tests, and does not include discussion of explosive compounds and degradation products or CSME chemical analysis results, which will be presented elsewhere.

2.0 INTRODUCTION

2.1 BACKGROUND

The Chemical Sensing in the Marine Environment (CSME) program targets the development of novel means to detect and locate unexploded ordnance in marine environments and to detect, characterize, and quantify explosives and their derivatives in seawater and marine sediments that result from manufacturing or disposal of explosive materials which contaminate marine environments or groundwater. It is anticipated that the technologies being developed in this program will have broad-based applications for monitoring environmental remediation of explosive contaminants and for manufacturing process stream monitoring. For example, information and technology developed in this program may be used to support the Mobile Underwater Debris Survey System (MUDSS), a system being developed to survey underwater explosive wastes as part of an effort to clean up Formerly Used Defense Sites.

The goal of the CSME program is the detection of trace levels of explosives and their degradation products in marine littoral environments. This involves developing an understanding of the influence of biological organisms on their distribution and fate, and the development of ultra-trace sampling techniques and strategies for studying these analytes in the near shore environment.

Because experiments during the initial phase of the CSME program have been conducted at a single fixed site, the selected sampling approach has been to pump samples to the surface, rather than use discrete sample collection. This simplifies sample collection, is capable of providing very large sample volumes, and is well suited for preconcentrating trace levels of analytes such as TNT in seawater by directly pumping the sample through solid phase extraction (SPE) membranes. This approach also provides important sampling flexibility and makes sample collection from a well defined grid feasible, as well as the collection of samples by divers using mobile "sampling wands" for collecting and pumping samples to the surface. This sampling process can be aided by the use of dye plumes for visualization by underwater video and/or by Navy divers. Once collected, the samples can either be analyzed on-site or packaged for express shipment to participating labs.

2.2 REPORT ORGANIZATION

This report is divided into several sections addressing the configuration of field tests conducted during the initial phase of the Chemical Sensing in the Marine Environment program in 1996-7. It should be pointed out that this is limited to the configuration of field tests, and does not include discussion of explosive compounds, their degradation products or CSME chemical analysis results. These will be presented

elsewhere. Following the summary and introduction in Sections 1 and 2, which outline the overall scope of the program, Section 3 covers Test Site Selection, including the criteria used in site selection. Section 4 presents the sampling approach used for CSME measurements. Detailed discussion of the various CSME test configurations is given in Section 5, and includes configurations for the three prototype tests, the two primary tests and the long term study. Finally, conclusions and recommendations regarding the test site and test configurations used during the initial phase of the CSME program are presented in Section 6.

3.0 TEST SITE SELECTION

Selection of suitable test sites for field experiments was a key decision for the first phase of the CSME Program. While the use of more than one test sites was initially considered, it became apparent that the selection of a single site that could meet program requirements would provide important advantages. This would include simplified logistics, capability for pre-configuration and staging of test structures and apparatus from one test to the next, advantages of familiarity with the site for both scientists and Navy divers, and the potential for conducting long term studies.

Specific criteria used for selection of a site for CSME program experiments included the following:

- Site availability for an extended series of tests
- Oceanographic conditions, especially water clarity and the presence of moderate currents (5-20 cm/sec)
- Presence of a pier or other structure providing ready access to seawater at depths of 12-50 feet
- Site infrastructure, including adequate AC power, facilities for equipment set-up and storage, work space for 15-20 scientists, availability of accommodations in the vicinity for test participants
- Logistics for travel to/from the site, shipping of equipment and supplies to the site, and overnight express shipment of samples to participating laboratories
- Suitable climate/weather for year-round use

The initial site considered for the CSME Prototype experiments was at CSS in Panama City, Florida. Here, a short pier extending into St. Andrew Bay (near Alligator Bayou) provides easy access to the bay, a platform for equipment setup, AC power, and proximity to a wide range of excellent support facilities (shops, equipment storage, meeting rooms, accommodations, etc.). However, while the nominal depth off the end of the pier is 10-12 feet, this is a dredged area surrounded by much shallower water (several feet) and does not provide suitable currents for the experiments. Poor underwater visibility for observation during experiments was also a factor. Finally, St. Andrew Bay itself is an (uncontrolled) open area with public access by boaters, making the placement of longer term experiments insecure.

Based on limitations of the Panama City site for CSME experiments, evaluation visits were made to several other potential sites during March 1996. These included sites on San Clemente Island off the coast of California, Monterey Bay and at Kaneohe Bay on Oahu. Of these, the San Clemente Island and Kaneohe Bay sites were the most promising. Potential Monterey Bay sites were problematic at best, as they are all

within a defined marine wildlife sanctuary, lacked a pier or other good on-site facility for staging the experiments, and are uncontrolled areas with public access.

The San Clemente Island NOTS pier and Kaneohe Bay Marine Corps Air Station sites both proved to be potentially viable for the Prototype tests, with each having pier access to water of sufficient depths, adequate water clarity, proximity to facilities for staging the experients, and a degree of controlled access. In most key comparisons, the San Clemente Island (SCI) site faired better than Kaneohe Bay MCAS. Advantages for SCI included superior water clarity, much better pier (with catwalks near water level underneath pier), easy access to a range of water depths to 35', extensive shoreside facilities at the pier including space for labs and a Navy Dive locker, and much better public access control (i.e. all of SCI is controlled access, with further controlled access road to NOTS pier site from shore, and posted restricted area out to 500 yards off-shore). The key advantage for Kaneohe Bay was better logistics with numerous commercial air links and close proximity to the Honolulu metropolitan area (although commercial overnight express delivery services are limited to West Coast only, with two day service to rest of CONUS).

Based on the above observations and considerations, the San Clemente Island site was selected for the CSME experiments. Weighing strongly in favor of SCI were superior oceanographic conditions, pier facilities, and public access control allowing undisturbed placement of longer term experiments. Logistical limitations for SCI centered around travel and transport were considered to be solvable by advanced planning and coordination with NRaD personnel. For example, low cost weekly barge service is available for large items, and coordination with the afternoon weekday flight to the mainland allows next day express delivery to nearly all U.S. cities.

4.0 SAMPLING APPROACH

The long range objective of the Chemical Sensing in the Marine Environment (CSME) program is the detection of trace levels of explosives and their degradation products in marine littoral environments. This involves developing an understanding of the influence of biological organisms on their distribution and fate, and the development of sampling techniques and strategies for studying these analytes in the near shore environment. The more immediate objective of the CSME experiments reported here has been to explore requirements for sampling and detecting trace levels of explosive compounds in seawater.

In response to these needs, the present CSME experiments have focused on placing underwater sources of trace levels of explosives, sampling seawater for these analytes from the plumes generated by underwater currents, and performing trace level measurements on the collected samples using various techniques. The use of pier access to near shore waters combined with fixed placement of the source has provided important flexibility for these experiments. This has made it possible to control source levels and release rates, to perform dye visualization experiments of plume evolution using underwater video, to use pumps to acquire large sample volumes of up to 100 liters, and to monitor/record experimental conditions with an array of current meters and video cameras.

The two source types used in these experiments were a pumped source for metering known concentrations of analyte(s) and dye using peristaltic pumps, and "surrogate" sources with known levels of analyte(s) applied to a painted surfaces which were then immersed in seawater. The pumped source consisted of a spiral coil of black 1/4" soaker hose about 30 cm in diameter attached to an adjustable stand. After positioning underwater by Navy divers, and in the presence of weak to moderate currents (5 to 10 cm/sec), dissolved analyte (and dye) can be pumped to the source to produce an underwater plume. The "surrogate" sources consist of painted barrels with a sprayed on coating of analyte(s) which is released into seawater when immersed. Here, current direction is monitored by current meter readouts and video observation of a "windsock" indicator.

Samples are acquired by pumping through 1/2" i.d. hard polyethylene lines, with typical (unrestricted) flow rates of eight liters per minute. Various sampling configurations were used including fixed arrays with selection of particular sampling heads from the pier, or the diver positioned sampling. Once acquired, samples can be directly analyzed or extracted for analysis, or preconcentrated by passing them through a solid phase extraction membrane.

Passive sampling approaches were developed by ORNL. These included passive samplers fabricated from solid phase extraction membranes held between

screens or perforated plates to provide contact with seawater. On recovery, the membranes can be removed from the passive sampler and extracted in the usual way. ONRL also developed several biological based "preconcentrators" in the form of phytoplankton and phytoplankton, either contained in dialysis bags or loaded on glass fiber filters. On recovery, the organisms can be extracted.

5.0 TEST CONFIGURATIONS

5.1 BACKGROUND

The long range objective of the Chemical Sensing in the Marine Environment (CSME) program is the detection of trace levels of explosives and their degradation products in marine littoral environments. This involves developing an understanding of the influence of biological organisms on their distribution and fate, and the development of sampling techniques and strategies for studying these analytes in the near shore environment. The more immediate objective of the CSME experiments reported here has been to explore requirements for sampling and detecting trace levels of explosive compounds in seawater.

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5.2 PROTOTYPE I

The CSME Prototype I Test April 29-May 3 resulted in twenty one samples being collected from a source plume of analyte and Fluoroscein dye out to distances of 50' from the source at a water depths of 30-40'. On site analysis of some of the samples using IMS (Sandia) and a Flowthrough Immunoassay Sensor (NRL) demonstrated that the analyte could be detected. Aliquots (including material collected on filters and extraction disks) of thirteen of the collected samples were sent for more detailed analysis to participating labs by overnight express. Participating labs were ORNL (including Univ. Tenn), JPL, NRL, and Sandia, with filters only sent to CRREL, and samples for chlorophyll analysis to Rutgers. The experimental configuration consisted of pumps and other apparatus setup on a catwalk under the NOTS pier, a plume source placed underwater by divers, various sampling devices used to collect and pump seawater samples from the plume back to the pier, and monitoring by an underwater video camera and S4 current meter. The S4 current meter only worked intermittently, and we were unable to monitor currents during most of the test.

The source itself consisted of a spiral coil of black 1/4" soaker hose about 1' in diameter attached to an adjustable stand constructed of PVC pipe. This was positioned underwater by Navy divers and worked well with the generation of nicely defined plumes when the current direction was stable. Separate peristaltic pumps and 3/8" (1/4" i.d.) polyethylene lines were used to meter solutions of analyte and dye to the source with typical flow rates of 500 ml/min each. An additional seawater pump and line were provided for dilution and flushing of the source. The output of this 100' long bundle of three lines was mixed near the source by passing through a static in-line mixer before being released to form a plume.

The original plan for collecting samples called for use of a 10' by 10' rig with twelve attached 100' long 5/8" o.d. (1/2" i.d.) hard polyethylene sample tubes. This rig was prepared and placed by the divers, but the plan had to be modified during the test due to irregular and unpredictable currents which did not make it feasible to collect plume samples using the fixed rig. Instead, a 10' sampling wand at the end of a 100' polyethylene sample line was devised. This was positioned directly in the plume by a diver at various (measured) distances from the source. This approach worked well, limited only by the diver's visibility of the plume and the length of the sampling line. The collected output of the sampling line was then passed through an in-line Fluorometer to monitor dye content and collected in 4 liter sampling jugs.

As Prototype I neared completion a night dive was conducted to test the feasibility of performing experiments at night. This would enhance capability to conduct experiments during optimal tide and current conditions. The test was a success. Navy divers were able to see the dye plume using their hand lights and could follow the plume at least 100'.

5.3 PROTOTYPE II

The CSME Prototype II Test was conducted July 30-August 2, 1996 at NOTS pier on San Clemente Island. Compared to the earlier Prototype I test, Prototype II used improved sample storage and preservation methods (including silanized sample containers), was better instrumented (S4 current meter and two underwater video cameras), used a new nine inlet sampling "wand" for collecting samples, new analytes were included, significantly more on-site extraction of samples was performed, lower levels of analyte were used, a variety of passive samplers were deployed, and preliminary efforts to sample a "surrogate" source were made. As in the Prototype I test, apparatus was setup on a catwalk under the NOTS pier, using a "wand" sampler positioned by divers to pump seawater samples from the plume formed by the underwater source. During the test sixteen samples were collected from plumes out to distances of 50' from the source at a water depths of 30-40', including a single large sample of 60 liters sampled at 20' using a source analyte level one thousandth that used in Prototype I (extracted onto a 90 mm disk). A 24 liter sample was taken near an improvised "surrogate" source which had been surface treated with a small amount of various analytes. On-site analyses of many of the samples were performed using IMS (Sandia) and a Flowthrough Immunoassay Sensor (NRL). These demonstrated that analyte could be detected at the lower source levels used in this test (typically one fifth that of Prototype I). Extraction disks were used for all sixteen of the collected samples, along with some one liter seawater sample aliquots (for Sandia). These were sent to participating labs for more detailed analysis. The participating labs were Sandia, ORNL (including Univ. Tenn), NRL, JPL, CRREL and NAVEOD TECHDIV, with samples for background analysis to Rutgers.

The source was the same as that used earlier in the Prototype I test, consisting of a spiral coil of black 1/4" soaker hose about 1' in diameter attached to an adjustable stand constructed of PVC pipe. This was placed about 30' out from the end of NOTS pier in about 35' of water by Navy divers. Three peristaltic pumps with separate 3/8" (1/4" i.d.) polyethylene lines were used to meter solutions of analyte and fluorescein dye to the source with typical flow rates of 50-500 ml/min each. For Prototype II in-line flow meters were added to improve accuracy. The output of the 100' long bundle of three lines was mixed near the source by passing through a static in-line mixer before being released to form a plume.

An improvised "surrogate" source was made from a painted can by the surface application of various analytes in a 7" wide band around the circumference of the can (about 1,630 cm^2). The "surrogate" source was placed (upside down) on a camera mounting bar above the other source at a height of about 8 feet from the seafloor. A small amount of dye released from the other source was used to establish visual direction of the current to aid sampling by the diver 1-2' from the "surrogate".

A new nine inlet sampling wand was developed for the Prototype II test. This consisted of a cluster of nine 0.25" i.d. polyethylene tubes arranged in an "X" pattern 60 cm across, the sampling tubes being about 15 cm apart (one in the center with two on each arm). This provides sampling from a "grid" of point in the plume, rather than from the single "point" used in Prototype I. During a test, the sampling head is positioned in the plume by a diver at various (measured) distances from the source. The nine inlets feed into a 0.5" i.d. polyethylene sample line 100' long which is connected to a pump on the pier. In a few cases an additional 90' of line was added. The collected output of the sampling line was then passed through an in-line Fluorometer to monitor dye content and collected in silanized 4 liter sampling jugs.

Various passive samplers were also deployed during the test at distances up to 20'. These passive samplers included devices fabricated using solid phase extraction disks or fibers (e.g. polystyrene-divinyl benzene-reverse phase). These were deployed on weighted lines with floats (ORNL), and a fiber mounted in a flowthrough housing attached to the "wand" sampler (JPL). ONRL also deployed several biological based "preconcentrators" in the form of both dialysis bags containing phytoplankton and phytoplankton loaded glass fiber filters. These bioaccumulation filters consisted of either cellulose dialysis bags containing Vibrio harveyi, Amphora coffeaformis, and Skeletonemia costatum, or glass fiber filters loaded with the same bacteria and algae. Other experiments were performed to support laboratory aquarium experiments on the metabolism and partitioning of analytes.

5.4 PROTOTYPE III

The CSME Prototype III Test was conducted September 23-27, 1996 at the NOTS pier site on San Clemente Island, with the focus of the test being on sampling of analyte residues released from surface coatings on 55 gal. drum "surrogates". Compared to the earlier Prototype I and II tests, much larger 50-100+ liter samples were collected and directly processed on-line using a newly devised technique where samples were concentrated by pumping them through four (or two in the case of 50 liter samples) 90mm SPE membranes in parallel. The four SPE membranes (extraction disks) were then combined for elution with acetonitrile into a single, 20mL volume (representing a preconcentration factor of up to 5000). This was designed to achieve detection limits in the parts per trillion (ppt) range. A total of 27 of these large samples were collected and processed during Prototype III (including controls). Passive samplers were also used during the test, along with small lab blanks and "spikes".

For Prototype III, both "short term" and "long term" sampling positions were set up. The "short term" position was in the same location as in earlier test, about 30' from the end of the pier in 35' of water. The "long term" position was 35' to the right of the "short term" position as viewed from the pier, at a compass heading of 120 degrees magnetic.

The short term test position was surrounded by a video monitored array of eight labeled "sampling positions" (consisting of multiple inlet sampling structures prepared by NRaD) surrounding the surrogate source position near the pier. Each sampling position was similar to the nine inlet sampling "wand" used in Prototype II and was on a separate stand for positioning by Navy divers. The use of multiple inlets on each sampler was designed to help ensure that a representative sample was collected, while the use of eight sampling positions allowed the best sampling positions to be selected from the pier (in response to shifts in current direction based on observation of a "windsock" by the two underwater video cameras and S4 current meter data). There were two sampling manifolds controlled by valves each feeding two of the four 90mm extraction disks from alternate (odd or even numbered) sampling positions. Thus two adjacent sampling positions would normally be selected for simultaneous sampling during a test (e.g. lines 3 and 4). This approach was designed to accommodate the long sampling times needed to collect these very large seawater samples, including the need for back-to-back repetitive collections at start of each experiment to follow the time evolution of the source. Such large sampling requirements would otherwise be beyond reasonable limits for sampling supported by divers.

Initial sampling system tests were performed on Sept. 24th using a 55 gal. drum wrapped with a soaker "blanket" (air mattress punched with holes) using pumped sources of analyte and dye. This was designed to allow the plume from such a source to be observed by underwater video, including collection by the sampling array to validate procedures and the use of a "windsock" indicator for current direction.

The first short term test was begun on Sept 24th with the sampling positions placed 5' from the source. On-site analyses of the samples using Sandia's IMS really paid off here, as early blanks showed a relatively strong signal, which was traced back to a contaminated graduate cylinder used in preparing the extraction disks. Without this on-site capability, many other samples might have been contaminated, seriously affecting the test.

The second short term test began Sept 25th with the sampling positions 5' from the source. For the final short term test on Sept 26th, sample positions were moved into 2.5' from the source.

The long term test surrogate position was setup about 35' from the short term site. This position was designed for close in sampling (at about 6") by a nine inlet diver manipulated wand sampler. Here, 50+ liter samples were taken and processed real-time on the pier. A series of passive samplers were also used. The long term source itself was placed the morning of September 25th, for sampling during Proto III with additional extended sampling over a period of weeks via the use of passive samplers.

Except for the preliminary tests which used a pumped source of analyte and dye for checking out the sampling systems, coated 55 gal. drum surrogate sources prepared by CRREL were used. These had sprayed on coatings of analyte. Of these surrogate sources, three were used for short term tests, and one for long term testing, with a total of 16 large seawater samples taken and processed. Five large 50-100+ liter blanks were also taken during Proto III, along with four large spiked samples prepared in silanized glass carboys on the dock using known levels of analyte. The spiked samples were directly pumped through the sampling system for concentration by extraction disks.

Following on-site extraction with acetonitrile into a total volume of 20 mL, the extract was split into 5 mL aliquots for on-site analysis by Sandia's IMS and shipping to participating labs for outside analysis. These samples were shipped in glass vials under blue ice to Sandia, ORNL, NRL, and CRREL.

The processing of large sample volumes meant that background organics were also extracted and concentrated. In fact, the extraction disks were observed to become distinctly yellow after use, presumably due to collection of "gelbstoff". Fluorescence from these materials presented significant background problems for the NRL Flowthrough Immunoassay Sensor.

Various passive samplers were also employed during the Prototype III test. These included "sandwich" devices (ORNL) fabricated using extraction disks for pre-concentrating aqueous samples deployed on weighted lines with floats. Of these a total of 18 were deployed, two on each of the short term tests (at the sampling head positions), and 4 successive sets of three on the long term test at distances ranging from 1-5 feet. Six extraction fibers mounted in protective housings were also used (JPL). These were attached to sampling head positions during the short term tests.

5.5 TEST 1

The CSME Prototype Test 1 was conducted November 5-12, 1996 at the NOTS pier site on San Clemente Island. This was the first test where a realistic test object (source) was used, with the focus of the test being on sampling and analysis of analyte release rates. The test began with dye measurements and visualization studies performed using a realistic "shell" modeling the geometry of the source. Tests on Nov 7-8 included measurements with pumped analyte as well as calibration "spikes" in seawater.

On Nov 9, the source itself was placed about 30' from the end of NOTS pier in 35' of water, as in earlier tests. This was surrounded by a video monitored array of eight labeled "sampling positions" with multiple inlets, including the sampling manifold and extraction setup developed in Prototype III. Each sampling position was on a

separate stand for positioning by Navy divers, allowing selection of sampling positions based on current direction observed by a "windsock" monitored by underwater video cameras and current meter data. This allowed large seawater samples to be directly processed using 90mm extraction disks. Some thirteen of these large external samples were collected during Nov 9-11 at distances of 1-10', using both the sampling array and diver manipulated "wands".

Variability in the currents suggested that it might be difficult to obtain reliable information on the "decay" rate of the source from "external" measurements only. Consequently a scheme was devised for "internal" sampling of the source to monitor decay in source strength over time, and thirty samples were taken over a period of about 70 hours at intervals as close as 15 minutes. These included 12, 9, 8 and 1 samples taken on Nov 9th through 12th, respectively.

5.6 TEST 2

The CSME program's Test 2 was conducted February 5-11, 1997 at NOTS pier on San Clemente Island. The primary objective of Test 2 was to determine chemical contaminant strength of a test source including measurements to assess long term aging effects, and dilution and dispersal of contaminants in the near field (to a few meters). This, coupled with additional studies related to subsequent dispersal and the chemical fate of contaminants in the far field, completed a key part of the understanding needed for assessments in the CSME program.

During Test 2, the source was placed on the bottom in about 35' of water about 30' from the end of NOTS pier (oriented due north). Measurements of the internal volume of the source coupled with dye studies show that the internal volume is flushed on average time scales of about 10 minutes. This readily allows contaminants from the interior of the source to be released into the surrounding seawater. Dye visualization experiments show that these will form well defined plumes whose direction depends on the direction of underwater currents.

At the beginning of Test 2, fluorescein dye studies using discrete samples were conducted February 7th with four data sets covering two current directions. In these experiments a surrogate source was first pumped full of 100 ppm dye solution, then the dye shut off to follow the decay profile. These data allowed assessments of the flushing time of the source.

During February 8-10, two types of chemical contaminant samples were collected by pumping seawater up to a catwalk underneath NOTS pier. "Internal" samples were directly pumped from the interior of the source through a small line to follow time evolution of source strength, and "external" samples to monitor

concentrations in the near field were collected using a special sampling rig at typical distances of about 5' from the source.

"Internal" samples of 250 mL were obtained by pumping through a 1/4" i.d. line connected to the interior of the source (after first flushing with one liter of seawater to clear the line). "External" samples were collected by pumping from a sampling rig consisting of a video monitored array of eight "sampling positions" consisting of 1/2" i.d. lines connected to multiple inlet "wands" (numbered 1 through 8), clustered in the best current direction for the 090 degree current. The magnetic directions of the eight wands from the source were 000, 067.5, 090, 112.5, 180, 225, 270, and 315. The direction of the current was monitored using current meters and underwater video of a "current sock" to guide selection of the two best wands for sampling.

The multiple inlets of each wand help ensure that representative samples are collected, while the selection of the two best sampling positions based on the direction of the current allowed for the long sampling times needed to collect and process large 100 liter samples. This approach also help insure that local meanders of the plume are captured. The samples themselves were processed by directly pumping them through a manifold and four 90 mm RPA extraction disks for preconcentration of the analytes of interest. This allows the extract from a 100 liter seawater sample to be concentrated into a 40 mL volume of acetonitrile, giving a preconcentration factor of 2500x. The volume of seawater actually sampled and extracted was monitored by physically collecting the filtrate in a catch basin with volume marks.

Background seawater samples were collected before the source went into the water on Feb 8th. The first internal samples from the source were collected at time intervals of about 15 minutes after the source went into the water. The first external samples were taken at one hour intervals after the source entered the water, and the next two at two hour intervals. Internal samples were also taken directly after each of the external samples. The next day, four external samples were taken along with eight internal samples, with the final series of internal samples taken at 20 minute intervals over two hours during a steadily weakening constant direction current. On the final day of Test 2, two internal samples were taken.

On-site analyses of samples during Test 2 was performed using high pressure liquid chromatography (CRREL) and a Flowthrough Immunoassay Sensor (NRL). Here, internal samples were directly analyzed without preconcentration. The external samples were extracted into 40 ml of acetonitrile giving a 2500x preconcentration factor. On-site analyses were used to confirm the detection of analyte under the given experimental conditions. However, the primary mode of analysis for Test 2 was the shipping of both pH stabilized seawater samples and extracted samples in acetonitrile to participating labs by FedEx for detailed analysis.

5.7 LONG TERM TEST

The Long Term Test began during Test 2 on February 8, 1997 and ran until retrieval on June 23-24, with a goal of assessing long term aging effects on source strength. The test configuration provided an extended measurement period of more then 19 weeks, with intervals between measurements ranging from 15 minutes at the beginning of the test to weekly.

For Long Term Test placement, the source was moved to a fixed location about 5' from the end of NOTS pier during the last task of Test 2, where it was secured. The Long Term Test employed weekly internal sampling of the source over an extended period of time, with express shipping of internal samples to Sandia, CRREL, NRL and ONRL for analysis. These were unfiltered seawater samples stabilized by pH adjustment.

In the protocol for the Long Term Test, samples were collected by pumping from the interior of the source via a 1/4" i.d. poly line, first flushing the line with a liter of seawater before collecting the sample. A single sample of 500 mL was then collected, and subsequently partitioned into a 40 mL sample vial (untreated) for NRL, and a 250 mL bottle containing a pre-measured amount of concentrated sodium bisulfate solution for pH adjustment (to pH 2). The 250 ml sample was then partitioned into a 40 mL silanized vials for shipping to the various labs (each protected by a small mailing tube). This procedure ensured that each lab would receive an aliquot of the same (preserved) sample. One of the NRL samples was not preserved to avoid interference with the analytical method. This sampling approach for the long term test was made feasible by a combination of the relatively high concentrations of analyte(s) and the short interval for overnight FedEx shipping to the labs.

6.0 CONCLUSIONS AND RECOMMENDATIONS

New methods for sampling and detecting trace levels of explosives from unexploded ordinance in seawater were developed and demonstrated in the CSME program. This included a large manifold pumping system which allowed sampling and solid phase extraction of up to 100 liters of seawater in 15-30 minutes. This system allows detection to parts-per-trillion levels, and can be monitored by underwater video and current meters to select preferred sampling stations. Diver manipulated "wands" for the collection of large seawater samples were also demonstrated. Such techniques may have future application for the study of other types of organic compounds in seawater.

Selection of NOTS pier on San Clemente Island as the site for CSME field experiments played a key role in the success of the first phase of the CSME Program. The generally excellent oceanographic conditions and year-round weather, relative isolation of the site, extensive physical facilities at the pier, and superb on-site support of NRaD divers and other personnel made possible test configurations and experiments which would not have been feasible at any of the other sites considered. For example, it's difficult to imagine how the Long Term Test could have been conducted at any of the other sites considered.

Among specific features of the NOTS pier site used for the experiments were good water clarity, which allowed routine use of underwater video to monitor and record all experiments. The pier itself has an extensive system of catwalks underneath which provided an excellent and comfortable platform (with plenty of AC power) for setting up apparatus and running experiments. A cluster of buildings at the foot of the pier, provide full dive locker and a berthing facility for divers, plenty of space with power and running water to setup laboratory equipment, and secure storage space for equipment and supplies between experiments. This situation helped to maximize continuity between tests and allowed for rapid (and routine) setup of experimental apparatus. Along with oceanographic conditions and pier facilities, public access control at SCI also allowed for the placement of longer term experiments. Logistical limitations for SCI centered around travel and transport, but were dealt with by advanced planning and coordination with NRaD personnel. Here, the weekly barge service allowed a large laboratory van from Sandia to be brought on site for the experiments. Perhaps most importantly, coordination with the afternoon weekday flights from SCI to the mainland allowed for next day express delivery of samples all of the participating laboratories, including those on the East Coast.

Also important was the "can do" attitude and excellent teamwork exhibited by CSME scientists, NRaD divers and support personnel. While much of this can be attributed to good program management and leadership by ONR, it also seemed to be fostered by the relative isolation of SCI (minimizing distractions), common eating and

berthing facilities for the CSME science team, and increasing familiarity with the NOTS pier site. This really paid off in rapid and creative development of approaches to get around problems that arose (these often evolved over discussions at breakfast). Some examples include the development of an alternative "wand" sampler during Prototype I, improvised large sample trials and "surrogate" sources during Prototype II, and the development of an "internal" source sampling system during Test 1. The dive support team also exhibited proactive involvement in the project, suggesting and then demonstrating night dive capability in tests during Prototype I, allowing experiments to be performed under optimal current conditions. The use of a single site with good staging and storage facilities also contributed to a rapid evolution of improvements in sample collection and processing approaches, such going from batch mode extractions to direct in-line processing of large seawater samples through extraction disks.

Based on results from the CSME program, it is strongly recommended that the use of a single, carefully selected site be considered for any future extended series of field tests, whenever this is compatible with experiment needs. This can simplify logistics, allow test structures to be staged for rapid setup, and provide important advantages of familiarity with the site for both scientists and other support personnel, helping to focus creative effort on sampling method development and solutions to technical problems.