Fabrication of a Portable Large-Volume Water Sampling System To Support Oil Spill Nrda Efforts

3 authors, including:

James Payne

Payne Environmental Consultants, Incorporated, Encinitas, CA, United States

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James R. Payne
Payne Environmental Consultants, Inc.
317 No. El Camino Real, Suite 201
Encinitas, California 92024 U.S.

Timothy J. Reilly
Industrial Economics, Inc.
2067 Massachusetts Avenue
Cambridge, Massachusetts 02140 U.S.

Deborah P. French
Applied Science Associates, Inc.
70 Dean Knauss Drive
Narragansett, Rhode Island 02882 U.S.

ABSTRACT: *A field-portable water-sampling system was designed and fabricated for collecting adequate volumes of seawater to meet the quantitation requirements to support Natural Resource Damage Assessment (NRDA) toxicity determinations and modeling efforts following an oil spill. This system is a significant improvement to conventional water sampling equipment and includes the ability to filter water samples at the time of collection, thereby providing critical differentiation between truly dissolved constituents and dispersed oil droplets. The system can be quickly and easily deployed from shoreline structures (piers and breakwaters) and/or vessels of opportunity to provide essential data during the early stages of a spill. Likewise, data collected with the system can be used to document dispersant effectiveness and provide information relating to seafood exposure, tainting, and toxicity issues.*

In many oil-spill NRDA efforts, water-column effects from dissolved components and dispersed oil droplets have not been adequately quantified or documented because: (1) samples are not obtained early enough after the spill event; (2) insufficient volumes are collected; and (3) the wrong constituents are analyzed. Generally, EPA hazardous-materials sampling approaches are followed, leading to inadequate sample sizes (e.g., 40 mL for volatile component analyses and 1 L samples for dissolved/dispersed constituents). Analytically, EPA semivolatile gas chromatography/mass spectrometry (GC/MS) SW-846 Method 8270 is often specified for polynuclear aromatic hydrocarbons (PAH). These sample sizes are not large enough to meet the detection limits required for most marine hydrocarbon analyses (de Lappe et al., 1980; Payne, 1997 and references therein), and the EPA PAH target analyte list does not include the majority of alkyl-substituted one-, two-, and three-ring aromatics that are the primary dissolved constituents actually present in the water column following an oil spill (Sauer and Boehm, 1991).

As a result, water column effects are often written off as being short-lived or insignificant. Alternatively, impacts are often assessed by computer modeling efforts with limited field validation. In either event, there is inadequate profiling of the extent and duration of petroleum hydrocarbon exposure to marine organisms. Furthermore, when adequate volumes of water have been collected and the proper target analytes have been specified, provisions have not been taken to differentiate between truly dissolved components and dispersed oil droplets. Consequently, later data analyses are unreliable in their ability to reflect conditions as they actually existed during the early stages of the spill. For example, PAH analyses of unfiltered water samples are confounded by the facts that: (1) a significant, but unknown fraction of discrete oil droplets in the water column will rise to the surface with time; (2) high levels of dispersed oil droplets will raise detection limits of dissolved PAH; and (3) it is impossible to determine how much of the PAH is in the truly dissolved state where it will persist as a toxic fraction to exposed organisms and how much is simply associated with slightly less toxic oil droplets that are subject to relatively rapid removal by resurfacing. The equipment and field implementation approach described in this paper can provide samples that are not subject to the aforementioned problems.

Equipment design considerations, fabrication, and use

Oil:water partitioning behavior -- dissolution of PAH. When crude oils or refined petroleum products are spilled in the marine environment, a number of natural oil weathering processes occur, including spreading, evaporation, dissolution, dispersion of whole-oil droplets into the water column, photochemical oxidation, water-in-oil emulsification, microbial degradation, adsorption onto suspended particulate material, ingestion by organisms, sinking, and sedimentation. From NOAA-sponsored wave tank experiments (Payne *et al*., 1983, 1984; Payne and McNabb, Jr., 1984) and measurements completed in the field following several major oil spills and blowouts (summarized in Payne 1997; French, 1998), it is known that water-column concentrations of both dissolved aromatics and dispersed oil droplets can reach concentrations in the hundreds of µg/L (parts per billion (ppb)) during the first 12 to 48 hours following a spill. Furthermore, concentrations of individual PAH can persist in the water column at much lower levels for several weeks or months (as long as the oil or distillate product remains on the water surface or stranded on shorelines) following a spill.

Sample size requirements to yield minimum detection limits that support NRDA modeling efforts. Based on an extensive literature review of toxicity models and available data to estimate additive toxicity of PAHs in oil (French, 1998), 96-hour LC_{50} values were derived for the sum of 22 selected 2- and 3-ring aromatics and their respective alkyl-substituted homologues. Calculated additive 96-hour LC_{50} data for crustaceans, fish, and other invertebrates were obtained for 8 different oils and other refined products. Interestingly, all 8 oils yielded about the same 96-hour LC_{50} values for the sum of the 22 PAHs dissolved in the water at 25° C (e.g., an approximate mean of 10 µg/L for sensitive crustaceans and 100 to 200 µg/L for species of average sensitivity).

Typically, toxicologists use a conservative 1% of the 96-hour LC_{50} concentration to estimate a threshold concentration for no toxic effects (i.e., a no-observable-adverse-effects level) (Calabrese and Baldwin, 1993). Therefore, the sum of the concentrations of the 22 selected 2- and 3-ring aromatics above which an effect might be expected would be in the range of 0.1 to 2 µg/L. Taking the more conservative value and the relative percent of the 22

selected PAH in No. 2 fuel oil and Alaska North Slope crude oil, a minimum per-component detection limit in the range of 1 to 5 ng/L (or lower) should be obtained to best support NRDA modeling efforts (Payne, 1997). Unfortunately, such detection limits are lower than most commercial laboratories routinely report, particularly when extracting a 1-L sample.

Lower typical detection limits can be obtained by implementing a few minor changes in sampling and analytical protocols. By increasing the sample volume extracted from 1 to 4 L (nominal 1 gallon), reducing final solvent extracts from 1 mL to a nonroutine, but easily workable 250 µL, and injecting a larger sample volume (2 versus 1 µL) into GC/MS instrumentation operating in the selected ion monitoring (SIM) mode, detection limits can easily reach the required 1 to 5 ng/L range (Payne, 1997). As such, the minimum volume requirement for any water sampling system to support NRDA efforts must be at least 4 L (or a nominal 1 gallon).

In addition to improving the detection limit, another advantage to larger sample sizes is in the differentiation of dissolved PAH and dispersed oil droplets. Specifically, as sample size is increased, more representative samples are obtained. Dispersed droplet distributions are more heterogeneous than dissolved components, and as a result, larger sample volumes can provide better samples to characterize water column impacts. Finally, filtration of seawater to differentiate dissolved and dispersed components is facilitated by larger sample volumes, both from a standpoint of sample handling at the time of collection and from ease of laboratory analyses.

Sampler construction and materials considerations. Figure 1 is a schematic diagram of the Portable Large-Volume Water Sampling System (PLVWSS). This design is based on the approach used by Payne *et al*. (1984) during numerous wave-tank studies and during the NOAA Launch 1273 investigation of oil/suspended particulate material (SPM) interactions following the *Exxon Valdez* oil spill (Payne *et al*., 1991). Figure 2 presents a photograph of the assembled unit contained in a specially fabricated wooden cruise box/work station designed to facilitate easy transport and secure the pump, inline trap, and water sample bottle during use. The filtration unit and tubing are contained in a separate cruise box of similar dimensions.

Stainless steel "tee" with ball valve for purge (backflush) through sampling tube during deployment through air-sea interface.

Flexible FEP-lined vacuum tubing attached to 5 m stainless steel sampling tube with disposable end cap (plug) for near surface (to 5 meters) sampling. End cap is blown off with oil-free compressed air (supplied from a SCUBA tank) back pressure after passing through air-sea interface.

The FEP-lined vacuum tubing can also be attached to a specially fitted 10 L Go-Flo Bottle® for deeper water samples obtained with conventional hydrowire, if desired.

Flexible FEP-lined vacuum tubing.

Two-holed Teflon® stopper with Viton® "O"-ring.

Stainless steel 293 mm-diameter Millipore® filter holder for 0.7 μm glass-fiber filters to allow separate analyses of dispersed oil droplets and dissolved PAH in water samples.

3.8 L (1 gal) amber glass water-sampling bottle.

| Portable Generator or Ship's 110 VAC Power Supply | Vacuum Pump | In-Line Charcoal Filter and Water Trap |

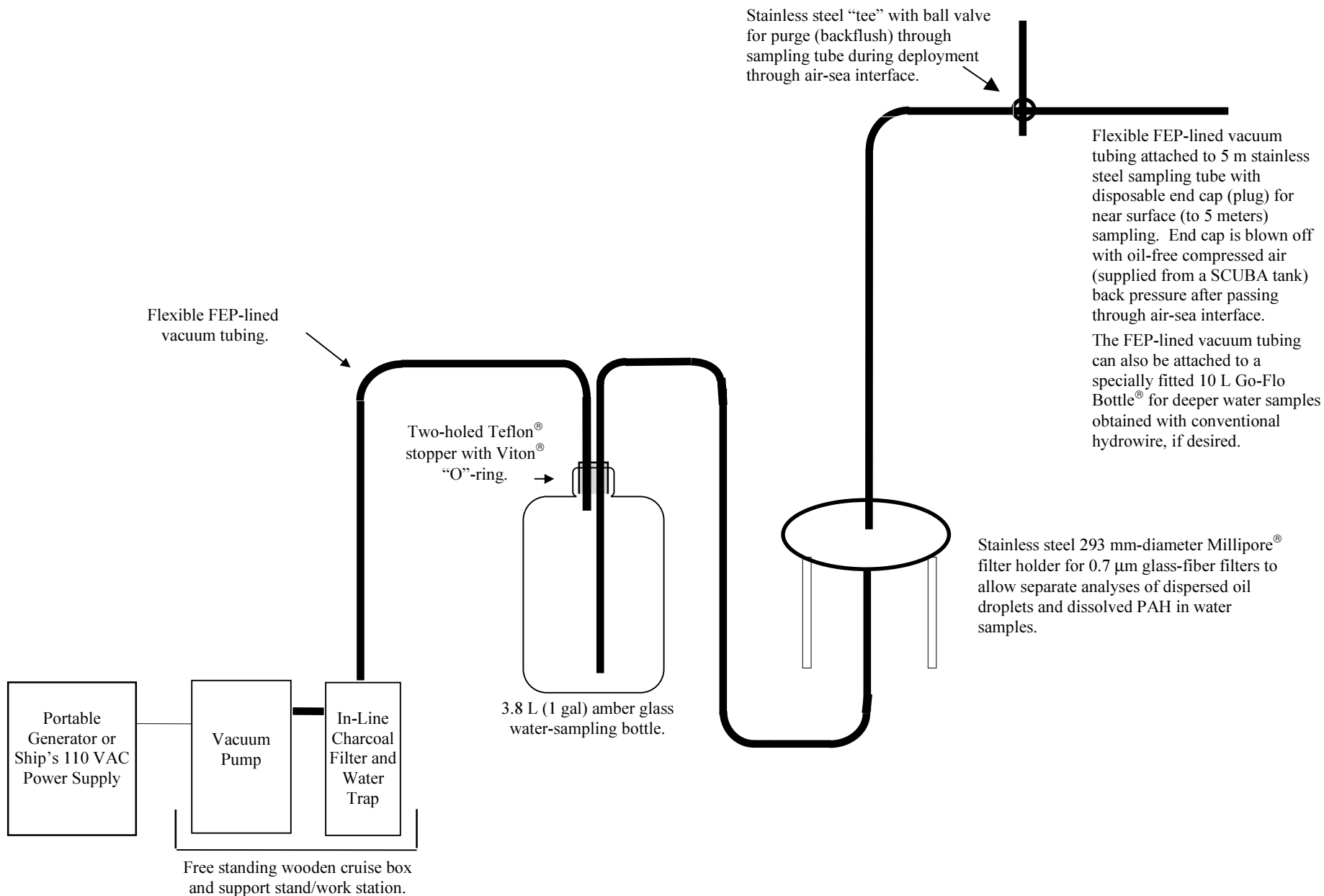Free standing wooden cruise box and support stand/work station.

Figure 1. Schematic diagram of the Portable large-Volume Water Sampling System.

The PLVWSS is constructed entirely of noncontaminating, chemically resistant, and easy-to-clean materials (e.g., stainless steel, Teflon®, Viton®, and Fluoropolymer (FEP) tubing and connections). The sampling tube is 3/8-inch-diameter stainless steel tubing, which can be solvent-rinsed between sampling stations, if desired. All ½-inch-I.D. (3/4-inch-O.D.) tubing used to connect individual components of the PLVWSS upstream of the sample bottle is FEP-lined Tygon® tubing. This tubing is extremely flexible, does not collapse under vacuum (27 inches Hg), and has been shown by GC/MS analyses of system blanks not to contribute any background organics. The 293-mm-diameter Millipore® filter unit (containing a 0.7-µm pore-size glass fiber filter) is constructed entirely of 316 stainless steel. The tubing from the sample bottle to the in-line charcoal trap and vacuum pump is ¼-inch corrugated FEP, which has the inert properties of Teflon® but is flexible and does not collapse under vacuum. The entire sampling train upstream of the sample bottle can be solvent-rinsed to eliminate potential for carry-over contamination between samples (Payne *et al.*, 1984; 1991). The 0.7-µm pore-size glass-fiber filters (Pall-Gelman Sciences, Inc., part number X11085) have been shown not to contribute significant background contamination (Payne *et al.*, 1984), and they effectively separate the truly dissolved constituents from the particulate (oil droplet) phase (Gordon *et al.*, 1973; Wells and Sprague, 1976). While background contamination of samples from the glass-fiber filters has not been a problem in the past, the additional precaution of kiln-firing the filters at 300° C for 2 hours before use is recommended in light of the improved sensitivity of modern analytical instrumentation. The filters are no longer kiln-fired during the manufacturing process (M. Sayer, personal communication, 1998), so the filters used with the PLVWSS have been kiln-fired by the analytical laboratory, wrapped in solvent-rinsed aluminum foil, and then stockpiled with the sampler for use in the field.

The use of a large-diameter (29.3 cm) filter system is important because it ensures that the seawater sample does not have to pass (or be filtered) through a standing layer of oil. With this system, the captured oil droplets are widely dispersed on the filter, and the majority of the water passes through the filter without being forced to pass through a standing oil phase (as might be the case on smaller-diameter filters). This prevents the potential and artifactual extraction (leaching) of additional dissolved PAH constituents during sample filtration at the time of collection.

The two-holed stopper used to seal the sample bottle during vacuum pumping is made of Teflon® with a Viton® "O-ring." The Viton® "O-ring" provides a better seal, but care must be taken not to expose it to acetone during cleaning.

The combined in-line charcoal filter and water trap (Cole-Parmer Instrument Company, Inc., part numbers E-01508-93 and E-01508-27) between the glass sample bottle and the vacuum pump serves two functions. First, it protects the vacuum pump from water damage if the water-sample bottle should be inadvertently overfilled, and second, it prevents potential back-diffusion of vacuum pump-oil vapors into the sample bottle. In the system

described in this paper, this problem is further eliminated by the use of a Gast® Model DAA-V175-EB oil-less vacuum pump. The cruise boxes were coated with three layers of a noncontaminating water-based cross-linked acrylic paint (Break-Through® by Vanex, Inc.) that was designed for use in cleanrooms and other high-performance applications that require an extremely inert painted surface.

Field implementation. The PLVWSS can be deployed from shoreline for intertidal/subtidal stations as well as from a small boat (e.g., a Boston Whaler or fishing vessel) to document water-column effects farther from shore. Electrical power for the vacuum pump is provided by a commercial portable generator for shoreline applications or the "research" vessel's own 110-volt AC power supply, if available. Obviously, if a portable generator is used, it should be positioned downwind from sampling operations.

For near-surface samples (to 5-m depths), the flexible FEP-lined vacuum tubing is attached to a 5-m stainless steel sampling tube that is closed at the water sampling end with a disposable cork or Viton® stopper. After deployment of the sampling tube through the air-sea interface, backpressure (oil-free air supplied from a scuba tank) is applied through a "tee" with a stainless steel ball valve to blow off the end cap (stopper). Alternatively, oil-free air forced through the open end of the sampling tube during deployment can also prevent internal contamination from the surface microlayer or any obvious oil slicks. Once the sampling tube is positioned at the desired depth, the vacuum system is turned on and the 4-L sample is drawn through the 0.7-µm glass-fiber filter and into the sample bottle. This process takes about 5 to 10 minutes, providing a more representative sample than a one-time grab. At that time, the 0.7-µm glass-fiber filter is carefully removed and stored in solvent-rinsed aluminum foil for later solvent extraction and analysis of the dispersed oil phase (freezing is recommended as the best sample-preservative method). The dissolved-phase water sample can then be stored on ice, acidified, or poisoned with 50 to 100 mL of methylene chloride for shipment to the analytical laboratory.

When used in connection with a Teflon®-lined 10-L Go-Flo Bottle® (preferably equipped with quick-connect fittings for carbon-filter purge valves and stainless steel drain valves) or other more traditional water sampling equipment, the PLVWSS can be used to process deeper (i.e., greater than 5 m) water samples to allow depth profiles to be obtained. In this case, the flexible ½-inch FEP-lined Tygon® tubing is simply attached to the drain valve on the Go-Flo Bottle®, and the contents of the sampler are vacuum-pumped directly into the 293-mm-diameter filter and water bottle as before. To minimize potential airborne contamination of the sample, it is recommended that the purge valve on the Go-Flo Bottle® be connected to a carbon filter to provide clean air for volume replacement during draining.

Results and discussion

As of this writing, the PLVWSS as physically configured in Figure 2 has not been used in an actual spill event. To demonstrate the type of information that can be obtained

from a prototype sampler that used the same filtration system, Figure 3 presents flame ionization detector (FID) gas chromatographic profiles of the surface oil, the dispersed oil droplets, and the dissolved-phase (filtered seawater) samples obtained after 48 hours of oil weathering in an outdoor flow-through wave tank system (Payne *et al.*, 1984).
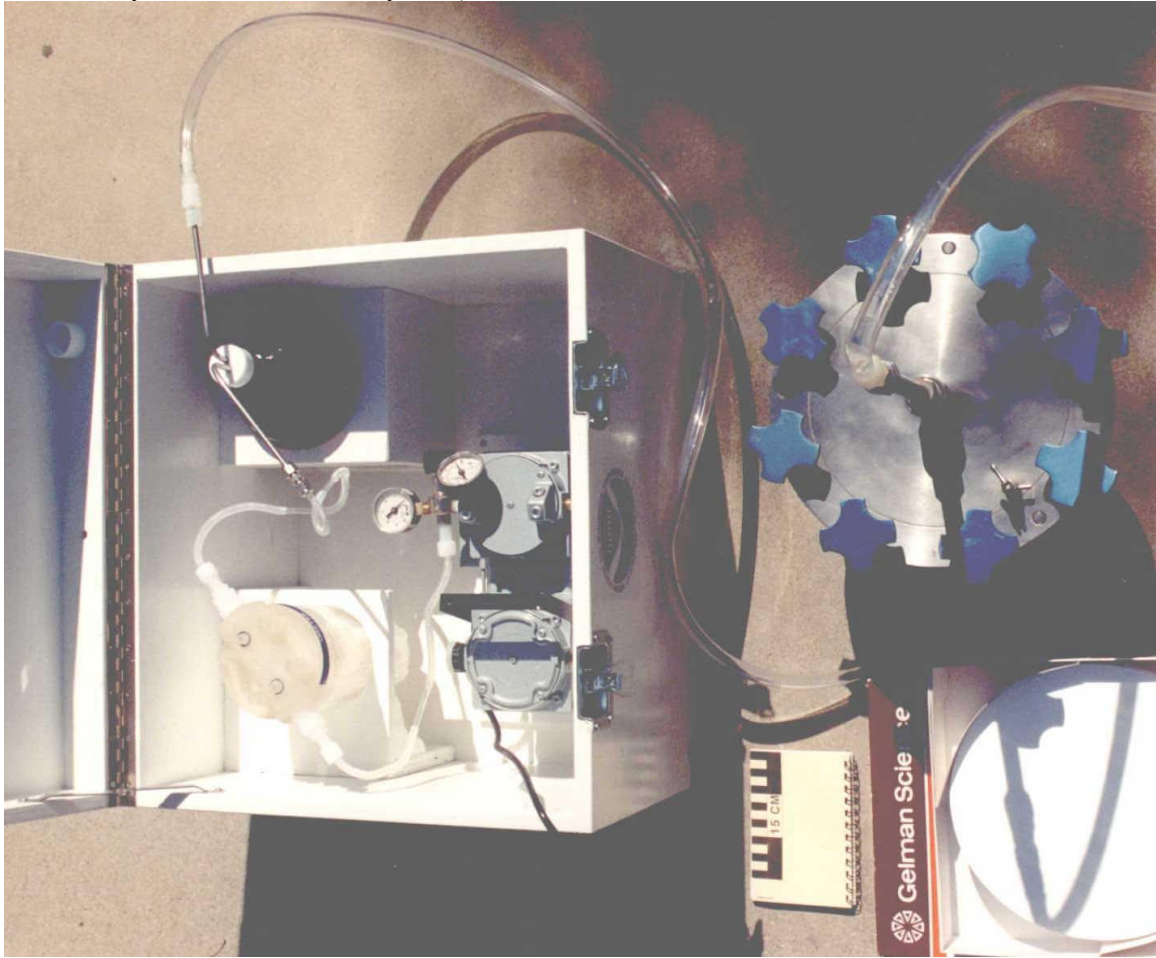

Figure 2. Portable Large-Volume Water Sampling System assembled for filtration/capture of dispersed oil droplets and collection of a 4-L (nominal 1 gallon) sample of dissolved hydrocarbon components. The vacuum pump, in-line trap, and glass sample bottle are secured in position within the cruise box/work station. The 293-mm-diameter filter unit, 0.7-µm glass-fiber filters, and PFE-lined tubing are carried in a second cruise box/work station of similar dimensions. Commercially available and pre-cleaned 1-gallon glass sample bottles are shipped separately.
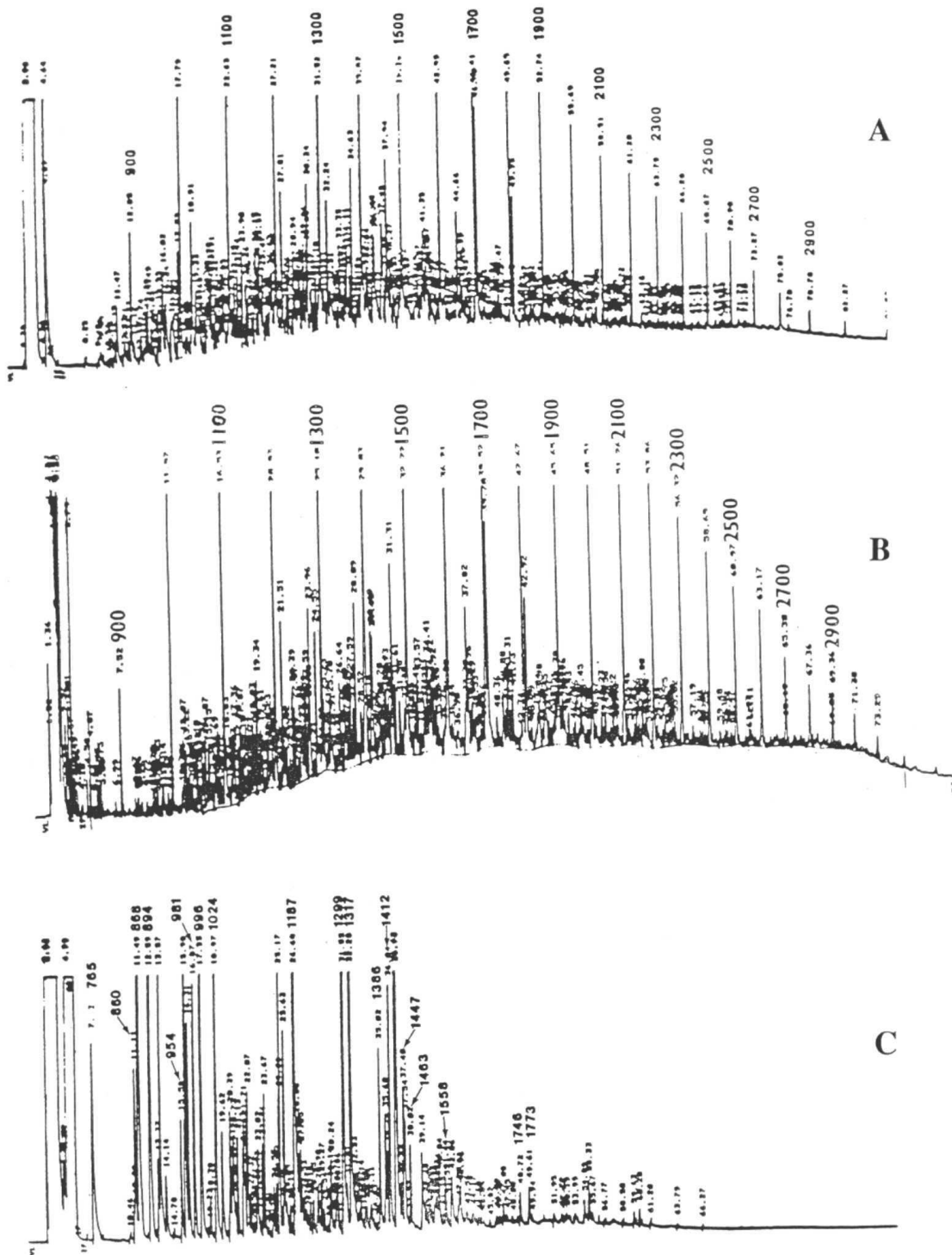
Figure 3. Flame ionization detector gas chromatographic profiles of surface oil (**A**), dispersed oil droplets (**B**), and dissolved components (**C**) collected with a prototype Portable Large-Volume Water Sampling System after 48 hours of oil weathering in flow-through wave-tank experiments. Kovats retention indices are printed above the predominant n-alkanes in **A** and **B** and the dissolved PAH in **C**.

After 48 hours of weathering, the surface oil (Figure 3A) had lost all components below n-C$_9$ (Kovats Index 900; Kovats, 1958) by a combination of evaporation and dissolution processes. Not surprisingly, the chemical composition of the dispersed oil droplets filtered from the water-column at the same time (Figure 3B) is nearly

identical to that of the surface (source) oil. Notwithstanding the fact that most oils will not readily sink, fresh oil can be temporarily dispersed/driven into the water column by wind and wave turbulence. In such instances, however, droplets above a certain size range (generally greater than 20 μm or 0.02 mm) will quickly resurface in the absence of turbulence. Then, as the surface oil viscosity increases due to water-in-oil emulsification or mousse formation, it becomes increasingly difficult for wind-driven waves to plunge discrete oil droplets into the water column. Instead, as the oil weathers, the oil/water interfacial surface tension decreases from approximately 27-35 dynes/cm to approximately 5-14 dynes/cm. At this stage, small (0.001 to 3 mm) oil flakes and droplets can be slowly torn off the surface of the emulsified mousse accumulations. These flakes and droplets either remain on the water surface or are dispersed by turbulence into the upper mixed layer of the water column.

The chemical composition of the dissolved phase (filtered seawater) is drastically different from either the surface oil or the dispersed oil droplets collected at the same time, and Figure 3C shows the preferential dissolution of alkyl-substituted benzenes, naphthalenes, phenanthrenes/anthracenes, and dibenzothiophenes in the Kovats Index 765 to 1800 range. The total resolved aromatic hydrocarbon concentration in the 0.7-μm filtered-seawater sample was 74 μg/L compared to a concentration of 110 μg/L for the aliphatics (primarily n-alkanes) in the dispersed oil droplets. Had a simple "grab" sample of unfiltered water been analyzed, it would have appeared "enriched" in aromatics compared to the surface oil; yet, it would have been impossible to give an accurate accounting of PAH exposures to water-column organisms due to uncertainties regarding the relative proportions of dissolved versus oil-phase PAH constituents and oil droplet resurfacing. As noted above, whole oil droplet dispersion becomes self-limiting with increases in viscosity. Thus, after 9 to 12 days, the concentrations of n-alkanes from dispersed oil droplets in the wave tanks declined to less than 5 μg/L, while the truly dissolved PAH components were still between 35-45 μg/L.

Only by including provisions for filtering large-volume seawater samples through a filter of 0.7-μm (or smaller) pore-size at the time of collection can such detailed information about PAH exposures to water-column organisms be obtained.

Conclusions

Both dissolved and particulate (oil-phase) PAH can be sublethal or acutely toxic to numerous marine organisms. As such, PAH concentrations should be documented, especially if commercially or ecologically important species (e.g., herring, salmon, clams, lobster) are present and spawning at the time of an oil spill event.

The PLVWSS is simple, easy to use, and highly portable. It can be transported with stockpiled supplies (commercially available 1-gallon amber-glass bottles and glass-fiber filters) by air for arrival on-station within 12 to 24 hours of notification of a spill event. It can be deployed

from shoreline features, and for offshore surface (1 to 5 m) samples, it can be used on any "vessel of opportunity" without the need for A-frames, winches, or other oceanographic equipment. If 110 volt AC power is not available from the vessel (or for shoreline stations), electrical power can be supplied from a portable generator positioned down-wind of the sampler. As such, the PLVWSS can be utilized quickly during the first hours or days of a spill event, when dissolved PAH and physically dispersed oil-droplet concentrations are at their highest.

With the PLVWSS described in this paper, contentious issues of water-column exposures can be taken out of the realm of speculation and instead be supported by hard data. In addition, with accurate measurements of dissolved-phase PAH and dispersed oil-droplet concentrations at specific intervals (e.g., 24, 36, 48, and 72 hours) into a spill event, it will be possible to enhance the predictive capability of modeling efforts. Specifically, these data will support accurate hindcasting to peak PAH concentrations and exposure durations that are known to occur in the first 8 to 24 hours of a spill. Finally, water samples collected with the PLVWSS could be used by NOAA Scientific Support Coordinators and Biological Assessment Teams for evaluation of dispersant effectiveness or other remediation approaches such as *in situ* burning.

Acknowledgments

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Author

Dr. James Payne has over 25 years experience in oil and chemical pollution studies and services. He is President of Payne Environmental Consultants, Inc., which is currently assisting NOAA, the U.S. National Park Service, and California's Office of Oil Spill Prevention and Response with NRDA issues.