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A fiber optic-based fluorometer system is described that uses a pulsed laser to induce fluorescence and a time-gated linear photodiode array coupled to a spectrograph for rapid measurement of fluorescence emission spectra and fluorescence decay times. Data is presented from studies conducted in San Diego Bay where the system has been used for real-time *in situ* measurements of temporal and spatial variability of petroleum hydrocarbons in seawater. Results show that the optical fiber fluorometer system is capable of direct quantification of low level (parts-per-billion diesel fuel marine equivalent) concentrations of petroleum hydrocarbons.

Analysis times for measurement of complete fluorescence emission spectra are fast (tens of milli-seconds) and compare with the temporal response characteristics for temperature and conductivity sensors that are used for measuring standard physical hydrographic parameters. Results obtained with the fiber optic fluorometer system during a mapping study in San Diego Bay show good correlation with GC-MS analysis of total polycyclic aromatic hydrocarbons (PAHs) measured on discrete samples collected during the study.

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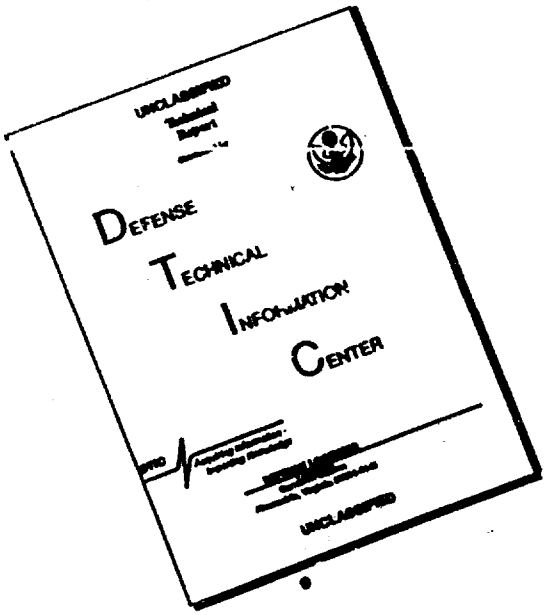

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LASER- INDUCED FLUORESCENCE OVER OPTICAL FIBERS FOR REAL-TIME *IN SITU* MEASUREMENT OF PETROLEUM HYDROCARBONS IN SEAWATER

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Abstract

A fiber optic -based fluorometer system is described that uses a pulsed laser to induce fluorescence and a time-gated linear photodiode array coupled to a spectrograph for rapid measurement of fluorescence emission spectra and fluorescence decay times. Data is presented from studies conducted in San Diego Bay where the system has been used for real-time *in situ* measurements of temporal and spatial variability of petroleum hydrocarbons in seawater. Results show that the optical fiber fluorometer system is capable of direct quantification of low level (parts-per-billion diesel fuel marine equivalent) concentrations of petroleum hydrocarbons.

Analysis times for measurement of complete fluorescence emission spectra are fast (tens of milli-seconds) and compare with the temporal response characteristics for temperature and conductivity sensors that are used for measuring standard physical hydrographic parameters. Results obtained with the fiber optic fluorometer system during a mapping study in San Diego Bay show good correlation with GC-MS analysis of total polycyclic aromatic hydrocarbons (PAH's) measured on discrete samples collected during the study.

Introduction

For many years it has been possible to make *in situ* measurements of important physical hydrographic parameters in the marine environment. CTD (conductivity-temperature-depth) systems are routinely used to measure vertical profiles of temperature and salinity in the ocean. CTD's can also be towed from a surface platform or mounted in submersible vehicles in order to measure horizontal variability. CTD temperature and conductivity sensors have been designed to have rapid response characteristics and support high sampling rates (ca. 10 Hz). These systems are routinely used for mapping small scale variability in physical hydrographic conditions.

Interest in environmental issues has increased the requirement for sensors that can measure parameters of environmental concern. The need to map chemical plumes in order to locate and discriminate sources of contamination as well as better understand the distribution and fate of chemical contaminants has intensified the demand for chemical sensors that respond on the same time and space scales as sensors on CTD systems. However, at present there are almost no chemical sensors that meet the requirements for rapid response time and reversibility. Oxygen and pH sensors probably come the closest, but these two chemical variables do not provide a direct measure of chemical contaminants of environmental concern (eg., petroleum hydrocarbons, chlorinated organic compounds, trace metals, etc.). In order to map the distribution of a chemical pollutants it is usually necessary to collect discrete samples and send them to a laboratory for subsequent analysis. There are several critical shortcomings to this approach: (1) Because chemical data from the laboratory is generally not available for weeks to months after samples are collected there is a lack of real-time chemical information to guide the sampling program. (2) The sparsity of chemical data that is a direct limitation of discrete sampling does not normally provide enough information to discriminate small

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scale features that can be used to track plumes or distinguish sources.

For the reasons discussed above we have embarked on a program to develop real-time sensor systems for *in situ* chemical measurements. This paper describes efforts to develop a fiber optic based fluorometer system that permits real-time *in situ* measurements of petroleum hydrocarbons in seawater.

Methods

Instrumentation. A schematic of the pulsed-laser fiber optic-based fluorometer system is shown in Figure 1. Details of the system have already been described [1,2]. In brief, UV light from a pulsed N_2 laser that operates at 337 nm with a pulse width of 0.8 nsec and a pulse energy of 1.4 mJ is coupled into the central fiber of a 10 m long fused silica, bifurcated seven-fiber bundle. Fluorescence stimulated in the sample by the laser pulse is collected by six other fibers that are concentrically distributed around the excitation fiber. This signal is returned to the instrumentation setup where it is dispersed spectrally using a polychromator and measured with a linear photodiode array. A triggering photodiode coupled with a fast pulser delay generator is used to control the gating of the detector. Analysis times are rapid. Read out of a fluorescence emission spectrum requires approximately 16 msec.

The system offers several advantages compared with non-time gated systems. Because the detector is only active for a period of 20 nanoseconds, coordinated with the arrival of the fluorescence signal at the detector, contributions to the signal from

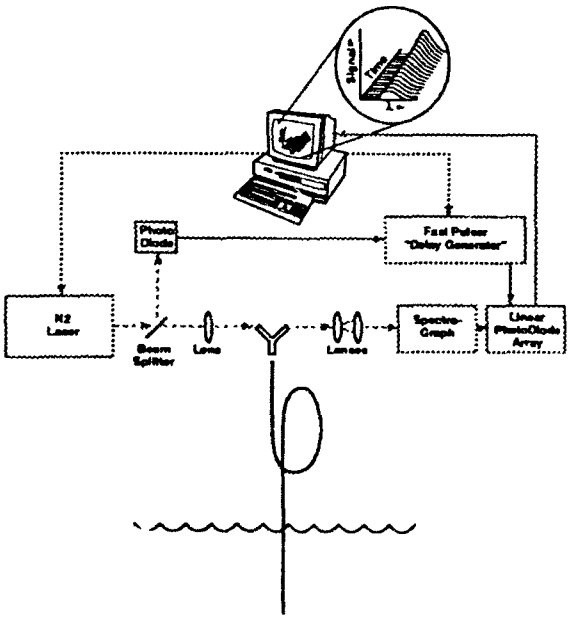

Figure 1. Schematic of fiber optic-based fluorometer system.

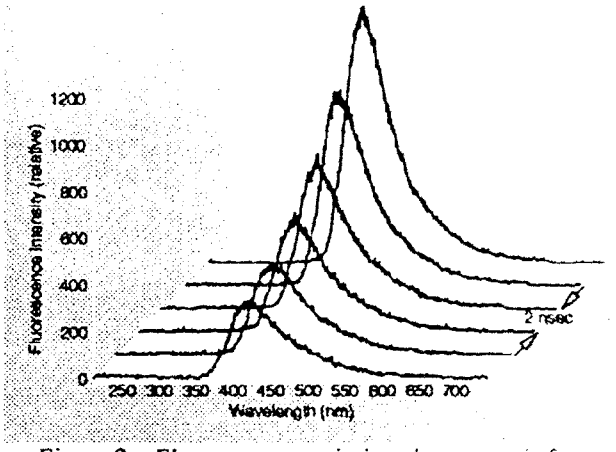

Figure 2. Fluorescence emission-decay matrix for diesel fuel marine in water.

ambient background light are negligible. Also, by incrementing the delay generator for successive laser pulses it possible to measure the fluorescence decay time of the fluorescence event.

A representative data set measured with the fiber fluorometer system is presented in Figure 2. This example shows the fluorescence emission-decay matrix for diesel fuel marine (DFM) in water. The data set was generated by collecting six sequential spectral scans with each successive scan incrementally delayed relative to the laser pulse by 2 nsec. The utility of measuring fluorescence decay times is that different compounds that contribute to the observed fluorescence signal have different decay times. Differences in fluorescence decay times are particularly useful for resolving fluorescence emission signals for compounds that cannot be resolved spectrally. We have shown that it is possible to distinguish several PAH's in oxygenated seawater on the basis of fluorescence decay times [1]. PAH's are important environmentally because they are components of petroleum hydrocarbon products and are also formed via incomplete combustion of fossil fuels. Many have well documented carcinogenic behavior [3].

Results

A study was conducted in which the pulsed-laser fiber optic fluorometer system was used to measure petroleum hydrocarbon fluorescence over a tidal cycle from a moored survey craft near the mouth of San Diego Bay. Measurements with the fiber optic system were made using a 10 meter long "bare-ended" fiber bundle mounted in an instrument well that penetrated the hull of the survey craft (Fig. 3). The probe was positioned approximately 1 meter below the surface of the water. The end of the fiber was shielded by a slotted PVC sheath that keep kelp from collecting on the probe and also provided a constant background (Fig. 4). A photograph of the fiber optic sensor system installed onboard the NOSC survey craft is shown in Figure 5. The fiber

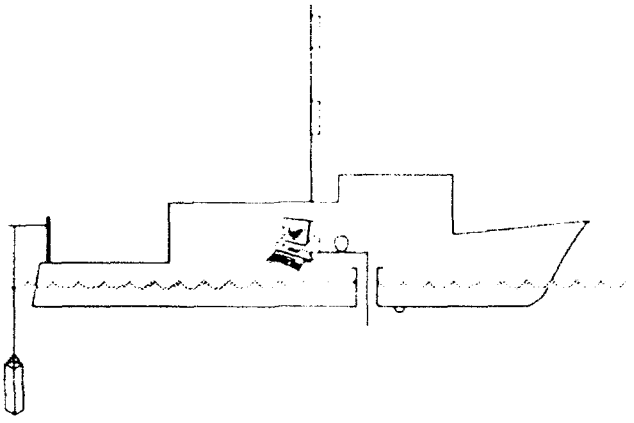

Figure 3. Schematic of survey craft used for tidal monitoring study showing fiber optic fluorescence probe mounted in instrument well. Intake for a pumped fluorometer system was attached to CTD instrument package deployed from stern.

optic probe was calibrated before and after the experiment by immersing it in a beaker containing seawater and adding known quantities of DFM. Response was linear over the range of 0 to 50 parts-per-billion (Fig. 6). For the field study a complete emission spectrum was recorded every 5 minutes for 26.5 hours (Fig. 7). A time series plot over the tidal cycle shows that the maximum fluorescence emission intensity measured with the fiber optic system (top panel on Figure 8) closely tracked fluorescence measured during the same time period with a conventional flow through fluorometer (Turner Designs, Inc.)(middle panel, Fig. 8). The Turner fluorometer was equipped with filters optimized for measuring oils fluorescence: excitation (254 nm, 50 nm bandpass) and emission filters (260 nm, 50 nm band pass). Inspection of the data in terms of the tidal height measured using a fathometer onboard the survey craft (bottom panel, Fig. 8) shows that in general high fluorescence values, (ie., higher

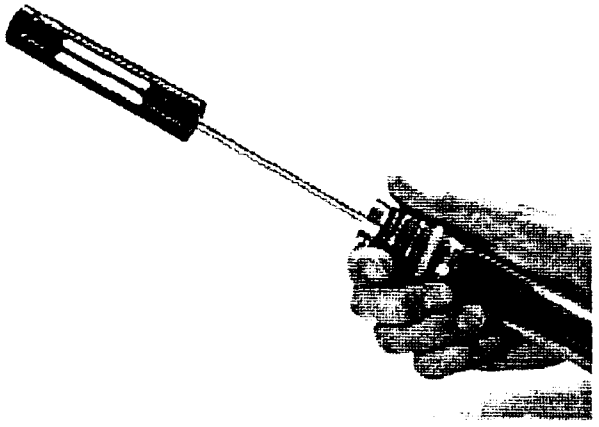

Figure 4. Photograph of fiber optic probe showing slotted sheath that was used to protect sensor from abrasion and provide a constant seawater volume

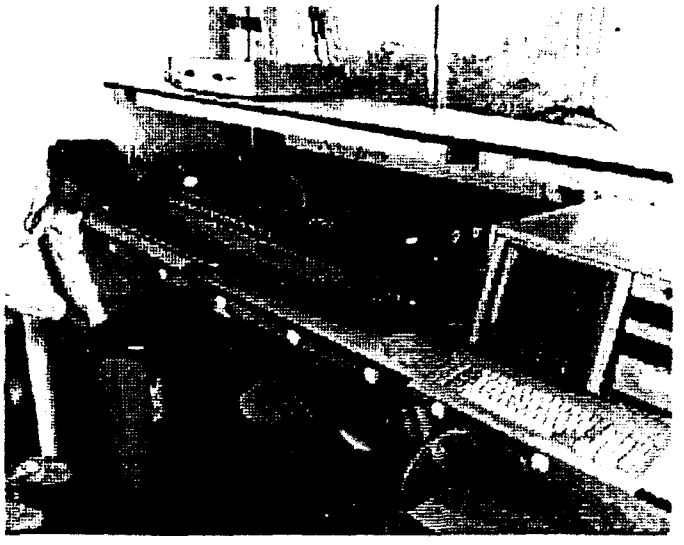

Figure 5. Photograph of laboratory on survey craft showing fiber optic sensor system. The operator is lowering the fiber optic probe into the instrument well.

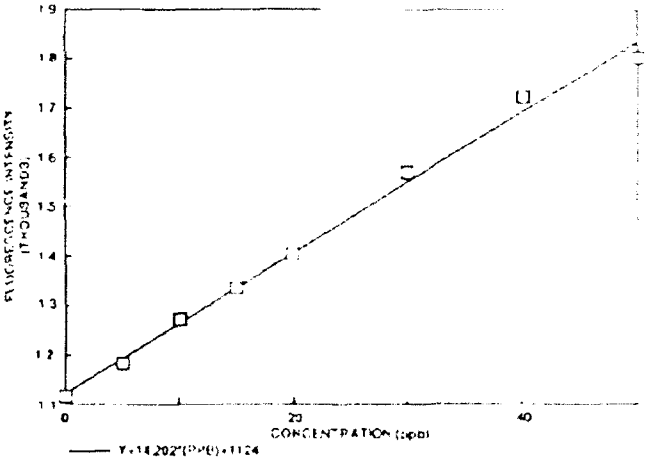

Figure 6. Calibration of the fiber optic sensor system with Diesel Fuel Marine (DFM) in seawater

concentrations of aromatic hydrocarbons were observed at low ebb tide, when contaminated water is leaving the San Diego Bay. Conversely, lowest fluorescence signals (lowest concentrations of aromatic hydrocarbons) were observed during high flood tide, when relatively clean ocean water was flowing past the survey craft into the bay. It is important to note that these measurements show that the concentration of petroleum hydrocarbons changed by nearly an order of magnitude at a single location over a single tidal period. This study demonstrates the feasibility of making long term (24 hours) direct *in situ* fluorescence measurements

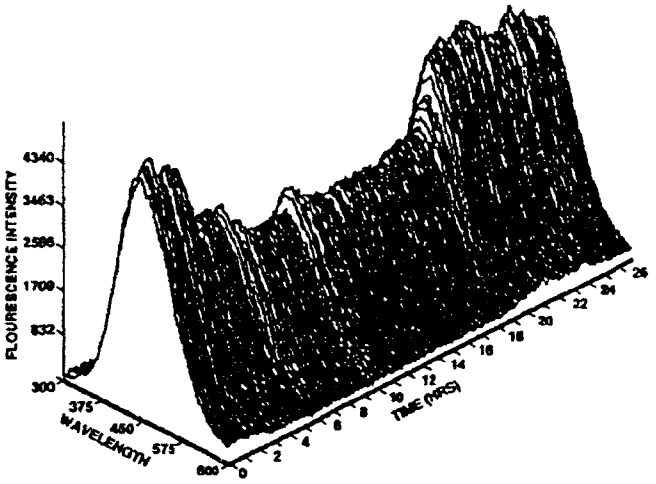

Figure 7. Fluorescence emission spectral scans measured with fiber optic sensor system over a tidal cycle near the mouth of San Diego Bay. A measurement was recorded every 5-minutes for 26.5 hours.

in seawater using pulsed-laser excitation over optical fibers. The advantage of the fiber optic system is that it is not necessary to pump water on-board the survey craft; hence, there is no problem with contamination/or sorption related to the pumping system. This would also make it possible to multiplex several fibers to the same instrument in order make nearly simultaneous measurements at numerous locations with a single instrument. Another important advantage of the fiber optic system described in this report is that is possible to rapidly collect the complete fluorescence emission spectrum induced in the sample. In contrast, conventional flow through fluorometers presently only measure a single emission band. Additional information contained in the emission spectrum and/or the emission decay matrix can be used for distinguishing different petroleum products and/or different contaminant sources.

More recently, the fiber optic sensor system described in this report was used to conduct underway mapping of petroleum hydrocarbon distributions in San Diego Bay. Fluorescence measured over the optical fiber mounted in the transducer well of the survey craft is shown plotted on a map of San Diego Bay in Figure 9. The position of the craft (determined automatically using a microwave positioning system) is represented by the base of a vector whose height represents the measured fluorescence intensity. Figure 10 shows a an enlargement of the portion of the survey made in the vicinity of Shelter Island and Commercial Basin and in the waters just outside these embayments. Both of these areas contain marinas with large numbers of recreational and small commercial boats. Measured fluorescence intensitites are much higher within these embayments, suggesting that the boats and their associated support facilities are a source of

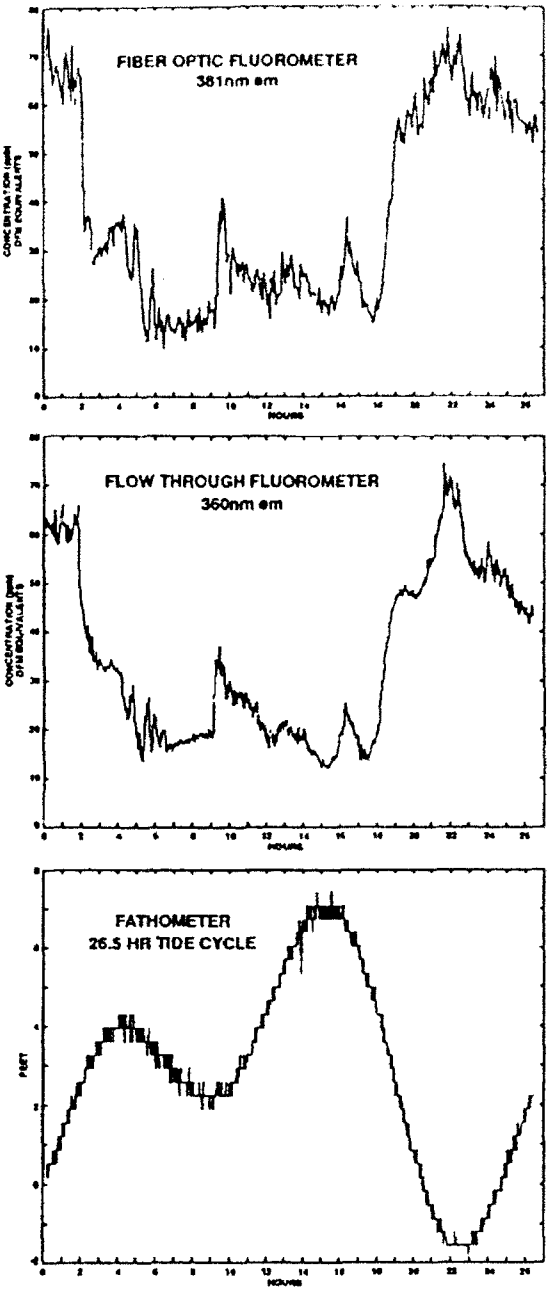

Figure 8. Comparison of direct in situ fluorescence measurements in seawater using the fiber optic probe vs. oils fluorescence measured using a conventional flow-through fluorometer over a tidal cycle in San Diego Bay. Data is plotted relative to tidal height recorded using a fathometer mounted on the hull of the survey craft.

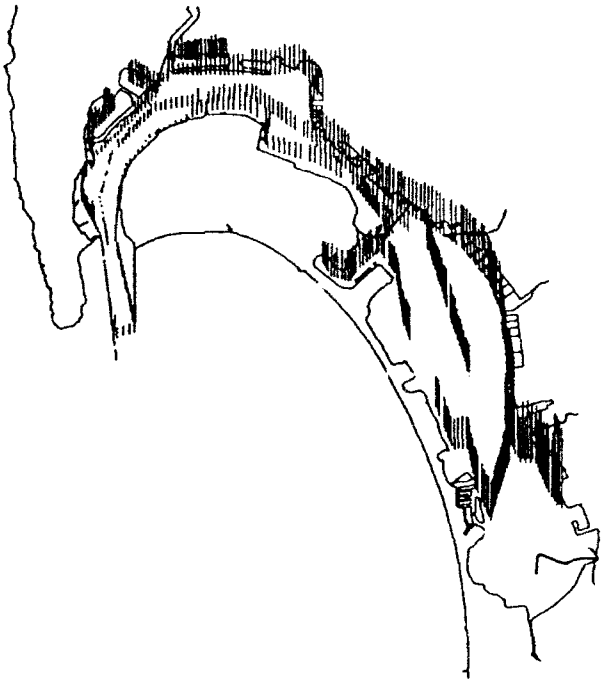

Figure 9. Map of San Diego Bay showing relative fluorescence values measured along cruise transect with fiber optic fluorometer system. The position of the craft at the time of measurement is indicated by the location of the base of a vertical vector whose height represents the measured fluorescence intensity.

petroleum contamination. No problems were experienced due to bubbles or other particles interfering with the fiber optic probe as it was moved through the water. This work sets the stage for fabrication of a fiber optic array that can be rapidly multiplexed as it is towed through the water to provide nearly simultaneous sampling at multiple depths.

Comparison of fluorescence intensities measured using the fiber optic fluorometer with results from GC-MS analyses of total polycyclic aromatic hydrocarbons (PAH's) on discrete samples collected during the mapping survey shows (Figure 11) a strong correlation between the real-time fluorescence measurements and conventional laboratory GC-MS analyses. Total PAH concentrations were determined by summing the concentration of individual PAH analytes quantified by GS-MS. Detail of the GS-MS analytical procedure and the list of PAH compounds quantified is presented elsewhere [4].

Summary and future work

The laser induced fiber optic fluorometer system described in this report offers the possibility of rapid *in situ* determination of low (ppb) concentrations of petroleum hydrocarbon compounds directly in seawater. Analysis times on the order of tens of milli-seconds are similar to response times for temperature and conductivity sensors on conventional CTD systems and exceed response times of most oxygen and pH sensors. Thus, the fiber optic sensor system permits *in situ* chemical measurements for the same scales of temporal and spatial variability that are possible with CTD systems. In the future the capability of multiplexing many fibers coupled to the same measurement instrument will permit multi-dimensional real-time mapping of pollutant distributions.

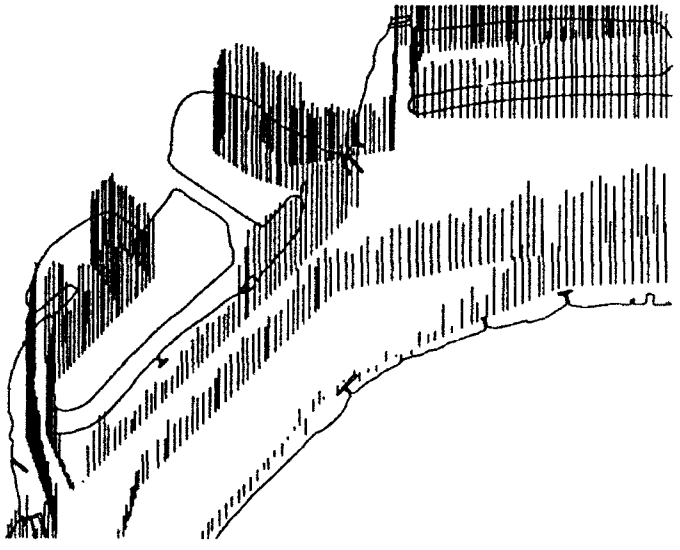

Figure 10. Enlargement of Shelter Island/Commercial Basin area of San Diego Bay showing higher fluorescence values within embayments realative to lower values in the main channel.

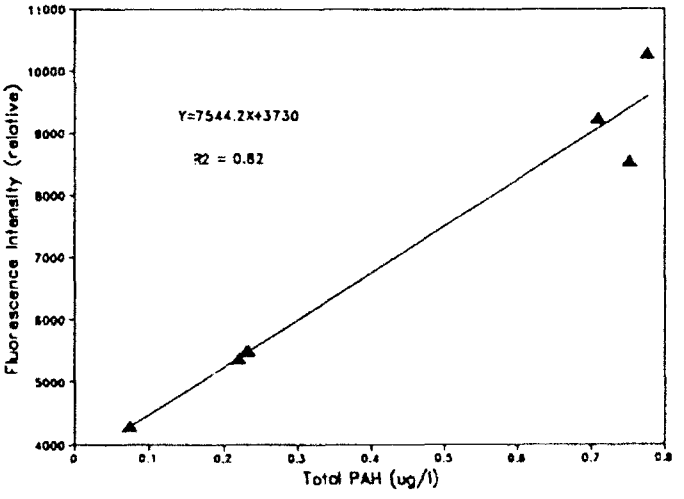

Figure 11. Fluorescence intensities measured with the fiber optic fluorometer system versus total PAH concentrations measured by GC-MS on discrete samples collected during the survey.

Other work is in progress to extend the fluorescence techniques reported here to chemical species that do not normally fluoresce. Efforts are underway to develop fluorogenic indicator systems that will permit the determination of trace transition metal ions through detection of fluorescent metal-indicator complexes. A novel system of constantly renewing the indicator a the probe tip has already been reported that provides excellent response times and is completely reversible on time scales of 1 sec [5].

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