USGS

WATER RESOURCES RESEARCH GRANT PROPOSAL

1. **Title.** Assessment of Chemical Pollution and Bioavailability in Pearl Harbor Using Supercritical Gluid and Immunochemical Methods

2. **Focus Categories.** Water quality, aquatic and environmental protection.

3. **Keywords.** bioavailability, monitoring, PCB, PAH, ELISA, supercritical fluid extraction.

4. **Duration.** 01/01/1999-12/30/1999.

5. **Federal funds requested.** $40,000.

6. **Non-Federal (matching) funds pledged.** $80,000.

7. **Principal investigators(s) name(s), university, city, and water resource institute.**

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8. **Congressional district of university where the research is to be conducted.**

The Southeastern/Island region.

9. **Statement (2 paragraphs maximum) of critical regional water problems.**

Contaminated sediment is a prominent and serious problem in many watersheds in the U.S. and throughout the world. Approximately 10% of the sediment underlying U.S. surface waters is sufficiently contaminated with toxic pollutants to pose potential risks to aquatic organisms, humans and wildlife (EPA, 1998). Water bodies affected include streams, lakes, harbors, near shore areas, and oceans. Among the many pollutants, those often found in high concentrations are polychlorinated biphenols (PCBs), heavy metals including mercury, organochlorine pesticides, and polycyclic aromatic hydrocarbons (PAHs). The risk posed by contaminated sediments must be identified, accessed, and remediated. The EPA has identified four critical research areas for sediments and water quality. Two of the four areas are to: (1) incorporate measures of chemical bioavailability into future sediment monitoring programs, and (2) develop better

sediment monitoring and assessment tools (EPA, 1998). Each of these areas will be addressed in the proposed project. Monitoring of pollutants in sediments and salt water remains very difficult. Complete removal of PCBs, PAHs, and pesticides from sediments is a significant analytical challenge due to the complexity of the matrices and analytes (Chester et al., 1996). Most solvent extraction methods require multiple concentration and cleanup steps prior to detection. Therefore, they are tedious, and generate tremendous amount of solvent wastes. In addition, conventional analytical chemistry methods for quantification of organic pollutants such as gas chromatography-mass spectroscopy (GC-MS) are time consuming and expensive. We have recently developed a supercritical fluid extraction (SFE) method for quantitative recovery of nonpolar and polar chemicals in soils, and immunoassays (enzyme linked immunosorbent assays, ELISAs) for detecting trace levels of PAHs, PCBs and atrazine in water. These new methods are of significance in environmental protection and management at the local, state, regional, and national levels. SFE has advantages of selectivity, efficiency, use of non-toxic carbon dioxide (CO_2), and cost-effectiveness. ELISAs are fast, simple, sensitive, specific, and economical often allowing in-the-field rapid analyses by non-chemists while producing high sensitivity and accuracy.

Pearl Harbor is one of the largest sheltered harbors in the USA and the only harbor wholly owned and controlled by the U.S. Navy. The facility contains numerous maintenance service facilities and has been the site of continuous Navy operations for more than 50 years. Previous investigations by Navy contractors have analyzed sediment samples from the harbor and found tributyltin, a single PCB (Aroclor 1254), significant levels of total PAHs, and several phthalates (plasticizers). Other samples contained low levels of DDT degradation products. Chlorinated pesticides were not detected. Significant amounts of total sulfides were also detected in most sediment samples indicating anaerobic biological activity. Ammonia was also found in most sediment samples. Detectable concentrations of several metals (arsenic, cadmium, chromium, copper, lead, mercury, nickel, and zinc) were also found. TCLP analyses for the same metals found all below reporting limits. Despite the presence of all these chemicals, the water column has not been found to be highly toxic (less than allowable) and fish tissues were not such that specific advisories were required or adverse biological effects were expected. This indicates that not all of the chemicals are bioavailable. Additionally, in 1996 there was a oil spill of 16,000 gallons (bunker fuel oil No. 6) in a stream near its mouth into the harbor from a Chevron oil pipeline that passes through to a nearby electric-power generating plant. The heavy oil initially sank and most was recovered. No other oil spills have been reported in the area. All of these findings can be expected from such a large harbor facility which has been in service for as many years and has serviced as many vessels in as many different maintenance facilities. The Pearl Harbor sediment and associated water column are ideal sources of "real" samples for conducting research into rapid and easy immunochemical techniques (suitable for field use) for extraction, identification, and quantification of toxic organic chemicals for both pollutant monitoring and assessment of bioavailability.

10. Statement (2 paragraphs maximum) of the results, benefits, and/or information expected to be gained during the performance period and by the end of the project, if of longer duration, and how they will be used.

This project will evaluate and optimize a novel SFE procedure to effectively extract pollutants from contaminated sediments for hazard assessment, remediation monitoring, and bioavailability research. It will also develop and evaluate several ELISAs for rapid and large throughput monitoring of pollutants in salt water and sediment extracts. This project will study the use of these sophisticated methods in actual real-world environmental applications. Both SFE and ELISA will be applied for bioavailability studies of PCBs and PAHs. The ELISA methods will allow cost effective pollutant analyses in the field and in some cases eliminate the need for costly and lengthy laboratory procedures. Bioavailability will be estimated by assessing the quantity of chemicals in the water column, the sediment pore water, and the readily and non-readily available adsorbed fractions on the sediment solids in isotherm experiments and biodegradation kinetic studies as well as by quantifying biodegradation products.

Use of SFE and ELISA will immediately reduce environmental pollution and risk associated with the analysis process because they generate minimal quantities of hazardous solvent wastes. They are simple, fast, large sample throughput and thus cost-effective. Pearl Harbor in Hawaii is heavily polluted and thus selected as a model site for the study. The project will collect data on the status of chemical pollution and bioavailability, and degree of remediation necessary in the Pearl Harbor water column and sediment. Success of the project will enable extension of the technologies to studies of other contaminated coast and harbors. In recent years, ELISAs and SFE have shown great promise for various environmental monitoring applications.