Contaminants of human origin are ubiquitous constituents of coastal waters. More and more frequently scientists and regulators ask, “How much of a given contaminant is acceptable?” “Acceptable,” a rather subjective term, is often defined as a level of contaminant that does not pose a threat to the sustainability or stability of an ecosystem. In practice, this usually means demonstrating that the contaminants do not harm key, sensitive species, often by comparing toxicity data with concentrations measured in the field. However, as we learn more about coastal environments, it is clear that such simple predictive measurements are complicated by a variety of factors. These include differences in the physiology of organisms used in culture experiments and those present in the field, effects of water chemistry on bioavailability of the contaminants, which may vary from place to place, and spatial and temporal variability in the distribution of contaminants.

My group’s particular interest is variability in the distribution and biological availability of contaminants in dynamic coastal environments. Coastal regimes are complex physical systems, with mixing processes that can lead to considerable spatial and temporal variability in contaminant distributions, presenting a real challenge for ecological assessment studies. Moreover, such variability leads to strong gradients in other chemical parameters that may affect toxicity. For example, copper is toxic to many organisms, but its toxicity is ameliorated by high levels of manganese and iron (which compete with copper for uptake sites on cell surfaces), whose distributions are also highly variable in coastal waters.

Currently, regulatory attention is focused on episodic inputs of contaminants into harbors and estuaries. During events like floods or harbor dredging, pulses of contaminants may be injected into the water column, raising concentrations to toxic levels. Rainstorms in urban areas generate large volumes of contaminant-laden runoff. Waste load allocation models, based on high levels of contaminants measured in discharge waters, indicate serious problems for such receiving waters as rivers, estuaries, and harbors, where these compounds end up. Applications of such models by regulatory agencies often lead to costly remediation measures.

Interestingly, there are few measurements in harbors showing how contaminant concentrations change during such events, so many critical questions are now addressed only in models. For instance, how fast are contaminant pulses dissipated by physical mixing processes? For how long are sensitive organisms exposed to high levels before dissipation occurs? Where, in complex urban environments, are the worst sources?

In order to answer these questions, scientists need large data sets to determine how contaminants vary at numerous locations within an estuary or harbor during storm events. Since collection of discrete samples is costly and logistically difficult, we have been working with an in situ, passive sampling probe to study the distribution and bioavailability of trace metals in harbors.

What is an “in situ passive sampling probe?” Basically, it is a small object containing a specialized solid material that absorbs trace metals or other chemicals from the surrounding water. It involves no mechanical process, only diffusion and the chemicals’ affinity for the solid phase—hence the term passive. The rate at which the target chemicals diffuse into the probe is proportional to their concentration in the water, and can be calibrated. Thus, deployment of the probes for a fixed period of time (from several hours to several days) provides a mean concentration.
of a contaminant at that location over that time period.

Such a device has several important features. It is cheap (no moving parts or electronics), so it can be deployed in substantial numbers in a harbor, providing sufficient coverage to be useful to a physical oceanographer. It can be tailored to the contaminant under investigation, through selection of solid phase materials with specific properties. Finally, the devices can be coupled with sophisticated shore-based methodologies for analysis. For instance, samples collected using our device can be analyzed by inductively coupled plasma mass spectroscopy, enabling over a dozen elements to be measured on a single sample. Thus, we can track variability in several contaminants as well as other metals that influence bioavailability such as manganese and iron.

Michael Twiss, a postdoctoral fellow partially supported by RCRC, evaluated the probes for measurement of copper, zinc, cadmium, and lead in harbors of Falmouth, MA, San Diego, CA, and Norfolk, VA. He showed that in contaminated harbors the probes yield highly reproducible measurements consistent with measurements of reactive metal species by other techniques. The Office of Naval Research, one of the sponsors of this research, is particularly interested in copper, because it poses an important regulatory problem for naval installations, particularly during episodic events.

Several other groups in the MIT-WHOI community have active programs in this type of work, and some interesting collaborations may develop in the future. For example, Roger François and Bill Martin (Marine Chemistry and Geochromistry Department) are using similar devices to obtain high resolution profiles of metals in sediment pore waters, and Phil Gschwend (MIT) and Rocky Geyer employ a conceptually similar probe to study organic contaminants in harbors.

I am planning to use the probes to study metal mobilization in Boston Harbor and surrounding areas during such episodic events as combined sewage overflows and dredging activities, with support from the Environmental Protection Agency and in collaboration with the Massachusetts Water Resources Authority.

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