Draft
Contaminant Monitoring Refinements to the Design of the National Water Quality Monitoring Network For U.S. Coastal Waters and their Tributaries

The National Water Quality Monitoring Council (Council) has produced a design for the National Water Quality Monitoring Network for U.S. Coastal Waters and their Tributaries (the Network) as called for in the U.S. Ocean Action Plan. The Network is a framework for linking water quality monitoring in coastal bays, estuaries and the Great Lakes with observations in upland areas and offshore waters, and includes freshwater flows and contaminant input from inland and coastal rivers, ground water, and from atmospheric deposition. Wetlands and coastal beaches are also included in the design (1).

This report examines the current Network design report and proposes refinements to the list of contaminants to be monitored in the water column, bottom sediment and in fish tissues.

The Coverage of Contaminants in the Network design document

The Network design document originally listed major categories of contaminants that related to toxic contamination and to habitat degradation. The revised Network design lists more specific chemicals and metals in those same categories, but instead of simply specifying them for monitoring; it specifies that managers must become knowledgeable of the locations and concentrations of the chemicals specified. Monitoring is, of course necessary to gaining this knowledge, but once understood, need not be continued with the same intensity or frequency. This understanding is necessary in the following resource components: estuaries, near shore coastal waters, offshore coastal waters, Great Lakes, rivers, ground water, and atmospheric deposition.

Table 3-1 of the Network design gave examples of contaminant groups to be included in the Network monitoring includes: metals and metalloids, bulk organics, volatile organic compounds, pesticides, halogenated hydrocarbons, polycyclic aromatic hydrocarbons, and contaminants of new and emerging concern.

One of the key design characteristics of the Network is the linkage among various resource compartments. Within these compartments, risks must also be considered through the exposure pathways of water, sediment, and fish tissue. Although it may not be appropriate to monitor all contaminant groups in all components, some of the same measurements should be made in more than one of the resource components.

Toxicity[1] of some metals in freshwater increases, for instance, in saltwater, often a downstream compartment. Many of these contaminants are no longer legally discharged but persistent in the environment. Fish tissue contamination is a particularly important exposure pathway because it often magnifies the concentrations found in water or sediment. Exposures through this pathway can, in some instances, be mediated through avoiding or reducing fish consumption. In these instances, information from monitoring is critical.

Monitoring water resources to meet the designated use goals of a region are made more complicated by the fact that there are as many as 100,000 chemicals that have been registered for use in commerce in the United States over the past 30 years, and the numbers are similar in the EU and Japan. (2) Of these, about 15,000 are classified as food additives, cosmetics, pharmaceuticals, and pesticides.

Toxicity varies according to the chemical structure of the compound as well as with exposures through one or more of the pathways noted above. Important

[1] Toxicity is often subdivided acute toxicity (the adverse effects resulting from a single exposure to a substance), carcinogenicity, cholinesterase inhibition, developmental or reproductive toxin or an endocrine disruptor.

elements of exposure are persistence and the degree to which and the contaminant bioaccumulates.

This report establishes the contaminants important to implementing national water quality policies, notes those important for the protection of public health and the environment due to the exceedance of water quality standards and the contamination of fish tissues, and shows how those concerns can affect choices to monitor sediments that are a source of those contaminants. The relationship of these sources to those measured from atmospheric deposition is discussed.

Monitoring At Regional and National Scales

Water quality standards are the foundation of the water quality-based control program mandated by the Clean Water Act. Water Quality Standards define the goals for a waterbody by designating its uses, setting criteria to protect those uses, and establishing provisions to protect water quality from increases in those pollutants. A water quality standard consists of four basic elements:

1. designated uses of the water body (e.g., recreation, water supply, aquatic life, agriculture),
2. water quality criteria to protect designated uses (numeric pollutant concentrations and narrative requirements),
3. an antidegradation policy to maintain and protect existing uses and high quality waters, and
4. general policies addressing implementation issues (e.g., low flows, variances, mixing zones).

Section 303(c)(2)(B) of the Clean Water Act requires States and authorized Tribes to adopt numeric criteria for §307(a) priority toxic pollutants for which the Agency has published §304(a) criteria, if the discharge or presence of the pollutant can reasonably be expected to interfere with designated uses. The §307(a) list contains 65 compounds and families of compounds, which the Agency has interpreted to include 126 priority toxic pollutants.

In addition to narrative and numeric (chemical-specific) criteria, other types of water quality criteria include:

- Biological criteria: a description of the desired aquatic community, for example, based on the numbers and kinds of organisms expected to be present in a water body.
- Nutrient criteria: a means to protect against nutrient over-enrichment and cultural eutrophication.
- Sediment criteria: a description of conditions that will avoid adverse effects of contaminated and uncontaminated sediments.

The routine monitoring of contamination in water, fish tissues, and sediment in waterbodies is intended first, to establish the status of current levels of contamination and to allow annalists to combine these levels with exposure estimates and knowledge of the toxicity of the various chemicals to understand their risks. Embedded in this process is the research needed to establish analytic methods that support the completion of these tasks.

Monitoring at the national scale is also associated with the many regulatory programs for controlling new sources of these chemicals and for assessing their impacts. Selected contaminants or classes of them are slated for special management attention. The task is complicated by the reality that environmental reservoirs of pollutants from past sources are often actively mobilized and transferred from one media to another. New chemicals are constantly being developed, and the mechanisms for screening them are imperfect.

To best meet national regulatory needs, monitoring must designed to be statistically valid and should lead to information that can guide regional studies and management actions.

Regional scale studies are usually centered on establishing the status of concentrations and fluxes of chemicals in waters using as guidance, the national criteria or standards adopted by state governments. This interest will often be see as concerns for chemical contaminants responsible for listing waterbodies as impaired or threatened on a jurisdictions' 303(d) list, or in chemical contaminants responsible for finfish and shellfish consumption advisories. In this context, regional monitoring will most likely be used with some form of adaptive management in which monitoring leads to action, and then to more monitoring to assess the results of that action. This cycle is seen in Virginia (3) and in many regional programs (4, 5, 6, 7). In many cases, the management action will be to cease monitoring because the contaminant in question is not found at levels sufficient to cause concern. In others, regional status reports will examine both overall contaminant levels of concern and identify the temporal and spatial variations of those levels, and further explore

the sources of the contamination. Over successive cycles, the monitoring must look at changes in contaminant levels that may be prompted by either changes in emissions or in natural events such as drought or the movement of sediment deposits because of floods or storms. To accomplish this, regional studies will usually examine more specific analytes such as specific PCB congeners or may use specific sediment quality screening data and techniques.

The Network does not envision that regional monitoring will play an initial role in assessing contaminants of emerging concern because these are often without adequate risk profiles and often need to have laboratory methods developed before they can be adequately monitored. For this reason, the Network design assumes that Federal research programs will perform these functions and does not specify contaminants of emerging concern among its analytes. Regional monitoring programs can, however, provide critical functions as test beds for portions of the Federal assessments.

The Great Lakes program has emphasized its estimates of the mass loading of various pollutants. This approach would appear to be easily communicated and to provide the technical basis for program responses. It also can also provide the long-term record needed for explaining the direction of monitoring programs as they evolve over time. Regional needs will also include monitoring to detect change over time and space, and support source identification and help assess the impact of remedial actions. Regional studies also provide important test beds, prototyping studies of concerns before they rise to the level of national interest.

Contaminant monitoring should be conducted with a full appreciation of its relatively high cost, and the issues covered in the various phases of the monitoring program should be well documented as context for evolving future priorities.[2]

Choosing Chemicals to Monitor

The goal of the refined Network design is to extend the current knowledge of the concentrations and loads of contaminants and establish a basis for determining differences in those concentrations over time. Because the extent of current knowledge varies widely by waterbody, and the sources of contamination vary as well, the choice of contaminants to monitor will vary also.
The Network design stresses that, while the need is to characterize and understand the risks that chemicals impose on water bodies, the list of monitored analytes is not static, and that it will evolve as the concentrations of these chemicals are better understood. As the analyte list evolves, it can greatly reduce or eliminate the monitoring for risks that are either low or are adequately characterized. The evolving list can accommodate new analytic techniques, new concerns about a chemical's toxicity, or changes in exposures to them. Altered exposures might be seen in new patterns in a chemical's environmental fate through sediment movements via storms or flooding, or to altered patterns of either manufacture or use that effect these elements of risk.

The list of contaminants to monitor was compiled by merging several lists, and then sorting them into the categories used in the Network design document and into the three principle media (water, fish tissue, and sediment). The process then assigned them to either regional or national concern or both. Table 1 shows the sequence of lists used and the logic employed to include or exclude items on them.

To avoid unnecessary monitoring while also assuring that concentrations of contaminants are well understood, the Council proposes that monitoring agencies adopt the practice of adapting their current list of analytes to reflect levels found in past monitoring.

The Council was impressed at the difficulty of specifying the pesticides that should be monitored. This difficulty arises from the fact that the use of each pesticide is dependent upon land uses, cropping patterns, and to some extent, the popularity of competing pesticide products. Organic contaminants in pesticides

Ongoing assessments of contaminants of emerging concern by both the U.S. Geological Survey in its Chemical Prioritization System (8), in the Environmental Protection Agency's National Target Analyte Strategy (9), by the Delaware River Basin Commission (10), and by Muir and Howard (2) were noted, but not used. They reflect sorting processes, however, that need to be carefully watched. These studies focus on organic chemicals by examining the levels of detection in controlled studies, the persistence of toxic properties, the volume of

[2] The Virginia Department of Environmental Quality annually reports the status of The Reduction of Toxics in State Waters to the General Assembly (3) This report includes both analytic costs and repeated reference to monitoring designs that minimize the costs to characterize the risks of toxic pollution.

Table 1. Selection of Analytes

Category	Use in the Network List	Citation
Criteria Pollutants	Chemicals for which EPA has issued criteria were classified as such and retained on the list.	Current National Recommended Water Quality Criteria, http://www.epa.gov/waterscience/criteria/wqcriteria.html#cmc
California Toxics Rule	Considered covered by the entry above	40CFR131.36, http://www.epa.gov/waterscience/standards/ctr/index.html
National Status and Trends Network Analytes	Current NS&T analytes in tissue and sediment were noted and retained Former NS&T analytes not found on other lists were omitted due to the low occurrences of these chemicals found by this program	National Status & Trends Program Committee Worksheets http://ccma.nos.noaa.gov/stressors/pollution/nsandt/mw_contaminants.html
Pesticides	Pesticides included in the report Pesticides in the Nation's Streams and Ground Water were retained. Of these, 18 pesticides were dropped from the list because monitored levels showed levels below benchmarks noted in the report for both aquatic life and human health impacts.	Reference 11
Organics	EPA Persistent Bioaccumulative Toxics Chemical List	Reference 12
	Contaminants in the Great Lakes Binational Toxics Strategy were retained	Reference 13
Fish Tissue	Great Lakes National Program Office Fish monitoring analytes were included except the specific PCB congeners listed	Contaminants in Top Predator Fish http://www.epa.gov/glnpo/glindicators/fishtoxics/topfishb.html
	US EPA Chemical Contaminant Data for Use in Fish Advisories were included	Reference 9
	FDA Action Level were included for Fish tissues	http://www.cfsan.fda.gov/~lrd/fdaact.html (Eight contaminants)

Sediment Contaminants	EMAP PAH Analytes in sediments	References 14,15,16,17,18
Atmospheric Deposition	IADN monitoring as summarized on the organics and trace metals tables.	Reference 19
Contaminants of Emerging Concern	Three lists were examined but not used pending further study at the national level	References 2, 8, 9, 10
NAWQA Analytes	This long list provided useful information on methods but was not used to establish priorities aside from the pesticides noted above	Reference 20

the chemicals produced, and their likelihood of bioaccumulating in the food chain. New programs that employ such procedures as computational toxicology continue to review the potential impacts of their release in the environment.

The approach to the sorting of existing lists of chemicals to produce recommendations for both national and regional studies in water, fish tissue[3] and sediment were as follows:

Chemicals were assembled on a single list shown in Table 2 showing the agency and the circumstances of their listing. Then, a category was assigned using the highest level of authority associated with the entry. The final List is in Table 2. A chemical that is cited as an emerging concern but that also had EPA criteria issued would be assigned the EPA criteria category since it is a more immediate reason to monitor the chemical. While some categories were chosen over others, all attributes were listed in the tables used to assemble the list.

Regional Lists

Regional list of analytes are critical to establishing accurate assessments of local water quality. Current monitoring needs to be established in the context of pervious monitoring that justifies both the selection of what is to be monitored and what has been sufficiently monitored in the past.

Great Lakes Water Quality Agreement (),calls for the "virtual elimination" of discharges of persistent toxic substances into the Great Lakes Basin. Pursuant to this agreement, the 1997 Great Lakes Basin. The Great Lakes Binational Toxics Strategy () sets reduction targets for the following toxic substances:
All of the chemicals are listed in Table CP-3.

Delaware River Basin Commission (6) has been active in monitoring toxic organics in several categories and has also been examining contaminants of emerging concern(). The coverage of PCBs and dioxins, furans, and fluorinated chemicals is impressive:

- PBDEs in water, sediment and tissue
- PCDDs and PCDFs in water and in tissue
- PBDEs in tissue
- PCDDs + PCDFs water
- PFOA/PFOSs in tissue

[3] Fish tissue should be interpreted to include bivalve tissues. The work group discussed whether it should use " biota" instead of fish tissues since monitoring bivalve species offer several advantages over fish. Fish metabolize many organic contaminants to a greater extent than bivalves, and it is often hard to find common fish species in different locations and many fish species found in estuarine or marine systems migrate considerable distances seasonally, making it very difficult to know the source of the contaminants.

Regional Monitoring Program for Water Quality in San Francisco Bay (RMP) is responsible for much of the ambient water quality monitoring administered by the San Francisco Estuary Institute (21). The list of contaminants was developed in consultation with the San Francisco Regional Water Quality Control Board and NPDES permit holders. The list largely focuses on contaminants with ambient water quality criteria; although several constituents have been eliminated based on no detect values. In addition, the RMP has included a number of emerging contaminants for which ambient water quality criteria do not exist (e.g., polybrominated diphenyl ethers, perfluorinated compounds, etc.).

The RMP has monitored contaminants in water and sediment annually since 1993; the program switched to probabilistic sampling of water and sediment in 2002. Water and sediment analyses focus on trace elements and organics. Organics monitored include PAHs, PCBs, PBDEs (both sum and individual), and synthetic biocides (e.g., cyclopentadienes, chlordanes, DDTs, HCHs, diazinon, etc) (21).

Additionally, the RMP monitors contaminants in bivalves, bird eggs, small fish, and sport fish. Bivalves are monitored for the same organics as water and sediment samples. Bird (tern and cormorant) eggs are monitored for mercury, PFOS, PBDEs, and pesticides. Sport fish are analyzed for mercury, PCBs, PBDEs, chlordanes, DDTs, and dieldrin. Small fish are analyzed primarily for mercury.

The Chesapeake Bay Toxics 2000 Strategy (5) recognizes the patchy nature of toxics concentrations across the Chesapeake and includes both a list of toxics of general concern and more detailed lists of toxics discovered to be limiting designated water uses under section 303(d) of the Clean Water Act.

This strategy refines a response to the characterization of toxics concerns into the following categories:

- Regions of Concern (hot spots)
- Areas with Low Probability for Adverse Effects
- Areas of Emphasis (early warning signs/areas where living resources may be affected)
- Areas with Inconclusive or Insufficient Data

Methods

Extensive lists of laboratory method have been assembled, but not yet arrayed. Most of these methods allow the detection of multiple analytes, and thus contaminant levels can be quantified for these families of chemicals with little increase in cost. These relationships often determine the list of analytes adopted by monitoring organizations.

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