

Guidance for Implementation of Trace Elements National Synthesis within the National Water- Quality Assessment Program

by Trace Elements National Synthesis Planning Team

EXECUTIVE SUMMARY

The Trace Elements National Synthesis Planning Team (TENSPT)—a group of 10 individuals from the Water Resources Division, Biological Resources Division, and Geologic Division of the U.S. Geological Survey (USGS)—met three times during 1997–98 to develop and document a national perspective for implementation of trace element studies within the National Water-Quality Assessment (NAWQA) Program.

Five issues related to trace elements in surface and ground water systems emerged from group discussions to form the framework of a national synthesis effort, and detailed approaches for addressing these issues were developed. The issues are: (1) characterization of reference conditions, (2) effects of urbanization, (3) human exposure from consumption of water and fish, (4) effects of coal and metal mining and remediation, and (5) regional occurrence and distribution of mercury. Mercury was considered separately because of its unique mode of atmospheric transport and concerns regarding aquatic ecosystem health. A ranking process resulted in assigning a greater importance to the first three issues than to the last two.

Characterization of Environmental Settings

In order to evaluate broad scale effects of land based factors on water quality, one of the first and most important tasks to accomplish is a characterization of important environmental settings (a process referred to as stratification). Because trace elements ultimately originate from geologic sources, the stratification design for most trace element issues will be driven by geology. However, there are at least two difficulties in using this approach. First, geologic maps typically are complex representations of large numbers of geologic mapping units, many of which contribute similar trace element signatures to water and sediment. Second, only one published national geologic map is likely to be available in digital format in the time frame needed for early Trace Elements National Synthesis planning, and Alaska and Hawaii are not included in this coverage. Thus, we recommend that a major long-term goal of Trace Elements National Synthesis be to facilitate classification of the geology of the entire United States into a reasonable number of categories based on trace element associations (lithochemical units).

Until improved geologic coverages are available, we suggest that ecoregions be used as the top level of stratification for trace elements studies and that geology be utilized at the second level. It is likely that ecoregion boundaries will follow those for major geologic divisions and that Study Units will be familiar enough with local geology to be able to provide information to allow some aggregation of geologic mapping units into lithologically consistent units with regard to trace element composition.

The above approach will work for evaluating reference conditions, effects of urbanization, human exposure from consumption of water and fish, and effects of mining and remediation, although some of these issues will require additional, issue-specific levels of stratification. In this regard, population density is recommended for stratification of urban areas; water use is suggested for stratification with regard to human exposure; and production data and locations of active, remediated, and abandoned mines are advocated for stratification of mined areas.

The characterization of important environmental settings for studying mercury requires a slightly different tack than that outlined above. Atmospheric transport generally is more influential than geology in regulating mercury inputs to watersheds, and wetland density provides considerable control on mercury methylation in aquatic systems. Thus, these factors become critical in the stratification design for understanding the environmental chemistry of mercury.

Trace Elements of Interest

The following 25 trace elements were determined to be of interest from a national synthesis perspective:

Aluminum	Mercury
Antimony	Molybdenum
Arsenic	Nickel
Barium	Radium-224, 226, 228

Beryllium	Radon-222
Boron	Selenium
Cadmium	Silver
Chromium	Thallium
Cobalt	Titanium
Copper	Uranium
Iron	Vanadium
Lead	Zinc
Manganese	

The decision to include each trace element was based largely on (1) existence of guidelines for protection of aquatic life (bed sediment, water) and/or human health (edible fish tissue, drinking water), (2) availability of analytical techniques, and (3) usefulness in interpreting data for other trace elements (especially for bed sediment).

Questions to be Addressed

The TENSPT agreed upon a number of pertinent questions that might be addressed by each of the five trace element issues of interest. The questions tend to fall into two widely divergent categories: (1) those of importance to all issues and to most media (sediment, tissue, water), and (2) those of importance to a limited number of issues and to selected media. The following four questions are addressed by all issues for all or most media:

- What are the occurrence and distribution of trace element concentrations (including mercury) in bed sediment, tissue, surface water, and ground water in environmental settings of importance to the NAWQA Program?
- How do concentrations of trace elements (including mercury) in bed sediment, tissue, surface water, and ground water compare among environmental settings? Can patterns be distinguished on a regional or national basis?
- How do trace element concentrations (including mercury) in fish tissue, surface water, and ground water compare with current or proposed standards or guidelines for the protection of human health.
- How do trace element concentrations (including mercury) in bed sediment, tissue, and surface water compare with current or proposed standards or guidelines for the protection of aquatic life.

The TENSPT recommends that studies that address these questions be given higher priority than those that specifically address questions of more limited extent. However, to the degree that other questions can be answered through data collection efforts organized around the above questions, such efforts should be encouraged.

Integration with NAWQA Program Components

The TENSPT organized work elements related to the five trace element issues around standard NAWQA Program components (retrospective analyses, bed sediment and tissue surveys, BFSs, surface water synoptic studies, LUSs, SUSs), and established relative priorities for the work elements within a given trace element issue. Although none of the work elements encompasses all five trace element issues, several were ranked either as moderate or highest priority for a majority of the five issues. They are trace elements in bed sediment (including reconstructed trends of trace elements in reservoir sediment cores), mercury in fish fillets, and trace elements in the used ground water resource (Study Unit Surveys). The TENSPT recommends that studies related to these work elements be considered of greater importance than the others. In addition, two work elements — synoptic studies of trace elements in multiple media along gradients of controlling factors and a retrospective analysis of mercury in fish and bed sediment — complement the first two recommended work elements and also should be seriously considered for implementation.

Operational Recommendations

Filtration of Water Samples

The U.S. Environmental Protection Agency (USEPA) sampling protocol for drinking water calls for collecting unfiltered samples, whereas the current NAWQA protocol requires filtration of water samples through a 0.45-micrometer capsule filter. Recent USGS research on trace elements in areas affected by acid mine drainage have demonstrated that the small pore sizes (on the order of 0.001 micrometers) employed in tangential flow filtration result in a more scientifically defensible procedure when determination of truly dissolved trace elements is important. Thus, the TENSPT recommends that the NAWQA Program support the testing of tangential flow filtration in collaboration with the Office of Water Quality during early fiscal year 1999. In the interim, all ground water sampling at NAWQA sites should follow the existing, capsule filter approach. Although we recognize that a change in the filtration protocol may make comparisons among sites and over time difficult, we feel that the more realistic estimates of dissolved inorganic constituents from tangential flow filtration will compensate for data comparison problems.

Organism and Tissue Type

No single tissue or organism can be expected to meet all NAWQA objectives for trace elements. The current protocol of sampling fish livers is a widely utilized approach in the investigation of potential effects of trace elements on fishes, but a rigorous assessment of the strengths and weaknesses of the liver data in meeting NAWQA objectives is still needed. Thus, major modifications to the current protocol should not occur without a review of the stated objectives and a reconsideration of the relative priorities. With this in mind, the TENSPT makes the following recommendations:

1. Continue the current NAWQA protocol of collecting fish livers for 1997 Study Units.

- Document any changes to recommended National Target Taxa (NATT).
- Have the Trace Elements National Synthesis Team (TEST) interact with appropriate technical experts to determine target taxa that can be interpreted on a national basis.
- Give serious consideration to regional target taxa (especially for 2001 Study Units).
- Have the TEST (a) analyze trace element concentrations in bed sediment and tissue from the first 10-year NAWQA cycle to evaluate the usefulness of the data with regard to NAWQA objectives and (b) recommend a modified tissue protocol by October 2000.

2. Have 1997 Study Units collect fillet samples in addition to livers.

- Submit fillet samples to participating States for mercury analysis.
- Archive frozen fillet samples from all fish at a central location (to be determined).
- Pursue funding options for analyzing frozen fillets for total mercury.

Extraction of Bed Sediment

When acid volatile sulfide (AVS) from a dilute hydrochloric acid extraction at room temperature exceeds simultaneously extracted metals (SEM), interstitial dissolved concentrations of certain metals are not expected to be toxic to biological communities living in or near the streambed—a hypothesis that has been demonstrated for cadmium and nickel, and proposed, based on equilibrium considerations, for copper, lead, mercury, and zinc. As part of the National Sediment Quality Inventory, the USEPA has used AVS-SEM to differentiate between Tier 1 (adverse effects are probable) and Tier 2 (adverse effects are possible) sites. Because the utility of the AVS-SEM procedure has not been widely documented and the extraction procedure is radically different from the total digestion currently used by the NAWQA Program, the TENSPT recommends that the AVS-SEM extraction be evaluated as part of proposed studies of water quality effects along a gradient of urbanization. The recommendation is consistent with suggested studies of ecological effects along such gradients made by the Ecological Synthesis Planning Team. Results from this study should allow an assessment of the utility of AVS-SEM procedure to the NAWQA Program and an evaluation of its correlation with measurements of ecological conditions.

INTRODUCTION

In 1991, the U.S. Geological Survey (USGS) began the National Water-Quality Assessment (NAWQA) Program to document the quality of the Nation's water resources, to determine how water quality is changing with time, and to provide an understanding of the effects of human activities and natural factors on water quality (Leahy and others, 1993; Leahy and Thompson, 1994). The NAWQA Program is assessing water quality in more than 50 of the Nation's largest river basins and aquifers, known as Study Units (fig. 1; table 1). Collectively, the Study Units cover about one-half of the United States and include sources of drinking water used by about 70 percent of the U.S. population.

NAWQA studies rely heavily on the use of nationally consistent study designs and methods of sampling and analysis. Such consistency allows regional and national assessments to be conducted for priority water quality issues and, thus, provides the basis of National Synthesis activities within the NAWQA Program. Active National Synthesis investigations of nutrients, pesticides, and volatile organic compounds (VOCs) currently (1998) are underway, and plans are being developed to provide study designs for ecology and trace elements. The latter effort is the focus of this report.

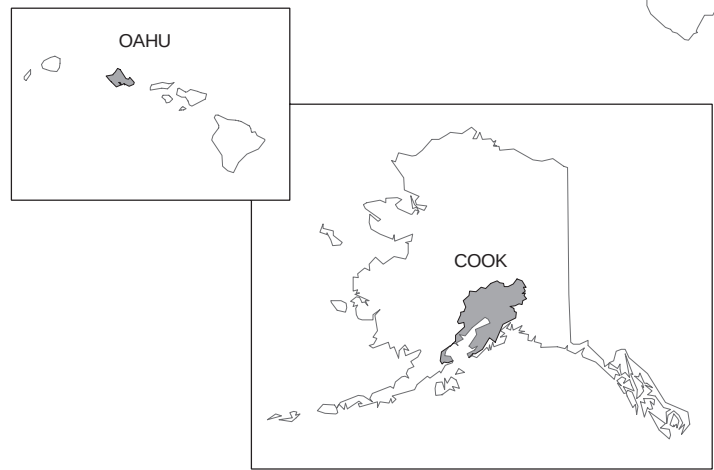


Figure 1. Locations of National Water-Quality Assessment Program Study Units

Table 1. National Water-Quality Assessment Study Units

Abbreviation	Name	Year Started
ACFB	APALACHICOLA-CHATTAHOOCHEE-FLINT RIVER BASIN	1991
ALBE	ALBEMARLE-PAMLICO DRAINAGE	1991
CCPT	CENTRAL COLUMBIA PLATEAU	1991
CNBR	CENTRAL NEBRASKA BASINS	1991
CONN	CONNECTICUT, HOUSATONIC, AND THAMES RIVER BASINS	1991
GAFL	GEORGIA-FLORIDA COASTAL PLAIN	1991
HDSN	HUDSON RIVER BASIN	1991
LSUS	LOWER SUSQUEHANNA RIVER BASIN	1991
NVBR	NEVADA BASIN AND RANGE	1991
OZRK	OZARK PLATEAUS	1991
POTO	POTOMAC RIVER BASIN	1991
REDN	RED RIVER OF THE NORTH BASIN	1991
RIOG	RIO GRANDE VALLEY	1991
SANJ	SAN JOAQUIN-TULARE BASINS	1991
SPLT	SOUTH PLATTE BASIN	1991
TRIN	TRINITY RIVER BASIN	1991
USNK	UPPER SNAKE RIVER BASIN	1991
WHIT	WHITE RIVER BASIN	1991
WILL	WILLAMETTE BASIN	1991
WMIC	WESTERN LAKE MICHIGAN DRAINAGE	1991
ALMN	ALLEGHENY AND MONONGAHELA BASINS	1994
CAZB	CENTRAL ARIZONA BASINS	1994
EIWA	EASTERN IOWA BASINS	1994
KANA	KANAWHA-NEW RIVER BASIN	1994
LERI	LAKE ERIE-LAKE ST. CLAIR DRAINAGE	1994
LINJ	LONG ISLAND AND NEW JERSEY COASTAL DRAINAGES	1994
LIRB	LOWER ILLINOIS RIVER BASIN	1994
MISE	MISSISSIPPI EMBAYMENT	1994
PUGT	PUGET SOUND BASIN	1994
SACR	SACRAMENTO BASIN	1994
SANT	SANTEE BASIN AND COASTAL DRAINAGES	1994

Table 1. National Water-Quality Assessment Study Units—Continued

Abbreviation	Name	Year Started
SCTX	SOUTH CENTRAL TEXAS	1994
SOFL	SOUTHERN FLORIDA	1994
UCOL	UPPER COLORADO RIVER BASIN	1994
UMIS	UPPER MISSISSIPPI RIVER BASIN	1994
UTEN	UPPER TENNESSEE RIVER BASIN	1994
ACAD	ACADIAN-PONTCHARTRAIN	1997
DELR	DELAWARE RIVER BASIN	1997
DLMV	DELMARVA PENINSULA	1997
GRSL	GREAT SALT LAKE BASINS	1997
LTEN	LOWER TENNESSEE RIVER BASIN	1997
MARK	MIDDLE ARKANSAS RIVER BASIN	1997
MIAM	GREAT AND LITTLE MIAMI RIVER BASINS	1997
MOBL	MOBILE RIVER AND TRIBUTARIES	1997
NECB	NEW ENGLAND COASTAL BASINS	1997
NROK	NORTHERN ROCKIES INTERMONTANE BASINS	1997
SANA	SANTA ANA BASIN	1997
SHPL	SOUTHERN HIGH PLAINS	1997
UIRB	UPPER ILLINOIS RIVER BASIN	1997
YAKI	YAKIMA RIVER BASIN	1997
YELL	YELLOWSTONE BASIN	1997
CACI	CANADIAN-CIMARRON RIVER BASINS	-
CHEY	CHEYENNE AND BELLE FOURCHE BASINS	-
KANS	KANSAS RIVER BASIN	-
KNTY	KENTUCKY RIVER BASIN	-
NPLT	NORTH PLATTE BASIN	-
UARK	UPPER ARKANSAS RIVER BASIN	-

Background

The Trace Elements National Synthesis Planning Team (TENSPT) was formed in September 1997 to develop and document a national perspective for implementation of trace element studies within the NAWQA Program. The TENSPT met three times: October 20–22, 1997, in Denver, Colorado; January 5–8, 1998, in Menlo Park, California; and March 30–April 2, 1998, in Denver, Colorado. The charter that guided the activities of the TENSPT was refined at the first meeting and is provided in Appendix A. It was officially issued by the Chief, NAWQA Program, on November 21, 1997.

Members of the TENSPT included:

- Dennis A. Wentz, TENSPT Leader, Water Resources Division (WRD), Oregon District, Portland, Oregon (dawentz@usgs.gov),
- William G. Brumbaugh, Environmental Chemist, Biological Resources Division (BRD), Environmental and Contaminants Research Center, Columbia, Missouri (william_brumbaugh@usgs.gov),
- Roger Fujii, Research Chemist, WRD, California District, Sacramento, California (rfujii@usgs.gov),
- Dennis R. Helsel, Trace Elements National Synthesis Project Chief, WRD, Denver, Colorado (dhelsel@usgs.gov),
- Arthur J. Horowitz, Research Chemist, WRD, Atlanta, Georgia (horowitz@usgs.gov),
- Michael T. Koterba, NAWQA Quality Assurance/Quality Control Project Chief, WRD, Baltimore, Maryland (mkoterba@usgs.gov),
- James S. Kuwabara, Hydrologist, WRD, National Research Program (NRP), Menlo Park, California (kuwabara@usgs.gov),
- Richard B. Wanty, Research Chemist, Geologic Division (GD), Denver, Colorado (rwanty@usgs.gov),
- Timothy L. Miller (ex officio member), Chief, NAWQA Program, WRD, Reston, Virginia (tlmiller@usgs.gov), and
- William G. Wilber (ex officio member), National Synthesis Coordinator, NAWQA, WRD, Reston, Virginia (wgwilber@usgs.gov).

Two additional people played key roles as leaders of subgroups that developed plans for specific issues designated by the TENSPT:

- David P. Krabbenhoft, Research Hydrologist, WRD, Wisconsin District, Middleton, Wisconsin (dpkrabbe@usgs.gov), and
- Peter C. Van Metre, Research Hydrologist, WRD, Texas District, Austin, Texas (pcvanmet@usgs.gov).

Finally, there were a number of others who contributed importantly to the development of this document by providing critical thinking and review of concepts. These people include: Carol Couch (WRD, Atlanta, Georgia), Kent Crawford (WRD, Lemoyne, Pennsylvania), Rod DeWeese (BRD, Denver, Colorado), Bob Goldstein (WRD, Mounds View, Minnesota), Marty Gurtz (WRD, Raleigh, North Carolina), Blair Jones (WRD, Reston, Virginia), Sam Luoma (WRD, Menlo Park, California), Tom May (BRD, Columbia, Missouri), Mark Munn (WRD, Tacoma, Washington), Chris Schmitt (BRD, Columbia, Missouri), Terry Short (WRD, Menlo Park, California), Alan Welch (WRD, Carson City, Nevada), and Jim Wiener (BRD, LaCrosse, Wisconsin).

Identification of Issues

After refining the charter, the TENSPT focused its efforts on review and evaluation of important environmental concerns (issues) related to trace elements in ground and surface water systems. Eight such issues were identified. They are (in the order presented at the first meeting):

1. characterization of trace element concentrations in reference areas,
2. effects of urbanization on trace element concentrations,
3. effects of mining and remediation on trace element concentrations,
4. effects of agricultural activities on trace element concentrations,
5. regional occurrence and distribution of mercury concentrations (this was considered as a separate issue largely because of its unique mode of atmospheric transport and because of concerns regarding aquatic ecosystem health),
6. trace element loads to receiving water bodies, such as reservoirs and/or estuaries,
7. exposure of humans to trace elements through consumption of water and fish, and
8. exposure of predatory animals to trace elements through consumption of prey.

The above issues were prioritized on the basis of answers to the following eight questions:

1. Does the issue address problems and/or needs of regional or national importance?
2. Does the issue have a clearly defined user and/or audience?
3. Is the issue a Federal responsibility?
4. Is it appropriate for the NAWQA Program (as opposed to another Federal program) to address the issue?
5. Can the issue be studied within the framework of the NAWQA Program?
6. Is it important to study the issue now (instead of, for example, 10 years from now)?
7. Will study results contribute to an information or data base of lasting value for addressing concerns related to water quality?

8. Will study results enhance the ability of the USGS to conduct future water quality studies?

Based on the above prioritization process, five issues—characterization of reference conditions, effects of urbanization, effects of mining and remediation, regional occurrence and distribution of mercury, and human exposure from consumption of water and fish—separated from the rest sufficiently to consider them within the framework of a national synthesis effort. All issues were rated high with regard to the eight questions listed above. The issues related to agricultural activities, loads to receiving water bodies, and exposure of predatory animals scored lower than the other five issues, primarily because of low ratings with regard to questions 1 (regional or national importance), 2 (clearly defined user and/or audience), and 6 (important to study now, as opposed to later).

The five priority issues were then ranked by the TENSPT on a relative scale. This process yielded three issues of primary importance (reference conditions, urbanization, human exposure) and two issues of secondary importance (mining and remediation, regional occurrence and distribution of mercury). Subgroups were formed to elaborate the individual issues and to develop plans for integrating each into a Trace Elements National Synthesis.

GENERAL CONSIDERATIONS

Detailed plans for the five priority trace element issues are provided under Description of Issues. Prior to presentation of these plans, three general topics—Characterization of Environmental Settings, Trace Elements of Interest, and Data Base Limitations—that are relevant to all issues, are discussed.

Characterization of Environmental Settings

In order to evaluate broad scale effects of land based factors on water quality, one of the first and most important tasks to accomplish is a characterization of important environmental settings (a process referred to as stratification). Previous NAWQA stratification designs typically have been based on ecoregions, geology, and land use (Gilliom and others, 1995). Ecoregions have been useful for characterizing natural environmental settings; however, categorization of land use in relation to human activities has provided the primary basis for studies of nutrients, pesticides, and VOCs. An example of a stratification scheme emphasizing both ecoregions and land use is shown for the Willamette Basin Study Unit (fig. 2). Generalized geology was utilized at the second level of stratification in this design to allow separation of the Willamette Valley ecoregion into two important aquifers (basin fill deposits and the Columbia River Basalt Group) for ground water studies; however, the two land use levels control the details of the stratification design.

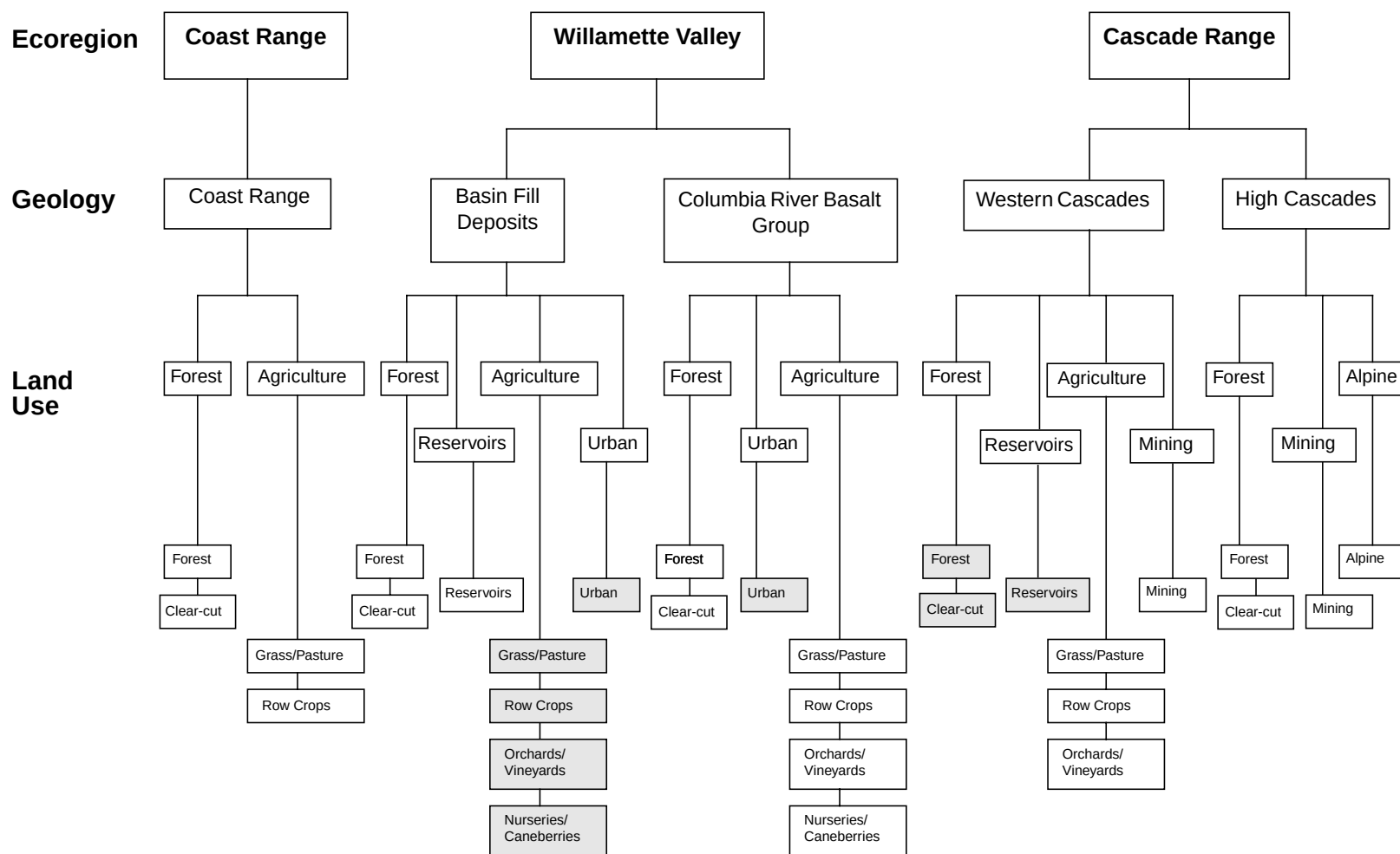


Figure 2. Stratification scheme for the Willamette Basin (most important strata for nutrient and pesticide studies are shaded).

Unlike pesticides and VOCs, which are anthropogenically derived, trace elements occur naturally in geologic materials. In fact, geologic materials are the ultimate sources of all trace elements found in sediment, biota, and water. Human activities simply redistribute trace elements, often at appreciably elevated concentrations. Thus, any stratification scheme for studying trace element concentrations must be driven largely by geology. As an example, a possible alternate approach to stratification of the Willamette Basin, using geology to optimize the design for trace element studies, is shown in figure 3. Using this approach, the most important geologic mapping units would be selected under level three (level two of geology) for study.

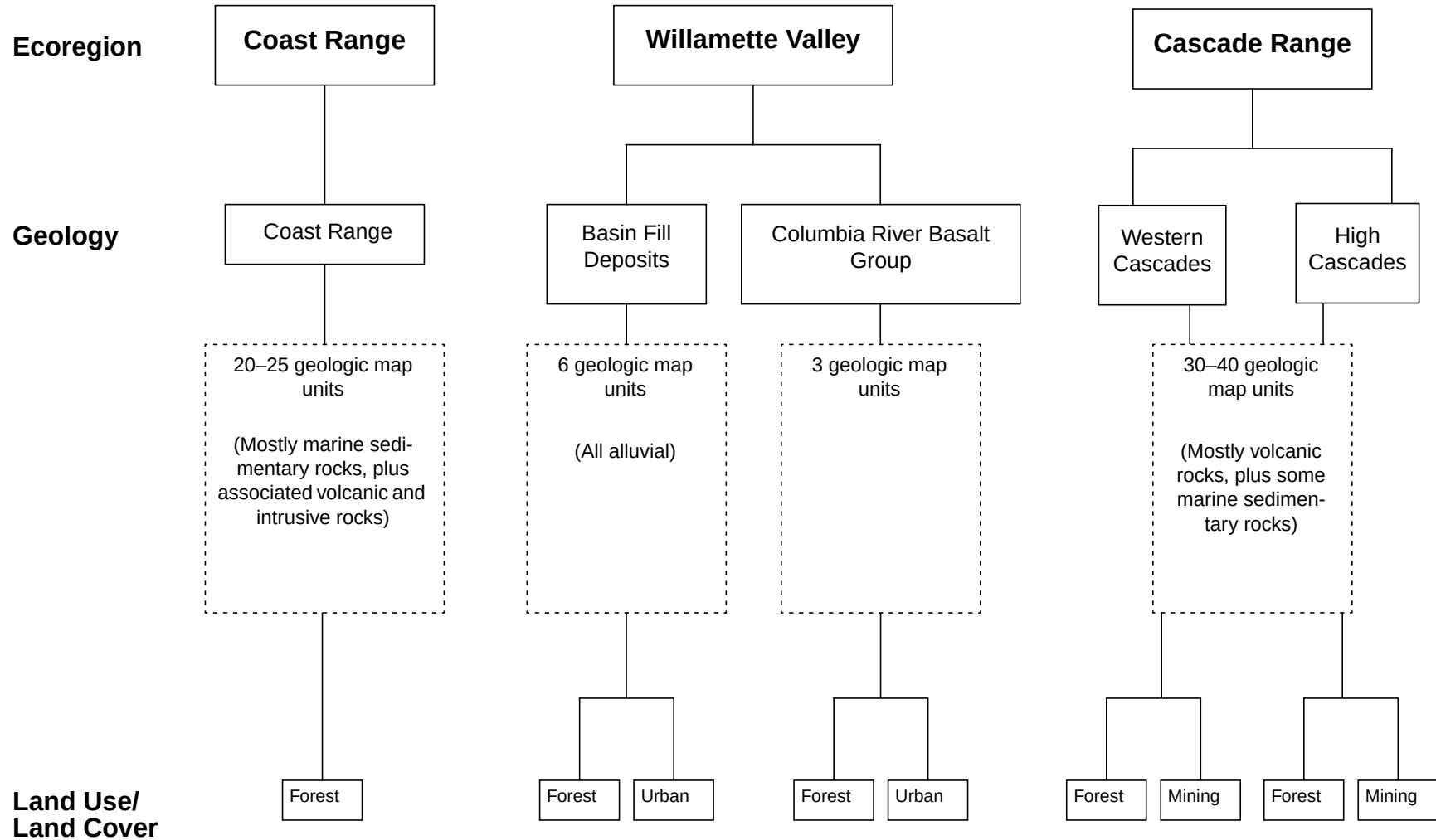


Figure 3. Stratification scheme for characterization of trace elements in the Willamette Basin.

As suggested in figure 3, a major difficulty with using geologic information to drive stratification is that most geologic maps contain a large number of geologic mapping units, many of which contribute similar trace element signatures to water and sediment. Raines and others (1996) have attempted to address this problem by aggregating geologic mapping units into compositionally classified lithologic units based on generally known lithology, mineralogy, and weathering processes. They produced a series of five maps describing subjective levels (low, medium, high) of calcium carbonate, base metals (cadmium, copper, lead, molybdenum, zinc), iron-aluminum-magnesium, potassium, and phosphate for the Pacific Northwest region (California, Idaho, Montana, Nevada, Oregon, Utah, Washington, and Wyoming). Robinson (1997) used a similar approach to aggregate bedrock geologic units of the New England region (Connecticut, Maine, Massachusetts, New Hampshire, New York, Rhode Island, and Vermont) into 26 lithochemical units based on susceptibility to weathering.

Unfortunately, we know of no existing or planned effort to produce a nationally consistent classification of geologic mapping units based on their trace element signatures. Such an effort will be critical for the Trace Elements National Synthesis Team (TEST) to develop and test hypotheses related to national or regional trace element issues. Thus, we recommend that a long-term goal of Trace Elements National Synthesis be to facilitate classification of the geology of the entire United States into a reasonable number of lithochemical units based on trace element associations and their susceptibility to weathering.

Several ongoing GD activities designed to update and refine traditional bedrock geologic maps of the United States (B.R. Johnson, U.S. Geological Survey, oral commun., 1998) could ultimately benefit the stratification design for Trace Elements National Synthesis. However, the only national geologic map likely to be available in the time frame needed for initial Trace Elements National Synthesis planning is that of King and Beikman (1974), which exists in ARC/INFO format (U.S. Geological Survey, modified February 4, 1998). Alaska and Hawaii are not included in this coverage.

Until improved geologic coverages are available, we suggest that the 79 Level III ecoregions described by Omernik (1987) be used as the top level of stratification for trace element studies and that geology be utilized at the second level (see, for example, fig. 3). At the third level of stratification, land uses, such as urbanization and mining, become important considerations. If, as is likely in many instances, ecogregion boundaries follow those for major geologic divisions, this approach will be internally consistent, and it will be consistent with the general approach used previously by most Study Units. It is assumed that Study Units will be reasonably familiar with the geology of their area and will be able to provide information to allow some aggregation of geologic mapping units into lithologically consistent units with regard to trace element composition. The TEST should work closely with Study Units to ensure a maximum level of consistency with regard to these aggregations.

An early effort that the TEST should undertake is a determination of the areal extent of designated environmental settings (specifically, unique combinations of ecoregions and geology) within the United States, within all Study Unit boundaries, and within Study Units containing important urban or mined areas. Knowing the relative ranks of environmental settings within each of these three categories will help determine those settings of primary importance to the NAWQA Program and will enable the TEST to advise Study Units regarding the importance of specific environmental settings when design choices must be made.

Trace Elements of Interest

The TENSPT has designated 25 trace elements that are of interest from a national synthesis perspective (tables 2a and 2b). Most of these had been suggested previously by Hirsch and others (1988) or had been agreed upon by a group of USGS scientists convened in April 1997 to begin preliminary discussions with regard to Trace Elements National Synthesis planning (D. R. Helsel, U.S. Geological Survey, written commun., 1997). Beryllium and thallium were added to the composite list from these two sources because of existing drinking water maximum contaminant levels (MCLs) (U.S. Environmental Protection Agency, 1996); titanium was included because of its utility in interpreting concentrations of other trace elements in bed sediment (Horowitz, 1991).

Table 2a. Trace elements of interest to the National Water-Quality Assessment Program—Bed sediment and tissue

[MRL, method reporting limit; NWQL, National Water Quality Laboratory]

Trace Element ^a	Circular 1021, Table 3 ^b	Trace Elements National Synthesis Meeting (April 1997) ^c	Range of Upper Screening Values for Bed Sediment (in µg/g) ^d	Sediment Probable Effects Levels (in µg/g) ^e	NWQL Bed Sediment Schedule 2400 ^f (MRLs in µg/g)	NWQL Tissue Schedule 2200 ^g (MRLs in µg/g)
Aluminum	X	X	-	-	0.005%	1
Antimony	X	-	200	-	.1	.1
Arsenic	X	X	41.6-700	17.0	.1	.1
Barium	X	X	-	-	1	.1
Beryllium	-	-	-	-	1	.1
Boron	X	X	-	-	-	.2
Cadmium	X	X	4.21-9.60	3.53	.1	.1
Chromium	X	X	160-370	80.0	1	.5
Cobalt	-	X	-	-	1	.1
Copper	X	X	108-1,300	197	1	.5
Iron	X	X	-	-	.005%	1
Lead	X	X	112-660	91.3	4	.1
Manganese	X	X	-	-	4	.1
Mercury	X	X	.70-2.1	.486	.02 ⁱ	n / a ⁱ
Molybdenum	X	X	-	-	2	.1
Nickel	X	X	42.8-51.6	35.9	2	.1
Radium-224 ^h	-	-	-	-	-	-
Radium-226	-	X	-	-	-	-
Radium-228	-	X	-	-	-	-
Radon-222 ^h	X	X	-	-	-	-
Selenium	X	X	-	-	.1	.1
Silver	X	X	1.77-6.1	-	.1	.1
Thallium ^h	-	-	-	-	-	-
Titanium ^h	-	-	-	-	.005%	-
Uranium	-	X	-	-	.05	.1
Vanadium	X	-	-	-	2	.1
Zinc	X	X	271-1,600	315	4	.5

^a Elements in bold are biologically essential (B.F. Jones, U.S. Geological Survey, written commun., 1998; J.S. Kuwabara, U.S. Geological Survey, written commun., 1998; T.M. Short, U.S. Geological Survey, written commun., 1998)

^b Hirsch and others (1988)

^c Preliminary list of trace elements of interest (D. R. Helsel, U.S. Geological Survey, written commun., 1997)

^d Range of values used by the U.S. Environmental Protection Agency (1997) to describe concentrations, above which affects on biota are likely [apparent effects threshold-high (AET-high), Barrick and others (1988); probable effects level (PEL), Florida Department of Environmental Protection (1994); effects range-median (ERM), Long and others (1995)]

^e Environment Canada (1995)

^f Elements shown, plus 25 additional, available from GD, Branch of Geochemistry for \$680

^g Available from NWQL for \$570

^h Radium, radon, and thallium are elements of interest in water (table 2b) but not in bed sediment and tissue; titanium is of interest in bed sediment, but not in water or tissue

ⁱ Total mercury in bed sediment or tissue is available as a separate determination from the Wisconsin District Mercury Research Laboratory for \$100; methyl mercury is available for \$150

**Table 2b. Trace elements of interest to the National Water-Quality Assessment Program—
Water**

[LC, laboratory code; MCL, maximum contaminant level; MRL, method reporting limit; NWQL, National Water Quality Laboratory; WDMRL, Wisconsin District Mercury Research Laboratory]

Trace Element ^a	Circular 1021, Table 3 ^b	Trace Elements National Synthesis Meeting (April 1997) ^c	Guidelines for Protection of Freshwater Aquatic Biota (in µg/L) ^d	Drinking Water MCLs (in µg/L) ^e	Guidelines for Drinking Water ^f	NWQL Filtered Water (shaded cells indicate Schedule 2703 ^g) (MRLs in µg/L)
Aluminum	X	X	-	-	-	1
Antimony	X	-	-	6	5	1
Arsenic	X	X	190	50 ^j	10	1
Barium	X	X	-	2,000	700	1
Beryllium	-	-	-	4	-	1
Boron	X	X	-	(candidate) ^k	300	- ^r
Cadmium	X	X	.37	5	3	1
Chromium	X	X	10 ⁱ	100 ^l	50	1
Cobalt	-	X	-	-	-	1
Copper	X	X	3.5	1,300 ^m	2,000	1
Iron	X	X	-	-	-	10 ^s
Lead	X	X	.54	15 ^m	10	1
Manganese	X	X	-	(candidate) ^k	500	1
Mercury	X	X	.012	2 ⁿ	1 ^q	WDMRL ^t
Molybdenum	X	X	-	-	70	1
Nickel	X	X	49	-	20	1
Radium-224 ^h	-	-	-	5 pCi/L for Ra-226 and Ra-228 combined ^o	-	.1 pCi/L (LC 799) ^u 1 pCi/L (LC 850) ^v
Radium-226	-	X	-		-	
Radium-228	-	X	-		-	
Radon-222 ^h	X	X	-	(pending) ^p	-	26 pCi/L (LC 1369) ^w
Selenium	X	X	5.0	50	10	1
Silver	X	X	.32	-	-	1
Thallium ^h	-	-	-	2	-	- ^r
Titanium ^h	-	-	-	-	-	-
Uranium	-	X	-	(pending) ^o	-	1
Vanadium	X	-	-	(candidate) ^k	-	- ^r
Zinc	X	X	32	-	-	1

^a Elements in bold are biologically essential (B.F. Jones, U.S. Geological Survey, written commun., 1998; J.S. Kuwabara, U.S. Geological Survey, written commun., 1998; T.M. Short, U.S. Geological Survey, written commun., 1998)

^b Hirsch and others (1988)

^c Preliminary list of trace elements of interest (D. R. Helsel, U.S. Geological Survey, written commun., 1997)

^d Telliard (1996); based on dissolved concentrations assuming a hardness of 25 mg/L as CaCO₃, except for mercury and selenium, which are based on total recoverable concentrations because these elements are bioaccumulative (Martha Prothro, U.S. Environmental Protection Agency, written commun., 1993); based on chronic toxicity, except for silver, which is based on acute toxicity because a chronic toxicity guideline is not available

^e U.S. Environmental Protection Agency, 1996; U.S. Environmental Protection Agency, revised August 4, 1998

^f World Health Organization (1993)

^g Available from NWQL for \$291

^h Radium, radon, and thallium are elements of interest in water, but not in bed sediment and tissue; titanium is of interest in bed sediment (table 2a), but not in water or tissue

ⁱ Chromium (VI)

^j Arsenic MCL under review; final MCL to be established by January 2001 (U.S. Environmental Protection Agency, revised July 29, 1998)

^k The trace elements listed on the contaminant candidate list are 3 of 20 contaminants, from which the U.S. Environmental Protection Agency will select 5 or more and determine by August 2001 whether to regulate them (U.S. Environmental Protection Agency, revised April 9, 1998)

^l Total Chromium

^m Copper and lead MCLs under review; final MCLs to be established by fall 1998 (U.S. Environmental Protection Agency, revised August 6, 1998)

ⁿ Inorganic mercury

^o Radium-226/radium-228 MCL under review; uranium MCL to be established; final decisions to be made by November 2000 (U.S. Environmental Protection Agency, revised January 26, 1998)

^p Radon-222 MCL to be established by August 2000 (U.S. Environmental Protection Agency, revised March 3, 1998)

^q Total mercury

^r The potential for incorporating boron, lithium, strontium, thallium, and vanadium into schedule 2703 is being evaluated (Ed Zayhowski, U.S. Geological Survey, written commun., 1998); estimated MRLs are not yet available

^s Included as part of NWQL schedules 2701 (\$169; surface water) and 2750 (\$211; ground water)

^t Available from WDMRL for \$100

^u Available from NWQL for \$173

^v Available from NWQL for \$214

^w Available from NWQL for \$57

Because most of the trace elements recommended for inclusion in a national synthesis effort can occur at environmentally important concentrations in bed sediment, aquatic biota (tissue), and the water column, tables 2a and 2b are organized similarly. The first two columns of both tables show the trace elements recommended by Hirsch and others (1988) and by those who attended the April 1997 planning meeting. The middle columns describe selected published guidelines for environmental trace element concentrations in various media. These guidelines are included to provide some information about concentrations of concern; however, they are not necessarily espoused over other published guidelines. The last column (or two) lists minimum reporting levels for those trace elements included either in standard National Water Quality Laboratory (NWQL) analytical schedules or otherwise available through the NWQL during 1998.

Data Base Limitations

The National Water Information System (NWIS) data base—currently used to store trace element concentrations in water, sediment, and tissue—has a number of limitations with regard to the efficient storage, retrieval, and interpretation of trace element concentrations. For example, codes for distinguishing total and methyl mercury are available for water, but not for sediment or tissue. Aqueous concentrations of specific oxidation states can be stored for only a limited number of trace elements, including chromium III and VI and iron II and III; however, codes for storing concentrations of species, such as arsenic III and V or selenium IV and VI, are not available. Total trace element concentrations in bed sediment can be accommodated, but codes for fractions removed by specific extraction procedures generally are not available. For aquatic biota, organism-specific information, such as taxon, whether a sample consists of one individual or a composite, the number of individuals comprising a composite, and tissue type (whole, fillet, or specific organ), cannot be readily stored. The TENSPT recommends that these data base issues be resolved by the TEST by obtaining the appropriate codes for storing all necessary data as soon as possible.

DESCRIPTION OF ISSUES

The following five sections—Characterization of Reference Conditions, Effects of Urbanization, Human Exposure from Consumption of Water and Fish, Effects of Mining and Remediation, and Regional Occurrence and Distribution of Mercury—provide detailed discussions of the major issues recommended for study within the context of a Trace Elements National Synthesis effort. For ease of comparison, each section is organized similarly. Included are a general description of the issues, brief statements of the questions to be addressed, a discussion of possible approaches to stratification, and specific recommendations regarding work elements to be conducted within each major issue.

A table summarizing highlights of the recommended work elements is included in each section as a focal point for discussion. The work elements are categorized as surface water or ground water (drinking water or fish tissue for the human exposure issue), and they are listed in order of priority, from highest to lowest, within each of the categories. Prioritization of work elements within each of the five major issues was based on scientific value, policy relevance, feasibility, and compatibility with the current NAWQA design. These priorities are relative, rather than absolute. Although it is recognized that resource constraints may not allow all work elements to be conducted during a given 3-year NAWQA high intensity phase (HIP) of data collection or even during a given 10-year cycle of all NAWQA Study Units, it is recommended that all work elements be conducted eventually.

Total costs have been estimated for each work element to provide additional information to help in decision making. Cost estimates include field data collection and processing and laboratory analysis, and they have been adjusted to include indirect charges. Cost estimates are based on the assumptions and information provided in Appendix B. Because of the differences in approaches to cost computations and personnel management among the various USGS offices where Study Unit staff are located, estimated work element costs are not intended to apply directly to any given Study Unit. However, they provide an internally consistent procedure for determining relative costs among work elements.

Following the discussions of the five major trace element issues is a section titled Integration of Issues. It is here that the individual issues are aggregated and considered in a holistic context. Recommendations provided in that section form the basis for the Trace Elements National Synthesis to be conducted as part of the NAWQA Program.

Characterization of Reference Conditions

The reference conditions subgroup consisted of Denny Wentz (subgroup leader), Art Horowitz, Michael Koterba, Jim Kuwabara, and Rich Wanty. In addition, Marty Gurtz (WRD, Raleigh, North Carolina) provided important input to development of this section of the report.

Issues

The primary driving forces behind society's interest in trace element concentrations in reference areas are a desire to better evaluate (1) effects of human activities on the environment, and, conversely, (2) effects of the environment on the human condition. Only by understanding the nature of trace element distributions under relatively pristine conditions can informed decisions be made regarding the impacts of activities, such as urbanization or mining, on water quality. For example, it is important to recognize that trace element concentrations in mineralized, but unmined, areas may be naturally elevated to levels that adversely affect aquatic communities or otherwise impair beneficial uses of streams. Similarly, without a knowledge of background trace element concentrations, it becomes difficult to evaluate the practicality and enforceability of drinking water and aquatic life standards or the effectiveness of proposed remediation strategies.

An unambiguous discussion of reference conditions requires the consistent use of terms that are well defined with regard to perceived levels of human impact. In this report, “reference condition” is a general term used to describe the highest water quality (lowest trace element concentrations) that can be attained in a given environmental setting and against which comparisons can be made to determine impairment of beneficial use, especially from land use changes. Background, minimally impaired, and baseline, but not pristine, reference conditions (see Glossary) are recognized in relation to trace element concentrations in surface and ground water systems. Reference conditions are measured at reference sites, such as a stream cross-section or well, and are inferred to larger hydrologic systems, such as a watershed or aquifer; these larger hydrologic systems are referred to as reference areas.

General Questions

The following general questions were constructed to best represent the recommended issues related to trace element concentrations in reference areas.

1. What are the occurrence and distribution of trace element concentrations in water, bed sediment, and aquatic biota from reference areas located in environmental settings of importance to the NAWQA Program?
2. How do trace element concentrations in a given medium (water, bed sediment, aquatic biota) differ among environmental settings?
 - a. What are the background concentrations characteristic of each environmental setting? Can the natural factors that regulate these concentrations be identified?

- b. How well can background concentrations in geologically heterogeneous reference areas (characterized by more than one environmental setting) be predicted based on measured concentrations in geologically homogeneous areas?
 - c. What spatial patterns over regional or national scales can be distinguished?
 - d. What temporal trends over seasonal, annual, and decadal scales are evident?
3. How do trace element concentrations from urban and mined areas, or from areas with other land uses important to the NAWQA Program, compare with concentrations from reference areas? How do trace element concentrations from undisturbed mineralized areas compare with concentrations from areas having little or no mineralization?
4. How do trace element concentrations from reference areas compare to existing and proposed guidelines for (a) protection of aquatic life, and (b) exposure to humans from drinking water and edible fish? (Answering this question will help to determine if there are areas of the U.S. where current water quality guidelines cannot be attained.)

Stratification

Factors related to the design of trace element studies in reference areas generally are covered under Characterization of Environmental Settings (this report). A few additional guiding principles are presented below.

Environmental settings for evaluating reference conditions are defined as specific combinations of ecoregions and geology. Thus, they are ecoregionally and geologically homogeneous by definition. Land cover in these settings should be natural and stable, with minimal human disturbance. Ideally less than about 5 percent of the area should be impaired by land use related to human activities, and sampling sites should be located as far downgradient as possible from any such activities. All human influences, both recent and historical, should be documented and quantified.

Reference areas should be as similar as possible to areas with which comparisons of trace element concentrations will be made. Surface water reference sites should be located on low order streams, and drainage basin areas should fall in the range of 50–500 km², as recommended by Gilliom and others (1995).

In some Study Units, it may be difficult to find reference areas that satisfy all of the above criteria. In these situations, we recommend that serious consideration be given to locating reference areas outside, but in close proximity to, the Study Unit boundary. Considerable effort may be necessary to find such areas that are representative of important environmental settings found within the Study Unit.

Environmental settings of national importance to the NAWQA Program should receive the highest priority for sampling. Other priorities include regionally important environmental settings and those of importance to specific Study Units.

Recommendations

Summary Table

Six work elements, or data collection activities, were recommended by the reference conditions subgroup for consideration as part of the Trace Elements National Synthesis. They are summarized in table 3. Further details regarding each work element are provided in the following text.

Trace Elements in Streambed Sediment

Evaluation of trace element concentrations in streambed sediment should be the first work element conducted under surface water studies related to characterization of reference conditions. Trace element concentrations in bed sediment are most likely to represent upstream geologic conditions, and the data will allow an early determination of the general adequacy of the selected reference sites for further studies. This work element can be integrated readily into the bed sediment and tissue occurrence and distribution survey described by Gilliom and others (1995) and typically done during summer and autumn low flow preceding the first year of the HIP. By selecting a few additional (reference) sites, or by substituting reference sites for some of the traditional occurrence survey sites, impacts on personnel, time, and fiscal resources should be minimal.

Table 3. Summary table for characterization of reference conditions

[Priority: ***, highest; **, moderate; *, lowest.]

COST^a	WORK ELEMENT^b	QUESTION^c	TRACE ELEMENTS^d	PRIORITY
Surface Water				
\$4,400 (3 sites)	Trace elements in stream-bed sediment	Occurrence and distribution in streambed sediment Determination of background concentrations in important environmental settings Ability to predict concentrations for sites with heterogeneous environmental settings Comparison with urban / mined areas Comparison with guidelines for protection of aquatic life	Schedule 2400, total mercury, methyl mercury	***
\$2,500 (3 sites)	Mercury in fish fillets	Occurrence and distribution in fish fillets Comparison with urban / mined areas Comparison with guidelines for edible fish tissue	Total mercury	**
\$13,100 (3 sites—2 visits each)	Trace elements in surface water	Occurrence and distribution in surface water Range of annual variation in surface water Comparison with urban / mined areas Comparison with guidelines for protection of aquatic life Comparison with drinking water guidelines	Schedule 2703, iron ^e , radium-226 (radium-228 at selected sites)	**
\$3,900 (3 sites)	Trace elements in fish livers	Occurrence and distribution in fish livers Comparison with urban / mined areas	Schedule 2200	*

Table 3. Summary table for characterization of reference conditions—Continued

[Priority: ***, highest; **, moderate; *, lowest.]

COST^a	WORK ELEMENT^b	QUESTION^c	TRACE ELEMENTS^d	PRIORITY
Ground Water				
\$23,200 (30 wells)	Trace elements in the used ground water resource	Occurrence and distribution in used ground water resource Comparison with drinking water guidelines	Schedule 2703, iron ^e , radium-226, radon-222 (radium-228 at selected sites)	***
\$6,800 (5 wells)	Trace elements in shallow ground water	Occurrence and distribution in shallow ground water from reference settings Comparison with urban / mined areas	Schedule 2703, iron ^e , radium-226, radon-222 (radium-228 at selected sites)	*

^a Approximate 1998 fiscal year cost per Study Unit for sample collection, processing, and analysis.^b Listed from highest to lowest priority for surface water components first, then for ground water components.^c See text for detailed statements of questions.^d See tables 2a and 2b for list of trace elements associated with the various schedule numbers.^e Included as part of schedules 2701 and 2750, which typically are analyzed as part of surface water and ground water studies, respectively.

The site selection process for bed sediment and tissue occurrence and distribution surveys previously has been designed to maximize the probability of detecting high concentrations of important constituents from anthropogenic sources. To adequately evaluate trace element concentrations in bed sediment from reference areas, modifications to this design must be included, as discussed under Stratification, p. ____.

Objectives

Objectives of studies of trace elements in streambed sediment from reference areas are to (1) determine background concentrations characteristic of specific environmental settings, (2) allow prediction of concentrations in streams where data have not been collected, (3) provide a basis for evaluating effects on streams draining basins with important land uses, and (4) provide information against which to compare existing and proposed guidelines and remediation strategies for the protection of aquatic life that ingest sediment.

Approach

We recommend that 2–4 reference sites be chosen by each Study Unit (average, 3 per Study Unit) for inclusion in the bed sediment and tissue occurrence and distribution survey. This will ensure that about 45–60 reference sites are sampled during each NAWQA cycle. The actual number of reference sites selected within a given Study Unit will depend on many factors, including the number of important environmental settings represented in the Study Unit, the availability and accessibility of potential sites, the relative importance of reference versus impaired sites, and the funding level of the Study Unit, among others. Sufficient replication to allow quantification of within-setting variability of important environmental settings should be provided.

Reference sites that have existing data and that are part of other networks should be chosen when they meet NAWQA Program guidelines. For example, sites located in experimental watersheds administered by the U.S. Forest Service; sites sampled as part of the U.S. Environmental Protection Agency's (USEPA) Environmental Monitoring and Assessment Program; and sites included in the USGS's Hydrologic Benchmark Network or the National Science Foundation's Long-Term Ecological Research Program are prime candidates. Sites in national parks, national forests (particularly designated wilderness areas), and protected watersheds that provide surface drinking water supplies also are excellent choices. Other organizations or agencies that may be administering programs with protected watersheds include the National Audubon Society, Nature Conservancy, and Agricultural Research Service.

Bed sediment samples for analysis of trace element concentrations from reference sites should be collected following standard NAWQA protocols outlined by Shelton and Capel (1994, rev. 1996) and Gilliom and others (1995). Samples should be analyzed for total trace element concentrations, using NWQL schedule 2400 (table 2a). In addition, a 100-ml subsample of composited wet, but unsieved sediment should be sent to the Wisconsin District Mercury Research Laboratory (WDMRL) for analysis of total and methyl mercury. Results from these analyses will help provide a nationwide perspective of the percentage of total mercury present in bed sediment as the methylated form and will contribute to an understanding of the significance of mercury methylation in the environment.

Mercury in Fish Fillets

Mercury concentrations should be analyzed in fillets from edible fish collected at all sites sampled for analysis of trace elements in streambed sediment. Fillets should be analyzed for total mercury only, as the methylated form of mercury in fish tissue is known to account for 95 to 99 percent of the total mercury concentration (Huckabee and others, 1979; Bloom, 1992). To minimize impacts on Study Unit resources, fish tissue sample collection should be integrated into the bed sediment and tissue occurrence and distribution survey; however, fillets may be frozen and analyzed up to one year after collection. Advantages of delaying analysis of mercury in fish fillets include (1) allowing ample time to evaluate trace element concentrations in other media to provide an assessment of the suitability of the reference sites for continuing studies, and (2) deferring analytical costs to a fiscal year when resources may be more readily available.

Objectives

Objectives of studies of mercury concentrations in fish fillets from reference areas are to (1) document background concentrations, (2) compare concentrations with those in fish collected from streams draining other land uses, and (3) compare concentrations with guidelines for fish consumption by humans.

Approach

A composite sample of five to eight fish should be collected following standard NAWQA protocols outlined by Crawford and Luoma (1993). Fillets should be removed and processed following the general procedures recommended under Sampling and Processing Fish Fillets for Assessment of Risk to Human Health (this report). Resident predator fish species typically eaten by humans are preferred for fillet analysis. Because these fish represent a different trophic level than those typically collected for analysis of trace elements in livers, some additional field effort generally will be required.

Fillet samples should be frozen and stored at -20°C (Crawford and Luoma, 1993) or sent immediately to the WDMRL. Because results from the mercury analyses may suggest that samples be later analyzed for other trace elements or ancillary constituents, we recommend that fillet samples from all fish be archived by storing at -20°C following mercury analysis.

Costs for this work element assume a separate effort for fillet sample collection. If the fish to be processed for analysis of mercury in fillets are collected at the same time as those to be processed for analysis of trace elements in livers, some cost savings will be achieved.

Trace Elements in Surface Water

Filtered trace element concentrations should be determined for stream water obtained from all sites where streambed sediment is collected. Streams should be sampled at least twice (during seasonal low and high flows) to estimate annual concentrations ranges. Shiller and Boyle (1987) note that annual discharge extremes may not be the most important streamflows for characterizing minimum and maximum dissolved trace element concentrations in all rivers; however, these conditions probably provide at least a first approximation to annual concentration ranges for reference streams, where yearly variability is expected to be small. Additional samples may be necessary if variability is high and precise characterization of the environmental setting is important. Low flow samples should be collected as part of bed sediment and tissue occurrence and distribution surveys; collection of high flow samples will require an additional visit to each site.

Objectives

Objectives of studies of trace element concentrations in streams draining reference basins are to (1) document background concentrations, (2) determine the range of annual concentrations, (3) compare concentrations with those in streams draining other land uses, (4) compare concentrations with guidelines for protection of aquatic life, and (5) compare concentrations with drinking water guidelines.

Approach

Collection and processing of surface water samples for trace element analyses should be consistent with guidelines presented by Horowitz and others (1994). In addition, Shelton (1994, rev. 1996) provides NAWQA Program guidelines for collection of stream samples for analysis of organic and inorganic compounds. Samples should be filtered following recommendations given under Filtration of Water Samples (this report).

To provide data for most trace elements with existing USEPA MCLs and for those on the current USEPA contaminant candidate list, stream samples from reference sites should be analyzed for NWQL schedule 2703 (table 2b), schedule 2701 (major cations and anions, including iron), and radium-226. In addition, field measurements of water temperature, pH, specific conductance, alkalinity, and suspended sediment should be made (Shelton, 1994, rev. 1996). Acidity should be measured at mineralized reference sites that are paired with sites located downstream from mined areas.

A separate sample for analysis of radium-228 should be collected and archived. Because radium isotopes in surface water are likely to be important only in areas with uranium and phosphate deposits (Hem, 1985), this sample should be analyzed only if radium-226 is detected. Radium-228 has a half-life of 5.75 years and will lose approximately 1 percent of its activity after 30 days.

Total cost is based on collection and analysis of 2 samples for dissolved trace elements in surface water at each of 3 sites. Analysis of radium-228 would be additional.

Trace Elements in Fish Livers

Analysis of trace elements in fish livers is part of the standard NAWQA design for assessment of water quality occurrence and distribution (Crawford and Luoma, 1993; Gilliom and others, 1995), and it is recommended that this approach be continued by the 1997 Study Units (see Organism and Tissue Type, this report). Trace elements should be analyzed in fish livers collected at all reference sites sampled for streambed sediment. To minimize impacts on Study Unit resources, fish sample collection should be integrated into bed sediment and tissue occurrence and distribution surveys. As with fish fillets, livers may be frozen and analyzed up to one year after collection.

Objectives

Objectives of studies of trace element concentrations in fish livers from reference areas are to document background concentrations and to compare concentrations with those in livers from fish collected from streams draining other land uses.

Approach

Fish should be collected and processed following standard NAWQA protocols outlined by Crawford and Luoma (1993); however, the National Target Taxa (NATT) list given by Crawford and Luoma (1993) and by Gilliom and others (1995) should not be followed. Rather, carp and suckers are considered priority taxa for liver collection because they are bottom feeders and because they are ubiquitous across the continental U.S. (p. ____). Samples should be analyzed for trace element concentrations using NWQL schedule 2200 (table 2a).

Trace Elements in the Used Ground Water Resource

Study Unit (or Subunit) Surveys (SUSs) are intended to evaluate the chemical quality of the most important ground water resources in terms of present and future water use (Gilliom and others, 1995). Because drinking water supply probably is the most critical use considered when designing SUSs, and because SUSs typically consist of existing wells that draw water from some distance below the water table (and, thus, that is somewhat isolated from activities at the land surface), land use effects on quality of ground water from SUS wells are expected to be less than those measured by other NAWQA ground water networks. Therefore, SUSs generally should be useful for evaluating background trace element concentrations associated with the used ground water resource, and we recommend that trace element analyses be included as part of all SUSs.

The actual determination of which SUS wells represent reference conditions will, to some extent, depend on an evaluation of concentrations of all chemical constituents measured in the sampled ground water. For example, ground water with measurable concentrations of pesticides and/or VOCs and with ages of a few years or less could easily be contaminated by anthropogenic trace element sources, whereas ground water with no detectable pesticides or VOCs and with ages of several tens of years or more would be more likely to represent true reference conditions.

Objectives

Objectives of analyzing trace elements in ground water from SUS wells are to document concentrations in the used ground water resource and to compare concentrations with drinking water guidelines.

Approach

The overall design of the SUS, well selection, and sample collection and processing should follow the guidelines presented by Gilliom and others (1995), Lapham and others (1995), and Koterba and others (1995). All samples for trace element analysis should be filtered following recommendations given under Filtration of Water Samples (this report).

All SUS wells should be sampled for trace elements unless there are known contamination issues that would compromise the utility of the data to describe trace element concentrations in ground water from reference areas. Such issues typically are related to the sampling of existing wells, which are commonly used in SUSs. For example, wells constructed of low-grade metal casings or including submersible pumps with metal parts, metal pressure tanks, or water softeners, although suitable for the collection of some types of chemical constituents, generally would be unacceptable for many trace elements.

The age of the water from all SUS wells sampled for trace elements should be established. The chlorofluorocarbon (CFC) technique (Busenberg and Plummer, 1992; Plummer and others, 1993) is recommended. Samples should be collected and analyzed as described in U.S. Geological Survey Office of Water Quality / Office of Ground Water Technical Memorandum 95.02 (1994).

In addition to radon-222 and NWQL schedule 2750 (major cations and anions, including iron), which typically are collected as part of the standard SUS sampling protocol, ground water samples from SUS wells should be analyzed for schedule 2703 and radium-226 (table 2b). This approach will provide data for most trace elements with existing USEPA MCLs and for those on the current USEPA contaminant candidate list. Field measurements of water temperature, pH, specific conductance, and alkalinity should be made, and turbidity should be measured if trace elements are to be analyzed (Koterba and others, 1995). Acidity should be measured at mineralized reference sites that are paired with sites located downgradient from mined areas.

A separate sample for analysis of radium-228 should be collected and archived. Because radium isotopes are likely to be important only in certain deep aquifers or in water associated with uranium and phosphate deposits (Hem, 1985), this sample should be analyzed only if radium-226 is detected.

The total cost for collection and analysis of 30 samples for dissolved trace elements in SUSs does not include the cost of schedule 2750 or radon-222, which normally are determined for all SUS wells as part of the standard NAWQA sampling protocol. Costs for radium-228 also are not included.

Trace Elements in Shallow Ground Water

Land Use Studies (LUSs) are designed to assess the chemical quality of recently recharged (within about the last 10 years) ground water (Gilliom and others, 1995). Studies of trace element concentrations in shallow ground water from reference settings can be integrated into traditional NAWQA LUSs by sampling 5 additional wells in recharge areas under natural land cover (reference wells), or by substituting 5 wells located in such areas for 5 of the 30 wells that normally would be sampled in the land use setting of interest. Reference wells should be located in areas with geologic and hydrologic settings that are similar to those of the land use setting. Ideally, the reference wells should be located beneath natural land cover representative of past conditions in the land use setting, and, if possible, the reference area(s) should be adjacent to the land use setting.

Objectives

The objectives of sampling reference wells as part of LUSs are to document trace element concentrations in ground water beneath reference settings and to compare these concentrations with those from important land use settings of interest to the NAWQA Program.

Approach

As for the SUS, the overall design of the LUS should follow guidelines presented by Gilliom and others (1995). We suggest that 5 reference wells be substituted for 5 land use wells when the total number of wells for a given LUS approaches the optimum of 30, but that an additional 5 reference wells be installed if the number of land use wells approaches the lower limit of 20 recommended by Gilliom and others (1995). This approach will maximize the ability of the LUS to characterize ground water quality in reference settings without sacrificing information on ground water quality in important land use settings.

Reference wells will not necessarily be included in all LUSs. Also, it may be possible to use the same reference wells for more than one LUS, if the geologic and hydrologic settings where reference wells are located are representative of historical conditions for each land use setting of interest. If each Study Unit were to sample 5 reference wells as part of 1 or 2 LUSs, data would be available for 75–150 reference wells during each NAWQA cycle. The TEST and other National Synthesis Teams will provide guidance and coordination for determining which LUSs proposed by Study Units should include associated reference wells.

Selection and installation of LUS reference wells should follow guidelines given by Lapham and others (1995), and sample collection and processing should follow guidelines provided by Koterba and others (1995). Ground water samples to be analyzed for trace elements should be filtered following recommendations given under Filtration of Water Samples (this report); age dating should be done using the CFC technique wherever feasible (see Trace Elements in the Used Ground Water Resource, p. ____).

Ground water samples from reference wells should be analyzed for NWQL schedule 2703, radium-226, and radon-222 (table 2b), in addition to schedule 2750 (major cations and anions, including iron). This approach will provide data for most trace elements with existing USEPA MCLs and for those on the current USEPA contaminant candidate list. Field measurements of water temperature, pH, specific conductance, and alkalinity should be made, and turbidity should be measured if trace elements are to be analyzed (Koterba and others, 1995). Acidity should be measured at mineralized reference sites that are paired with sites located downgradient from mined areas.

A separate sample for analysis of radium-228 should be collected and archived. Because radium isotopes are likely to be important only in certain deep aquifers or in water associated with uranium and phosphate deposits (Hem, 1985), this sample should be analyzed only if radium-226 is detected.

The total cost for collection and analysis of 5 samples for dissolved trace elements in LUSs does not include costs for radium-228 or for NWQL 2750; the latter normally is determined for all LUS wells as part of the standard NAWQA sampling protocol.

Effects of Urbanization

The urbanization subgroup included Pete Van Metre (subgroup leader), Roger Fujii, and Denny Wentz. In addition, Ted Callender (WRD, Reston, Virginia), Terry Short (WRD, Menlo Park, California), and Carol Couch (WRD, Atlanta, Georgia) provided important input to development of this section of the report.

Issues

Of the five major trace element issues selected for study, the issue related to effects of urbanization is somewhat unique. The NAWQA Program has been evaluating various effects of urbanization on water quality since the program's inception (Squillace and others, 1996; Tate and Heiny, 1996; Van Metre and Callender, 1996; 1997b; Kolpin and others, 1998; Lopes and others, 1998; Wentz and others, 1998), and design documents for urban studies in Study Units that began during fiscal year 1994 have been published (Squillace and Price, 1996; Lopes and Price, 1997). In particular, trace elements, organochlorine compounds, and semivolatile compounds typically are analyzed in bed sediment from surface water fixed and synoptic sites (Gilliom and others, 1995), some of which are in urban areas. Except for the organochlorine compounds, a similar analytical schedule is being recommended for future studies of ecological community structure along gradients of urban land use (Cuffney and others, in press). Thus, for consistency with previous and proposed NAWQA studies, two of the work elements discussed in this section recommend collection and analysis of organic compounds in bed sediment, in addition to trace elements.

General Questions

Four general questions should be addressed with regard to trace elements in urban settings:

1. What are the occurrence and distribution of trace element concentrations in bed sediment and aquatic biota along gradients of urban land use in various environmental settings?
2. What long-term trace element trends are evident in sediment from in urban settings?
3. What are the risks posed to humans and biota by anthropogenic releases of trace elements in urban settings?
4. What anthropogenic loads of trace elements are contributed to streams and receiving water bodies from urban areas?

Occurrence, distribution, and trends are fundamental building blocks of the NAWQA design and are a necessary first step toward understanding sources and cause-effect relationships. Risks to humans and biota are major underlying reasons for most interest in occurrence and distribution of contaminants in the environment. In areas where occurrence, distribution, and trends are well understood, and where risks to (or effects on) humans or aquatic biota have been identified, an evaluation of trace element loads is a logical next step to help to evaluate the magnitude and variability of source contributions.

To answer questions 1, 2, and 3, a combination of sediment coring in reservoirs and lakes, and synoptic surveys of bed sediment and fish tissue in streams is proposed. Sediment coring currently (1998) is underway in selected major urban areas of the U.S. (Van Metre and Callender, 1997a), and synoptic surveys are proposed for the same urban areas. The synoptic surveys would be similar to current NAWQA bed sediment and tissue studies, which measure hydrophobic organic compounds and total trace elements, but they also would include analyses of extractable metals in bed sediment. Results from these studies could be used to help evaluate risks to aquatic biota in surface waters. Occurrence in shallow ground water and risks posed to people from drinking ground water containing high concentrations of trace elements would be addressed by including trace element analyses as part of urban LUSs.

Stratification

The stratification presented here attempts to account for the major environmental variables that could affect three groups of hydrophobic or particle reactive contaminants in urban aquatic systems: trace elements, organochlorine compounds (including chlorinated pesticides and polychlorinated biphenyls or PCBs), and polycyclic aromatic hydrocarbons (PAHs). Several major environmental variables have been identified that relate to the occurrence, distribution, and trends of trace elements and hydrophobic organic compounds in urban streams and lakes. These variables include the density and age of urbanization, urban land use type (commercial, residential, industrial), use and release history of trace elements or hydrophobic organic compounds, physiographic setting, climate, and hydrologic conditions. At the national scale, two environmental variables are used for stratification. The first is climate, following the approach of Lopes and Price (1997). They based a national stratification of urban sites on climate because it captures much of the hydrologic and regional variability of the country. The second variable is ecoregion as delineated by Omernik (1987). Ecoregions incorporate much of the physiographic variability (including geology) that can be important for understanding trace element background concentrations.

Lopes and Price (1997) used mean annual precipitation, snowfall, and temperature in a cluster analysis to group 268 metropolitan statistical areas (MSAs) (U.S. Bureau of the Census, 1994) with populations over 50,000 into 17 different climatic settings.

[Lopes and Price (1997) note that “An MSA is a geographic area that may include several counties and is comprised of a large population nucleus and adjacent communities that have a high degree of economic and social integration with that nucleus; not all cities with a population greater than 50,000 are considered MSAs.”] For each climatic setting, those MSAs within NAWQA Study Units and with populations over 250,000 were identified. An additional step applied here is to overlay these MSAs with ecoregions delineated by Omernik (1987).

Based on a combination of climatic settings, ecoregions, population, and NAWQA Study Units, 13 urban areas are recommended for sampling (tables 4 and 5). The areas recommended have the following characteristics:

1. They represent each of the climatic settings that contain a large portion of the urban population of the U.S. (table 4). At least one urban area from each climatic setting that contains more than 1 percent of the U.S. population (see Lopes and Price, 1997; figure 4) was selected.
2. They represent most of the ecoregions that contain a large portion of the urban population of the U.S. (table 5). The five ecoregions with the largest total MSA populations

Table 4. Metropolitan Statistical Areas in NAWQA study units, listed by climatic setting
[Shaded areas are proposed for sediment coring studies and for bed sediment and tissue synoptic studies.]

Metropolitan Statistical Area ¹	Climatic Setting (Lopes and Price, 1997)	Population in 1992	Ecoregion (Omernik, 1987)	Number of Coring Sites Sam- pled as of 1998 (Pro- posed Sites in Paren- theses)	NAWQA Study Unit ²
Los Angeles-Riverside-Orange Co, CA	4	15,047,770	SOUTHERN AND CENTRAL CA PLAINS AND HILLS	(3)	SANA
Phoenix-Mesa, AZ	4	2,330,353	SOUTHERN BASIN AND RANGE		CAZB
Sacramento-Yolo, CA	4	1,563,374	CENTRAL CA VALLEY		SACR
Las Vegas, NV-AZ	4	971,169	SOUTHERN BASIN AND RANGE	2	NVBR
Denver-Boulder-Greeley, CO	6	2,089,321	WESTERN HIGH PLAINS	2	SPLT
Salt Lake City-Ogden, UT	6	1,128,121	WASATCH AND UINTA MOUNTAINS	3	GRSL
Dallas-Fort Worth, TX	9	4,214,532	TEXAS BLACKLAND PRAIRIES	2	TRIN
San Antonio, TX	9	1,378,619	TEXAS BLACKLAND PRAIRIES	1	SCTX
Oklahoma City, OK	9	983,612	CENTRAL OKLAHOMA / TEXAS PLAINS		CACI
Austin-San Marcos, TX	9	901,048	CENTRAL TEXAS PLATEAU		SCTX
Chicago-Gary-Kenosha, IL-IN-WI	11	8,410,402	CENTRAL CORN BELT PLAINS	(3)	UIRB
Detroit-Ann Arbor-Flint, MI	11	5,245,906	S MICHIGAN / N INDIANA TILL PLAINS	2	LERI
Minneapolis-St. Paul, MN-WI	11	2,617,973	NORTH CENTRAL HARDWOOD FORESTS	3	UMIS

Table 4. Metropolitan Statistical Areas in NAWQA study units, listed by climatic setting—Continued
[Shaded areas are proposed for sediment coring studies and for bed sediment and tissue synoptic studies.]

Metropolitan Statistical Area ¹	Climatic Setting (Lopes and Price, 1997)	Population in 1992	Ecoregion (Omernik, 1987)	Number of Coring Sites Sam- pled as of 1998 (Pro- posed Sites in Paren- theses)	NAWQA Study Unit ²
Pittsburgh, PA	11	2,406,452	WESTERN ALLEGHENY PLATEAU		ALMN
Milwaukee-Racine, WI	11	1,629,420	SOUTHEASTERN WISCONSIN TILL PLAINS		UIRB
Hartford, CT	11	1,121,462	NORTHEASTERN COASTAL ZONE		CONN
New York-Northern New Jersey-Long Island, NY-NJ-CT-PA	15	17,951,400	NORTHEASTERN COASTAL ZONE	4	LINJ
Philadelphia-Wilmington-Atlantic City, PA-NJ-DE-MD	15	5,938,528	NORTHERN PIEDMONT		DELR
Washington-Baltimore, DC-MD-VA-WV	15	6,919,572	NORTHERN PIEDMONT	2	POTO
Seattle-Tacoma-Bremerton, WA	15	3,131,392	PUGET LOWLAND	3	PUGT
Cincinnati-Hamilton, OH-KY-IN	15	1,865,002	INTERIOR PLATEAU		MIAM
Bridgeport, CT (NECMA)	15	1,629,789	NORTHEASTERN COASTAL ZONE		CONN
Kansas City, MO-KS	15	1,616,930	CENTRAL IRREGULAR PLAINS		KANS
Indianapolis, IN	15	1,424,050	EASTERN CORN BELT PLAINS		WHIT
Dayton-Springfield, OH	15	961,547	EASTERN CORN BELT PLAINS		MIAM
Boston, MA-NH (NECMA)	16	5,669,802	NORTHEASTERN COASTAL ZONE	(3)	NECB

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Table 4. Metropolitan Statistical Areas in NAWQA study units, listed by climatic setting—Continued
[Shaded areas are proposed for sediment coring studies and for bed sediment and tissue synoptic studies.]

Metropolitan Statistical Area ¹	Climatic Setting (Lopes and Price, 1997)	Population in 1992	Ecoregion (Omernik, 1987)	Number of Coring Sites Sam- pled as of 1998 (Pro- posed Sites in Paren- theses)	NAWQA Study Unit ²
Cleveland-Akron, OH	16	2,890,402	ERIE / ONTARIO LAKE PLAIN		LERI
Providence-Fall River-Warwick, RI-MA (NECMA)	16	914,627	NORTHEASTERN COASTAL ZONE		NECB
Albany-Schenectady-Troy, NY	16	872,290	NORTHERN APPALACHIAN PLA- TEAU AND UPLANDS		HDSN
Miami-Fort Lauderdale, FL	17	3,309,246	SOUTHERN FLORIDA COASTAL PLAIN		SOFL
Atlanta, GA	17	3,142,857	SOUTHEASTERN PLAINS	2 (2)	ACFB
Tampa-St. Petersburg-Clearwater, FL	17	2,107,271	SOUTHERN COASTAL PLAIN		GAFL
Orlando, FL	17	1,304,700	SOUTHERN COASTAL PLAIN	(2)	GAFL
Charlotte-Gastonia-Rock Hill, NC-SC	17	1,212,393	SOUTHEASTERN PLAINS		SANT
Jacksonville, FL	17	952,566	SOUTHERN COASTAL PLAIN		GAFL
Raleigh-Durham-Chapel Hill, NC	17	909,232	SOUTHEASTERN PLAINS		ALBE
West Palm Beach-Boca Raton, FL	17	900,655	SOUTHERN FLORIDA COASTAL PLAIN		SOFL
Birmingham, AL	17	858,531	SOUTHWESTERN APPALACHIANS		MOBL

¹Metropolitan Statistical Areas shown are those within NAWQA Study Units and with 1992 populations greater than 850,000.

²See table 1 for Study Unit names; see figure 1 for Study Unit locations.

Table 5. Ecoregions with Metropolitan Statistical Areas (MSAs) located in NAWQA Study Units, listed by total ecoregion population
[Shaded entries are proposed for sediment coring studies and for bed sediment and tissue synoptic studies.]

Ecoregion ¹ (Omernik, 1987)	Number of MSAs within Ecoregion	Total Population of MSAs	Number of Coring Sites Sampled as of 1998 (Pro- posed sites in parenthe- ses)	Urban Area(s) Proposed for Sampling
NORTHEASTERN COASTAL ZONE	11	28,818,556	4 (3)	New York, NY Boston, MA
SOUTHERN AND CENTRAL CA PLAINS AND HILLS	6	24,805,194	(3)	Los Angeles, CA
NORTHERN PIEDMONT	8	15,327,870	2	Washington, D.C.
SOUTHEASTERN PLAINS	27	12,957,263	2(2)	Atlanta, GA
CENTRAL CORN BELT PLAINS	8	9,962,180	3	Chicago, IL
ERIE / ONTARIO LAKE PLAIN	10	7,818,656		
S MICHIGAN / N INDIANA TILL PLAINS	7	7,555,589	2	
SOUTHERN COASTAL PLAIN	12	6,832,027	(2)	Orlando, FL
TEXAS BLACKLAND PRAIRIES	3	5,784,711	2	Dallas, TX
SOUTHERN FLORIDA COASTAL PLAIN	6	5,417,645		
WESTERN GULF COASTAL PLAIN	6	5,295,443		
INTERIOR PLATEAU	9	5,143,568		
CENTRAL CA VALLEY	9	4,693,893		
EASTERN CORN BELT PLAINS	7	4,626,717		
SOUTHERN BASIN AND RANGE	4	4,109,262	2	Las Vegas, NV
WESTERN ALLEGHENY PLATEAU	6	3,399,501		
PUGET LOWLAND	2	3,269,305	3	Seattle, WA
INTERIOR RIVER LOWLAND	4	3,038,943		

Table 5. Ecoregions with Metropolitan Statistical Areas (MSAs) located in NAWQA Study Units, listed by total ecoregion population—Continued
[Shaded entries are proposed for sediment coring studies and for bed sediment and tissue synoptic studies.]

Ecoregion ¹ (Omernik, 1987)	Number of MSAs within Ecoregion	Total Population of MSAs	Number of Coring Sites Sampled as of 1998 (Pro- posed sites in parenthe- ses)	Urban Area(s) Proposed for Sampling
NORTH CENTRAL HARDWOOD FORESTS	4	3,028,601	3	Minneapolis, MN
WESTERN HIGH PLAINS	6	3,012,947	2	Denver, CO
MIDDLE ATLANTIC COASTAL PLAIN	7	2,833,341		
SOUTHEASTERN WISCONSIN TILL PLAINS	6	2,782,808		
WESTERN CORN BELT PLAINS	9	2,262,047		
CENTRAL IRREGULAR PLAINS	6	2,217,277		
WILLAMETTE VALLEY	2	2,187,761		
MISSISSIPPI VALLEY LOESS PLAINS	3	1,924,191		
CENTRAL APPALACHIAN RIDGES AND VALLEYS	8	1,890,537		
CENTRAL OKLAHOMA / TEXAS PLAINS	3	1,810,284		
NORTHERN APPALACHIAN PLA- TEAU AND UPLANDS	6	1,677,159		
MISSISSIPPI ALLUVIAL PLAIN	2	1,489,216		
WASATCH AND UINTA MOUNTAINS	2	1,403,187	3	Salt Lake City, UT
SOUTHWESTERN APPALACHIANS	2	1,264,082		
SOUTH CENTRAL PLAINS	7	1,207,842		
HURON / ERIE LAKE PLAIN	3	1,174,028		
CENTRAL TEXAS PLATEAU	2	1,155,909		
CENTRAL GREAT PLAINS	6	1,025,789		

¹Ecoregions shown are those with total populations greater than 1,000,000.

are represented by at least one urban area in each; two urban areas are located in the ecoregion with the largest MSA population.

3. They represent the large-scale geographic diversity of the country. Some smaller urban areas—for example, Las Vegas, Salt Lake City, Orlando, and Minneapolis—are therefore included instead of some larger eastern (for example, Philadelphia) and southern (for example, Miami) cities (table 5).

Reservoir or lake coring has been conducted (as of 1998) or is proposed for each of the 13 urban areas selected for study. The numbers of coring sites sampled or proposed for sampling are listed in tables 4 and 5.

Recommendations

Summary Table

Four work elements related to trace element studies in urban areas were recommended by the urbanization subgroup. They are summarized in table 6 and are discussed in detail below.

Table 6. Summary table for effects of urbanization

[Priority: ***, highest; **, moderate; *, lowest; NWQL, National Water Quality Laboratory]

COST^a	WORK ELEMENT^b	QUESTION^c	TRACE ELEMENTS^d	PRIORITY
Surface Water				
^e	Reconstructed trends in hydrophobic contaminants using sediment cores	Variations of trace elements and hydrophobic organic compounds in bed sediment as a function of time and urban land use changes Rates of accumulation of trace elements and hydrophobic organic compounds in urban watersheds	NRP schedule similar to schedule 2400; NWQL LC8375 (organochlorine compounds and PAHs)	***
\$110,000 (30 sites)	Synoptic studies of hydrophobic contaminants in bed sediment and tissue along urban gradients	Occurrence and distribution of trace elements in bed sediment and tissue and hydrophobic organic compounds in bed sediment along urban gradients Biological effects of trace elements and hydrophobic organic compounds in urban streams Identification of urban settings where contaminants are major factors in biological health	Schedule 2400, total mercury, methyl mercury; acid volatile sulfide—simultaneously extracted metals; NWQL LC8375; schedule 2200	**
\$33,000 (1 site)	Trace element loads at urban intensive fixed sites	Loads and yields of trace elements from urban areas Anthropogenic contributions to trace element loads Relationships between trace element loads and occurrence, distribution, and rates of accumulation in downstream receiving water bodies	NRP schedule similar to schedule 2400	*

Table 6. Summary table for effects of urbanization—Continued
 [Priority: ***, highest; **, moderate; *, lowest; NWQL, National Water Quality Laboratory]

COST^a	WORK ELEMENT^b	QUESTION^c	TRACE ELEMENTS^d	PRIORITY
Ground Water				
\$30,000 (30 wells)	Trace elements in shallow urban ground water	Occurrence and distribution of trace elements in shallow ground water from urban areas Potential health risks from urban sources of trace elements in drinking water?	Schedule 2703, iron ^f , radium-226 (total mercury, radium-228 at selected sites)	*

^a Approximate 1998 fiscal year cost per Study Unit for sample collection, processing, and analysis.

^b Listed from highest to lowest priority for surface water components first, then for ground water components.

^c See text for detailed statements of questions.

^d See tables 2a and 2b for list of trace elements associated with the various schedule numbers.

Cost per lake or reservoir is \$21,000–\$35,000, depending on number of lakes sampled per trip, age of lake (affects number of samples per core), and land use setting (reference lakes/reservoirs require fewer samples); costs would likely be to the Trace Elements National Synthesis Team, rather than to Study Units.

Included as part of schedule 2750, which typically is analyzed as part of ground water studies.

Reconstructed Trends in Hydrophobic Contaminants using Sediment Cores

A nationwide NAWQA study using reservoir and lake sediment cores to evaluate historical trends of hydrophobic contaminants has been underway since 1992 (VanMetre and Callender, 1997a). The pilot study (1992-96) used paleolimnological techniques to describe natural and anthropogenic changes to water quality in reservoir drainage basins (Van Metre and Callender, 1996; 1997b). Techniques used include radiochemical dating of sediment cores; analysis of major, minor, and trace elements, chlorinated organic compounds, and PAHs; and interpretation of various sedimentological and geomorphic properties of cores. In one setting, historical changes in diatoms and pollen also were evaluated (Bradbury and Van Metre, 1997). Full implementation of the Reconstructed Trends National Synthesis study began in fiscal year 1997.

Objectives

The two primary objectives of the Reconstructed Trends National Synthesis study and of the work element recommended here are to (1) identify trends, or lack of trends, in surface water for hydrophobic, particle reactive constituents (including trace elements, hydrophobic organic compounds, and, to some extent, nutrients), and (2) characterize relationships between contaminant trends and major land uses, including urban, agricultural, and, to a limited extent, mined lands. Other goals of the present work element are to determine rates of accumulation of trace elements and hydrophobic organic compounds in urban watersheds (for example, regional atmospheric versus local fluvial sources), to identify major sources of these contaminants in urban watersheds, and to evaluate effects of regional scale pollution controls.

Approach

Several minor adjustments were made to the originally proposed urban areas selected for study of reconstructed trends in order to make them consistent with the national scale stratification described above. Urban reservoirs and lakes have been, or will be, sampled in 17 urban areas across the U.S., including 2 or more lakes or reservoirs in each of the 13 areas identified in tables 4 and 5, 2 sites in Detroit-Ann Arbor, and 1 site each in San Antonio, Anchorage, and San Diego.

Ideally, reservoirs sampled will have been constructed before about 1960, will not have been dredged or drained, and will have a defined contributing drainage where land use is known over time. Reservoirs that are part of water supply diversion and transfer networks will be avoided: this can be a particular problem in the West, where water diversions from other drainages commonly are routed through reservoirs. Where natural lakes are sampled (Minneapolis and Seattle, to date), lakes with larger ratios of drainage area to lake surface area are preferred over lakes with smaller ratios. Larger ratios lend several advantages to coring studies, including a better chance for dominance of fluvial inputs over direct atmospheric inputs, and higher sedimentation rates (Van Metre and others, 1997).

Within each urban area, two or three reservoirs or lakes typically will be selected to characterize suburban and older urban contaminant sources and atmospheric reference conditions. Conceptually, old urban sources are represented by residential and light commercial land uses that were developed prior to about 1950. These watersheds may contain high population density areas, such as row houses or apartments, and they may be served by mass transit systems. Old urban areas make up a large part of many major urban areas and can have distinctly different contaminant histories than newly urbanizing areas. Suburban sources, in contrast, are represented by basins dominated by residential and commercial land uses that were developed after about 1950 and are typified by the suburban sprawl surrounding many cities. Many of these watersheds contain considerable nonurban land.

Urban indicator sites (in this case, lakes or reservoirs) ideally will drain small basins (10–100 km²) with homogeneous land use and represent a range in population densities. Industrial areas and point sources of contaminants will be avoided for urban indicator sites. However, in some cases, urban integrator sites, which generally drain considerably larger areas (10–100 percent of the Study Unit) and are influenced by upstream industrial land use and point sources, will be sampled instead of, or in addition to, older urban indicator sites.

Atmospheric contaminant transport is especially important in urban areas with poor air quality, and reference lakes and reservoirs are therefore selected to characterize local atmospheric inputs to watersheds in or near major urban areas (Callender and Van Metre, 1997; Van Metre and others, 1997). Contaminants, such as lead, mercury, PAHs, and PCBs, can be transported by short and long range atmospheric pathways from sources ranging from cars to power plants. Determining the source of a particular contaminant (local runoff versus regional atmospheric pollution) requires a good understanding of regional levels of atmospheric fallout.

Synoptic Studies of Hydrophobic Contaminants in Bed Sediment and Tissue Along Urban Gradients

The occurrence and distribution of trace elements in bed sediment as a function of gradients in urban land use, and the associations between urban trace element concentrations and biological exposure and accumulation, are not well known (Cuffney and others, in press). In order to refine these relationships, synoptic surveys of bed sediment and tissue must be designed to provide statistical power at the Study Unit level. This recommendation affects design considerations at both the national scale (how many and which urban areas to sample) and the local scale (how many and what types of sites to sample). Greater numbers of samples than the 15–20 currently collected to assess occurrence and distribution are necessary at the Study Unit level because variability in concentrations of contaminants among urban areas can be large. This variability can greatly complicate or preclude development of statistical relationships between anthropogenic factors and water quality when samples from multiple urban areas are combined nationwide.

Objectives

Specific objectives of this work element are to (1) determine how trace element concentrations in bed sediment and tissue, and concentrations of hydrophobic organic compounds in bed sediment, vary locally (along urban gradients), regionally, and nationally, (2) define the relationships between biological exposure and concentrations of trace elements and hydrophobic organic compounds in bed sediment in urban streams, and (3) document urban settings where trace elements and hydrophobic organic compounds are a major factor in biological health or risk. Results from this work element also may help to identify major sources of trace elements and hydrophobic organic compounds to urban streams and evaluate effects of regional scale pollution controls.

Approach

The synoptic approach presented here is consistent with that proposed by the Ecological Synthesis Planning Team (ESPT) (Cuffney and others, in press) for ecological studies along urban gradients. The approach will yield statistically large numbers of samples (about 30 sites) in each of the 13 major urban areas (tables 4 and 5). Site selection in each urban area should target a range in density or intensity of urban land use, from reference basins (10–20 percent of sites) to dense commercial/residential basins. A few industrial indicator sites and urban integrator sites, including receiving water bodies, could be sampled.

It should be recognized that factors not easily captured by a single urban density variable could affect the occurrence and distribution of contaminants in urban settings. These factors include the age of development, previous land use, and type of urban development. For these reasons, site selection should be made with at least two data analysis approaches in mind, namely relationships between contaminant occurrence and distribution and (1) continuous land use gradients (for example, population density or percent impervious cover) or (2) land use class variables (for example, residential, commercial, or industrial categories).

Site selection should be performed by the Study Unit in consultation with the ESPT, TEST, and other national synthesis teams. Basins selected should:

1. cover a range in population densities, major land use classes, and ages of development;
2. have drainage areas of about 10–100 km²;
3. allow sampling of continuously or nearly continuously flowing streams; and
4. include some receiving water bodies (lakes, reservoirs, bays, estuaries).

Sampling should follow standard NAWQA protocols for bed sediment (Shelton and Capel, 1994, rev. 1996) and tissue (Crawford and Luoma, 1993). At about 30 sites in each urban area, bed sediment should be analyzed for total trace element concentrations (NWQL schedule 2400, table 2a) and for concentrations of selected metals with known urban sources and biological impacts using the acid volatile sulfide-simultaneously extracted metals (AVS-SEM) technique (see Extraction of Bed Sediment, this report). In addition, bed sediment should be analyzed for organochlorine compounds in selected urban areas (where high concentrations are known to occur based on historical data) and for PAHs in all urban areas (NWQL laboratory code 8375). Trace elements should be analyzed in fish livers from all sites (schedule 2200).

Because of the resource intensive nature of the proposed urban gradient studies, we recommend that pilot investigations be done during fiscal year 1999 in two of the Study Units that began in fiscal year 1997. The pilot investigations will allow an evaluation of the ability of such studies to discern variations in total and extractable trace elements and (total) hydrophobic organic compounds in bed sediment and aquatic biota, variations in ecological responses, and relationships among the various concentrations and responses.

Selection of Study Units for participation in the urban gradient pilot studies should be done in conjunction with the ESPT, TEST, and other national synthesis teams. Four of the 8 Study Units recommended by the ESPT for consideration for these studies (Cuffney and others, in press) also are included in the group of 13 Study Units recommended by the TENSPT (tables 4 and 5). These four Study Units (GRSL, NECB, SANA, and UIRB) represent the best opportunities for integration of objectives related to studies of trace elements, hydrophobic organic compounds, and aquatic ecology.

Trace Element Loads at Urban Intensive Fixed Sites

Accurate quantification of trace element loads in urban streams will require event based sampling of both suspended sediment and filtered water. Typically, the mass of trace elements in the suspended phase is much greater than in the filtered phase (Horowitz, 1995; Garbarino and others, 1995). At relatively low suspended sediment concentrations, however, a significant portion of the trace element load can still be transported in the filtered phase (Garbarino and others, 1995). Therefore, concentrations of trace elements in both phases must be sampled and analyzed.

Objectives

The objectives of this work element are to (1) determine loads (and yields) of trace elements in urban streams, (2) evaluate anthropogenic contributions to trace element loads, and (3) determine relationships between trace element loads and the occurrence, distribution, and accumulation of trace elements in bed sediment and aquatic biota in downstream receiving water bodies.

This work element is recommended for urban areas where (1) there is a good understanding of the occurrence and distribution of trace elements in bed sediment and aquatic biota, (2) there is a good understanding of trace element trends, and (3) the occurrence, distribution, and trends suggest that concerns (or risks) for the health of humans or biota are posed by anthropogenic contributions of trace elements.

Approach

Large temporal and flow-related variations in suspended sediment concentrations in streams complicate the computation of accurate trace element loads. An important consideration in sampling design, however, is that variations in concentrations of trace elements per gram of sediment, at least in larger rivers (Graf and others, 1996; A.J. Horowitz, USGS, oral commun., 1998), appear to be small. For example, concentrations of dissolved and suspended trace elements were determined for 57 streamflow samples from 9 sites in New Mexico and Arizona in and near the Puerco River. Concentrations of suspended sediment varied more than an order of magnitude; however, concentrations of radium, thorium, and uranium in the suspended sediment varied by a factor of two or less; and, coefficients of variation for chromium, copper, and lead ranged from 10 to 20 percent (data from Graf and others, 1996). Because of the large variability but small analytical cost associated with suspended sediment concentrations, and the small variability but large analytical cost associated with trace element concentrations in the suspended sediment, a sampling strategy was adopted for the Puerco River study that measured suspended sediment concentrations frequently (discrete samples over storm events) and trace element concentrations in suspended sediment infrequently (composite samples over storm event). It is recommended that the same strategy be evaluated for its applicability to the present work element.

Site selection would follow guidelines used to select urban intensive fixed sites (Gilliom and others, 1995; Lopes and Price, 1997). Sites located upstream from reservoir or lake coring sites are preferred. This pairing of load sites with sites for determining trends from lake cores will allow several valuable comparisons, including (1) concentrations in suspended sediment in streams with those in recently deposited sediment in receiving water bodies, and (2) loads (and yields) in streams with accumulation rates in lake and reservoir sediment cores. Because of associated costs and labor, only one or two urban load sites would be monitored in a given urban area. Each urban area will require a reference site in order to estimate the anthropogenic component of the trace element loads from local fluvial sources. Depending on the relationship between the stream network and the pattern of urbanization, the reference site could either be a paired watershed in a similar geologic setting or a site upstream on the same stream as the urban site.

Collection and processing of filtered phase samples will be accomplished using existing NAWQA protocols. The two most likely approaches for collecting suspended sediment for chemical analysis are centrifugation and filtration. The USGS National Stream Quality Accounting Network (NASQAN) Program (Hooper and others, 1997) uses centrifugation. This procedure has the advantages of high sediment recoveries (80–98 percent) and simple field protocols for collection of large volumes of whole water, which are shipped to the laboratory for further processing (Horowitz and others, 1989). One disadvantage of the procedure is the need to estimate the suspended sediment concentration of the sample so that the appropriate amount of water can be collected. The second approach for sampling suspended sediment employs filtration of large volumes of water (200 L) through 0.5-micrometer teflon filters (P.C. VanMetre, U.S. Geological Survey, oral commun., 1998). The sediment is washed from the membranes and freeze dried prior to chemical analysis. Advantages of the filtration approach are reasonable sediment recoveries (mean, 80 percent for 10 samples), faster separation of the phases than for centrifugation, and no need for prior knowledge of suspended sediment concentrations. One disadvantage of filtration is a more time consuming and complicated on-site protocol than for centrifugation. Either or both of these methods could be used by the NAWQA Program.

Because much of the trace element load in urban settings is likely to be transported on sediment and because much of the sediment movement occurs during storms, most of the sampling at urban sites should be event based. The design that yields the cost estimate shown in table 6 is for trace element analysis of 12 samples collected over a 1-year period; 6 samples would be collected bi-monthly, and 6 would be collected during storm events. More frequent samples would be collected for analysis of suspended sediment. Because of the assumed smaller variability in the concentrations of trace elements per unit mass of suspended sediment at reference sites, only six samples would be collected per year. Again, these samples would be supplemented by more frequent sampling for suspended sediment.

Trace Elements in Shallow Urban Ground Water

Trace element concentrations in water from urban LUS wells could fill an important data gap with regard to drinking water. Water providers are mandated by the USEPA and the States to measure concentrations of priority pollutants in finished drinking water supplies, and there are efforts in some States to evaluate source water supplies. These efforts are directed at public water suppliers, thus covering most surface water supplies and large ground water supplies; however, they generally miss individual home owners with private wells. Shallow ground water supplies in and near developing areas are susceptible to contamination and are more likely to be untreated, unregulated, and not analyzed (particularly for trace elements) than are other types of water supplies.

Objectives

The objectives of this work element are to describe the occurrence and distribution of trace elements in shallow ground water in relation to urban land use, and to provide the data necessary to evaluate trace element risks posed to humans owing to their drinking water from aquifers underlying urban areas.

Approach

To address the above objectives, we recommend adding trace elements (NWQL schedule 2703) to current schedules analyzed as part of urban LUSs. Only USGS installed monitoring wells that are nonmetal should be sampled. Samples should be filtered following recommendations given under Filtration of Water Samples (this report).

Human Exposure from Consumption of Water and Fish

The human exposure subgroup consisted of Dennis Helsel (subgroup leader), Roger Fujii, and Bill Brumbaugh. Input on drinking water issues was received from Marilee Horn (WRD, Pembroke, New Hampshire) and Glenn Patterson (WRD, Reston, Virginia). Input on mercury in fish tissue and the choice of tissues for sampling was received from numerous individuals.

Issues

An important issue related to trace elements in the aquatic environment is the extent to which humans are exposed to unhealthy levels of these constituents. The two most likely pathways are ingestion of drinking water and consumption of fish. The USEPA currently (1998) has existing or pending drinking water MCLs for 14 trace elements (including radionuclides) and is considering MCLs for at least 3 other trace elements (table 2b). In 1997 (the latest year for which data are available), mercury alone accounted for 1,782 of 2,299 fish advisories in the U.S. (U.S. Environmental Protection Agency, 1998b)

Unlike synthetic chemicals, many trace elements are essential to life in small quantities, yet these same elements can create health problems, or can even become toxic, at higher doses. Therefore, levels of exposure, rather than simple detections, are of primary interest for trace elements in relation to human health.

The USGS has a long history of measuring chemicals in natural waters. These waters are often also source waters—waters used as inputs to public water treatment systems or pumped by domestic wells with minimal treatment. NAWQA's primary interest is the occurrence, distribution, and trends of chemicals in natural waters. Such information complements the vast data bases of chemical concentrations in finished water supplies collected by the USEPA, State regulatory agencies, and the water supply industry. Data on chemical concentrations in natural waters provide direct answers to questions, such as "What are people drinking?", for small, unregulated domestic supply wells found primarily in rural areas of the country and for minimally treated supplies, largely ground water supplies, served to the public. For larger, primarily surface water supplies, these data answer questions regarding the amounts of trace elements entering the treatment process.

General Questions

Questions that provide some specifics for the above issue discussion were determined to be:

1. What are the occurrence and distribution of trace elements in source waters (from ground water) as a function of human and natural environments?
2. What are the occurrence and distribution of trace elements in source waters (from surface water) as a function of human and natural environments?
3. What are the occurrence and distribution of trace elements in edible fish tissue? How do concentrations relate to those in bed sediment?

4. Can patterns in trace element concentrations used to answer the three previous questions be explained by patterns in the natural terrain or human activities?

Question 3, above, addresses the utility of trace element concentrations in bed sediment, as currently collected by the NAWQA Program, and asks whether these data are of use in determining whether high concentrations might occur in fish tissue at a given location. The fourth question seeks to identify factors that might be associated with exposure to high or low concentrations of trace elements.

Stratification

An indication of the importance of ground water as a drinking water source in NAWQA Study Units is needed to construct a stratification design for question 1 above. The location and extent of principal aquifers of the U.S. (Miller, 1998) should be useful in this regard. In addition, population served by ground water supply and the amount of ground water withdrawn in each Study Unit can be used to determine the relative importance of ground water as a drinking water source. These data were extracted from the USGS Water Use data base for 1990 (Marilee Horn, U.S. Geological Survey, written commun., 1998) and are summarized by Study Unit in decreasing order of population served in table 7. (Table 7 should be updated to reflect water use during 1995, when that information becomes available.) A similar approach could be used to rank Study Units with regard to surface water used as drinking water (question 2 above).

Table 7. Ground water use for National Water-Quality Assessment Study Units during 1990¹

[1997 Study Units in bold]

Study Unit ²	Population Served by Ground Water (thousands)	Ground Water Used (millions of gallons per day)
GAFL	7,971.1	1,176.92
LINJ	7,377.2	670.36
SOFL	4,854.8	863.92
NECB	2982.5	290.49
MISE	2,853.7	442.39
UMIS	2,558.3	389.41
SANJ	2,528.2	644.55
DELR	1751.8	483.39
SCTX	1,717.7	317.93
CAZB	1,710.9	350.32
MIAM	1696.6	224.28
UIRB	1592.9	314.56
ACAD	1503.7	253.02
SANA	1359.1	298.97
MOBL	1324.6	202.24
PUGT	1,247.7	229.64
ALBE	1,097.1	130.88
RIOG	1,088.6	281.67
CONN	1,055.7	175.24
EIWA	1,048.3	134.93
LIRB	1,030.3	150.34
WHIT	934.0	124.19
SACR	914.9	233.17
SANT	868.7	122.75
CACI	863.1	117.59
GRSL	841.1	248.15
OAHU	828.9	161.13
OZRK	743.1	127.98
LIRB	726.1	103.68
KANS	724.0	118.27

Table 7. Ground water use for National Water-Quality Assessment Study Units during 1990¹—Continued
[1997 Study Units in bold]

Study Unit ²	Population Served by Ground Water (thousands)	Ground Water Used (millions of gallons per day)
LSUS	700.1	76.75
SHPL	685.8	104.15
POTO	683.8	99.46
UTEN	677.4	90.67
DLMV	659.8	79.46
WMIC	655.9	104.86
NROK	640.7	177.84
MARK	625.9	112.49
ALMN	624.9	115.65
CNBR	604.9	167.21
ACFB	579.5	97.49
TRIN	534.0	92.43
LTEN	449.9	74.05
HDSN	446.1	106.69
WILL	437.0	72.51
USNK	347.9	82.01
SPLT	290.2	58.40
KANA	287.2	33.07
NVBR	270.1	82.47
REDN	268.9	38.31
CCPT	236.7	65.79
YAKI	187.2	36.54
NPLT	159.8	40.23
CHEY	143.8	21.06
UARK	113.9	23.54
KNTY	113.2	15.46
YELL	109.3	21.06
COOK	96.8	14.09
UCOL	67.6	14.57

¹Data from Marilee Horn, U.S. Geological Survey, 1998

²See table 1 for Study Unit names.

A stratification tool that should be useful for questions related to fish consumption is information on locations of fish advisories for trace elements (U.S. Environmental Protection Agency, 1998b). Because mercury is the primary contaminant of concern in fish tissue, stratification for fish consumption studies will be similar to that discussed under Regional Occurrence and Distribution of Mercury (this report).

Recommendations

Summary Table

Seven work elements or activities related to human exposure to trace elements are described (table 8). Details regarding each work element are provided in the following text.

Trace Elements in the Used Ground Water Resource

SUSs of randomly selected wells provide a general look at concentrations of contaminants across a large area (geohydrologic unit) of a Study Unit. Past Study Units have occasionally measured trace elements in SUS wells, but this was optional. The TENSPT recommends that trace elements become part of the standard analytical schedule for any SUS that samples water from aquifers that are used, or that could be used, for public or domestic supply. Actual supply wells are of highest priority for sampling, but other SUS wells also should be sampled and analyzed for trace elements if the ground water is representative of that available for supply.

Table 8. Summary table for human exposure from consumption of water and fish

[Priority: ***, highest; **, moderate; *, lowest.]

COST^a	WORK ELEMENT^b	QUESTION^c	TRACE ELEMENTS^d	PRIORITY
Drinking Water				
\$32,400 (30 wells)	Trace elements in the used ground water resource	Occurrence and distribution in source ground water used for public or domestic supply Comparison with drinking water guidelines Geographic patterns in source waters	Schedule 2703, iron ^e , radium-226, radon-222 (radium-228 at selected sites)	***
\$51,400 (30 wells)	Trace elements in shallow ground water from urban and mined areas	Occurrence and distribution in source ground water used for public or domestic supply, or in ground water overlying aquifers used for public or domestic supply Relationship between concentrations of trace elements and land use	Schedule 2703, iron ^e , radium-226, radon-222 (radium-228 at selected sites)	**
^f	Retrospective analysis of trace elements in source waters	Occurrence and distribution in source water used for public supply of major population centers Comparison with drinking water guidelines Consumption of water containing concentrations above levels of concern Geographic patterns in source waters Relationships of concentrations in source waters to those in finished water supplies	Not applicable	**

Table 8. Summary table for human exposure from consumption of water and fish—Continued

[Priority: ***, highest; **, moderate; *, lowest.]

COST^a	WORK ELEMENT^b	QUESTION^c	TRACE ELEMENTS^d	PRIORITY
\$3,500 (1 site)	Trace elements at basic fixed sites near water supply intakes	Occurrence and distribution in source surface water used for public supply Comparison with drinking water guidelines Consumption of water containing concentrations above levels of concern Geographic patterns in source waters Relationships of concentrations in source waters to those in finished water supplies	Schedule 2703, iron ^e , radium-226 (radium-228 at selected sites)	*
Fish Tissue				
^f	Retrospective analysis of mercury in fish	Occurrence and distribution in edible fish Comparison with guidelines and / or standards Geographic patterns in fish	Not applicable	***
\$16,800 (20 sites)	Mercury in fish fillets	Occurrence and distribution in fillets from predator fish Comparison with guidelines and / or standards Geographic patterns in fillets from predator fish	Total mercury	**
\$6,800 (__ sites)	Trace elements in fish fillets at selected sites	Occurrence and distribution in fillets from edible fish Geographic patterns in fish fillets Relationships to background concentrations	Schedule 2200	*

^a Approximate 1998 fiscal year cost per Study Unit for sample collection, processing, and analysis.^b Listed from highest to lowest priority for drinking water components first, then for fish tissue components.^c See text for detailed statements of questions.^d See tables 2a and 2b for list of trace elements associated with the various schedule numbers.^e Included as part of schedules 2701 and 2750, which typically are analyzed as part of surface water and ground water studies, respectively.^f Costs for retrospective analyses would likely be to the Trace Elements National Synthesis Team, rather than to the Study Units.

Objectives

Objectives of analyzing trace elements in ground water from SUS wells are to (1) document the occurrence and distribution of concentrations in ground water used for public or domestic supply, (2) compare concentrations with drinking water guidelines and/or standards, and (3) determine if geographic patterns in concentrations in source waters can be related to geologic or human factors.

Approach

Issues related to use of SUS wells for sampling trace element concentrations in ground water are covered under Characterization of Reference Conditions (this report). NAWQA protocols of Lapham and others (1995) and Koterba and others (1995) should be followed. Samples should be filtered following recommendations given under Filtration of Water Samples (this report) and analyzed for NWQL schedule 2703 (table 2b), schedule 2750 (major cations and anions, including iron), radium-226, and radon-222. A sample for radium-228 should be collected and archived; this sample should be analyzed if radium-226 is detected.

The total cost for analysis of 30 samples for dissolved trace elements does not include radium-228. Analyses of radon-222 and constituents included in schedule 2750 typically are done as part of the standard SUS protocol, so these costs also are not included. The additional cost of field sampling should be minimal.

Radium-224 in drinking water currently is being considered for regulation by the USEPA (M.J. Focazio, U.S. Geological Survey, oral commun., 1998). This isotope has an extremely short half-life (3.6 days), and it probably has been overlooked, even when present in important amounts. Because the NWQL currently (1998) does not analyze for radium-224, and because many analytical and quality control concerns exist, the TENSPT is not recommending analysis of radium-224 at this time. However, it should be reconsidered in the future, as sampling and analytical capabilities improve.

Trace Elements in Shallow Ground Water from Urban and Mined Areas

The objective of NAWQA LUSs is to document relationships between shallow ground water quality and land use at the land surface above. Areas that are preferentially selected for sampling include either the used ground water resource or ground water that overlies a deeper used resource. If certain LUSs are expected to document elevated trace element concentrations in shallow ground water, they should be conducted early in the HIP. Examples might include urban or mining LUSs. It is TENSPT's recommendation that trace elements be part of the analytical schedule for all LUSs in these two types of land use settings.

Objectives

Objectives related to human exposure to elevated trace elements in shallow ground water include (1) determination of the occurrence and distribution of concentrations in ground water (a) used for public or domestic supply or (b) overlying aquifers used for public or domestic supply, and (2) defining relationships between concentrations and land use. The second objective requires a comparison with trace element concentrations in ground water from reference wells.

Approach

The approach for an urban LUS related to trace elements is consistent with the existing NAWQA urban LUS design, namely installation of 30 wells at random locations within an area defined as recently suburbanized and overlying potential or existing water supplies (Squillace and Price, 1996). One deviation from the existing design is the selection of five of the wells to be located in reference areas. For more detail, see Characterization of Reference Conditions (this report).

The approach for a mining land use study is outlined under Effects of Mining and Remediation (this report). Again, 5 reference wells should be selected from the 30 total wells to allow comparisons that will highlight the added influence, if any, of mining and/or remediation on trace element concentrations. As with the SUSs, samples from LUS wells should be filtered following recommendations given under Filtration of Water Samples (this report) and analyzed for NWQL schedule 2703 (table 2b), schedule 2750, radium-226, radon-222, and, possibly, radium-228.

The total cost for this work element does not include radium-228 (to be analyzed only if radium-226 is detected). The estimate also does not include the cost for schedule 2750 and radon-222, which typically are done as part of the standard LUS protocol.

Retrospective Analysis of Trace Elements in Source Waters

The USGS historically has published summaries of the quality of water (primarily major ions) consumed by the public in major cities of the United States (Durfor and Becker, 1962). Responsibility for ensuring the adequacy of finished water supplies resides with the USEPA, which regulates practices of the water utilities. However, the USGS continues to monitor the quality of natural surface and ground (source) waters used throughout the United States for human consumption (as well as for other purposes). In addition, many larger utilities collect information on the quality of water coming into their facilities prior to treatment. Aggregation of existing information on trace elements in source waters, and an evaluation of what is known and what is not known about them, are the first steps in assessing the occurrence and distribution of trace element concentrations in water used for public supply across the United States and for determining how many persons might be exposed to high concentrations.

Robinson and Horn (1998) conducted a pilot study of 201 public water suppliers in portions of 11 States to determine what information might be available from them on source water quality. Information on trace elements in source waters was collected by many utilities, but on an infrequent (often annual) basis. These data, when combined with other data from State public health laboratories and from the USGS, could provide a picture of the quality of source waters for many cities. Information from the USGS can augment the information available for smaller public or private systems, where data are scarce. Differences in sample collection and laboratory analytical techniques between the myriad sources of data add confusion that must be overcome before a picture of the quality of source waters can be obtained.

Alan Welch and Marilee Horn (U.S. Geological Survey, written commun., 1998) are conducting an analysis of existing data on concentrations of arsenic in ground water across the United States, which when combined with information on population served in each area, will lead to estimates of how many persons are exposed to specific levels of arsenic in their drinking water supply. A similar approach could be applied to other trace elements, and the analysis could be expanded to evaluate exposure for people served primarily by surface water supplies.

Objectives

An evaluation of existing information on trace elements in source waters will allow (1) determination of the occurrence and distribution of concentrations in source waters used as public supplies for major population centers, (2) comparison of concentrations with drinking water guidelines and/or standards, (3) determination of the numbers of people consuming water with concentrations above levels of concern, (4) analysis of geographic patterns in concentrations in source waters, (5) comparison of concentrations in source waters with those found by water utilities in finished supplies at the same locations, and (6) analysis of patterns of concentrations in relation to human health effects (as noted by agencies, such as the National Institutes of Health and the Centers for Disease Control). Of primary concern will be a determination of the extent to which each objective can be met with available data versus which can be adequately met only after collection of new data.

Approach

Building on the work by Robinson and Horn (1998), water utilities and the USEPA will be contacted and asked to supply information on trace element concentrations in source waters, as well as on methods of sample collection and laboratory analysis. A subset of the utilities will be asked for information on finished waters, as well. At the same time, similar requests will be made to organizations like the Association of State and Territorial Public Health Laboratory Directors. USGS data will be combined with previous information, and the entire data set will be made available to all who contributed.

Trace Elements at Basic Fixed Sites near Water Supply Intakes

Once the extent of information on trace elements in public supplies is known (see previous work element), it may become necessary to collect additional information on trace elements in surface water supplies. Although intakes for public supplies often draw water from impoundments, which have not been sampled consistently by the NAWQA Program to date, some basic fixed sites (BFS) are located near public supply intakes. By collecting samples for trace element analysis from these sites, a considerable amount of information on the delivery of trace elements to surface water supply systems can be added to that currently collected (on approximately an annual basis) by utilities.

Objectives

Objectives related to trace elements in surface waters at BFS are similar to those for assessment of source water using existing data. They include (1) determination of the occurrence and distribution of concentrations in surface water used for public supply, (2) comparison of concentrations with drinking water guidelines and/or standards, (3) determination of the numbers of people consuming water with concentrations above levels of concern, (4) analysis of geographic patterns in concentrations in source surface water, (5) comparison of concentrations in source surface water with those found by water utilities in finished supplies at the same location, and (6) analysis of patterns of concentrations in relation to human health effects (as noted by agencies, such as the National Institutes of Health and the Centers for Disease Control).

Approach

Filtered stream water samples should be collected and analyzed for trace elements twice annually, once during low flow and once during high flow, at each BFS determined to be near a public supply intake. This will provide a first approximation to the annual range of concentrations to be expected, though conditions other than flow can affect trace element concentrations (Shiller and Boyle, 1987). Filtration procedures should follow the recommendations given under Filtration of Water Samples (this report).

Procedures for collection and processing of surface water samples for trace elements must be consistent with existing NAWQA guidelines. See Characterization of Reference Conditions (this report), for more detail. NWQL schedule 2703 should be used for analysis, in addition to schedule 2701 (major cations and anions, including iron), and radium-226 (table 2b). Radium-228 should be analyzed if radium-226 is detected. The estimated cost for this element does not include the cost associated with schedule 2701 (part of the standard protocol for BFS sampling) or analysis of radium-228.

Retrospective Analysis of Mercury in Fish

Federal, State, and local agencies collect fish for analysis of mercury. Their objectives are to determine whether mercury levels exceed guidelines or standards for fish consumption, and, if so, to post advisories so that people will not catch and eat fish with harmful levels of mercury. Fish consumption advisories due to mercury contamination exist for 40 States (U.S. Environmental Protection Agency, 1998b); however, to date, no one has aggregated this information to interpret it in light of the geomorphic, chemical, and human characteristics that may be driving the processes causing mercury contamination. The extent and quality of existing information should be determined, as its existence is a frequently noted argument against collecting new data. Problems likely to dominate the data analysis include use of multiple collection protocols, varying species and ages of fish, differences in tissue types analyzed, differences in analytical methods used, and differing reporting limits.

Objectives

Objectives satisfied by evaluation of existing information on mercury in edible fish include (1) determination of the occurrence and distribution of concentrations in edible fish, (2) comparison of concentrations with fish consumption guidelines and/or standards, (3) analysis of geographic patterns in source or environmental variables in relation to patterns in the distribution of concentrations in fish, and (4) analysis of patterns in human health effects in relation to patterns in the distribution of concentrations in fish. As with the work element on Retrospective Analysis of Trace Elements in Source Waters, an important determination will be the degree to which the objectives can be addressed with available data as opposed to requiring collection of new data.

Approach

Federal and State agencies will be contacted and their data on mercury in fish will be obtained and evaluated. Data on mercury in streambed sediment will be acquired at the same time. If suitable for analysis and interpretation, the data will be put into a single data base. Ancillary information on field and laboratory methods will help determine whether the data can be aggregated and interpreted together. Needs for additional information will be noted as the above objectives are addressed. The results should provide valuable insight into data collection needs for this issue, and how existing data collection could be augmented by the USGS or others to provide a more complete and consistent coverage for the Nation.

Mercury in Fish Fillets

Total mercury concentrations in fillets from edible predator fish should be analyzed for every site where bed sediment and tissue samples are collected as part of bed sediment and tissue occurrence and distribution surveys. This collection is a separate effort from that for other trace elements in fish, asiatic clams, or other target taxa currently being done in the NAWQA Program. Present protocols place livers from ubiquitous bottom-feeding fish, such as carp and suckers, highest in priority for evaluating occurrence and distribution of trace elements in tissue. For issues of human health, however, levels of mercury in fish fillets (typically from predator fish of local origin) are of greater importance.

Objectives

Objectives related to evaluation of mercury in fish fillets include (1) determination of the occurrence and distribution of concentrations in edible predator fish fillets, (2) comparison of concentrations with fish consumption guidelines and/or standards, and (3) analysis of geographic patterns in source or environmental variables in relation to patterns in the distribution of concentrations in predator fish fillets.

Approach

Protocols for the collection of fish can be found in Crawford and Luoma (1993). A composite sample of five to eight fish should be collected, and fillets should be removed and processed following the procedures recommended under Sampling and Processing Fish Fillets for Assessment of Risk to Human Health (this report). It is anticipated that 20 sites per Study Unit will be sampled one time.

Total mercury concentrations will be interpreted in light of their relation (if any) to methyl mercury concentrations in bed sediment (proposed for analysis under Mercury in Bed Sediment, p. __), concentrations of other trace elements in bed sediment and aquatic biota (collected as part of current bed sediment and tissue occurrence and distribution surveys), and geographic characteristics and mercury sources for the sampling area. A portion of all fish tissue samples should be archived by freezing at -20°C so that subsequent trace element analyses can be performed, if necessary. For more detail on the approach, see similar work element under Regional Occurrence and Distribution of Mercury (this report).

Trace Elements in Fish Fillets at Selected Sites

At ___ selected locations where bed sediment samples have been collected, fish fillets should be analyzed for trace elements, in addition to mercury. Other elements, including arsenic, cadmium, lead, selenium, and tributyl tin, are of public health concern in fish fillets (U.S. Environmental Protection Agency, revised March 9, 1998), and information on concentrations in livers already being collected by NAWQA will need to have concurrent measurements in fillets to establish levels that humans are exposed to through fish consumption. And, although not as ideal as trace element concentrations in whole fish, concentrations in fillets will give a reasonable estimate of the levels predatory wildlife are exposed to when eating fish.

Objectives

Objectives related to evaluation of trace elements in fish fillets include (1) determination of the occurrence and distribution of selected trace element concentrations in fillets from edible fish, (2) analysis of geographic patterns in source or environmental variables in relation to patterns in the distribution of concentrations, and (3) comparison of concentrations with those in fish fillets from reference areas.

Approach

Methods for sampling are those of Crawford and Luoma (1993). It is likely that analysis of multiple trace elements will require different fillet processing procedures than those discussed for mercury under Sampling and Processing Fish Fillets for Assessment of Risk to Human Health (this report). The USEPA (revised March 9, 1998) has recommended procedures that may be useful.

NWQL schedule 2200 (table 2a) should be used for laboratory analysis of trace elements in fish fillets. Except for tributyl tin, which currently (1998) is not analyzed by the NWQL, this schedule includes all of the trace elements suggested by the USEPA for analysis in fish and shellfish contaminant screening programs (U.S. Environmental Protection Agency, revised March 9, 1998). Archived portions of the sample should remain frozen for future analysis. The sites from which frozen, archived fillet samples will be selected and analyzed will be determined by which sites had elevated concentrations of trace elements in bed sediments.

Effects of Mining and Remediation

The mining subgroup consisted of Michael Koterba (subgroup leader), Dennis Helsel, Art Horowitz, Jim Kuwabara, and Rich Wanty. Barbara Ruddy (WRD, Denver, Colorado), and Stan Church, Blaine Cecil, Hal Gluskoter, and others (GD, Reston, Virginia) assisted in this effort.

Issues

In general, an evaluation of the occurrence and distribution of trace elements in water resources associated with mining can help to address at least five major questions or issues:

- (1) What is the current water quality in mined areas?
- (2) How has water quality in mined areas changed over time?
- (3) How do trace element concentrations in areas affected by active mining compare to those in undisturbed mineralized areas, remediated areas, abandoned mine areas, or areas impacted by other human activities (for example, urbanization)?
- (4) What areas are least (or most) sensitive to mining?
- (5) Among the areas currently or likely to be mined, which have historically reflected significant effects on trace element concentrations downgradient from mined areas?

A sixth issue, adverse effects due to acid mine drainage from abandoned hard rock mines, currently is being addressed by the USGS and the Bureau of Land Management (S.E. Church, U.S. Geological Survey, written commun., 1998). The NAWQA Program should support of this effort.

Of the five issues identified for possible study, the first four generally received the widest support from the TENSPT, primarily because these issues are perceived to be more feasible and more compatible with current (1998) NAWQA Program objectives and design approaches than is the fifth issue. The fifth issue incorporates regional effects of mining on downgradient water resources and is more likely to provide information on the ultimate effects of mining on water resources potentially used for drinking water supply. Water resource demands in areas where mining occurs typically are low and reflect rural population needs, and the NAWQA Program generally would not target these areas for study. But impacts that involve acid mine drainage and mine tailings can extend well beyond the mined area and could affect water quality at drinking water intakes or in reservoirs. Therefore, the issue of downgradient impacts on water quality should be seriously considered as the NAWQA Program develops efforts related to water supply.

Regardless of the issue(s), three things are necessary for the NAWQA Program to conduct a national or regional assessment related to mining. First, there must be a demonstrated need for the NAWQA Program to address mining. Second, the NAWQA Program must develop a national or regional stratification of environmental settings for areas in which mining has occurred, is occurring, or is likely to occur. Third, the stratification design must include an assessment of reference conditions and the water quality associated with these conditions. This is particularly critical for mining because of the potential for unmined, highly mineralized areas to adversely affect the quality of water resources.

General Questions

The following general questions were developed by members of the TENSPT and the mining subgroup. They reflect the issues previously cited.

(1) What are the occurrence and distribution of concentrations of trace elements and related constituents in bed sediment, aquatic biota, ground water, and surface water for mined, and possibly reclaimed, areas?

(2) How do trace element concentrations vary seasonally, or from year to year, among mining settings or among mining types (for example, coal versus metal)?

(3) How do trace element concentrations compare with those in other media in the same mining setting or with those associated with other types of human activity (for example, urbanization)? How do trace element concentrations compare with historical data collected at the same sites?

(4) Which trace elements, individually or as a group (a mining signature), best indicate (a) effects of mining and/or remediation on water quality, (b) effects of increased mining intensity, and (c) differences among mined, reclaimed, and background areas?

(5) (a) What are the downgradient effects of mining on trace element concentrations in water being used or available for use? (b) Do effects differ with mining intensity, environmental setting, or background conditions in a predictable manner? (c) What are the effects of remediation on trace element concentrations? Is there evidence that remediation is successful, i.e. that water quality of remediated areas is similar to or approaching that of reference areas?

(6) How do trace element concentrations compare with guidelines for protection of aquatic life or humans (from exposure to drinking water and/or fish)?

Stratification

Major mining activities in the United States can be grouped into four major classes—coal, oil and gas, industrial minerals (nonmetallic minerals, such as sand and gravel), and metallic minerals or metals (sometimes referred to as hard rock minerals). There are important differences among these classes with regard to the general scale of mining impacts.

Industrial mining encompasses (1) many different commercial products that are used in construction materials, fertilizers, cosmetics, and abrasives, and (2) numerous local mining operations that are conducted at relatively small scales (generally less than about 10 km²) in diverse environmental settings. Because their effects on water resources generally are localized, industrial minerals were not included in this initial consideration of mining.

Extraction activities associated with coal, oil and gas, or metals typically are more regional in nature than those for industrial minerals. For each of these former types of mining, either a single large operation or the combined effects of a number of smaller operations can lead to water resources problems that extend well beyond the area of resource extraction. For oil and gas extraction, the major problem is disposal of brines, which generally is regulated through permits at the well head or point of extraction. In contrast, coal and metal mining often involve considerable disturbance of the earth's surface; these areas contribute nonpoint source runoff in a manner similar to the agricultural and urban areas that have been the subject of previous NAWQA Program investigations. For these reasons, the mining subgroup focused its preliminary efforts on coal and metal mining.

Coal Mining

Since the early 1960s, there has been a steady increase in national coal production (fig. 4). The increase is a result of changes in Federal policy on coal leasing that began in the 1960s, an effort to reduce the Nation's dependency on foreign oil in the 1970s, and the continued increase in demand for electricity from steam-generated, coal-fired power plants following World War II (Hudson and Van Haveren, 1989; Palmquist, 1989).

Most of the coal produced since the 1960s has come from five major areas of known coal reserves (fig. 5; table 9).¹ Because of the Clean Air Act and, to a lesser extent, the Clean Water Act initiated in the 1970s, most of the increased coal production has come from low sulfur coal deposits. A significant part of this increased production has been from mining on Federal lands (fig. 6), which occur predominately in the western United States. In addition to the major increased coal production in the West, coal production remains high in the eastern United States, particularly in the Appalachian region (table 9), and is expected to remain high for the next several decades (U.S. Geological Survey, 1996).

¹Alaska potentially has some of the largest coal reserves in the Nation and, perhaps, the highest quality (low ash and low sulfur) coal. Currently, Alaska's annual production accounts for about 15 percent of that produced in the continental United States, but production is expected to double within the next few years.

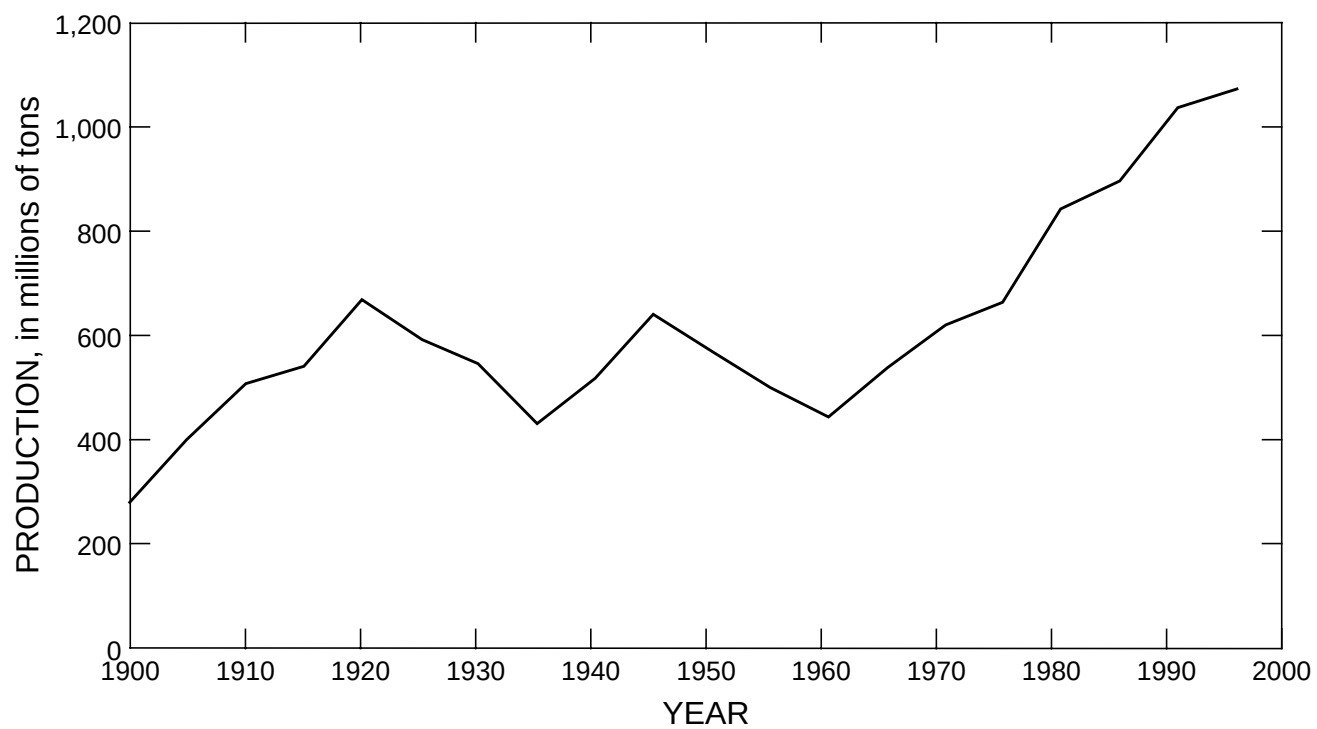


Figure 4. Coal production in the United States, 1900–96 (data from U.S. Geological Survey, 1996).

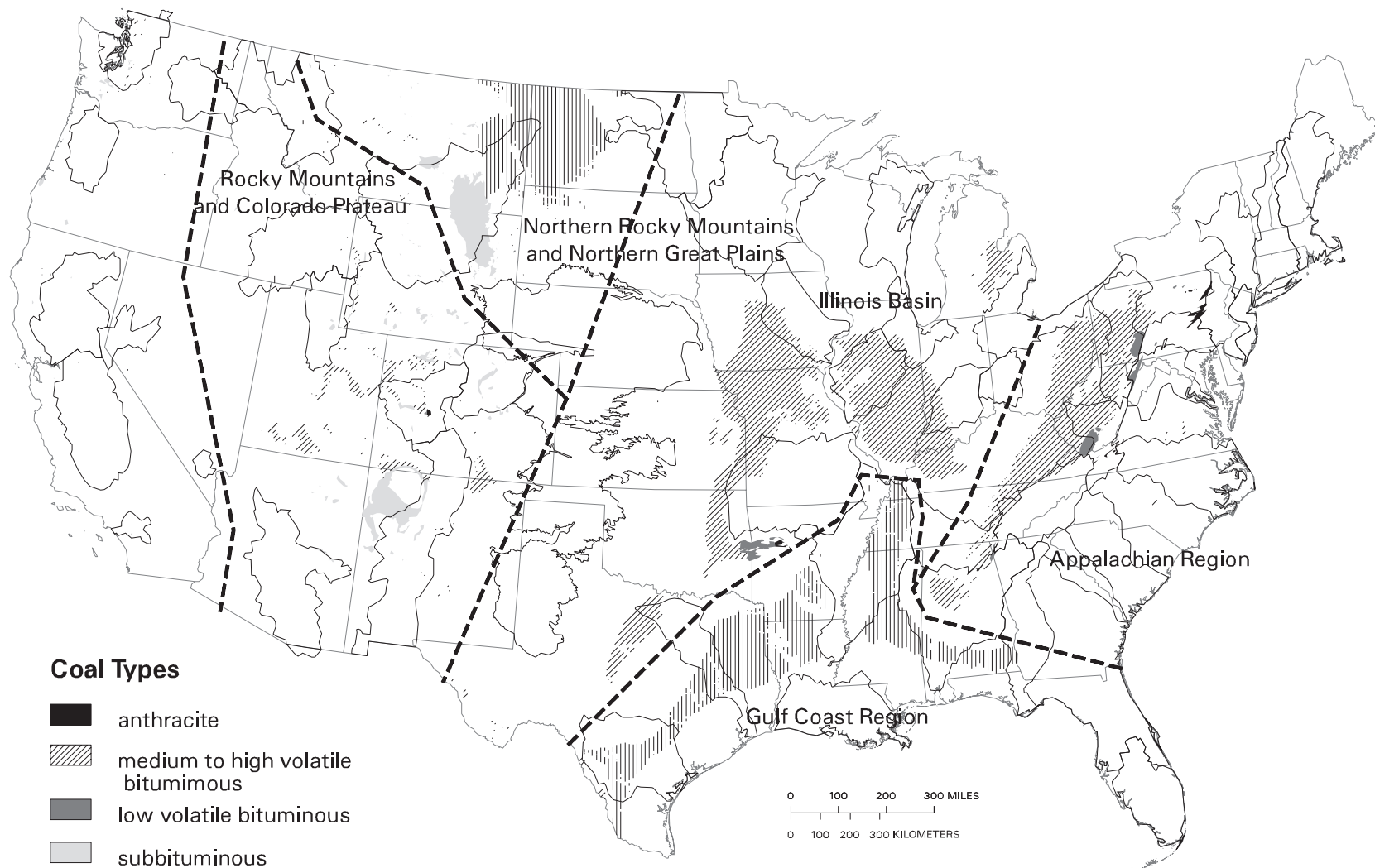


Figure 5. Areas of Known coal resources in relation to National Water-Quality Assessment Study Units (after U.S. Department of Interior, 1975).

Table 9. Coal production in the United States¹

Coal region	1994 production (millions of short tons)	Percentage of total production
Appalachian Region—Central to Northern	400	40
Illinois Basin	121	12
Gulf Coast Region	57	6
Rocky Mountains and Colorado Plateau	80	8
Northern Rocky Mountains and Northern Great Plains	300	30
Other	42	4
Totals	1000	100
Alaska	145	-

¹Except for Alaska, production data are from 1994 (U.S. Geological Survey, 1996). Alaska data are for 1996 (Gary Striker, U.S. Geological Survey, written commun., 1998).

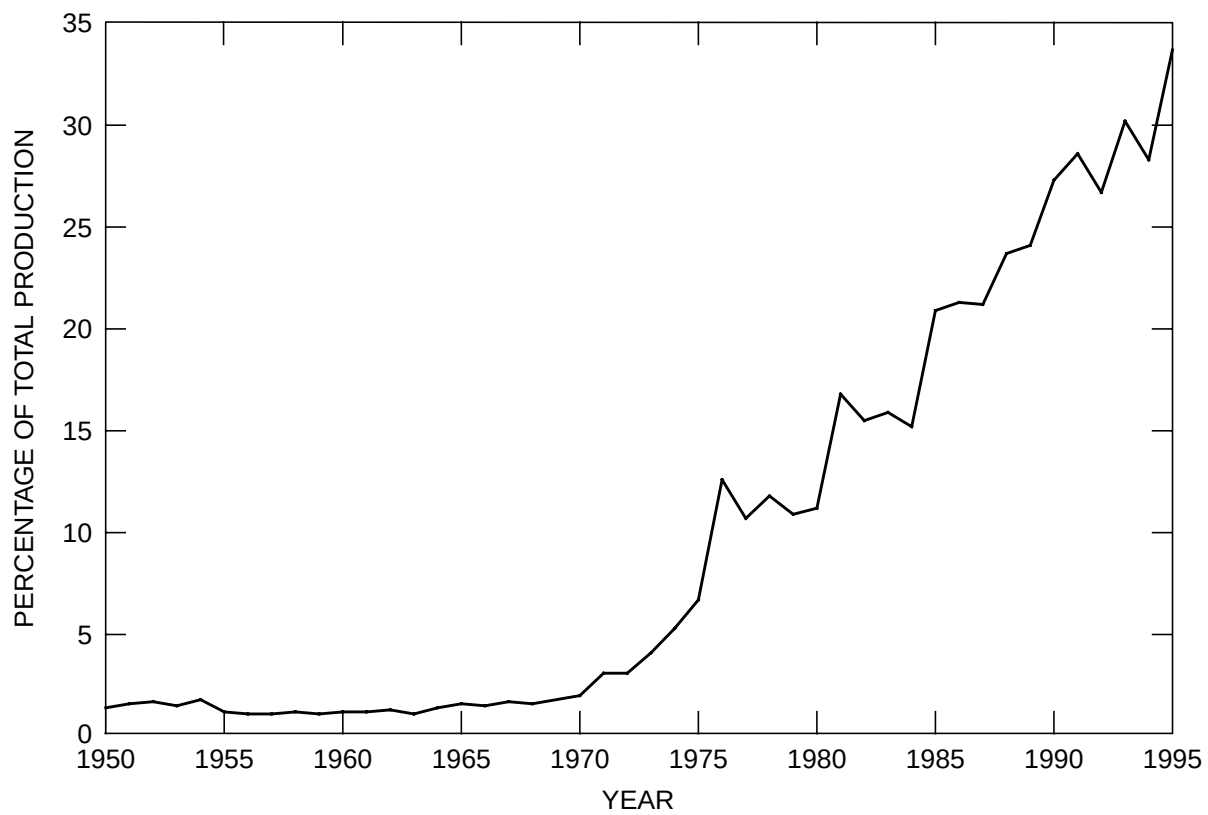


Figure 6. Coal production from Federal lands, 1950–95 (data from U.S. Geological Survey, 1998).

A recent significant change in coal production in the East is serial “mountain top” mining, which began in West Virginia and is now being introduced into Virginia, Kentucky, and Tennessee (American Broadcasting Company, Nightline, April 21, 1998, “Digging Deep”, Transcript Number 4411, 9 p.). Under this type of mining, the entire overburden of each of a series of adjoining mountain tops is displaced into adjacent valley headlands. Currently (1998), there are 75 mountain top mining operations in West Virginia. At least a third of these are considered to be massive, whereby the mining reduces the mountains to an area of low terraces or rolling hills. Mountain top coal mining has raised a number of concerns at State and Federal levels, and one of these is the effect of this type of mining on concentrations of trace elements and related constituents in drainage from these areas.

The increasing role that Federal lands play in national coal production in the West and the introduction of large-scale, mountain top mining operations into a number of States in the East are two important reasons for the NAWQA Program to consider the inclusion of coal mining in its assessment of the Nation’s water resources. A third reason is related to complications that result from the duality of roles that the Department of Interior plays in relation to coal mining in the United States. On the one hand, the Department of Interior, through the actions of the GD, has long supplied information to the Nation on the location and quality of coal. On the other hand, the Department of Interior also has the responsibility to assess the effects of coal production on Federal lands (U.S. Department of Interior, 1975).

The Coal Hydrology Program—the first national assessment of the potential effects of coal mining on water resources in the continental United States—was completed in the mid-1980s, in response to the 1977 passage of the Surface Mining Control and Reclamation Act. Under the Coal Hydrology Program, the U.S. Geological Survey and the Bureau of Land Management examined the quality of water and sediment in more than 60 areas distributed among four of the five coal regions (excluding the Gulf Coast Region; fig. 5) in the continental United States (Britton and others, 1989). This study indicated that in many locations, the water quality in mined areas was different from that in unmined areas and that there were either mixed results or inadequate data to assess the effects of remediation. Helsel (1983) found that reclaimed coal mining areas produced water with iron and aluminum concentrations and pHs that were similar to those in unmined areas, but that sulfate concentrations and specific conductances were more like those in unreclaimed mined areas. Although trace elements were not analyzed, they might be expected to behave similarly to iron and aluminum. Van Haveren and Goolsby (1989) indicated that there remained a need to be able to identify the environmental sensitivity of areas to coal mining and to determine the long-term effects of remediation.

Data from the Coal Hydrology Program should be useful in the verification of a national or regional stratification for evaluating effects of coal mining. These data also might serve as the basis for a trend assessment, given that it has been 15–20 years since individual coal area studies were done.

A preliminary stratification effort indicates that the distribution of NAWQA Study Units throughout the United States, including Alaska, provides reasonable coverage of the known coal reserve areas (fig. 5). A total of 21 Study Units (table 10), or 4–8 Study Units per HIP (table 11), potentially could participate in a coal mining assessment.

Whether coal mining affects a major used, or a potentially used, water resource is a question to be answered. However, most areas in the U.S. that are associated with major coal mining activities (for example, the northern Appalachians and the northern Rocky Mountains and Great Plains) have been described as relatively rural and sparsely populated (Britton and others, 1989). The immediate impacts of mining in these areas are mainly to the surrounding rural surface and ground water supplies. However, results from the Coal Hydrology Program (Britton and others, 1989) indicate that long-term effects extend downgradient from areas with intensive mining and may affect water consumed by small communities or larger urban populations. The extent to which this occurs in each of the NAWQA Study Units is unknown.

Table 10. NAWQA Study Units representing coal regions and types

[l, low volatile; mh, medium to high volatile]

Coal region	Coal type	Coal type area (mi ²)	Coal type in Study Units (percent)	Study Unit(s) ¹
Appalachian	Bituminous, mh	56,000	46	ALMN, KANA, MOBL, KNTY, UTEN, LTEN
Interior	Bituminous, mh	108,000	24	LIRB, OZRK, EIWA, WHIT
Gulf Coast	Bituminous, mh	8,520	15	TRIN
Rocky Mountains and Colorado Plateau	Bituminous, mh	9,100	12	UCOL
Northern Rocky Mountains and Great Plains	Bituminous, mh	9,120(???)	32	CACI, UARK, USNK
Alaska	Bituminous, mh	140	79	COOK
Appalachian	Bituminous, l	3,140	63	ALMN, KANA, POTO
Northern Rocky Mountains and Great Plains	Subbituminous	16,000	81	YELL, CHEY
Alaska	Subbituminous	830	54	COOK
Gulf Coast	Lignite	80,000	45	MISE, SCTX, MOBL, TRIN
Northern Rocky Mountains and Great Plains	Lignite	47,000	20	YELL

¹See table 1 for Study Unit names.

Table 11. Timing of NAWQA Study Units in relation to a possible coal mining assessment

[l, low volatile; mh, medium to high volatile]

Coal type	Coal region	Study Unit ¹			
		FY91	FY94	FY97	Other
Bituminous, mh	Appalachian		ALMN, KANA, UTEN	LTEN, MOBL	KNTY
	Interior	WHIT, OZRK	LIRB, EIWA		
	Gulf Coast	TRIN			
	Northern Rocky Mountains and Great Plains	USNK	UCOL		CACI, UARK
	Alaska			COOK	
Bituminous, l	Appalachian	POTO	ALMN, KANA		
Subbituminous	Northern Rocky Mountains and Great Plains			YELL	CHEY
	Rocky Mountains and Colorado Plateau				
Lignite	Northern Rocky Mountains and Great Plains			YELL	
	Gulf Coast	TRIN	MISE, SCTX	MOBL	
	Alaska			COOK	

¹See table 1 for Study Unit names.

A high probability of adverse impacts on water quality should not be the sole reason for Study Unit participation in an assessment of coal mining effects. There are a number of Study Units that could provide useful reference (background) data because they contain suitably sized areas of unmined reserves. These reserves, which may be mined in the future, also should be factored into the process of Study Unit selection. For example, coal mining will soon begin in the COOK Study Unit in Alaska—perhaps not during the current HIP (1999–2001), but probably soon thereafter. Given that it will be at least 10 years before this Study Unit has another chance to address mining, the NAWQA Program is presented with a unique opportunity to begin collection of background data in relation to the proposed mining activities.

Perhaps the most lacking data, regionally and nationally, with regard to impacts of coal mining on water quality are those related to chemical and physical properties of overburden material. Depending on the locations, some historical (pre-1960s) overburden analyses are available. Also, lithochemical maps, such as those recently prepared for the Pacific Northwest (Raines and others, 1996) and New England (Robinson, 1997) areas, should prove useful for regional assessments of trace elements (see, for example, Ayotte and others, 1998).

Metal Mining

Metal mining² occurs extensively throughout selected parts of the western United States (fig. 7). In addition, there are major metal producing mines in the eastern half of the United States, particularly along the eastern edge of the Appalachians. Production in the East, however, is more widely dispersed than in the West (S.E. Church, U.S. Geological Survey, written commun., 1998).

Abandoned and failed metal mines pose serious water quality problems. A summary by Wuerthner (1998) indicates that about 557,000 abandoned metal mines in the U.S. are unreclaimed, with 12,000 miles of streams affected by mining wastes and an estimated minimum clean-up cost of 32 to 72 billion dollars. Wuerthner (1998) also notes that 66 abandoned mine sites are included in the Superfund National Priority List. In addition, more than 4,000 abandoned mining claims exist within units of the National Park system, including about 11,000 adits, 33,000 disturbed areas, and 5,000 miles of access roads.

²As used in this report, metal mining refers to extraction and processing of ore deposits that typically occur as native elements (for example, gold), sulfides (commonly, copper, lead, silver, and/or zinc), or oxides (for example, uranium and vanadium).

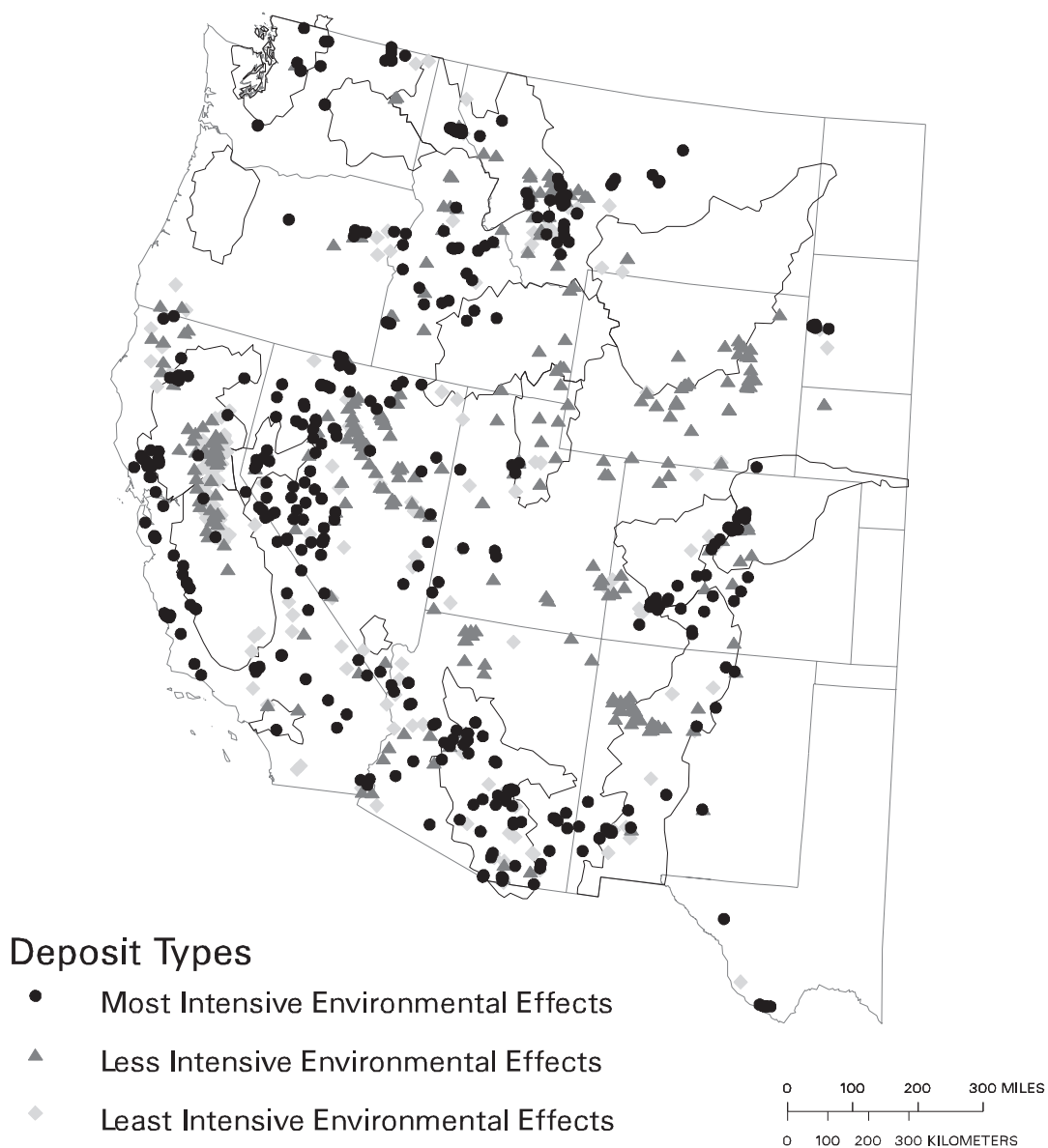


Figure 7. Metal producing mines in the Western United States in relation to National Water-Quality Assessment Study Units (S.E. Church, U.S. Geological Survey, written commun., 1998).

Some states are particularly hard-hit as a result of mine failures and abandoned mines. For example, a recent assessment of water resources in Colorado revealed that (1) most of the 90 streams that failed to meet State and Federal water quality regulations during 1998 did so because of mining related problems, and (2) of the approximately two dozen USEPA Superfund sites in the State, most were mining related (Rocky Mountain News, March 11, 1998). The Summittville Mine alone cost Colorado taxpayers \$130 million dollars during the last five years (Colorado Public Radio, March 13, 1998, "Metal Mining").

Problems similar to those in Colorado can be found in many areas throughout the West, and the western United States has been the focus of preliminary efforts to characterize hard rock mining (S.E. Church, U.S. Geological Survey, written commun., 1998). This region contains parts or all of 17 NAWQA Study Units (table 12); 6 Study Units each contain more than 10 major mining operations classified as likely to produce the "most intensive" environmental effects.

Table 12. Number of deposit types and intensity of environmental effects from hard rock mining in NAWQA Study Units (ranked according to sum of “most intensive” and “less intensive” environmental effects)

Study Unit ¹	Number of hard rock deposit types found within Study Unit boundary ²		
	Most intensive environmental effects	Less intensive environmental effects	Least intensive environmental effects
SACR	22	32	49
NROK	31	17	9
RIOG	10	21	9
CAZB	21	6	14
SANJ	10	14	49
SPLT	11	5	1
CHEY	8	7	3
NPLT	0	14	2
NVBR	9	4	0
YELL	0	13	2
GRSL	0	11	3
UCOL	8	2	3
USNK	3	6	1
CACI	7	1	0
PUGT	7	1	0
UARK	5	2	0
SANA	1	1	0

¹See table 1 for Study Unit names.

²S.E. Church, U.S. Geological Survey, written commun.,1998

As in the case for coal mining, the lack of existing mined sites should not preclude a Study Unit from active participation in studies related to metal mining effects. For example, a Study Unit might contain reference (background/mineralized) areas needed to aid in the characterization of the natural occurrence and distribution of trace elements, or it could contain areas suitable for mining at some future time.

It appears that there are a sufficient number of Study Units to provide an assessment of effects of metal mining on trace elements in the western United States. However, additional work needs to be done to characterize metal mining across the Nation in relation to the development of an environmental setting and stratification and to identify which Study Units might participate in an assessment of metal mining.

Data Requirements

On the basis of preliminary stratification results (tables 10 and 12), it appears that 21 Study Units could participate in a coal mining study, whereas 17 Study Units might participate in a study of metal mining. As 6 of these Study Units (CACI, CHEY, UARK, UCOL, USNK, and YELL) include both coal and metal mining, a total of 32, or more than one-half of all, Study Units potentially could be involved in a Trace Elements National Synthesis of mining areas, not including those where background or unmined reserves are determined to be important.

The participation of Study Units should be determined on the basis of key factors of the environmental setting and the geologic materials associated with the deposits that are mined. Toward this end, a description of data requirements and a strategy to begin development of a common environmental setting and stratification are proposed (table 13).

Table 13. Proposed data requirements and strategy to develop regional or national environmental setting and stratification for mining

Required data and information value for coal or metal mining	Sources of information
Quantify extent of resource: Known and probable resource reserves—geographic extent in United States, including Alaska, by known reserve region for coal and by ore body for metals.	USGS, GD, Coal Assessment Program and Mineral Resource Assessment Program. Production data should aid in the identification of areas that are unmined, recently mined, mined with a varied production history, or possibly mined out.
Quantify intensity of production: Production, per smallest unit area possible—Pre-1980s, recent (post-1979), and most recent (post-1990)	
Quantify nature of contaminants in disturbed material: Resource and overburden quality (per unit basis above) for trace elements, acid producing constituents (for example, reduced sulfur), alkaline producing constituents (for example, carbonate), and possibly other constituents	Same as above. Also lithochemical or surficial geochemical maps in some regions (see text) to identify potential sources of trace elements, acidity, and alkalinity.
Quantify advective transport potential: Climatic data (on county basis, if possible) for precipitation, and runoff and recharge potentials	Precipitation, various; runoff (W. A. Gebert, U.S. Geological Survey, written. commun., 1998); and recharge potential (D.M. Wolock, U.S. Geological Survey, written. commun., 1998)
Quantify hydrologic system potentially affected Water resources data Potential resource identification (water body) Surface Water (Hydrologic Units) and sinks (reservoirs) Ground water (Principal Aquifers)	USGS Hydrologic Units that contain mined area(s) and/or are immediately downstream from such areas. Principal Aquifers within mined areas (Miller, 1998).
Used resource (withdrawals or population served) Surface water Ground water	Water use data from USGS or State records. Population data from county census data.
Verify and revise with available data: Bed sediment, aquatic biota, and water quality	Coal Hydrology Program data; NAWQA data for pilot, FY91, FY94, and FY97 Study Units

Recommendations

The primary recommendation supported by all TENSPT members is to develop a comprehensive plan that describes the environmental settings and the stratification design for resources affected by coal and metal mining. In relation to development of this plan, it is recommended that the NAWQA Program support the mining related activities planned by the FY97 Study Units (ALMN, COOK, and KANA for coal; NECB, NROK, UCOL, and YELL for metals). These activities address important local water resource issues and will provide data and design information that should be useful for a Trace Elements National Synthesis.

The cooperation of the GD, Coal Quality Assessment and Mineral Resource Assessment Programs will be vital to the development of a stratification design. The Coal Quality Assessment Program has compiled coal quality and production (public and proprietary) data and identified areas of acid mine drainage potential that could help guide development of a national stratification for coal mining. In addition, work by the Mineral Resource Assessment Program to assess and prioritize abandoned mine lands for remediation from metal mining effects could be similarly useful for developing a stratification for metal mining.

Summary Table

Six work elements are summarized in table 14 in relation to their contribution to a Trace Elements National Synthesis on mining issues. The work elements are discussed in detail in the following pages. All costs include sampling reference (background) conditions as described under Characterization of Reference Conditions (this report).

Trace Elements in Streambed Sediment

Evaluations of trace element concentrations in streambed sediment are the first studies to be conducted under Effects of Mining and Remediation. These studies are part of the bed sediment and tissue occurrence survey described by Gilliom and others (1995) and are typically done during summer and autumn low flows preceding the first year of the HIP. The addition of two sites for each type of mining (coal or metal), or the substitution of these sites for traditional occurrence and distribution sites, would be expected: one site would represent mined conditions, and one site would be located in a corresponding reference (background) area. A maximum of four sites would be dedicated to evaluation of effects of mining.

Table 14. Summary table for effects of mining and remediation

[Priority: ***, highest; **, moderate; *, lowest.]

COST^a	WORK ELEMENT^b	QUESTION^c	TRACE ELEMENTS^d	PRIORITY
Surface Water				
\$5,900 (4 sites)	Trace elements in stream-bed sediment	Occurrence and distribution in streambed sediment Comparison with other mined settings or urban areas Determination of background concentrations Characterization of mining effects Comparison with guidelines for protection of aquatic life	Schedule 2400, total mercury, methyl mercury	***
\$3,400 (4 sites)	Mercury in fish fillets	Occurrence and distribution in fish fillets Comparison with other mined settings or urban areas Determination of background concentrations Characterization of mining effects Comparison with guidelines for edible fish tissue	Total mercury	**
\$17,200 (4 sites; 2 visits per site)	Trace elements in surface water	Occurrence and distribution in surface water Range of annual variation in surface water Comparison with other mined settings or urban areas Determination of background concentrations Characterization of mining effects Comparison with drinking water guidelines	Schedule 2703, iron ^e , radium-226, (radium-228 at selected sites)	**
_f	Synoptic studies of trace elements in bed sediment, tissue, and surface water along mining gradients	Occurrence and distribution in streambed sediment, aquatic biota, and surface water over a gradient of mining intensity Trend (change) assessment for coal mining sites Comparison with urban areas Determination of background concentrations Characterization of mining effects Comparison with guidelines for protection of aquatic life and human health	_f	*

Table 14. Summary table for effects of mining and remediation—Continued

[Priority: ***, highest; **, moderate; *, lowest.]

COST^a	WORK ELEMENT^b	QUESTION^c	TRACE ELEMENTS^d	PRIORITY
Ground Water				
\$69,600 (30 wells)	Trace elements in Land Use Studies	Occurrence and distribution in shallow ground water from remediated settings Comparison with urban areas Determination of background concentrations Comparison with used ground water resource and with drinking water guidelines	Schedule 2703, iron ^e , radium-226, radon-222 (radium-228 at selected sites)	***
\$20,100 (30 wells)	Trace elements in Study Unit Surveys	Occurrence and distribution in used ground water resource Determination of background concentrations Comparison with drinking water guidelines	Schedule 2703, iron ^e , radium-226, radon-222 (radium-228 at selected sites)	**

^a Approximate 1998 fiscal year cost per Study Unit for sample collection, processing, and analysis.^b Listed from highest to lowest priority for surface water components first, then for ground water components.^c See text for detailed statements of questions.^d See tables 2a and 2b for list of trace elements associated with the various schedule numbers.^e Included as part of schedules 2701 and 2750, which typically are analyzed as part of surface water and ground water studies, respectively.^f Costs and trace elements to be analyzed for full scale implementation will be based on pilot studies in selected Study Units (see text).

Objectives

Objectives of studies of trace elements in streambed sediment from mined areas are to (1) document their occurrence and distribution of concentrations in mined environmental settings, (2) compare concentrations between types of mining or with other human activities that contribute trace elements, (3) determine background concentrations characteristic of specific mined environmental settings, (4) provide a basis for characterizing effects on streams draining mined basins, and (5) compare concentrations with guidelines for the protection of aquatic life that ingest sediment. An ancillary benefit to be gained from conducting this work early in the HIP is that the information can be used to evaluate the suitability of sites as potential surface water indicator sites.

Approach

Each mining related site should be chosen to represent an environmental setting and hydrologic condition identified as relevant to National Synthesis or Study Unit needs. Sites should be on low order streams, and drainage basins should conform to the 50–500 km² range for indicator basins recommended by Gilliom and others (1995). Within these constraints, the basin should be as large as possible to allow for potential use as indicator sites for mining and to provide continued assessment of increases in mining activity. Basins should consist of natural, relatively stable land cover, with little human disturbance other than mining. The site for data collection also should be located to minimize the influence of any other human activities.

Reference sites should have environmental settings and mineralized conditions that correspond to those in the mined basins they are intended to reflect. Background basins should be similar in size and land cover to mined basins. In all other respects, reference basins should conform to recommendations provided under Characterization of References Conditions (this report), which include the potential selection of references basins outside, but in proximity to, the Study Unit boundary.

Bed sediment samples at mined and reference sites should be collected, processed, and analyzed following standard NAWQA protocols, as described under Characterization of References Conditions (this report).

Mercury in Fish Fillets

Because mercury often is associated naturally with mined metals or has been used historically in processing techniques in some mining operations (Nriagu, 1979), mercury concentrations should be determined in fillets from edible fish collected at all mining related sites sampled for analysis of trace elements in streambed sediment. (See also Characterization of Reference Conditions, this report, for details).

Objectives

Objectives of studies of mercury in fish fillets from mined areas are to (1) document occurrence and distribution of concentrations in mined environmental settings, (2) compare concentrations between types of mining or with other human activities that contribute mercury, (3) determine background concentrations characteristic of specific mined environmental settings, (4) provide a basis for characterizing effects on streams draining mined basins, and (5) compare concentrations with guidelines for fish consumption.

Approach

The protocols for fish collection, processing, and analysis are described under Characterization of Reference Conditions (this report).

Trace Elements in Surface Water

Trace element concentrations should be analyzed in filtered stream water collected once during low flow and once during high flow at all mined and background sites sampled for analysis of trace elements in streambed sediment, as discussed above. In addition, unfiltered samples should be incrementally titrated to determine the acid and base neutralization capacity. Field measurements of turbidity, water temperature, dissolved oxygen, pH, and specific conductance should be made.

Objectives

Objectives of studies of trace elements in streams draining mined areas are to (1) document occurrence and distribution of concentrations in mined environmental settings, (2) determine the approximate annual range in concentrations, (3) compare concentrations between types of mining or with other human activities that contribute trace elements, (4) determine background concentrations characteristic of specific mined environmental settings, (5) provide a basis for characterizing effects on streams draining mined basins, and (6) compare concentrations with drinking water guidelines. High flow samples collected early in the HIP could prove useful in selection of mining indicator and background BFSs and could indicate possible trace elements of concern for synoptic studies. Also, radium results will indicate the need to include analyses of this trace element at future indicator or synoptic sites.

Approach

Protocols for collection, processing, and analysis of surface water samples are described under Characterization of Reference Conditions (this report).

Synoptic Studies of Trace Elements in Bed Sediment, Tissue, and Surface Water Along Mining Gradients

Large-area, low flow synoptic studies that focus on mining effects are being proposed by two groups of Study Units: the ALMN and KANA in the Appalachian coal region, and the NROK, UCOL, and YELL in metal mining areas of the western Rocky Mountains. Data collection will include selected trace elements and other mining related constituents in bed sediment, aquatic biota, and water. Results from, and lessons learned during, these synoptic studies will be useful for developing guidance and cost estimates for future, large-scale synoptic studies along gradients of mining intensity.

In the proposed combined ALMN-KANA synoptic study, common types of data will be collected at 30 core sites in each Study Unit. These sites will be used to (1) establish current water quality conditions in relation to selected mining conditions in each region, (2) compare effects on water quality from mining low sulfur and high sulfur coal, and (3) establish the degree of mining effects upgradient from sites at the time data are collected to aid future trend assessments. In addition, data will be collected at an additional 60–120 sites to compare present water quality conditions with those determined in the early 1980s as part of the Coal Hydrology Program.

Trace Elements in Shallow Ground Water from Remediated Areas

The current NAWQA LUS design for ground water cannot effectively characterize the effects of underground mining because the design is focused on surficial aquifers in order to relate surficial land use to effects on shallow ground water. However, reclaimed mined land is a common end member to many mining operations, particularly coal mining operations regulated by the Surface Mining Control and Reclamation Act of 1977. Therefore, it is recommended that this be the focus of mining LUSs.

The recommendation that mining LUSs focus on reclaimed mined lands is logical for the following reasons:

(1) Reclaimed lands and the surficial remnants of mining were cited as two aspects of mining that warranted study in the summary of the Coal Hydrology Program (Van Haveren and Goolsby, 1989).

(2) The Nation has had about 25 years of reclamation activity, and an assessment of reclaimed lands is warranted to evaluate how closely water quality of remediated areas approaches that of unmined reference areas.

(3) Reclaimed lands represent an end member of the mining process, and, thus, determine to some extent the current limit to which work will be done to improve site conditions.

Objectives

Studies of trace element concentrations in ground water from mining LUSs will help (1) document occurrence and distribution of concentrations in mined and remediated environmental settings, (2) allow comparisons of concentrations in ground water from mined and remediated settings with concentrations in ground water from the used resource, ground water from other possible land uses, and surface water from synoptic studies, (3) determine background concentrations characteristic of specific mined and remediated environmental settings, (4) provide a basis for characterizing effects on the used resource, and (5) allow comparison of concentrations with drinking water guidelines.

Approach

Detailed guidance on the design, implementation, and cost of LUSs that focus on reclaimed mined lands will be aided by results from two proposed studies. The first is being conducted by the ALMN and KANA and involves LUSs that focus on reclaimed surface mines in the Appalachian coal region. In each case, 30 reclaimed sites will be selected from field inspections of over 100 candidate sites (in each Study Unit) where suitable water supply wells can be found downgradient from reclaimed mined land. Water quality samples and ancillary data from these sites currently are being analyzed and will be compared with SUS data also obtained for each Study Unit. The efficacy of the design will be evaluated as part of their analysis of these data.

The second LUS study in reclaimed mined lands is being planned by the NROK for tailings deposits from past metal mining activities. In this case, the design being considered is to install nested or multiport wells in reclaimed, metal-rich sediment that was deposited in the flood plain along the Cour d'Alene River. This LUS could be coupled with a flowpath study. This pilot effort will address an issue that has not been effectively addressed previously—the assessment of effects of this type of deposit on ground and surface water quality over a large area.

In relation to either LUS described above, a portion of the wells must be reference or background wells (see Characterization of Reference Conditions, this report). Ideally, for a reclaimed mined land study, these reference wells should be located beneath natural land cover and in the mineralized setting representative of pre-mining conditions for the mined (reclaimed) land use setting.

Guidance on collection, processing, and analysis of ground water samples from LUSs is provided under Characterization of Reference Conditions (this report). In addition, unfiltered samples will be incrementally titrated to determine acid and base neutralization capacity. Also, because their analytical cost is relatively high compared to other trace elements, radium-226 and radium-228 may be analyzed as part of only a few selected LUSs. The TEST will suggest LUSs where analyses of radium will provide useful information for national synthesis.

Trace Elements in the Used Ground Water Resource

Inclusion of trace element concentrations in SUSs that include mined areas provides a basis for comparing the quality of ground water associated with mined lands to the quality of ground water that generally is or could be consumed, particularly for rural domestic supplies.

Objectives

Objectives of analyzing trace elements in ground water from SUS wells are to (1) document occurrence and distribution of concentrations in the used or potentially used ground water resource, (2) determine background concentrations characteristic of specific mined environmental settings, (3) provide a basis for characterizing effects on the used resource, and (4) document concentrations in drinking water sources and compare them with drinking water guidelines.

Approach

Guidance on collection, processing, and analysis of filtered ground water samples from SUSs is provided under Characterization of Reference Conditions (this report). In addition, unfiltered samples will be incrementally titrated to determine acid and base neutralization capacity. Also, because their analytical cost is relatively high compared to other trace elements, radium-226 and radium-228 may be analyzed as part of only a few selected SUSs. The TEST will suggest SUSs where analyses of radium will provide useful information for national synthesis.

If the SUS is conducted to provide regional ground water data in relation to several different LUSs, including a mining LUS, then the total sample analytical cost is that associated only with the trace element analyses.

Regional Occurrence and Distribution of Mercury

The mercury subgroup consisted of Dave Krabbenhoft (subgroup leader), Bill Brumbaugh, and Jim Kuwabara. Jim Wiener (BRD, LaCrosse, Wisconsin) also provided important input to development of this section of the report.

Issues

Over the last decade, and especially over the last five years, mercury has become recognized as an important environmental contaminant, resulting in the issuance of a large number of fish consumption advisories in the U.S. as well as globally. In 1997, mercury accounted for 75 percent of the 2,299 fish advisories issued in a total of 40 States (U.S. Environmental Protection Agency, 1998b). The widespread nature of mercury contamination is primarily due to releases to the atmosphere, followed by long-range transport and atmospheric deposition to the earth's surface; however, point source releases (both natural and man related) can be important in some areas.

Mercury becomes a serious problem for humans and wildlife when it is transformed into methyl mercury by microbially mediated processes. Methyl mercury is extremely toxic, efficiently transferred to low trophic level organisms, and bioaccumulates as it progresses to higher trophic levels. As such, the so called “mercury problem” is really a “methyl mercury problem,” and understanding the controls on the partitioning, transformation, and bioaccumulation processes are the focus of most mercury related research today. To date, it remains difficult for scientists to predict *a priori* how an individual ecosystem, or ecosystem type, will respond in terms of mercury toxicity (methyl mercury production) or to varying mercury loads. This problem stems from large information gaps that currently exist in the mercury science base.

Current information needs regarding mercury in the environment fall into three broad categories.

1. Data availability—Human health consumption advisories for mercury in game fish are nationally and globally distributed. Mercury is by far the primary environmental contaminant leading to fish consumption advisories, yet information on mercury occurrence and distribution is scattered, and high quality studies have been conducted at only a limited number of sites. In addition, there are exceedingly few data available from the western two-thirds of the continental U.S. Although it is widely known that it is critically important to have information on methyl mercury in mul-

multiple environmental media (water, sediment, tissue), no national program is collecting this information.

2. Mercury sources and relative toxicity—Although most recent studies have concluded that the primary source of mercury to aquatic ecosystems is atmospherically derived, there have been few studies on systems where other likely mercury sources, such as those related to mining, also could be important. To date, it is unknown whether mercury from nonatmospheric sources is more or less likely to become methylated and subsequently bioaccumulate in the food web than mercury from atmospheric deposition.

3. Land use/land cover and water chemistry—Recent studies have demonstrated that land use and land cover can have a profound effect on the relative toxicity of mercury in aquatic ecosystems under otherwise equivalent source loads. Areas with high wetland densities have been shown to have a greater proportion of the total mercury burden as methyl mercury, and this can greatly exacerbate the relative rates of mercury bioaccumulation. The precise reasons for this remain unknown, although wetland environments are generally associated with elevated dissolved organic carbon and sulfate, and lower pH levels, all of which are correlated with mercury methylation.

General Questions

In response to the above identified information needs, the following questions were posed to help guide proposed work elements related to mercury for the TENSPT:

1. What are the occurrence and distribution of mercury and methyl mercury in bed sediment, fish tissue, and water?
2. Do levels of mercury in consumable fish tissue present a health hazard for humans and wildlife nationally, regionally, or locally?
3. As all NAWQA bed sediment samples to date have been analyzed for total mercury (which typically is mostly inorganic mercury), whereas methyl mercury is the form that bioaccumulates in fish tissue, should a correlation be expected between mercury in bed sediment and mercury in fish livers for NAWQA data?
4. What effects do mercury loading rate and source type (point versus nonpoint) have on mercury bioaccumulation?
5. What are the controls on partitioning of mercury between solid and solution, mercury speciation, and methyl mercury production in aquatic ecosystems, and can the major controlling factors be identified through sampling efforts on a variety of ecosystem types?
6. Can relative bioaccumulation rates of methyl mercury be compared across ecosystem types by sampling and analyzing mercury in whole standardized prey fish that are important in the trophic transfer of methyl mercury to higher trophic levels?
7. Although human fish consumption advisories are based on results from sampling large game fish, how do these levels of contamination compare with those in juveniles or typical prey species that are more likely to be the food base for piscivorous wildlife?

Stratification

The work element design and the stratification/prioritization of proposed data collection efforts utilize results from previous studies that have elucidated the dominant controls of mercury toxicity in the environment. Five primary factors consistently have been shown to affect mercury abundance, distribution, speciation, and bioaccumulation across five study areas in the U.S. and Canada (Gilmour and others, 1991; Hecky and others, 1991; Bodaly and others, 1993; St. Louis and others, 1994; Rudd, 1995; Hurley and others, 1995).

1. Landscape-scale factors can have an important controlling influence on mercury toxicity. A limited number of studies to date have shown the surprising result that more pristine areas generally tend to yield higher methyl mercury levels than developed areas (St.Louis and others, 1994; Hurley and others, 1995). This conclusion results, in part, because developed areas generally have lower wetland densities, and wetlands are a key location for mercury methylation in the environment. Similar studies have not been conducted over a wide range of environmental settings (climate, geology, geography, soils) to ascertain the transferability of these results.
2. Low pH levels have the general effect of allowing greater mobility and higher mercury concentrations in surface waters, which in turn increases the likelihood of mercury methylation.
3. DOC can be an effective complexing ligand for mercury, thus increasing its relative solubility in aqueous systems. However, DOC is a general category that includes the

myriad of aliphatic and aromatic compounds present in natural waters, and recent studies have shown that the quality (composition) of the DOC is more important than the quantity.

4. Sulfate reducing bacteria, which generally concentrate in sediment at or near the sediment-water interface under anoxic conditions, are the principal mercury methylating agent in natural systems. Thus, systems with more available sulfate generally will facilitate mercury methylation. However, sulfate reducing bacteria oxidize organic carbon and reduce sulfate to sulfide, which in turn can (self) limit mercury availability for methylation through mercuric sulfide complexation or precipitation.
5. To date, a most mercury studies have been conducted in areas remote from any known mercury point sources. As such, little is known about the roles of source types or source loads in controlling mercury toxicity. Even for those areas where the mercury source is known to be atmospheric deposition, so few studies have been conducted that it is not known if the atmospheric deposition gradient (fig. 8) manifests itself in terms of concentrated areas of high mercury levels in fish. NAWQA Study Units provide a unique opportunity to study mercury occurrence and distribution across a

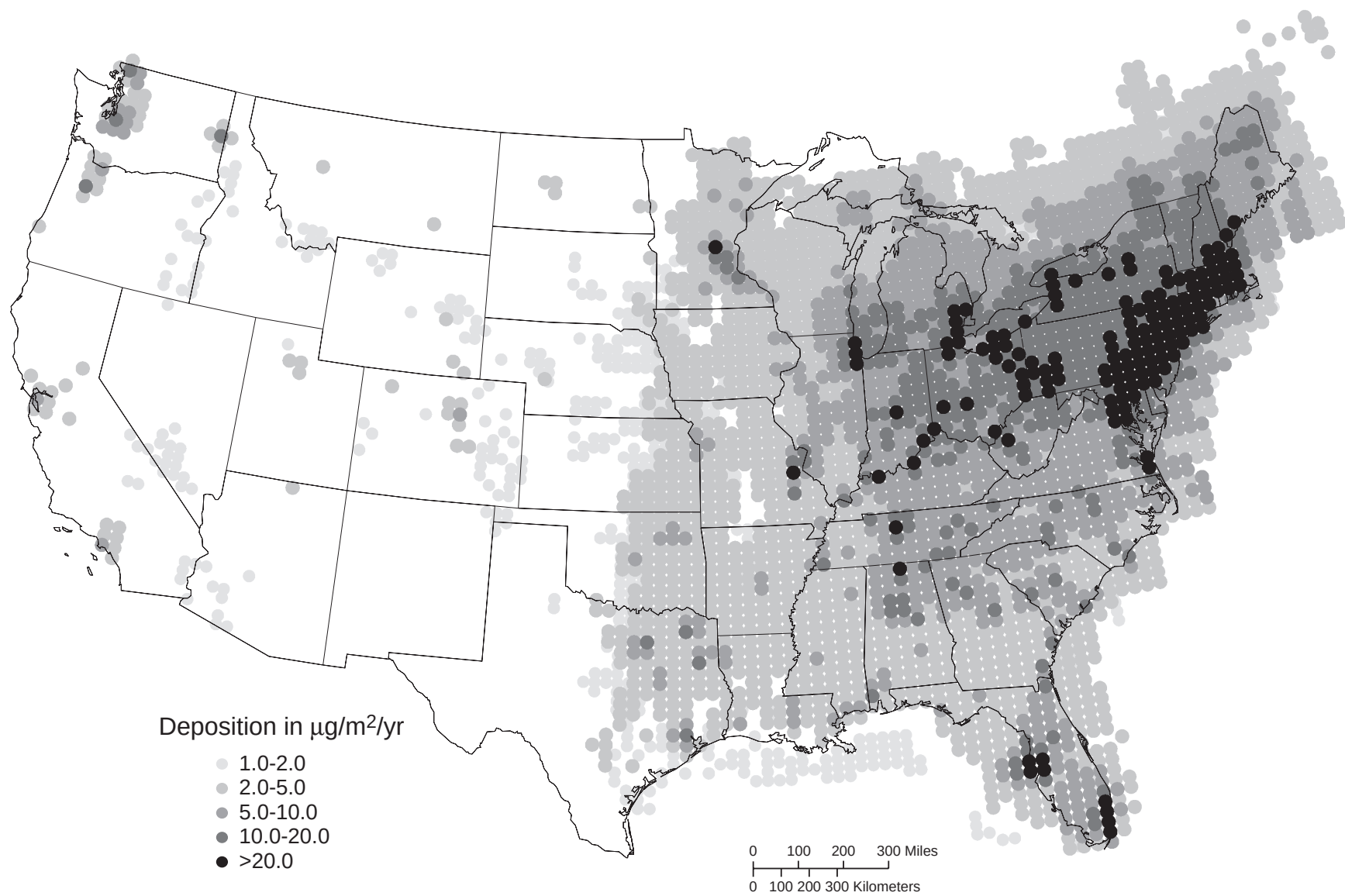


Figure 8. Atmospheric deposition of total mercury for 1997 (U.S. Environmental Protection Agency, 1998a).

range of wetland densities and source loads, including high loading rates due to point sources (see fig. 9).

Recommendations

Summary Table

To address the general questions and provide meaningful information that will help fill the data gaps that exist for mercury, five work elements, stratified according to the factors described above, are proposed. They are summarized in table 15 and are described in detail on the following pages.

Synoptic Studies of Mercury in Bed Sediment, Fish Tissue, and Surface Water Along Gradients of Loading and Wetland Density

This study will be a collaborative effort between the NAWQA Program and the National Mercury Project (funded by the Toxic Substances Hydrology Program) and will provide an opportunity to achieve complementary programmatic objectives. The NAWQA Program, with its highly trained, nationally dispersed personnel and existing water quality information, would interface well with the technical expertise and experience of scientists from the National Mercury Project. Together, both programs could make significant contributions toward filling many of the information gaps described above.

Table 15. Summary table for regional occurrence and distribution of mercury

[Priority: ***, highest; **, moderate; *, lowest]

COST^a	WORK ELEMENT^b	QUESTION^c	TRACE ELEMENTS^d	PRIORITY
Surface Water				
\$7,500 ^e (5 sites)	Synoptic studies of mercury in bed sediment, fish tissue, and surface water along gradients of loading and wetland density	Occurrence and distribution in bed sediment, fish fillets, and surface water Comparison with guidelines for protection of aquatic life and human health Comparison of bed sediment with fish fillets Effects of loading rates and source types on bioaccumulation Controls on mercury methylation and speciation	Total mercury in sediment, fish, and water; methyl mercury in sediment and water	***
f	Retrospective analysis of mercury in fish tissue and bed sediment	Occurrence and distribution in bed sediment and fish tissue Comparison with guidelines for protection of aquatic life and human health Comparison of bed sediment with fish livers Effects of loading rates and source types on bioaccumulation	Not applicable	***
\$7,800 ^e (10 sites)	Mercury in bed sediment	Occurrence and distribution in bed sediment Comparison of bed sediment with fish fillets Effects of loading rates and source types on bioaccumulation Controls on mercury methylation and speciation	Total mercury, methyl mercury	**

Table 15. Summary table for regional occurrence and distribution of mercury—Continued

[Priority: ***, highest; **, moderate; *, lowest]

COST^a	WORK ELEMENT^b	QUESTION^c	TRACE ELEMENTS^d	PRIORITY
Surface Water				
\$8,600 ^{e,g} (10 sites)	Mercury in fish fillets	Occurrence and distribution in fish fillets Comparison with guidelines for protection of aquatic life and human health Comparison of bed sediment with fish fillets Effects of loading rates and source types on bioaccumulation Comparison of bioaccumulation across environmental gradients Comparison of predator fish (consumed by humans) with prey fish (consumed by piscivorous wildlife)	Total mercury	**
\$10,000 ^e (10 sites)	Mercury in surface water	Occurrence and distribution in surface water Effects of loading rates and source types on bioaccumulation Controls on mercury methylation and speciation	Total mercury and methyl mercury in filtered and unfiltered samples	*

^a Approximate 1998 fiscal year cost per Study Unit for sample collection, processing, and analysis.^b Listed from highest to lowest priority for surface water components first, then for ground water components.^c See text for detailed statements of questions.^d See tables 2a and 2b for list of trace elements associated with the various schedule numbers.^e Costs include expendable sample collection supplies and consultation with staff from the Wisconsin District Mercury Research Laboratory.^f Costs for retrospective analysis would likely be to the Trace Elements National Synthesis Team, rather than to the Study Unit.^g Costs are based on duplicate samples at each site.

Objectives

The two primary objectives of this work element are to (1) provide mercury concentrations from multiple media (bed sediment, fish fillets, and surface water) using standardized collection and analysis methods for ecosystems across the U.S., and (2) identify ecosystem characteristics associated with high production and accumulation rates of methyl mercury.

The relative importance of mercury loading (type and source strength), water quality, and basin characteristics on mercury occurrence, speciation, and bioaccumulation across the U.S. would be examined. Although studies in Wisconsin suggest that basin characteristics are important, total variability in atmospheric deposition rates and water quality across Wisconsin are limited compared to national variability, and point source contributions are modest at best. Thus, these results may not be transferable to a national scale. Data from the proposed synoptic studies would provide the first comprehensive information on mercury for many areas of the Nation. Reliable data on methyl mercury and total mercury in sediment, aquatic biota, and water are available for probably fewer than 10 areas, and large areas of the Nation entirely lack data to infer existing or potential methyl mercury contamination.

Approach

A pilot study is proposed in which samples would be collected from approximately 5 indicator sites in each of (at least) 10 NAWQA Study Units that span the dominant east-to-west mercury atmospheric deposition gradient across the U.S. and that, in a few instances, have significant internal (point) sources of mercury. Study Units have been evaluated to reflect a wide array of watershed characteristics, such as wetland density, land use/land cover, soil types, and key water chemistry constituents (pH, dissolved organic carbon, and sulfate) that are suspected to affect mercury methylation and bioaccumulation. The 10 Study Units shown in figure 9 span the full range of mercury loading and wetland density gradients, but also provide a good range of other important environmental factors, such as climate and hydrology. Bed sediment, fish, and surface water should be collected within a few weeks of each other in order to document patterns in methyl mercury production and bioaccumulation, and their relations to site conditions. Data from this pilot study would provide the first available information on mercury for several of these basins, and this would be the first known sampling effort of its kind across the U.S.

Wetland Density	High		ACAD	SANT		
	Medium	COOK		NECB	LINJ	NVBR
			TRIN			
	Low	UCOL			ALMN	SACR
		Low	Medium			High
			(Atmospheric Source)			(Point Source)
			Mercury Loading			

Figure 9. Distribution of selected Study Units along gradients of wetland density and mercury loading. (See table 1 for Study Unit names.)

Fish may be collected by any means that does not compromise the specimen with regard to mercury contamination. Ideally, a composite sample of five individuals of a single, commonly found, freshwater, top predator species should be collected from each site. Fish should be uniform in size and 3 years of age. Prior to the sampling effort, estimates should be obtained for expected lengths of 3-year old fish for the body of water and species to be sampled. Largemouth bass are preferred; however, crappie, walleye, and yellow perch are good alternatives. If possible, the same fish species should be collected at all sites sampled.

Each fish should be rinsed in river/stream water, and all individuals from a site should be placed together in a heavy duty, clear plastic, zipper-style bag and sealed. The bag containing the fish should be placed into a second bag along with a waterproof label containing site/sample information recorded using a waterproof pen. The second bag should be sealed or secured with a heavy duty closure and the fish put on dry ice as soon as possible. All samples should be shipped overnight to the WDMRL for further processing and analysis of total mercury. Fillets will be removed and processed in the laboratory, as outlined under Sampling and Processing Fish Fillets for Assessment of Risk to Human Health (this report).

Bed sediment should be collected and processed using standard NAWQA protocols (Shelton and Capel, 1994, rev. 1996). The bulk sediment sample should be collected, accumulated in the glass compositing bowl, and homogenized with minimal disturbance. Two subsamples—one for total and methyl mercury analysis and another for analysis of AVS and organic carbon—should be removed from the homogenized composite sample prior to sieving. This approach is used to avoid possible changes in partitioning of methyl and inorganic mercury and to minimize oxidation of sulfide. The subsamples should be placed into containers provided by the WDMRL, stored in a darkened cooler (preferably with dry ice) as soon as possible, and shipped overnight to the WDMRL.

Water samples should be collected and/or in situ measurements made to quantify total mercury, methyl mercury, pH, sulfate, DOC, and DOC fractionation. Aqueous mercury samples should be collected using the parts-per-billion inorganic protocol (Horowitz and others, 1994); sample bottles will be provided by the WDMRL. All sample bottles for mercury will come double bagged and partially filled with 1 percent hydrochloric acid. The acid solution should be removed and properly disposed just prior to sampling. Sampling crews should execute clean-hands/dirty-hands techniques to remove the sample bottle from the two bags (stowing the bags closed, original inner bag inside outer bag, in a clean location while sampling).

Samples for mercury analysis should be taken from the centroid of flow by holding the bottles under water while wearing gloves provided by the WDMRL. To avoid possible contamination of water samples by surface films, the sample bottle should be uncapped and firmly resealed while fully submerged at the point of sample collection. Sample bottles should be rinsed three times using this procedure prior to filling with water for analysis. After filling, the sample container should be decanted to the container shoulder, placed back into the inner bag and outer bags (in that order), and stored in a darkened cooler. Samples for analysis of methyl mercury should be stored on dry ice, whereas samples for analysis of total mercury should be stored on frozen water and preserved with acid solution following instructions provided by the WDMRL. The water samples should be shipped overnight to the WDMRL.

Grab samples for analysis of sulfate, DOC, and DOC fractionation should be collected from the centroid of flow using the same procedure as outlined previously for collecting samples for mercury analysis. The sulfate and DOC samples should be field filtered using standard NAWQA methods (Shelton, 1994, rev. 1996), but DOC fractionation sample should be done on a whole water sample. The DOC fractionation sample should be collected by filling two 1-liter brown glass pesticide bottles (available from the NWQL) from the centroid. Ultra-clean techniques are not necessary while collecting this sample. The DOC and sulfate samples should be taken in the appropriate containers, depending on the analytical lab being used (NWQL or WDMRL). DOC samples (concentration and fractionation) should be shipped on ice (not frozen).

Retrospective Analysis of Mercury in Fish Tissue and Bed Sediment

Although many Federal, State, and local agencies collect fish for mercury analysis, and fish consumption advisories for mercury exist for 40 states (U.S. Environmental Protection Agency, 1998b), there has been no known attempt to aggregate this information or to interpret the data in terms of the factors, such as sources, land use/land cover, soils, and water chemistry, that control environmental mercury concentrations. Likely reasons that such a data compilation has yet to be conducted include quality assurance/quality control concerns; lack of readily comparable fish species, ages, and/or tissue types; multiple analytical techniques and reporting limits; or simply poor data base documentation and availability. Despite these concerns, some level of data synthesis for mercury concentrations in fish is critical for guiding new data gathering efforts.

A retrospective analysis of data on mercury in fish livers and bed sediment collected during the first complete cycle of the NAWQA Program is critical for assessing the efficacy of the currently prescribed NAWQA protocols. It is well known that almost all mercury in fish is methyl mercury, whereas, in most cases, sediment is dominated by inorganic mercury. In addition, methyl mercury can be incorporated into any living organism by bonding with sulfur groups, primarily on proteins. As such, methyl mercury preferably accumulates in muscle tissue, and to a lesser degree (amount unknown) in livers. Thus, it is assumed that a poor correlation between total mercury in bed sediment and in fish livers (or muscle) will result, but this needs to be tested.

Objectives

The objectives of this retrospective effort are to (1) use existing data bases to assess the occurrence and distribution of mercury concentrations in edible fish tissue and in fish livers, and (2) assess whether there are national or regional spatial patterns in these aggregated data bases that correlate with mercury sources or environmental controls.

Approach

Federal and State agencies will be contacted and their data on mercury in fish and streambed sediment will be obtained and evaluated as outlined under Retrospective Analysis of Mercury in Fish in the section on Human Exposure from Consumption of Water and Fish (this report).

Mercury in Bed Sediment

Bed sediment is a desirable medium for sampling mercury for several reasons. First, sediment tends to integrate environmental conditions and reflect dominant biogeochemical processes over longer periods of time than does water. Second, near surface sediment generally is the location of greatest mercury methylation in most aquatic ecosystems. Although actual measurements of mercury methylation are laborious and expensive, involving the use of radioactive mercury-203, it has been shown that a good proxy for estimating and comparing different sites for relative rates of methylation in sediment is to measure the percentage of the total mercury pool that is present as methyl mercury (Krabbenhoft and others, 1998). In this manner, confounding effects, such as varying amounts of mercury available for methylation, organic carbon (which naturally accumulates mercury due to the high affinity of mercury and methyl mercury for organic material), and AVS can be normalized, and across-site comparisons can be made.

Objectives

Objectives of this work element are to (1) generate a data base of mercury and methyl mercury concentrations in bed sediment from a variety of environmental settings across the U.S. using a consistent set of collection, processing, and analytical procedures, (2) estimate mercury methylation rates or susceptibility to methylation based on the ratio of methyl mercury to total mercury in bed sediment, and (3) test the utility of the organic carbon and/or AVS content of bed sediment for normalizing conditions among sites within Study Units and across Study Units.

Approach

Bed sediment should be collected at 10 sites using standard NAWQA protocols (Shelton and Capel, 1994, rev. 1996) and analyzed for total and methyl mercury, organic carbon, and AVS. [Note: the WDMRL is in the process of implementing analysis of AVS on a limited basis using the standardized procedures of Brumbaugh and others (1994); the procedure should be available by the fall of 1998.] Samples should be processed as described under Synoptic Studies of Mercury in Bed Sediment, Fish Tissue, and Surface Water Along Gradients of Loading and Wetland Density (this report).

Mercury in Fish Fillets

Mercury has become an important national issue, in part because of concerns regarding consumption of contaminated fish by humans and piscivorous wildlife. Most Federal, State, and local agencies collect sport (predator) fish muscle tissue or whole fish for evaluating exposure of humans to mercury. The NAWQA program, on the other hand, has promoted analysis of fish livers from ubiquitous bottom-feeding fish (for example, suckers and carp). Because livers are a concentration point for many trace elements, such data should optimize the likelihood of detecting trace elements and, thus, the ability to determine trace element occurrence and distribution. Because mercury is ostensibly the only trace element of widespread concern with regard to human health, the current NAWQA sampling design may not provide the necessary information to determine the occurrence and distribution of mercury concentrations to which humans are likely to be exposed.

Objectives

Objectives of evaluation of mercury in fish fillets are to (1) determine occurrence and distribution of concentrations in edible predator fish fillets, (2) compare concentrations with fish consumption guidelines and/or standards, and (3) evaluate geographic patterns in source or environmental variables in relation to patterns in the distribution of concentrations in predator fish fillets.

Approach

Guidance for the collection, processing, and analysis of fish, and for data interpretation, are provided under Trace Elements in Fish Fillets (p. ____). It is anticipated that 10 sites per Study Unit will be sampled one time. Because mercury concentrations in fish tissue are expected to be more variable than in other media, duplicate samples will be collected at each site to address this concern.

Mercury in Surface Water

Reliable data on mercury and methyl mercury concentrations in water from a variety of environmental settings currently do not exist, and this makes it difficult to establish and/or evaluate safe environmental limits for these constituents. Although mercury and methyl mercury concentrations in most surface waters are low (parts per trillion or less), bioaccumulation rates of methyl mercury are high, and toxicological concerns often result for humans or fish-eating wildlife. The USEPA wildlife protection criterion (???REFERENCE NEEDED???) for total mercury in water (12 ng/L) currently is under review, as almost all surface waters exhibit concentrations below this action level, yet fish consumption advisories for mercury have been posted in 40 states (U.S. Environmental Protection Agency, 1998b). For example, consumption of sport fishes from the Florida Everglades has been completely banned, yet the USGS data base on mercury in unfiltered and filtered water has over 4,500 entries with no concentrations exceeding the wildlife protection criterion.

It is widely accepted that mercury contamination is largely the result of atmospheric transport and deposition across the continental U.S. The mercury deposition pattern exhibits a strong east-to-west declining gradient, with notable exceptions around major urban centers (see fig. 8). However, it is unknown how or if this gradient is reflected in mercury concentrations in surface water. In addition, there are other potentially important mercury sources (urban runoff, abandoned precious metal mines, active and abandoned coal mines, geothermal areas, active volcanoes) that may play important roles in the occurrence, distribution, and speciation of mercury in surface water.

Objectives

The overall objective of this proposed work element is to establish a data base for mercury and methyl mercury in water from a variety of environmental settings that span gradients in source strengths, source types, and other factors that influence mercury speciation.

Approach

Water samples for filtered and unfiltered, total and methyl mercury should be collected using the standard USGS parts-per-billion inorganic protocol (Horowitz and others, 1994), with the additional requirement that sample containers and filtration equipment be made of Teflon and be cleaned with hot acid as prescribed by the WDMRL (Krabbenhoft and others, 1998). All standard USGS sampling devices, including the D77 or DH81, can be used for the collection of water samples for analysis of mercury provided they are subjected to the required cleaning procedure. For small (wadeable) streams, samples should be collected at the centroid of flow; for large streams, a composite sample should be collected using EWI practices and a pre-cleaned homogenization container (for example a 5-L Teflon bottle).

By collecting and analyzing samples for total and methyl mercury in filtered and unfiltered samples, partitioning coefficients can be calculated for these species for dissolved and suspended particulate phases. This information will allow an assessment of whether total mercury plays an important role in driving mercury methylation through calculations of the percent of total mercury as methyl mercury. Finally, these data can be tied to other data collected by the Study Units to assess whether commonly assumed water chemistry parameters (pH, sulfate, and dissolved organic carbon) have controlling influences on mercury methylation.

INTEGRATION OF ISSUES

One way to integrate the five major issues discussed in the preceding pages is to examine the various questions that have been posed and determine their commonalities with regard to the issues. As shown in table 16, this approach tends to partition the questions into two widely divergent categories: (1) those of importance to all issues and to most media (sediment, tissue, water), and (2) those of importance to a limited number of issues and to selected media.

Table 16. Summary of Interrelationships Among Questions and Issues Recommended for Trace Elements National Synthesis

[BS, bed sediment; GW, ground water; SW, surface water; T, tissue; bold type indicates issue/question/medium combinations that would be addressed by the shaded work elements in table 17]

Question	Issue				
	Character-ization of Reference Conditions	Effects of Urbaniza-tion	Human Exposure to Drink-ing Water and Fish	Effects of Mining and Reme-diation	Regional Occur-rence and Distribu-tion of Mercury
Occurrence and Distribu-tion	BS, T, SW, GW	BS, T, GW	T, SW, GW	BS, T, SW, GW	BS, T, SW
Comparison with other Environmental Settings	BS, T, SW, GW	BS, T	T, SW, GW	BS, T, SW, GW	BS, T, SW
Comparison with Guide-lines for Protection of Human Health	T, SW, GW	T, GW	T, SW, GW	T, SW, GW	T, SW
Comparison with Guide-lines for Protection of Aquatic Life	BS, SW	BS	-	BS, SW	BS, T
Annual Range of Concen-trations	SW	-	-	SW	-
Temporal Trends	-	BS	-	BS, SW	-
Prediction of Concen-trations in other Environ-mental Settings	BS, SW	-	-	-	-
Determination of Biologi-cal Effects	-	BS	-	-	-
Comparison of Source Water with Finished Water	-	-	SW, GW	-	-
Determination of Mining Signature	-	-	-	BS, T, SW, GW	
Determination of Down-gradient Effects	-	-	-	SW, GW	
Comparison of Bed Sedi-ment with Tissue	-	-	-	-	BS, T
Determination of Degree of Mercury Methylation	-	-	-	-	BS, SW

Questions that address specific issues and media are sometimes considered to be more relevant to decision making than broader questions. Such questions (category 2, above) are listed toward the bottom of table 16. However, before these questions can be answered with any degree of certainty, it is important to have a complete understanding of the occurrence and distribution of trace elements in the environment.

Occurrence and distribution assessments in the NAWQA Program are designed to document broad-scale spatial and seasonal variability of water quality conditions (Gilliom and others, 1995). They comprise the largest component of the first 3-year HIP in all Study Units. In addition, they are the foundation of most other NAWQA data collection efforts, including assessments of trends and evaluations of constituent sources, transport, fate, and effects. Questions related directly or indirectly to the occurrence and distribution of trace elements tend to fall into category 1 (above) and are listed toward the top of table 16.

The first four questions in table 16 address all issues and all or most media. They can be stated as follows:

- What are the occurrence and distribution of trace element concentrations (including mercury) in bed sediment, tissue, surface water, and ground water in environmental settings of importance to the NAWQA Program?
- How do concentrations of trace elements (including mercury) in bed sediment, tissue, surface water, and ground water compare among environmental settings? Can patterns be distinguished on a regional or national basis?
- How do trace element concentrations (including mercury) in fish tissue, surface water, and ground water compare with current or proposed standards or guidelines for the protection of human health.
- How do trace element concentrations (including mercury) in bed sediment, tissue, and surface water compare with current or proposed standards or guidelines for the protection of aquatic life.

The TENSPT recommends that studies that address the above questions be given higher priority than those that specifically address questions of more limited extent. However, to the degree that other questions can be answered through data collection efforts organized around the above questions, such efforts should be encouraged.

It is also important to recognize that some work elements are repeated under several of the five major issues previously discussed. For example, studies related to mercury in fish fillets are recommended under characterization of reference conditions, human exposure from consumption of water and fish, effects of mining and remediation, and regional occurrence and distribution of mercury. Although the specific objectives for each issue differ slightly, consideration must be given as to whether data collection efforts related to such a common theme would result in an aggregate priority that is higher than that suggested by the individual work elements. Trace element themes organized around common work elements and multiple issues provide potential for increased interpretive power and cost savings.

Thus, a second way to integrate the five major trace element issues is to examine their relative priorities in relation to standard NAWQA Program components (retrospective analyses, bed sediment and tissue surveys, BFSs, surface water synoptic studies, LUSs, SUSs) as represented by the work elements presented previously in the issue summary tables. This information is presented in table 17. Although none of the work elements encompasses all five trace element issues, several were ranked either as moderate or highest priority for a majority of the five issues. They are trace elements/mercury in bed sediment (including reconstructed trends in trace elements using sediment cores), mercury in fish fillets, and trace elements in the used ground water resource. These work elements are considered to be of greatest importance. Two additional work elements—synoptic studies of trace elements/mercury in multiple media along gradients of controlling factors, and a retrospective analysis of mercury in fish and bed sediment—complement the first two recommended work elements and also should be seriously considered for implementation.

Table 17. Summary of Interrelationships Among Work Elements and Issues Recommended for Trace Elements National Synthesis

[Priority: ***, highest; **, moderate; *, lowest; shaded work elements are considered to be of greatest importance]

Work Element	Issue					Range of (1998) Estimated Total Cost to Study Units
	Character- ization of Reference Conditions	Effects of Urbaniza- tion	Human Exposure to Drink- ing Water and Fish	Effects of Mining and Reme- diation	Regional Occur- rence and Distribu- tion of Mercury	
Retrospective Analyses						
Retrospective Analysis of Mercury in Fish and Bed Sediment	-	-	***	-	***	-
Retrospective Analysis of Trace Elements in Source Waters	-	-	**	-	-	-
Surface Water						
Trace Elements/Mercury in Bed Sediment	***	-	-	***	**	\$4,400– 7,800
Reconstructed Trends in Trace Elements using Sediment Cores	-	***	-	-	-	-
Mercury in Fish Fillets	**	-	**	**	**	2,500– 16,800
Synoptic Studies of Trace Elements/Mercury in Multiple Media Along Gradients of Control- ling Factors	-	**	-	*	***	7,500– 110,000
Trace Elements/Mercury in Surface Water	**	*	*	**	*	3,500– 33,000
Trace Elements in Fish Livers	*	-	-	-	-	3,900
Trace Elements in Fish Fillets	-	-	*	-	-	6,800
Ground Water						
Trace Elements in the Used Ground Water Resource	***	-	***	**	-	20,100– 32,400
Trace Elements in Shal- low Ground Water	*	*	**	***	-	6,800– 69,600

OPERATIONAL RECOMMENDATIONS

In addition to the five major trace element issues previously discussed, three operational recommendations were made that transcend the boundaries of the individual issues. These recommendations are discussed in the following sections.

Filtration of Water Samples

USEPA protocols for processing ground water samples vary from no filtration to filtration at pore sizes less than 0.45 micrometers, and they depend largely on the specific program (Barcelona and others, 1985; Brown and Teplitzky, 1995; U.S. Environmental Protection Agency, 1997a). Extremely slow pumping rates may be used to avoid collecting particulate material in ground water samples; however, the slow pumping rates and lack of purging raise concerns about whether the protocols result in samples of static well water rather than water moving through the aquifer.

The current NAWQA protocol requires filtration of water samples through a 0.45-micrometer capsule filter prior to analysis for dissolved constituents (Shelton and Capel, 1994, rev. 1996; Koterba and others, 1995). Use of this procedure is a fairly standard practice in environmental studies, provides a reasonable estimate of the dissolved fraction of many constituents under many hydrologic conditions, and avoids the inclusion of trace elements associated with large particulate matter when determining concentrations that are “bioavailable” in drinking water.

Horowitz and others (1992) have shown that filter type and diameter, filtration method, volume of sample filtered, suspended sediment concentration and particle size, and concentrations of colloidal material and organic matter all affect the amount of particulate matter that passes through a given filter to contribute to elemental concentrations operationally defined as “dissolved.” Generally, the smaller the pore size, the fewer fines that are allowed to pass, but the longer the time that is required in the field for filtration.

Recent advances in tangential flow filtration, and its common use in medical applications, have produced affordable filtration equipment with a nominal pore size of 0.001 micrometers (Hernandez and Stallard, 1988). USGS research projects studying trace elements in areas affected by acid mine drainage have used tangential flow filtration where determination of truly dissolved trace elements is important (Kimball and others, 1995). The small pore sizes used in this procedure should produce a more scientifically defensible approach for determining dissolved concentrations of trace elements.

Because of the perceived advantages of tangential flow filtration, the TENSPT recommends that this procedure be evaluated during early fiscal year 1999 for applicability to trace element studies within the NAWQA Program. Because a new protocol would need to be consistent with water quality monitoring needs outside the NAWQA Program, but within the WRD, the Office of Water Quality should be involved in the comparisons. The first step in the evaluation should be to compare split samples processed using both capsule and tangential flow filters. The study should compare results of the two methods for samples collected across a range of environmental settings within NAWQA Study Units. It should also identify associated quality assurance, quality control, and financial issues.

Prior to adoption of any new protocol, all water sampling at NAWQA sites should follow the existing, capsule filter approach. We recognize that any change in the filtration protocol will alter the nominal particle size included in the operationally defined dissolved fraction and that this may make comparisons among sites and over time more difficult than in the absence of such a change. However, we feel that the more realistic estimates of dissolved inorganic constituents likely to result from tangential flow filtration will more than compensate for potential data comparison problems.

Organism and Tissue Type

The choice of organism and tissue type for use in the bioassessment of trace element occurrence and distribution under the NAWQA Program has been difficult, as no single organism or tissue type can optimally address all possible objectives. Benthic invertebrates, such as mollusks and aquatic insect larvae, have a number of advantages for use in the biomonitoring of trace elements in aquatic ecosystems. These organisms are in intimate contact with the sediment where most trace elements accumulate, they bioaccumulate a number of trace elements reasonably well, and they are relatively immobile and, therefore, reflect localized contaminant concentrations. However, they are sometimes difficult to collect, are relatively short-lived, and are less relevant than fish in addressing potential health effects to humans. Thus, fish may be selected for use in biomonitoring, despite the fact that they accumulate some trace elements poorly and by a variety of uptake processes.

NAWQA Program Objectives, Fish Tissue Type, and Target Trace Elements

When sampling fish, the species or trophic functional group and the type of tissue to be analyzed must be determined. For the monitoring of trace elements in fish, various sampling approaches have been utilized, including the sampling of whole fish (Schmitt and Brumbaugh, 1990), fish muscle (U.S. Environmental Protection Agency, 1992), and fish liver (Crawford and Luoma, 1993; Evans and others, 1993). Small scale studies have included the analysis of kidney, gill, stomach, and other tissues, all of which can add to the understanding of the sources and routes of exposure.

The NAWQA sampling design should be influenced by the priorities for both program objectives and trace elements to be monitored. For example, sampling the fish fillet (muscle) is most important from the human health standpoint; however, only a few trace elements (primarily mercury and selenium) are known to accumulate significantly in fish muscle. In considering the health of organisms at higher trophic levels, the sampling of whole fish may be most appropriate because it is what piscivorous fish and waterfowl consume. For this objective, mercury and selenium are two of the most important trace elements because they are distributed fairly uniformly in fish and are most noted for bio-magnification. Finally, the liver is a logical choice for assessing the exposure to the organism selected for sampling because it is a deposition site for many trace elements, particularly those that are most acutely toxic (e.g. cadmium, copper, lead, and zinc).

In the original NAWQA sampling design for tissue (Crawford and Luoma,1993), human health aspects were considered a low priority for the program. Monitoring efforts of many States and the USEPA were already designed for the protection of human health. Therefore, fish livers were the most appropriate tissue to meet NAWQA Program objectives of determining trace element occurrence and distribution.

Sampling of Whole Fish

Apart from considerations of program objectives and the differential tissue accumulation of various trace elements, there are practical aspects to the sampling of whole fish to consider. Because a whole fish sample integrates all of the tissues from which trace elements may compartmentalize, it might be considered as the best all-around tissue for meeting the most objectives. However, bone and scales make sample homogenization much more difficult for whole fish, especially for larger specimens. Also, contamination of the tissue by ingested sediment is an important consideration (Brumbaugh and Kane, 1985; Lobel and others, 1991), especially for bottom feeding species, such as carp and suckers (Wiener and others, 1984; Haines and Brumbaugh, 1994). In extreme cases, contributions of selected trace elements from ingested sediment or detritus may overwhelm the concentrations in the whole body tissue. Because the trace elements associated with sediment may not be accumulated by the organism, the inclusion of ingested sediment in a whole fish may give misleading results concerning the bioavailability of the trace elements measured, as well as providing an artificial source of increased variability among serial replicate samples.

Because of the potential for contributions from ingested sediment and because homogenization is more difficult to accomplish for whole fish than for individual tissues, trace element concentrations for whole fish are likely to be more variable than for other tissues. Also, the size of the fish to be sampled is important depending on whether human health or food chain bioaccumulation is considered the highest priority. Larger fish are more likely to be consumed by humans but less likely to be consumed by predatory fish and waterfowl. Smaller fish would be better indicators of risk to predatory organisms. However, relatively young fish might be less useful for evaluating trends over the 10-year cycle of Study Unit activity in the NAWQA Program because of the greater likelihood that their trace element concentrations would be influenced by short-term, event-driven variations. Despite these considerations and potential problems, sampling of whole fish (particularly if uniform age classes can be obtained) is an option that deserves continued consideration under the NAWQA Program.

Sampling and Processing Fish Fillets for Assessment of Risk to Human Health

Many States have active monitoring programs for assessing the risk to human health from the consumption of fish. The vast majority of State fish consumption advisories for trace elements are due to mercury contamination. Many of the relatively few advisories for other trace elements are for shellfish near urban coastal regions (U.S. Environmental Protection Agency, 1997b). Therefore, the TENSPT recommends that sampling of fish fillets for assessment of risk to human health focus on the determination of mercury.

Because mercury typically bioconcentrates in fish muscle tissue (Goldstein and others, 1996), sampling of the muscle portion of the fillet (excluding skin and belly flap) is appropriate for assessing risk to humans from consumption of fish potentially contaminated with mercury, regardless of local preferences for fish preparation prior to consumption. Furthermore, because mercury has a propensity to bioconcentrate in fish muscle, the processing of fillets for mercury analysis is not prone to serious contamination (Bloom, 1992). Consequently, fillet removal for mercury analysis can be done without the extreme precautions generally required for analysis of other trace elements.

The following procedure, which is used at the USGS Environmental and Contaminants and Research Center, Columbia, Missouri (W.G. Brumbaugh, U.S. Geological Survey, written commun., 1998), is recommended by the TENSPT for processing of fillets for mercury analysis. Fillets should be removed with a good quality, high carbon steel fillet knife rinsed with dilute hydrochloric acid (1 percent, by volume) followed by laboratory grade, deionized water just prior to making the initial incision. Fish should be processed on a clean surface, such as a plastic cutting board, and any foreign material should be rinsed from the exterior of the fish before filleting. Age, size, and species of fish should be recorded.

A diagonal cut is made into the fish behind the pectoral fin until the backbone is felt. The knife blade is turned sideways, and a cut is made parallel to the backbone with the tip of the blade penetrating the skin just above and along the dorsal fin. The cut is continued to a point just short of the tail, so that the fillet is attached to the fish by the skin of the tail section. The fillet with skin attached is flipped over so the muscle faces up and the skin faces down. The muscle is removed from the skin by running the knife blade along the length of the fillet just above the skin layer.

A fillet removed following the above procedure should have been in contact only with the fillet knife. After removal, the fillet should be rinsed with laboratory grade, deionized water; the excess water should be allowed to drain before storage at -20°C. The fillet should be double bagged in zipper-seal plastic bags with any label(s) placed in the outer bag.

If possible, fillets should be removed in the laboratory to minimize contamination. Alternatively, fillets can be removed, rinsed, and frozen in the field. Fillets removed in the field should be rinsed with deionized water in the laboratory prior to homogenization for analysis.

It is likely that analysis of trace elements other than mercury will require different sample processing procedures than those outlined above. The USEPA (revised March 9, 1998) has recommended procedures that may be useful to the Trace Elements National Synthesis effort.

Sampling of Fish Livers

The sampling of fish livers has been used frequently for the assessment of trace element exposure to fish and is a component of the NOAA Status and Trends Program (Evans and others, 1993). Although fish livers may have minimal utility for assessing risks to human health, the concentrations of two of the trace elements that are of highest concern in fish muscle (mercury and selenium) often correlate strongly with the concentrations in the liver (Harrison and Klaverkamp, 1990; Goldstein and others, 1996). Most other toxicologically important trace elements are concentrated greatly in the liver in comparison to muscle tissue. Therefore, the liver is a logical sampling choice for assessing the exposure of the sampled organism to trace elements. The accumulation of trace elements in fish liver is generally indicative of systemic exposure, including waterborne and dietary routes. More importantly, physiological indicators of organism stress associated with heavy metal exposure have been linked to impaired liver function. Examples include increased lipid peroxidation and metallothionein induction in the liver, both of which are associated with tissue damage resulting from heavy metal exposure (Roch and others, 1982; Radi and Matkovics, 1988; Stegeman and others, 1992; Farag and others, 1995).

Despite the existence of an extensive literature on trace elements in fish livers, there may currently be insufficient data within the NAWQA Program to adequately evaluate the strengths and weaknesses of liver sampling for nationwide biomonitoring, and for straightforward interpretation of individual Study Unit data. Continued collection and evaluation of NAWQA fish liver data, along with a compilation of any pertinent existing literature data, should allow for better interpretation and would facilitate a reassessment of the liver sampling program at some later date. Because tissue monitoring is still an evolving science, there exists an opportunity for the NAWQA liver sampling effort to become an increasingly important biomonitoring component that could contribute significantly to the understanding of trace element exposure and uptake by fishes.

Taxa Considerations

Because trace elements are accumulated differently based on species and feeding habits, the interpretation of data collected for mixed species can be tenuous. Attempts to collect species that are common to all NAWQA Study Units, which would allow for a nationally consistent data set, have been minimally successful. This is a significant problem for all large-scale biomonitoring programs. In the current NAWQA tissue protocol, either carp or suckers are considered priority taxa because they are bottom feeders and they are the most ubiquitous fish across the continental U.S. However, some Study Units apparently have been unable or unwilling to collect either of these species. If it appears that the sampling of a nationally consistent fish species is unrealistic, a greater emphasis on regionally important (economically or otherwise) taxa should be considered. Target taxa based on regionally important species might, in fact, be more consistent with liver sampling because the liver is highly relevant in monitoring exposure and potential damage to the organism being sampled (as opposed to exposure to humans or higher trophic levels). Collection of taxa that are unique to one or a few Study Units should be avoided unless there is strong evidence that these taxa will be present at the vast majority of sampling sites within that Study Unit and that these are the only taxa that will allow multi-site comparisons within the Study Unit.

Summary

No single tissue or organism can be expected to meet all NAWQA objectives for trace elements. Different tissues should be sampled depending on the priorities of the objectives (assessing exposure to humans, to higher order organisms, or to sampled organisms) and the trace elements of greatest concern (mercury, selenium; or cadmium, copper, lead, zinc; or others). Sampling of livers is a widely utilized approach in the investigation of potential effects of trace elements on fishes, but a rigorous assessment of the strengths and weaknesses of the liver data in meeting NAWQA objectives is still needed. Thus, major modifications to the current tissue protocol should not occur without a review of the stated objectives and a reconsideration of the relative priorities. The ideal tissue sampling design would include whole fish (smaller specimens), fish fillets, and fish livers, from all sites. Because sampling all three tissue types is cost-prohibitive, the TENSPT makes the following recommendations:

1. Continue the current NAWQA protocol of collecting fish livers for 1997 Study Units.

- Document any changes to recommended National Target Taxa (NATT).
- Have the TEST interact with NAWQA regional biologists and other technical experts to determine target taxa that can be interpreted on a national basis.
- Give serious consideration to regional target taxa (especially for 2001 Study Units).
- Have the TEST analyze, in a timely manner, all trace element concentrations in bed sediment and tissue from the first 10-year NAWQA cycle to evaluate the

usefulness of the data with regard to NAWQA objectives. Analysis of the data should include a compilation of pertinent existing trace element concentrations in fish livers. Have the TEST recommend a modified tissue protocol for trace elements by October 2000 based on the data analysis.

2. Have 1997 Study Units collect fillet samples in addition to livers.

- Submit fillet samples to participating States for mercury analysis.
- Archive frozen fillet samples from all fish at a central location (to be determined).
- Pursue funding options for analyzing frozen fillets for total mercury.

Extraction of Bed Sediment

Trace elements historically have been recovered from sediment by total digestion, partial extraction, or sequential partial extraction (Horowitz, 1991). Total digestion dissolves the sediment matrix by heating with a combination of strong acids (typically hydrochloric, nitric, perchloric, and hydrofluoric), thus releasing trace elements from within the mineral lattice as well as from the particle surface. This procedure yields maximum trace element concentrations and does not differentiate between biologically available and unavailable forms. It is the procedure that has been used to date by the NAWQA Program (Arbogast, 1990).

Partial extractions typically use dilute acids, bases, complexing agents, and/or mild oxidizing agents at room or somewhat elevated (sub-boiling) temperatures to remove trace elements from the surface of sediment particles without appreciably attacking the matrix. In some situations, trace elements removed in this way have correlated with concentrations in organisms living in association with the sediment. For sediment containing carbonate minerals, care must be taken that the pH of the extraction fluid does not go above 1.5 (Luoma and Jenne, 1977) or some metals may precipitate.

Sequential extractions are a series of partial extractions of increasing chemical strength that are used to estimate various chemically reactive trace element fractions. A different fraction is removed with each chemical extractant (Tessier and Campbell, 1987).

Partial extractions, sequential or otherwise, are operationally defined procedures, and extracted trace element concentrations should not necessarily be expected to correlate to biological conditions at the site of sample collection. However, trace element concentrations derived from partial extraction procedures have the potential to better approximate bioavailable trace element fractions than do concentrations derived from total digestions because elements bound within the sediment matrix tend to be less easily removed than those on the particle surface. A major problem with all extraction procedures is that they are not selective (Horowitz, 1991).

As part of the National Sediment Quality Inventory, the USEPA (1997c) has used the AVS-SEM procedure, which involves extraction of sediment by dilute hydrochloric acid at room temperature, to evaluate the potential toxicity of divalent cadmium, copper, lead, mercury, nickel, and zinc in sediment. The USEPA notes that, according to Meyer and others (1994), AVS is a major chemical control on the activity and availability of these metals in interstitial waters of anoxic sediment. This, of course, assumes (1) the existence of chemical equilibria between the various divalent metals in interstitial water and their respective solid metal sulfides, and (2) that the major route of exposure to aquatic organisms is via the water column. The AVS-SEM procedure would not necessarily be expected to be applicable to organisms that are exposed to toxic divalent metals through ingestion of sediment.

DiToro and others (1990; 1992) have demonstrated no appreciable mortality to amphipods, snails, and oligochaetes from cadmium and nickel when AVS is greater than SEM. On the basis of chemical equilibria, they have predicted a similar lack of toxicity for divalent copper, lead, mercury, and zinc when AVS is greater than SEM. Only when SEM exceeds AVS are metals theoretically available to cause toxicity to biological communities living in or near the streambed. Hansen (1995) determined that when SEM exceeded AVS by more than 5, 80–90 percent of the cases exhibited toxic effects for crustaceans, and the USEPA (1997c) has used that criterion to differentiate between Tier 1 (adverse effects are probable) and Tier 2 (adverse effects are possible) sites based on chemical analyses of bed sediment.

Measurements of AVS-SEM are not widespread, and the utility of the procedure for divalent metals other than cadmium and nickel has not been documented. In addition, potential quality control problems have been noted when using the AVS-SEM procedure for copper and mercury (Brumbaugh and others, 1994; Brumbaugh and Arms, 1996). Finally, the extraction procedure is radically different from the total digestion currently used by the NAWQA Program.

Therefore, rather than suggest a wholesale change to a promising, but as yet unproven procedure, our recommendation is that the AVS-SEM extraction be implemented in one phase of the Trace Elements National Synthesis—the evaluation of bed sediment along a gradient of urbanization (see p. ____). This approach is consistent with similar recommendations by the ESPT (Cuffney and others, in press) and should be easy to integrate with proposed studies to evaluate ecological effects along such gradients. Sites selected for urban gradient studies will have the most complete record of ecological metrics and tissue contaminants, and they will represent a broad geographic coverage. Results from these studies should allow an assessment of the utility of AVS-SEM procedure to the NAWQA Program and an evaluation of its correlation with measurements of ecological conditions.

RECOMMENDED STAFF

To fully implement this plan for Trace Elements National Synthesis, the following staff will be required. A brief description of experience needed and duties is presented for each position. As many as possible of the staff should be located at the same duty station as the Chief, in order to insure interactive team synergy as the synthesis progresses. Staff are expected to be full-time (100%), except as noted. A total of 9 FTE are recommended.

Chief

Directs implementation of the Trace Elements National Synthesis. Selects and manages personnel. Meets with staffs of USEPA, American Water Works Association, and others in the drinking water community, and with State agencies in charge of fish advisories. Ensures that the synthesis effort is directed toward areas of value to the Nation. Develops cooperative efforts, if appropriate, with State and Federal agencies concerned with trace elements. Communicates with Study Unit staffs and tracks implementation of Study Unit efforts on trace elements. Prepares budgets and workplans in a timely manner. Coordinates with efforts of Geologic and Biological Resources Divisions related to trace elements. Advises staff on data analysis procedures. Integrates efforts on trace elements with other synthesis teams and the USGS Water Use Program.

Ground Water / Drinking Water Specialist

Leads synthesis efforts on ground water. Requires extensive expertise in geochemistry of trace metals and radionuclides in ground water systems. Develops a stratification of the United States by geochemical source regions, working with counterparts in GD and the Office of Ground Water. Evaluates and recommends field sampling protocols, as well as approaches to Study Unit Surveys and Land Use Studies for trace elements in ground water. Interprets results of Study Unit Surveys across Study Units, developing a regional/national picture of the distribution of trace elements. Communicates with health officials and epidemiologists to ensure that results of NAWQA efforts are useful to those disciplines.

Surface Water Specialist / Biologist

Leads synthesis efforts for surface water, particularly bed sediment and tissue surveys. Requires broad experience in collection and interpretation of trace elements in surface water, bed sediment, and aquatic biota. Develops a stratification of the United States by natural and human sources, working with counterparts within and outside the USGS. Evaluates and recommends sampling protocols for trace elements in fish tissue, working with Regional and Study Unit biologists and the Biological Resources Division. Works with the Office of Water Quality on all issues related to trace element sampling protocols. Interprets results of bed sediment and tissue occurrence and distribution surveys across Study Units, developing a regional/national picture of the distribution of trace elements. Communicates with the USEPA, State health officials, and aquatic ecologists to ensure that NAWQA efforts are useful to those disciplines.

GIS Specialist

Develops a national environmental setting for natural and human sources of trace elements. Works with other GIS specialists on NAWQA and District staffs to obtain, develop, and manipulate national data coverages relevant to national synthesis. Uses creativity and knowledge of digital data to develop new sets of ancillary data key to interpreting national-scale trace element data. Works with other team members to evaluate water quality and hydrologic data in relation to natural and human geographic settings. Compiles and evaluates existing trace element data available in a myriad of data bases from USGS (GD and WRD) and from other agencies. Writes and reviews technical reports interpreting water quality information using GIS.

Mercury Specialist (33% time)

Leads synthesis efforts related to mercury. Requires extensive expertise in the fate, transport, and analysis of mercury in the environment. Develops a stratification of the United States based on mercury input to and transport within watersheds. Works with the Surface Water Specialist and the USGS Toxics Substances Hydrology Program to interpret and publish reports on mercury in sediment and fish tissue across the United States, and to develop and implement sampling protocols for mercury in sediment and fish. With joint funding from the Toxics Substances Hydrology Program, performs laboratory analyses of mercury in sediment and fish.

Coring Trends Specialist

Plans and implements studies to characterize trends of trace elements and PAHs in lake and reservoir sediment across the United States. Requires experience in the collection and interpretation of sediment chemistry data, as well as characteristics of innovation and independence. Develops a stratification of reservoirs based on land use and natural conditions for the United States. Interprets data on trends and their possible causes, relates magnitudes of trends to sizes of sources, and authors papers on the same. Schedules data collection activities and supervises work of field crews. Insures that data are placed into the NAWQA data repository. Works with Study Unit chiefs and their staffs to integrate findings with those of the Study Units.

Coring support personnel (1.7 FTE)

Under supervision of the Coring Trends project specialist, plans and conducts field coring of lakes and reservoirs, maintains field equipment in working order, processes and analyzes samples for trace elements, and maintains data base.

Hydrologist

Data base support specialist. Works with surface water and ground water specialists to obtain and interpret existing and new data on trace elements. Maintains data bases for trace element data. Works with the GIS specialist to produce coverages of new ancillary data for interpreting trace elements. Oversees placement of all data onto the internet. Maintains web page as a resource for Study Units and an outreach tool.

Liaison / Specialized Expertise

This position, and the persons filling it, will change over time. It will be filled through term appointments and Intergovernmental Personnel Agreements.

Years 1–2: USEPA Liaison

Works at the Office of Science and Technology (OST), USEPA, Washington, DC, to integrate bed sediment and tissue activities in the NAWQA Program with those of the OST. Requires expertise in the interpretation of trace element and trace organic substances in sediment and aquatic biota. Communicates well with others. Co-authors reports with OST personnel. Keeps the Trace Elements National Synthesis Chief informed of all activities at OST of interest to the NAWQA Program. Presents NAWQA findings to OST for consideration. Develops opportunities for multiple Study Units to respond to OST needs.

Subsequent years: Trace Element Transport Specialist, IPA

University professor (part-time) and student help to model and explain the most important difficulties with observed occurrences of trace elements. Constructs, calibrates and verifies models. Applies results to areas of observed high occurrence of trace elements. Guides changes in NAWQA sampling over space and time to better understand the movement of trace elements from sources into important water supplies of the Nation. Co-authors reports with NAWQA staff.

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GLOSSARY

Aquatic life criterion — A water quality guideline for protection of aquatic life. Often refers to U.S. Environmental Protection Agency water quality criteria for protection of aquatic organisms.

Background — A reference condition that is as close to being unimpaired by human activities as can be found for a given environmental setting. The only human effects on trace element concentrations are from atmospheric deposition; other direct or indirect human influences are minor or nonexistent. Mineralized, but unmined, areas with naturally elevated trace element concentrations can be viewed as a special case of the background designation.

Baseline — A reference condition existing prior to (in time or space) the influence of a phenomenon whose effect is being measured. Conditions at reference sites described by this definition could be more than minimally impaired but may be quite useful for measuring effects of specific, well-defined inputs.

Basic Fixed Site (BFS) — A site on a stream at which streamflow is measured and samples are collected for temperature, specific conductance, suspended sediment, major ions and metals, nutrients, and organic carbon to assess the broad-scale spatial and temporal character and transport of inorganic constituents of stream water in relation to hydrologic conditions and environmental settings.

Bed sediment and tissue study — Assessment of concentrations of trace elements and hydrophobic organic compounds in streambed sediment and aquatic biota to identify potential sources and to assess spatial distribution.

Bioaccumulation — The biological sequestering of a substance at a higher concentration than that at which it occurs in the surrounding environment or medium. Also, the process whereby a substance enters organisms through the gills, epithelial tissues, dietary, or other sources.

Chlorofluorocarbons — A class of volatile compounds consisting of carbon, chlorine, and fluorine. Commonly called freons. Used in refrigeration mechanisms, as blowing agents in the fabrication of flexible and rigid foams, and, until recently, as propellants in spray cans.

Detection limit — The concentration below which a particular analytical method cannot determine, with a high degree of certainty, a concentration.

Domestic supply —

Drinking water standard/guideline — A threshold concentration in a public drinking water supply, designed to protect human health. As defined here, standards are U.S. Environmental Protection Agency regulations that specify the maximum contamination levels for public water systems required to protect the public welfare; guidelines have no regulatory status and are issued in an advisory capacity.

Ecoregion — An area of homogeneous climate, landform, soil, potential natural vegetation, hydrology, or other ecologically relevant variables.

Environmental framework — Natural and human-related features of the land and hydrologic system (such as geology, land use, and habitat) that provide a unifying framework for making comparative assessments of the factors that govern water quality conditions within and among Study Units.

Environmental setting — Land area characterized by a specific combination of natural and human-related features (for example, glacial till soils and row crop cultivation) that are relevant to water quality in the area of concern.

Finished water —

Geomorphic —

High Intensity Phase (HIP) —

Human health advisory — Guidance provided by U.S. Environmental Protection Agency, State agencies or scientific organizations, in the absence of regulatory limits, to describe acceptable contaminant levels in drinking water or edible fish.

Indicator site — A stream sampling site located at the outlet of a drainage basin with relatively homogeneous land use and physiographic conditions; most indicator site basins have drainage areas ranging from 20 to 200 square miles.

Integrator or mixed use site — Stream sampling site located at an outlet of a drainage basin that contains multiple environmental settings. Most integrator sites are on major streams with relatively large drainage areas.

Intensive Fixed Site (IFS) — Basic Fixed Site with increased sampling frequency during selected seasonal periods and analysis of dissolved pesticides for 1 year. Most NAWQA Study Units have one to two integrator Intensive Fixed Sites and one to four indicator Intensive Fixed Sites.

Land Use Study (LUS) — A network of existing shallow wells in an area having a relatively uniform land use. These studies are a subset of the Study Unit Survey and have the goal of relating the quality of shallow ground water to land use.

Maximum contaminant level (MCL) — Maximum permissible level of a contaminant in water that is delivered to any user of a public water system. MCLs are enforceable standards established by the U.S. Environmental Protection Agency.

Method Detection Limit (MDL) — The minimum concentration of a substance that can be accurately identified and measured with present laboratory technologies.

Mineralized —

Minimally Impaired — A reference condition with trace element concentrations that have been measurably increased due to the direct activities of humans within the immediate area. The determination of impairment should be made relative to the most sensitive beneficial use likely to be considered.

Minimum reporting level (MRL) — The smallest measured concentration of a constituent that may be reliably reported using a given analytical method. In many cases, the MRL is used when documentation for the method detection limit is not available.

Occurrence and distribution assessment — Characterization of the broad-scale spatial and seasonal distributions of water quality in relation to major contaminant sources and background conditions for surface and ground water.

Pristine — Webster's Ninth New Collegiate Dictionary (1990) defines pristine as "uncorrupted by civilization"; however, under current conditions of pollution redistribution by atmospheric transport (see, for example, Travis and others, 1989; Bonn, 1998), truly pristine watersheds probably do not exist anywhere in the world.

Public supply — Water withdrawn by public and private water suppliers for use within a general community. Water is used for a variety of purposes such as domestic, commercial, industrial, and public water use.

Reference condition — The highest water quality (lowest trace element concentrations) that can be attained in a given environmental setting and against which comparisons can be made to determine impairment of beneficial use, especially from land use changes.

Retrospective analysis — Review and analysis of existing data in order to address NAWQA objectives, to the extent possible, and to aid in the design of NAWQA studies.

Secondary maximum contaminant level (SMCL) — The maximum contamination level in public water systems that, in the judgment of the U.S. Environmental Protection Agency (USEPA), are required to protect the public welfare. SMCLs are secondary (nonenforceable) drinking water regulations established by the USEPA for contaminants that may adversely affect the odor or appearance of such water.

Sediment quality guideline — Threshold concentration above which there is a high probability of adverse effects on aquatic life from sediment contamination, determined using modified U.S. Environmental Protection Agency (1996) procedures.

Source water —

Speciation —

Stratification — Subdivision of the environmental framework. The Study Unit is divided into subareas that exhibit reasonable homogeneous environmental conditions, as determined by both natural and human influences.

Study Unit — A major hydrologic system of the United States in which NAWQA studies are focused. Study Units are geographically defined by a combination of ground and surface water features and generally encompass more than 4,000 square miles of land area.

Study Unit Survey (SUS) — Broad assessment of the water quality of major aquifer systems of each Study Unit. The Study Unit Survey relies primarily on sampling existing wells and, wherever possible, on existing data collected by other agencies and programs. Typically, 20 to 30 wells are sampled in each of three to five aquifer subunits.

Subunit Survey (SUS) — Same as Study Unit Survey.

Synoptic sites — Sites sampled as part of a short-term investigation of water quality during selected seasonal or hydrologic conditions to provide improved spatial resolution for critical water quality conditions.

Tailings — Rock that remains after processing ore to remove the valuable minerals.

Tangential flow filtration —

Water column study — Investigation of physical and chemical characteristics of surface water, which include suspended sediment, dissolved solids, major ions and metals, nutrients, organic carbon, and dissolved pesticides, in relation to hydrologic conditions, sources, and transport.

Water quality criterion — A specific level of water quality which, if reached, is expected to render a body of water unsuitable for its designated use. Commonly refers to water quality criteria established by the U.S. Environmental Protection Agency. Water quality criteria are based on specific levels of pollutants that would make the water harmful if used for drinking, swimming, farming, fish production, or industrial processes.

Water quality guideline — A specific level of water quality which, if reached, may adversely affect human health or aquatic life. These are nonenforceable guidelines issued by a governmental agency or other institution.

Water quality standard — State adopted and U.S. Environmental Protection Agency approved ambient standard for water bodies. Includes the use of the water body and the water quality criteria that must be met to protect the designated use or uses.

Water year — The continuous 12-month period, October 1 through September 30, in U.S. Geological Survey reports dealing with the surface water supply. The water year is designated by the calendar year in which it ends

and which includes 9 of the 12 months. Thus, the year ending September 30, 1980, is referred to as the 1980 water year.

APPENDICES

Appendix A. Charter

MEMORANDUM

TO: Study Unit Chiefs (1991, 1994, 1997), National Synthesis Team Leaders, NAWQA Leadership Team, NAWQA Planning Team, Regional Water Quality Specialists, and Trace Elements National Synthesis Planning Team

FROM: Timothy L. Miller, Chief, National Water-Quality Assessment Program

SUBJECT: Charter for the Trace Elements National Synthesis Planning Team

As the third set of National Water-Quality Assessment Program (NAWQA) Study Units begins intensive data collection in October 1998, a Trace Elements National Synthesis effort will be added as a focus for data collection and interpretation. Data collection for several trace elements has been part of the Program since our beginning, and has resulted in several Study Unit fact sheets, as well as other ongoing interpretation efforts. At issue, now, is how NAWQA should change to address trace element issues in response to this new national synthesis focus and to questions posed by external information needs, such as reauthorization of the Safe Drinking Water Act.

In February, Dennis Helsel was selected to lead the Trace Elements National Synthesis project. In order to ensure that the plan for this effort reflects the full expertise and capability of the Bureau, we are forming an ad hoc Trace Elements National Synthesis Planning Team (TENSPT) to receive and coordinate input from the many individuals and groups with expertise in this area.

As with the newly formed Ecological Synthesis Planning Team, the TENSPT will develop a synthesis plan; however, they will call on expertise from around the USGS and outside the Bureau to assist in this effort. Denny Wentz has agreed to assist Dennis Helsel by leading the planning team effort.

Below is the TENSPT Charter. Please note the section on "Structure and Composition of the Planning Team". The TENSPT will need to obtain assistance from others. If asked, please consider assisting the TENSPT in this important endeavor for NAWQA.

CHARTER for TRACE ELEMENTS NATIONAL SYNTHESIS PLANNING TEAM

A. ESTABLISHMENT

This document establishes an ad hoc Trace Elements National Synthesis Planning Team (TENSPT) and sets forth the purpose, scope, process, composition, and tenure for this team.

B. BACKGROUND

The long term goals of the NAWQA Program are to describe the status and trends in the quality of the Nation's surface and ground water resources and to provide a sound, scientific understanding of the primary natural and human factors affecting the quality of these resources. This information, which will be obtained on a continuing basis, will be made available to water managers, policy makers, and the public to provide an improved scientific basis for evaluating the effectiveness of water quality management programs and for predicting the likely effects of contemplated changes in land and water management practices.

The activities of the NAWQA program are organized to coincide with efforts at the Study Unit and national scales. Study unit investigations are the principal building blocks of the NAWQA Program. The full scale program will be accomplished through investigations of a set of 50-59 Study Units (major river basins and aquifer systems) distributed throughout the Nation that in aggregate account for a large percentage of the Nation's water use and population. To make the program manageable, the assessment activities in each of the Study Units will be done on a rotational, rather than a continuous basis. Only about one-third of the Study Units will be studied in detail at a given time.

The national benefits of NAWQA primarily accrue in two ways. First, there is the simple accumulation of high quality data from perennial assessments of some of the most important hydrologic systems of the Nation. In this respect, NAWQA Study Unit investigations could be independently designed to address the most critical water quality issues in each Study Unit. The second way that benefits of NAWQA accrue at the national level is through the process and results of national synthesis. The goal of national synthesis is to provide policy relevant water quality information that is more meaningful and complete at the national scale than the simple accumulation of independent water quality studies of individual hydrologic systems. The unique characteristic of the NAWQA Program that lends itself to national synthesis is the coordinated application of comparative hydrologic studies at a wide range of spatial and temporal scales. This approach is intended to simultaneously provide new insights into the status and trends of water quality and, more importantly, to improve our understanding of the physical, chemical, and biological processes and causal relationships. The linkage of information on status and trends with an understanding of environmental processes is a key design concept that is of fundamental importance to environmental management and policy development. National synthesis products are being developed from a combination of existing water quality and ancillary information, along with new findings from the NAWQA Study Unit investigations and regional synoptic surveys.

Two national synthesis projects began in fiscal year 1991; they are focused on pesticides and nutrients in surface and ground water. A third national synthesis project, focused on VOCs, began in 1994. Planning for trace elements and ecological national synthesis projects are presently (1997) underway. Trace element issues are currently of great interest to the U.S. EPA and States that are reconsidering regulatory levels for arsenic and radon, evaluating whether other trace elements warrant regulation in water and fish tissue, and investigating health effects of mercury and other elements in humans and animals. Therefore, a Trace Elements National Synthesis is not only essential to meeting the basic goals of the NAWQA Program, but the information produced by the synthesis could be of great value in addressing current and future management and regulatory issues of Federal and State agencies.

Implementation of a Trace Elements National Synthesis plan may require modest changes to the current design of Study Unit investigations and field protocols, and to the relation and coordination of activities among other national synthesis studies (pesticides, nutrients, VOCs, and

ecology). After approval of the plan by the NAWQA Leadership Team (NLT), the job of the ad hoc Planning Team will be complete, and it will dissolve.

C. PURPOSE AND SCOPE

The TENSPT will be responsible for preparing a written plan for Trace Elements National Synthesis in the NAWQA Program that will be presented to the NLT. The plan should include (but is not limited to) the following components:

I. IDENTIFICATION AND SUMMARY OF TRACE ELEMENT QUESTIONS REQUIRING NATIONAL OR REGIONAL APPROACHES

1. TRACE ELEMENT INFORMATION NEEDS OF WATER RESOURCE MANAGERS, POLICYMAKERS, AND THE GENERAL PUBLIC

- * Description of trace element information needs of other Federal and nonfederal agencies appropriate to regional and national synthesis
- * Role of trace element data in addressing key pieces of environmental legislation
- * Environmental standards, criteria, etc., that may require trace element data.

2. TRACE ELEMENT MONITORING ACTIVITIES OF STATE AND FEDERAL AGENCIES

- * Information required to avoid duplication of effort and enhance applicability of data collected to other programs.

II. PRIORITIZATION OF QUESTIONS TO BE ADDRESSED AS PART OF TRACE ELEMENTS NATIONAL SYNTHESIS

The Trace Elements National Synthesis plan will address hypotheses, objectives, and questions that are topically, regionally, or nationally significant. The plan will provide a prioritized list of questions. These priorities can guide NAWQA in the event that budget difficulties require identification of hypotheses/objectives/questions to be deferred. Criteria used for prioritization will be developed. Linkage of trace elements synthesis questions to other NAWQA syntheses, and to other Federal programs, will be addressed.

III. DESIGN ELEMENTS FOR TRACE ELEMENTS NATIONAL SYNTHESIS ACTIVITIES

The Trace Elements National Synthesis Plan will specify the appropriate spatial (regional, national) and temporal scales of questions to be considered. The plan will address the following elements.

1. ENVIRONMENTAL FRAMEWORK FOR TRACE ELEMENTS NATIONAL SYNTHESIS

- * Concepts for an environmental framework
- * Definition of population about which we are drawing inferences
- * Integration and reconciliation with environmental frameworks of other national synthesis studies
- * Existing frameworks for agriculture and urban areas
- * Additional requirements for trace elements synthesis
- * Conceptual organization of a trace elements synthesis environmental framework
- * Consideration of the role of minimally impacted and comparative reference settings
- * Consideration of land use aspects and how NAWQA will obtain a nationally consistent environmental framework
- * Other factors that may be important for addressing the critical questions/objectives of interest, such as human population distribution and point and nonpoint sources
- * Critical needs related to the above and plans for addressing these needs

2. SELECTION OF TARGET VARIABLES FOR TRACE ELEMENTS NATIONAL SYNTHESIS

- * Considerations include elements, forms, media, etc.
- * Criteria/rationale for selection of variables
- * Key characteristics of candidates
- * Application of criteria and resulting target variables

3. PLAN FOR RETROSPECTIVE ANALYSIS FOR TRACE ELEMENTS NATIONAL SYNTHESIS

- * Prioritized objectives and linkage of retrospective analysis to planned synthesis studies
- * Review of experience, progress, and products of 1991 and 1994 Study Units
- * Evaluation of existing approaches
- * Products (what can be accomplished from the first two sets of Study Units plus historical data)
- * Evaluation of quality of historic data
- * Availability of ancillary data from 1991 and 1994 Study Units
- * Time frame
- * Guidance requests for the 1997 Study Units, as appropriate

IV. IMPLEMENTATION PLAN FOR TRACE ELEMENTS NATIONAL SYNTHESIS

1. PLAN FOR STUDY UNIT ACTIVITIES

- * Determine the role of different Study Units in addressing specific Trace Elements National Synthesis objectives (e.g., not all Study Units may be equally important for addressing all objectives, particularly those of a regional scale)

2. RELATION OF TRACE ELEMENTS NATIONAL SYNTHESIS PLANS TO OTHER NATIONAL SYNTHESIS ACTIVITIES AND WRD PROGRAMS (NASQAN, BENCHMARK), GD, AND BRD EFFORTS

- * Trace elements in NAWQA urban studies and study unit surveys
- * Opportunities to enhance existing topical studies and objectives
- * Proposed role(s) of other synthesis efforts for accomplishing Trace Elements National Synthesis objectives
- * Potential for interdivisional collaboration

3. DATA BASE ELEMENTS NECESSARY TO SUPPORT TRACE ELEMENTS NATIONAL SYNTHESIS

- * Review of existing data base elements
- * Specification of new requirements and links with other data bases
- * Options, analysis, and recommendations for addressing needs

4. ANCILLARY DATA NEEDS FOR TRACE ELEMENTS NATIONAL SYNTHESIS

- * Prioritized list of potentially useful existing data bases
- * Brief description of selected data bases
- * Coordination with ancillary data bases of other national synthesis studies
- * Identification of other data needs
- * Options, analysis, and recommendations for meeting needs

5. PRIORITIZED LABORATORY ANALYTICAL METHODS, QUALITY CONTROL, AND OTHER NEEDS OF TRACE ELEMENTS NATIONAL SYNTHESIS

- * Definition of needs
- * Current laboratory and field capabilities in relation to stated goals and objectives
- * Relation to specific objectives
- * Options, analysis, and recommendations for meeting needs

6. GENERAL TIMEFRAME FOR COMPLETION OF TRACE ELEMENTS NATIONAL SYNTHESIS STUDIES

7. STAFFING PLAN FOR IMPLEMENTATION OF TRACE ELEMENTS NATIONAL SYNTHESIS STUDIES

- * Recommendations for areas of expertise for the synthesis team
- * Description of major work activities by position
- * Relation to Study Unit activities
- * Relation to ongoing State programs

8. 3-5 YEAR BUDGET WITH OPTIONS FOR IMPLEMENTATION OF TRACE ELEMENTS NATIONAL SYNTHESIS STUDIES.

D. PLANNING PROCESS

There are several elements to the planning process: (1) Structure of the planning process guided by the TENSPT; (2) timing for initial planning, internal and external reviews, and final revisions and recommendations to the plan; (3) authority of the team and its relation to the NLT; and (4) products from the planning process.

Structure and Composition of the Planning Team

To accomplish the planning process, this Charter establishes the Trace Elements National Synthesis Planning Team, which will consist of the following individuals:

Denny Wentz, Planning Team Leader, Portland, OR
Bill Brumbaugh, Environmental Chemist, BRD, Columbia, MO
Roger Fujii, Research Chemist, CA District, Sacramento, CA
Dennis Helsel, NAWQA Trace Elements National Synthesis Project Chief, Denver, CO
Art Horowitz, Research Chemist, NRP, Atlanta, GA
Mike Koterba, NAWQA QA/QC Project Chief, Baltimore, MD
Jim Kuwabara, Hydrologist, NRP, Menlo Park, CA
Rich Wanty, Research Chemist, GD, Denver, CO

Ex officio members -----Tim Miller, Bill Wilber

Ex Officio members will provide necessary linkages between the TENSPT and the NLT and provide advice and guidance where needed. Individuals may be added or removed from the TENSPT by recommendation of the Team Leader to the NLT.

Because this effort should be well integrated with other components of the program and to incorporate additional experience and perspectives from completed NAWQA Study Unit investigations and other national synthesis teams into the planning process, individuals from the following program components will be identified to serve as key resources and linkages:

1991, 1994, and 1997 Study Units
Nutrients National Synthesis Team
Pesticides National Synthesis Team
VOCs National Synthesis Team
Ecological Synthesis Planning Team
Numerous ongoing national efforts supported by the NAWQA Program and related to interpretation of trace elements in sediment cores, bed sediment, tissue, and ground water

Additional individuals, both within (NMD, GD, BRD, WRD) and outside the USGS, will be asked to act as key resources for the development of the Trace Elements National Synthesis Plan. Resource individuals will be called on to provide input and advice on specific topics and to provide suggestions related to draft plans prepared by the team. In particular, key resource individuals will be necessary to (1) review priorities of hypotheses/objectives/questions to be

studied, (2) provide technical expertise as required, (3) provide assistance with and review of implementation plans. Time commitments required of various resource individuals may vary considerably, and significant time commitments will be reviewed by the NLT and appropriate supervisors.

Planning Components and Timing

Beginning in October 1997, the TENSPT will convene to begin the planning process at the call of the team leader and the ex officio members. Because of the scope of work, it is anticipated that the planning and review process will require about 1 year to complete. One of the first tasks of the TENSPT will be to develop a work plan for completing the Trace Elements National Synthesis Plan, which will identify key tasks, individuals responsible for completing these tasks, and time lines for completing the tasks. This work plan will be reviewed by the NLT to ensure there is agreement on direction of the team and that the necessary resources are made available to complete the plan in a timely manner.

Authority

The TENSPT has authority to draft plans and make recommendations to the NLT. It is the responsibility of the TENSPT to interface with other groups both internal and external to the USGS including Study Units, national synthesis teams, the National Research Program, the National Water Quality Laboratory, and other agencies and universities as needed. The NLT responsibilities include: (1) ensuring that necessary staff time and resources are made available to complete the plan, (2) providing guidelines and identifying planning constraints, (3) reviewing and carefully considering recommendations in the plan at strategic times in the planning process and providing feedback to the team, (4) approving the plan after any necessary revisions are completed, and (5) tasking the Trace Elements National Synthesis project team leader to implement the approved plan.

Products

The principal product of this team is a peer reviewed document describing the recommended plan for trace elements synthesis in the NAWQA Program. Periodic progress reports will be provided at key milestones during the planning process.

TENURE OF THE PLANNING TEAM

The TENSPT is established and individual members serve at the discretion of the Chief, NAWQA. The tenure of the Team is expected to be about 1 year unless, based on the work plan, a different time schedule is approved by the NLT.

Appendix B. Assumptions for Determining Cost Estimates

A. Cost for quality control samples = 20 per cent of environmental sample cost.

B. Numbers of sites and/or samples for various component studies:

- LUS — 30 wells
- SUS — 30 wells
- Bed sediment — 20 sites
- Tissue — 20 sites
- BFS — 16 samples per year for two years
- Surface water synoptic studies — 20 sites

C. Personnel and time requirements, and equipment and supplies needed for field sampling are presented in table B-1.

Table B–1. Personnel and time requirements, and equipment and supplies needed for field sampling

Component	Personnel ^a	Average Time ^b	Equipment/Supplies Needed
LUS	GS-10 technician GS-5 technician	1 well per day	Turbidity meter and supplies (\$1,780) ^c
SUS	-		Turbidity meter and supplies (\$1,780) ^c
Bed sediment ^d	GS-10 technician GS-5 technician	2 sites per day	Minimal
Tissue ^d	GS-11 biologist GS-10 technician GS-5 technician	1.5 sites per day	Minimal
Surface water site ^e	GS-10 technician GS-5 technician	2.5 sites per day	Minimal

^aApproximate total salaries for personnel: GS-5, step 1 technician = \$190 per day; GS-10, step 6 technician = \$375/day; GS-11, step 3 biologist = \$375 per day.

^bThese are long-term average times for typically long (10+ hour) days.

^cThis is a one time cost for either LUS or SUS. If both LUSs and SUSs are done, only one \$1,780 assessment applies.

^dLarge (nonwadable) rivers will require significantly greater resources (time, money, personnel, equipment). Efficiencies with regard to time will be realized if the bed sediment and tissue sampling are done during the same site visit.

^eThese estimates are for sites sampled for only dissolved trace elements and associated ancillary data (field water quality, discharge, and, possibly, hardness).