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5. CHEMICAL ANALYSES

The assessment of risks associated with contaminated sediments at a specific site is limited by the available database. A comprehensive assessment of contaminated sediments requires both evaluation of the biological component (e.g., toxicity tests, lesions, developmental abnormalities, benthic community surveys) and chemical characterization at the study site. In many studies, either the biological or the chemical component is absent, limiting the quality of professional judgment that may be applied to assess risks.

One goal of the ARCS Program was to generate a large body of chemical data to complement extensive biological studies at the demonstration AOCs. It was recognized that ideally the sampling scheme should be complete spatially (horizontally as well as with depth) and that the analysis scheme should include the full range of chemicals that might be present at the site. Assessment of the depth of contamination was extremely important to ensure that any contamination that could be uncovered during site remediation would be handled properly.

To develop a strategy for sample collection and analysis, investigators should study the site history and gather relevant data that may indicate the identity and location of potential contaminants in sediments. Ideally, the contaminant history should be gleaned both from past environmental monitoring studies and a history of chemical loading to the drainage basin (e.g., based on agricultural, urban, industrial land use practices). Local experts may be able to provide additional information regarding potential contamination at a particular site. Selection of the appropriate analytical variables should also take into consideration available analytical methods and whether the new data will be comparable with historical data (assuming that the historical data meet current DQOs). Often practical considerations, such as use of the current methods for USEPA's priority pollutant list compounds, limit the selection of chemicals that may be evaluated.

Typical Great Lakes sites present multiple contamination problems that may have been explored to some degree during previous studies. For the five ARCS priority AOCs, historical data were gathered by the Corps (Brandon et al. 1991; Skogerboe et al. 1991; Lee et al. 1991; Simmers et al. 1991; Tatem et al. 1991). While these reports were not complete at the time that the list of potential contaminants of concern was developed, sufficient information was available to select the chemicals to be analyzed. Local experts were, and should always be, consulted regarding the identity and locations of sediment contaminants, as well as potential sources of those contaminants.

An exploratory screening-level study (see Chapter 4) should be completed first whenever possible to better target analyses of samples in cases where the historical database and

knowledge of the contaminants released to the system are limited. Screening-level analyses can help target areas requiring detailed assessments. When possible, screening-level studies should be initiated well in advance of more detailed assessment studies so that any major class of contaminants found in the system can be incorporated into the detailed study design. An exploratory screening-level study may also save money by narrowing the list of contaminants and areas to sample for the detailed assessment.

A detailed assessment is usually needed to determine appropriate remedial alternatives that may be cost effective for a given site. Spending too many project dollars for the detailed assessment, however, can leave too few dollars for remediation and post-remediation monitoring. Because remediation of contaminated sediments is often very costly, a great deal of money can be saved through accurate, comprehensive assessment activities. A tiered approach makes maximum use of available funds by quickly identifying potential concerns using relatively low-cost screening analyses and then focusing higher-cost, detailed analyses on high-priority sites. Sampling costs can often be minimized in such a program by collecting and archiving samples from all stations sampled in a screening survey, and then conducting detailed analyses on selected stations after concerns are better defined.

Factors that affect the bioavailability of contaminants should also be considered when developing the list of chemicals to be analyzed. In general, several sediment characteristics have been identified as major factors that will alter contaminant bioavailability (Landrum and Robbins 1990). Among these are the TOC and AVS content of sediments. The TOC concentration is used to estimate the partitioning of nonionic organic compounds between sediment solid fractions and pore water. The AVS theory of metals bioavailability in sediment is that sulfide can form an insoluble compound with many divalent metals (e.g., cadmium, copper, lead, nickel, zinc), thereby reducing the concentration of these metals that may be available to exposed organisms (Di Toro et al. 1990). Both TOC and AVS analyses are recommended, although there is still scientific debate about the use of AVS normalization in predicting the toxicity of metals. Additional analyses to characterize the bioavailability of sediment-associated contaminants may need to be considered in future assessments as new data become available from ongoing national research on bioavailability.

Chemicals not typically analyzed for may also be associated with sediment toxicity. Exploratory analyses for tentatively identified compounds should also be considered. These techniques employ use of GC/MS, liquid chromatography/mass spectrometry, nuclear magnetic resonance spectroscopy, and infrared spectroscopy. They will not be discussed here.

In some cases, chemical analyses will be performed not only on sediment samples, but also on tissue, elutriate, or pore water samples. The contaminant concentrations in tissue may be used in human health or ecological risk assessments, while the contaminant concentrations in elutriate or pore water samples may provide a better estimate of the contaminant concentrations to which benthic organisms are exposed.

METHOD SELECTION (GENERAL OVERVIEW)

Analytical techniques should be selected that produce reliable data, have adequate sensitivity to meet the required detection limits, and are cost effective. In addition, standard techniques such as those in *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods* (USEPA 1986b) should be used, when possible, to ensure that the data to be collected will be comparable with historical data. Other methods are needed for analyses of PCB congeners, methylmercury, and tributyltin (TBT), which are not addressed in standard USEPA methods. Recommended analytical procedures are discussed in the following sections. Approximate costs (in 1993) for common chemical analyses are provided in Table 5-1.

CONVENTIONAL VARIABLES

This section describes recommended analytical methods for the measurement of conventional (noncontaminant) variables in sediment and tissue samples.

Sediments

Total solids, grain-size distribution, and TOC are common analyses that are conducted to characterize sediments or to provide data used to interpret specific chemical analyses. Additional information on the use of these analyses to characterize sediments can be found in Chapter 4, *Screening-Level Analyses*, or in Plumb (1981).

The total solids content of sediments can be determined by oven-drying the sample at 105°C or by freeze-drying a subsample and calculating the ratio of dry to wet weight of the sediment. Grain-size distribution (e.g., the percent gravel [>2-mm diameter], sand [2 mm–62.5 μm], silt [62.5 μm–3.9 μm], and clay [<3.9 μm] content) of a sediment sample can be determined using a nest of sieves and pipette analysis or hydrometer.

After treating the sediment with hydrochloric acid (non-oxidizing acid) to remove carbonates, organic carbon can be determined as total carbon by combusting the sample at 800–1,000°C in an oxygen atmosphere and transferring the evolved CO_2 directly into a gas analyzer with either a thermal conductivity or infrared spectroscopy detector.

In addition to these more common analyses, AVS can be determined in sediments as described in Cutter and Oatts (1987) or Allen et al. (1991). These methods involve generation of hydrogen sulfide from sediment in 1N HCl, trapping the hydrogen sulfide, and quantifying by a number of possible techniques.

TABLE 5-1. APPROXIMATE COSTS FOR CHEMICAL ANALYSES

Parameter	Matrix	Methods	Cost[a] (1993)
Total solids	Sediment	Gravimetric	$15
Acid-volatile sulfides	Sediment	GC/PID	$75
Grain size	Sediment	Sieve and pipette	$65–$100
Total organic carbon	Sediment	Combustion	$50–$70
Lipid content	Tissue	Gravimetric	$25–$75
Moisture content	Tissue	Gravimetric	$25
Semivolatile organic compounds	Sediment Tissue Water or elutriates	GC/MS	$300–$700
Polynuclear aromatic hydrocarbons	Sediment Tissue Water or elutriates	GC/MS, SIM HPLC	$450 $175
PCB Aroclors® and chlorinated pesticides	Sediment Tissue Water or elutriates	GC/ECD	$200–$300
PCB congeners	Sediment Tissue Water or elutriates	GC/ECD	$300–$500
PCB coplanars	Sediment Tissue Water or elutriates	GC/ECD, HRGC/HRMS	$900–$1,500
PCDDs/PCDFs	Sediment Tissue Water or elutriates	HRGC/HRMS	$900–$1,500
Methylmercury	Sediment Tissue Water or elutriates	Ethylation, CVAF	$225
Butyltin compounds	Sediment Tissue Water or elutriates	Derivatization, GC/FPD	$400–$500
Metals	Sediment Tissue Water or elutriates	GFAA, ICP/MS, ICP/AES, CVAA or CVAF (mercury only), XRF	$300–$400 $70

Note: AES - atomic emission spectroscopy
CVAA - cold vapor atomic absorption spectroscopy
CVAF - cold vapor atomic fluorescence
ECD - electron capture detection
FPD - flame photometric detection
GC - gas chromatography
GFAA - graphite furnace atomic absorption spectroscopy
HPLC - high-pressure liquid chromatography
HRGC - high-resolution gas chromatography
HRMS - high-resolution mass spectrometry
ICP - inductively coupled plasma
MS - mass spectrometry
PCB - polychlorinated biphenyl
PCDD - polychlorinated dibenzo-*p*-dioxin
PCDF - polychlorinated dibenzofuran
PID - photoionization detector
SIM - selective ion monitoring
XRF - x-ray fluorescence

[a] Cost per sample. Costs per sample generally go down as more samples are analyzed.

Tissues

Moisture content in biological tissue can be determined gravimetrically by oven- or freeze-drying the samples and determining the ratio of dry to wet weight of tissue. Lipid content can be determined gravimetrically following a method derived from Bligh and Dyer (1959). A subsample of each tissue sample is extracted with a chloroform-methanol solution (a nonpolar-polar solvent combination) and centrifuged, and then the chloroform layer is drawn off and filtered. Care must be taken to ensure that the filter is rinsed with solvent so that lipids are not adsorbed. The organic filtrate is evaporated and the remaining residue is dried at 103°C. The method should be performed on a subsample of the same tissue homogenate used for organic chemical analyses to avoid introducing sampling variability into lipid-normalized concentrations of organic compounds.

Alternatively, the gravimetric weight of solvent-extractable organic material in tissue samples (i.e., lipid content) can be determined directly from the same extract used for analysis of semivolatile organic compounds, assuming that a combination of polar and nonpolar solvents is used in the extraction (e.g., acetone-dichloromethane or methanol-dichloromethane). Following separation of the organic and aqueous fractions of the tissue extract using a separatory funnel, and prior to additional extract cleanup (e.g., gel permeation chromatography [GPC]), a subsample not exceeding 1/40th of the total extract should be transferred to a pre-weighed aluminum dish, evaporated gently, and weighed.

Use of nonpolar solvents alone in the tissue extraction process will not extract the more polar lipids such as phospholipids. Further, the partitioning of nonpolar contaminants associated with the more polar lipids appears to be similar to that for nonpolar lipids (Gardner et al. 1990). Thus, if a completely nonpolar extraction is employed, the lipid content will be underestimated while the measured contaminant concentrations will be fairly complete, creating a positive bias in lipid-normalized concentrations. Overall extraction efficiency will also decrease because of the creation of emulsions between the nonpolar solvent and water in the tissue sample. To avoid these concerns, lipids in tissue samples should always be determined using a procedure that incorporates both polar and nonpolar extraction solvents.

Because lipid content may be calculated on a dry-weight basis by some researchers, the wet- to dry-weight ratio should be provided so that users of the data can convert between a wet- and dry-weight basis as required. The units used to report percent lipids content (wet or dry weight) should be clearly indicated on the data table.

Conclusions

The analysis of total solids, grain-size distribution, and TOC content should be required for all sediment samples. AVS analyses for sediment samples are optional but recommended. Other sediment analyses such as total volatile solids and ammonia content may

be appropriate as screening tests for sites that are expected to have substantial concerns with anoxia. All tissue samples should be analyzed for moisture content and percent lipid content.

ORGANIC COMPOUNDS

The three groups of organic chemicals that are frequently quantified in sediment samples include 1) nonchlorinated semivolatile organic compounds, which include PAHs; 2) PCBs and chlorinated pesticides; and 3) PCDDs and PCDFs. The usual sequence for analysis includes extraction with solvent, purification (cleanup) and separation by column chromatography or HPLC, and quantification by capillary column gas chromatography with detection by electron capture detection (ECD), mass spectrometry, or flame ionization detection (FID).

Nonchlorinated Semivolatile Organic Compounds

Nearly 200 nonchlorinated semivolatile organic compounds can be routinely analyzed by environmental laboratories, including phenols, phthalate esters, and PAH compounds. Among these compounds, those that appear to pose the greatest health risk are a number of the PAH compounds classified as B2 carcinogens by the USEPA (1993b) (e.g., benzo[a]pyrene, benz[a]anthracene, benzo[b]fluoranthene, chrysene, dibenz[a,h]anthracene, and indeno[1,2,3-cd]pyrene). For this reason, the ARCS Program focused primarily on analysis of PAH compounds.

The most widely used method for the analysis of semivolatile organic compounds is the USEPA Method 8270 described in USEPA (1986b). In addition, other USEPA methods for analyzing more specific groups of semivolatile compounds such as PAHs (USEPA SW-846 Methods 8100 and 8310) and phenols (USEPA SW-846 Method 8040) are designed to achieve lower detection limits than USEPA SW-846 Method 8270. NOAA also has a widely accepted set of methods for analyzing PAH compounds as part of the National Status and Trends Program (NOAA 1993).

Extraction

Extraction of sediment samples for the entire range of acid, base, and neutral semivolatile organic compounds is best conducted using a mixture of nonpolar and polar solvents (e.g., dichloromethane-methanol, dichloromethane-acetone, hexane-methanol) and sometimes in sequential extraction steps. The goal is to extract as completely as possible all compounds of interest while preserving their chemical structure for analysis. Polar solvents are necessary to extract polar (acid and base) compounds and to aid in removing water from the sediment matrix, which can interfere with the proper extraction of nonpolar compounds. Some extraction methods make use of anhydrous sodium sulfate as a drying agent to remove water from the sample prior to and during the extraction step.

USEPA SW-846 provides specific extraction procedures, including sonication (USEPA SW-846 Method 3550) and Soxhlet (USEPA SW-846 Method 3540) extraction. A sequential cold extraction technique on a roller table is specified by NOAA's National Status and Trends Program (NOAA 1989). Other extraction techniques may include derivatization to make compounds of interest detectable by more sensitive instruments, to minimize losses of relatively unstable compounds, and to eliminate potential matrix effects (e.g., interference from co-eluting nontarget analytes). Selected phenols, for example, can be extracted and derivatized to allow the use of analytical techniques that provide greater sensitivity (USEPA SW-846 Method 8040).

Tissue samples for semivolatile analysis are macerated prior to extraction using an appropriate tool such as a Tekmar Tissuemizer® or a stainless-steel blender. Samples are often thoroughly mixed with a drying agent such as anhydrous sodium sulfate and then extracted with either dichloromethane-acetone or dichloromethane as described above. Care should be taken to avoid caking of the tissue/desiccant mixture, which may hinder complete extraction.

To assess the efficiency of extraction and cleanup procedures, surrogate compounds are added to all samples and blanks prior to the extraction step. The surrogate compounds are either compounds that are similar in chemistry to the analytes of interest or deuterated analogs of the compounds of interest. The concentration of the compounds of interest can then be corrected for the recovery of the surrogate compounds. The laboratory should be clearly instructed either to provide analytical results that are recovery-corrected and report the recovery of the surrogate compounds for informational purposes, or to report the recovery of the surrogate compounds. Generally, recovery corrections are only applied when all of the major chemicals of interest have a directly analogous surrogate compound. Minimum requirements for use of surrogate compounds are listed in the USEPA methods; these compounds can be purchased through many major chemical suppliers.

Cleanup

Exhaustive extraction of sediment or tissue samples also brings into the sample extract organic and inorganic constituents other than those of interest. These constituents can interfere with the analysis being performed, but often can be removed or minimized through subsequent cleanup steps. If the entire range of polar and nonionic semivolatile organic compounds is of interest, then cleanup steps must be chosen with caution to avoid losing some of the compounds while removing interfering constituents. For PAH analyses, cleanup is usually accomplished by column chromatography using alumina and/or silica gels (USEPA SW-846 Methods 3611, 3630) or GPC (USEPA Method 3640), which will remove many pigments and macromolecules such as lipids, polymers, and proteins. Of these procedures, only GPC also minimizes loss of certain acid or base compounds that would be of interest for semivolatile organic compound analysis. The NOAA National Status and Trends Program (Krahn et al. 1988; NOAA 1989) uses an HPLC procedure as a final cleanup step for neutral organic compounds. This procedure

is somewhat more effective in removing interferences than column chromatography, especially for tissue samples that contain large amounts of lipids. The HPLC method also has the advantage of using far less solvent than is required for column chromatography. Therefore, the use of HPLC is recommended, when practical.

Other interferences, such as elemental sulfur, can be removed or reduced in a sediment sample extract by the addition of activated copper (NOAA 1989), tetrabutylammonium-sulfite (USEPA SW-846 Method 3660A), or mercury (USEPA SW-846 Method 3660A).

After the final cleanup step, extracts are reduced in volume to approximately 500 μL (depending on the detection limits required and the nature of the sample). Reduction of solvent volume can be performed using various techniques. The most common and probably the most reliable technique for removing 5–500 mL of solvent is the use of the Kuderna-Danish apparatus with Snyder columns. Zymark® is another tool that is available for reducing large volumes of solvent; however, losses of some semivolatile organic compounds have been found when using this technique. Final reduction of solvent to small volumes (i.e., 1–5 mL) can be achieved by using micro Snyder columns followed by a nitrogen-blowdown using a carefully controlled stream of nitrogen gas. Additional internal standards should be added at this point to assess any losses or variability due to the analytical quantification technique employed.

Analysis

Many commercial laboratories screen extracts prior to quantitative analysis by using GC/FID to assess the approximate concentration range of the extract. This procedure avoids contaminating sensitive instruments with high-concentration extracts that should be diluted prior to quantitative analysis.

Quantification of semivolatile organic compounds can be performed using a number of different techniques depending on the sensitivity and selectivity required. The method most commonly used is GC/MS in the full-scan mode. Detection limits using this method range from approximately 0.1 to 10 mg/kg (ppm). Alternatively, a selected group of compounds can be analyzed using selected ion monitoring (SIM), and sensitivity can be improved by up to 2 orders of magnitude, with detection limits for individual PAH compounds, for example, ranging from 1 to 10 μg/kg (ppb). GC/MS is a selective technique that makes positive identification of the chemical possible based on both structural and retention time characteristics.

Another option for the analysis of PAH compounds is HPLC (e.g., USEPA SW-846 Method 8310). This method provides increased sensitivity, with detection limits ranging from approximately 0.01 to 10 μg/kg (ppb). This HPLC technique is very cost effective when PAH compounds are the only constituents of interest and is subject to fewer chemical interferences than GC/MS analyses. HPLC and GC/MS provide comparable quantitative results for extracts that have been subjected to appropriate cleanup procedures (Prahl and Carpenter 1979).

Recommendations

GC/MS analyses (or specialized GC/MS-SIM analyses) are recommended for analyzing semivolatile organic compounds to minimize the influence of interfering substances that may remain after extract cleanup. Any of the analytical methods described in the previous section can be used to determine PAH compounds, although separate HPLC analyses may not be cost effective or needed if GC/MS analyses are used to quantify other semivolatile organic compounds.

PCBs and Chlorinated Pesticides

During the ARCS Program, discussion of PCB analyses focused on current understanding of the toxicity of specific PCB congeners relative to the PCB mixture as a whole. PCBs are a set of 209 different compounds—congeners, all of the possible combinations and variations of the biphenyl molecule substituted with one or more chlorine atoms. Only about 80–120 of these congeners occur to any significant extent in the environment. The toxicity of the individual congeners depends on the number and the placement of the chlorine atoms on the biphenyl. When neither of the phenyl rings contains a bulky chlorine atom on the ortho positions (adjacent to the other phenyl ring), the molecule can become planar—the rings are said to be coplanar. These coplanar congeners (International Union of Pure and Applied Chemistry [IUPAC] Nos. 77, 126, and 169) are particularly toxic. In addition, congeners with one ortho-chlorine can also become coplanar. While not as inherently toxic as the non-ortho-chlorine congeners, the much higher amount of these mono-ortho congeners means that the presence of these congeners may present a greater health hazard in the environment.

The following section describes the standard USEPA methods for extraction, cleanup, and analysis of PCB Aroclor® mixtures in sediment samples. Aroclor® was a trade name used by Monsanto Company for mixtures of PCBs with varying degrees of chlorination (e.g., 1242 represents 42 percent chlorine by weight). Quantification of individual congeners is also discussed.

Extraction

Chlorinated pesticides and PCBs may be extracted using either sonication (USEPA SW-846 Method 3550) or Soxhlet extraction (USEPA SW-846 Method 3540) procedures. This extraction can be performed simultaneously with that for nonchlorinated semivolatile organic compounds. When chlorinated pesticides and PCBs are the only chemicals of interest, however, a solvent mixture of hexane-acetone is often preferred in the Soxhlet extraction.

As with semivolatile organic compounds, surrogate compounds are added prior to extraction of chlorinated pesticides and PCBs to assess overall analytical efficiency. A number

of different surrogate compounds can be used; however, USEPA SW-846 Method 8080 recommends the use of dibutylchlorendate (DBC) (which can break down at high gas chromatography injector temperatures), decachlorobiphenyl (DCB), octachloronaphthalene (OCN), and tetrachloro-*m*-xylene (TCMX). At a minimum, one early eluting surrogate (e.g., OCN or TCMX) and one late eluting compound (e.g., DCB or DBC) should be used. When performing PCB congener-specific analyses, surrogate compounds should include PCB congeners that do not occur in environmental samples (e.g., IUPAC Nos. 103, 198, and 204). If appropriate, nonchlorinated semivolatile and PAH surrogate compounds may be added, this extract may also be used for analysis of those compounds, thus saving a separate extraction step.

Tissue samples for PCB and/or pesticide analysis should be treated identically to those for the analysis of nonchlorinated semivolatile organic compounds by first macerating the sample, drying the sample with anhydrous sodium sulfate or equivalent, and then extracting. Care should be taken to avoid caking of the tissue/drying agent mixture, which may hinder complete extraction.

Cleanup

Standard cleanup procedures that can be used for PCB/pesticide analysis include Florisil® column chromatography (USEPA SW-846 Method 3620) and the other HPLC, alumina/silica gel, and GPC cleanup techniques described above for nonchlorinated semivolatile organic compounds. Sulfur cleanup is particularly important for analyses of chlorinated compounds because the electron capture detector used for analysis of chlorinated hydrocarbons is sensitive to small amounts of elemental sulfur (USEPA SW-846 Method 3660). USEPA SW-846 Method 8080 provides further guidance on cleanup procedures to be used when analyzing for chlorinated pesticides, because some of these compounds are more polar than most PCB congeners and different cleanup methods may be needed to separate the pesticides from the PCBs. HPLC cleanup as described by Krahn et al. (1988) can also be used, but addition of a different surrogate compound (e.g., dibromooctafluorobiphenyl) is needed prior to this step to assess any loss to the HPLC system.

Some sediment samples from highly contaminated areas contain oils (hydrocarbons) that interfere with the quantification of pesticides or PCBs. A relatively rigorous cleanup can be achieved by using sulfuric acid to extract the hydrocarbons (USEPA 1981). This step will also degrade many pesticide compounds and, therefore, should be used only when analyzing for PCBs.

Analysis

Historically, the most common method used to quantify PCBs has been to analyze for PCB Aroclor® mixtures. PCBs as Aroclors®, as well as chlorinated pesticides, may be

quantified using USEPA SW-846 Method 8080. This method involves the use of capillary column gas chromatography/ECD.

Aroclor® analysis includes not only chromatographic requirements for quantification (e.g., correct retention times, peak shape) but pattern matching as well. Pattern matching is the comparison of the heights of dominant peaks in samples relative to the heights of the same peaks in an Aroclor® standard. These requirements can introduce a significant amount of uncertainty into the quantification because environmental samples exhibit "weathering" of the original Aroclor® pattern. This weathering is a result of selective degradation or other loss of congeners based on their physical and chemical characteristics.

Low molecular weight chlorinated compounds, for example, have higher vapor pressures and may evaporate from sediment or partition into aqueous media, resulting in a pattern that has a higher proportion of more chlorinated congeners as compared to an Aroclor® standard mixture. In these cases, analyst judgment is often used in determining a final concentration. In severely weathered samples, the total PCB concentration is less accurate, and interlaboratory variability is higher. Methods for computer-based multiple linear regression pattern matching have produced good total PCB results on weathered samples (Burkhard and Weininger 1987).

Analysis of individual PCB congeners alleviates the need for pattern recognition, because individual compounds are being quantified. A method using known amounts of up to 80 congeners in a specific combination of three Aroclor® mixtures (Mullin et al. 1984) was used for the ARCS Program to quantify a large number of PCB congeners. Total PCB concentrations obtained from the sum of the concentrations of PCB congeners determined by this method and the total PCB concentration determined by Aroclor® analysis were found by Mullin et al. (1984) to be comparable for all types of samples. This method is somewhat cumbersome, however, and the degree of confidence is reduced when there are substantial matrix interferences (such as might be encountered in Great Lakes AOCs). When such interferences are of concern, pattern matching methods can be applied to the data, and confirmation with a second capillary GC column can be added. Analyzing for a subset of congeners may be a more advantageous route. A subset of 20 PCB congeners, chosen for their potential toxicity and frequency of occurrence in the environment, has been recommended by NOAA for continued analysis in the National Status and Trends Program (NOAA 1993). All 209 congeners are available from at least some chemical suppliers (e.g., AccuStandard, Inc.). Specific mixtures, which make quantification more reliable, can be ordered. However, this method does not allow for calculating total PCB concentrations. This is a problem for some regulatory programs and for comparing PCB concentrations to historical data.

Analysis of all 209 congeners is problematic because of the difficulty in separating many of the individual compounds during chromatography. The coplanar congeners co-elute with other congeners that are generally present in significantly higher proportions and, therefore, mask the quantification of the more toxic congeners. A special separation step using carbon, and analysis using high-resolution mass spectrometry (HRMS), allows for

isolation of these compounds. This analysis procedure is similar to that used for PCDDs and PCDFs (USEPA SW-846 Method 8290) and is often performed at the same time. However, the cost of this analysis is high and unless PCDD and PCDF data are required, the cost is usually prohibitive for analysis of coplanar PCB congeners alone. New separation techniques, such as the use of polymeric C_{18} phases to separate congeners based on molecular shape (Sander et al. 1991) or polystyrene divinylbenzene bonded to $C_{60/70}$ fullerenes (Stalling et al. 1993) to enrich coplanar PCB congeners from sample extracts, may allow for a relatively simple analysis by liquid or gas chromatography. These methods are still under development.

The primary obstacle to analysis of PCB congeners, especially the more toxic coplanar PCBs, is the resolution of the individual compounds from other interferences as well as from each other. Currently, coplanar congeners are analyzed using a method similar to that used for analysis of PCDDs and PCDFs (USEPA SW-846 Method 8290), which employs high-resolution GC/MS. This method is costly and precludes analysis of most samples for the more toxic PCBs. More complex methods have been employed where the sample extract is chromatographed twice using tandem gas chromatographs (Duinker et al. 1988). Other methods involving reverse-phase separations of the extract on special carbon columns are currently under investigation (Tanabe et al. 1987). Because of the high cost of coplanar PCB analyses using HRMS, it was recognized that not all ARCS samples could be analyzed to resolve co-eluting coplanar congeners. As a result, the ARCS Program analyzed for PCB congeners in all samples but only conducted the more costly analyses to resolve co-eluting coplanar congeners in selected samples.

For chlorinated pesticides, a dual-column analysis (e.g., DB-5 and DB-608 or equivalent) is performed simultaneously and the results from both columns are compared. Pesticide results from the two columns should be within 50 percent of each other to be reliably reported.

Conclusions

Congener-specific analysis using NOAA's procedure (NOAA 1989) is recommended for routine PCB analyses of both sediment and tissue samples. This procedure can also be used to quantify concentrations of chlorinated pesticides. Additional analyses to resolve co-eluting coplanar congeners should be conducted on selected samples, if warranted by concerns at the site and if funding is available.

PCDDs and PCDFs

Extraction and cleanup of sediment samples for PCDDs and PCDFs can be accomplished using the isotope dilution method (USEPA SW-846 Method 8290; USEPA 1986b). Stable, isotopically labeled PCDDs and PCDFs are added prior to extraction as specified in USEPA SW-846 Method 8290. These compounds include one carbon-13 labeled isomer from each PCDD and PCDF homolog group. All PCDD and PCDF congeners

within these homolog groups are actually quantified based on the recovery of the stable, isotopically labeled compounds. The isotope dilution technique can be a very accurate method of quantification.

Samples are extracted with benzene for 18 hours using a Soxhlet extractor. Extracts then undergo an extensive cleanup procedure to remove interferences. This procedure involves three separate column chromatography steps using acidified silica gel, alumina, and AX-21 activated carbon on silica gel. Deuterium-labeled 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) is added prior to these enrichment steps to assess process efficiency. Two additional recovery internal standards are added after extract cleanup but prior to the final concentration of the extract.

PCDDs and PCDFs are quantified using capillary column high-resolution gas chromatography/HRMS, which enables detection limits of approximately 1–5 ng/kg (parts per trillion) for individual congeners. The data are acquired by SIM analysis of the groups of ion masses described in USEPA SW-846 Method 8290. Low-resolution mass spectrometry is often used (e.g., USEPA SW-846 Method 8280), but detection limits attained using this method (i.e., approximately 100–2,000 ng/kg [parts per trillion]) are higher than concentrations thought to be environmentally hazardous. Therefore, the recommended method for analysis of PCDDs and PCDFs is USEPA SW-846 Method 8290, which is the only standard method with adequately low detection limits needed for risk assessment.

ORGANOMETALLIC COMPOUNDS

Methylmercury

Bacteria in sediments can transform inorganic mercury into the more bioavailable form of methylmercury, which can then enter the aquatic food chain. Methylmercury concentrations can be determined in sediment and tissue using the method in Bloom (1989). This method is currently the most sensitive and reliable technique available.

Homogenized sediment samples are digested in a potassium hydroxide-methanol solution by heating at 60°C for 2–4 hours. Samples are allowed to cool, additional methanol is added, and the samples are mixed well by shaking. Undissolved solids are allowed to settle completely prior to analysis. An alkylating agent (sodium tetraethylborate) is added to the digestate to form a volatile methyl-ethylmercury derivative, which is purged onto graphitized carbon traps for preconcentration and the removal of interferences. The sample components are then separated on a cryogenic gas chromatography column, and the eluting mercury species are pyrolytically broken down to elemental mercury. The mercury is detected and quantified using a cold vapor atomic fluorescence (CVAF) technique, which is based on the emission of 254 nm radiation by excited Hg^0 atoms in an inert gas stream (Bloom 1989).

Butyltin Compounds

Butyltin compounds, primarily TBT, have been used as the active ingredient in antifouling bottom paint for boat hulls for the last two decades. Sediments in marinas and near boat or ship maintenance facilities are frequently contaminated with TBT and its breakdown products, monobutyltin and dibutyltin. The analytical method most commonly used involves solvent extraction and chemical derivatization prior to analysis.

Sediment samples are extracted with 0.2 percent tropolone in dichloromethane. The resulting extract is filtered through glass wool. The filtrates are derivatized using a Grignard's reagent (hexyl magnesium bromide) and purified using a Florisil® column. Quantification is accomplished using gas chromatography/flame photometric detection (Unger et al. 1986).

METALS

Procedures for analyzing metals in sediment, tissue, and elutriate/pore water samples are summarized in the following sections.

Sediments

To determine metals concentrations in sediment samples (except for mercury, discussed below), the sample matrix must be digested prior to qualitative and quantitative analysis. There are two options for digestion of the sediment sample: total acid digestion and strong acid digestion. Total acid digestion may be performed using either a combination of nitric, perchloric, and hydrofluoric acids (Method 200.4; USEPA 1983) or a combination of hydrofluoric acid and aqua regia (Rantala and Loring 1975). Although both total acid digestion methods result in the release of all mineral-bound metals (including those in crustal minerals) into solution, the method of Rantala and Loring (1975) is preferred by some laboratories because it does not require the special fume hood necessary for the use of perchloric acid as in Method 200.4 (USEPA 1983).

Strong acid digestion uses nitric acid and hydrogen peroxide (USEPA SW-846 Method 3050), but, unlike total acid digestion, does not break down all mineral (matrix) components. Therefore, the total acid digestion method is recommended for the analysis of sediment samples for the following reasons:

- Comparability among data sets is improved with total acid digestion (i.e., variable extraction efficiency due to variable grain size or sediment matrix effects is eliminated).
- The results using total acid digestion are more reproducible among different analytical laboratories.

- The total acid digestion procedure is consistent with the methods used by NOAA in the National Status and Trends Program.
- SRMs can be included as an element of quality assurance (not possible with strong acid digestion because the metal extraction is incomplete). Standard reference sediments are certified only for total metals.
- The potential loss of volatile metals during digestion is minimized by using an enclosed digestion chamber.

The strong acid digestion method does have three distinct advantages, however:

- Matrix interference during atomic absorption analysis is less of a problem using strong acid digestion than it is using total acid digestion.
- Laboratory safety is improved because the digestion bombs and hydrofluoric acid used in total acid digestion are not used in strong acid digestion.
- Lower limits of detection may be achieved with strong acid digestion because of matrix interference problems and method-imposed sample size limitations for total acid digestion.

Following digestion of the sediment sample, the metals (with the exception of mercury) in the resulting solution are analyzed by ICP/AES, ICP-mass spectrometry (ICP/MS), or graphite furnace atomic absorption spectroscopy (GFAA).

As an alternative to total acid digestion, the total metals content can be analyzed by freeze-drying a sediment sample, ball milling it to approximately 120 mesh, pelletizing it, and analyzing the sample using XRF (Nielson and Sanders 1983). Typically, detection limits achievable with XRF are higher than those achievable with the digestion methods and analysis by GFAA and are lower than those obtained by ICP.

In most cases, the appropriate analysis method for metals is chosen by considering both its ability to obtain the desired detection limit and the time and cost efficiency of the method. In general, XRF is the most time- and cost-efficient method because all metals are quantified from the same easily prepared subsample. XRF is also a nondestructive analysis. However, the detection limit for certain metals is occasionally unacceptable using XRF (e.g., cadmium and silver in both sediments and tissues; chromium, nickel, and lead in tissues only; selenium in sediments only). For these metals, the digested sample may be analyzed by GFAA or ICP/MS.

The analysis of mercury in sediments requires a separate digestion procedure using potassium permanganate as the oxidizing agent, with analysis by cold vapor atomic absorption spectroscopy (CVAA; USEPA SW-846 Method 7470).

If analyses for AVS are conducted to determine the bioavailability of metals in the sediment, then metals concentrations in the aqueous portion of the stillbottom should be determined after AVS distillation is complete. Current theories for metals bioavailability hold that these simultaneously extracted metals more accurately reflect the concentrations of metals that can form metal sulfides with AVS. The expense of this additional analysis may not yet be warranted, however, until the applicability of AVS measurements is confirmed.

Tissues

Tissue samples may be freeze-dried without loss of trace metals. Dried tissue may be analyzed by XRF, similar to sediments, for metals at concentrations greater than approximately 2 μg/g dry weight. For analysis of metals in tissue by GFAA, ICP/AES and ICP/MS, the tissue must be dissolved. Tissue digestion with nitric acid conducted in a sealed Teflon® container at elevated temperature and pressure is effective at dissolving metals without significant contamination.

Elutriate and Pore Water

With the exception of mercury, elutriates may be analyzed by ICP/AES, ICP/MS, or GFAA without any sample preparation. Zinc in the elutriates may be quantified using flame atomic absorption spectroscopy because the concentrations are often quite high.

Mercury may be analyzed using CVAF with gold amalgamation (USEPA Method 245.1) to provide detection limits at the sub-ng/L level. The mercury procedure employed for the ARCS Program included a bromine monochloride/UV oxidation procedure to oxidize the organic compounds prevalent in many of the Great Lakes samples (Bloom and Crecelius 1983). For pore water analyses, a preconcentration step with ammonium pyrrolidinedithiocarbamate (Bloom and Crecelius 1984) may be used prior to analysis by GFAA or ICP/MS to improve the detection limits for cadmium, copper, lead, nickel, and silver.

CONCLUSIONS

The ARCS Program conducted both chemical analyses and a number of toxicity tests on sediment samples. The chemical analyses were focused on employing the best currently available methods. Use of this approach resulted in several recommendations that may serve to improve the quality and information content of the chemical data for future monitoring and assessment studies.

Significant analytical problems occurred during the analysis of organic compounds in sediment samples that were heavily contaminated with hydrocarbons. During the preparation of some solvent extracts, some material precipitated when these sediment extracts were concentrated below a volume of 5 mL. Also, the high concentrations of hydrocarbons in extracts caused degradation of the HPLC cleanup columns and changed the properties of the carbon cleanup column used to process extracts for PCDDs and PCDFs. One option to avoid problems caused by high concentrations of hydrocarbons is to dilute the extracts for the initial gas chromatography analysis; however, this can significantly increase detection limits. A second option for PAHs and other semivolatile organic compounds is to use a secondary cleanup technique such as reverse phase C-18 columns in addition to GPC and prior to instrument analysis (Ozretich and Schroeder 1986). Additional cleanup using concentrated sulfuric acid to oxidize interfering compounds is helpful for PCB analyses only.

The recommended organic and inorganic analyses provide total concentrations of each contaminant in a matrix. Supplemental analyses that provide a better representation of the biologically available fraction of chemicals in a matrix, particularly the simultaneous extraction of metals during the extraction of AVS, may provide data that are more suitable for performing risk assessments. Additional research is required, however, before such analyses are recommended for routine use.

The level and complexity of chemical analyses necessary to complement the biological assessment component may vary from situation to situation, depending on the particular questions that need to be addressed. Improved analytical methods may make the choices simpler and more meaningful, from a toxicological perspective, but much development is still required. In general, the available chemical data have often been inadequate for risk assessment purposes. In particular, exploratory surveys that could be used to test for a wide array of toxicologically important compounds at a site have rarely been conducted. It is recommended that the selection of analytes be based on a complete survey of the literature for both previous monitoring and exploratory studies, as well as on available data regarding municipal and industrial discharges in the drainage basin for the site. This information, in combination with an exploratory study and best professional judgment, will provide the basis for selecting the appropriate contaminants and analytical methods.

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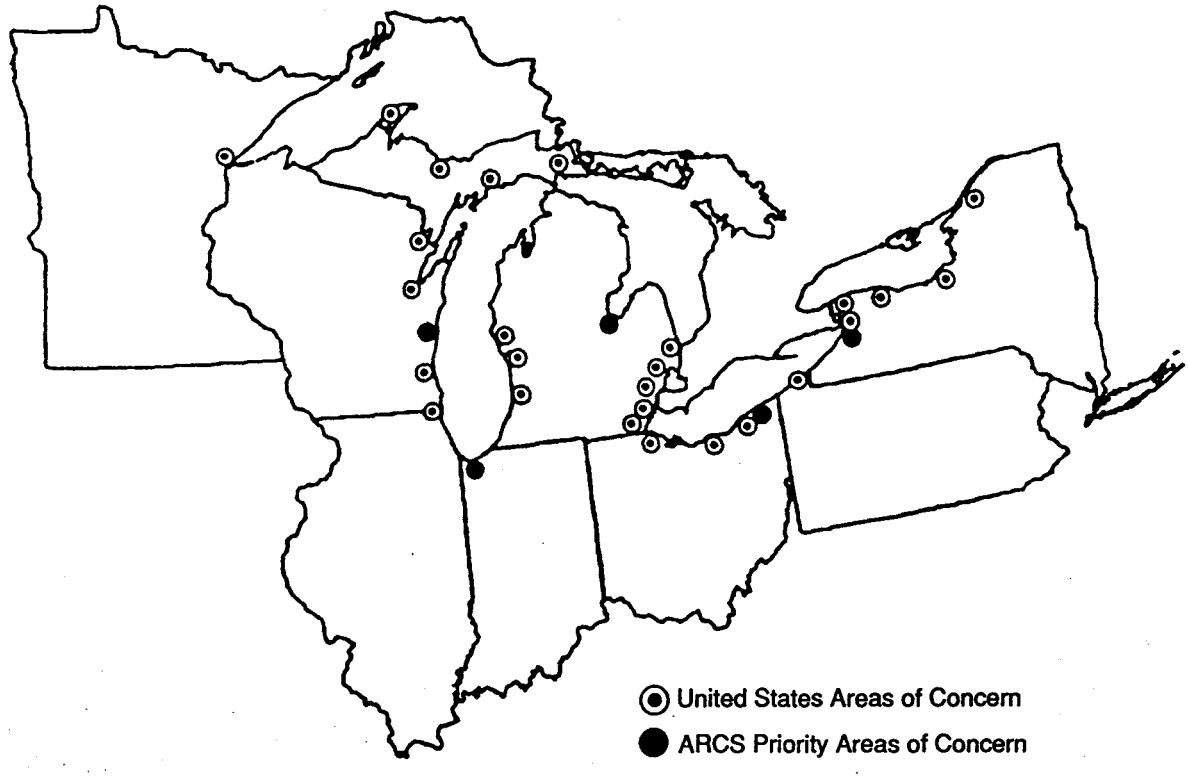

FINAL

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ASSESSMENT AND REMEDIATION OF CONTAMINATED SEDIMENTS
(ARCS) PROGRAM

ASSESSMENT GUIDANCE DOCUMENT

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ABSTRACT

This document provides guidance on procedures for assessing the nature and extent of sediment contamination as applied to areas in the Great Lakes region. The document was prepared by the Toxicity/Chemistry Work Group as part of the Assessment and Remediation of Contaminated Sediments (ARCS) Program, administered by the U.S. Environmental Protection Agency's (USEPA) Great Lakes National Program Office (GLNPO), in Chicago, Illinois.

Assessment of sediment contamination is intended to determine whether chemical concentrations in the sediments are sufficient to cause adverse effects on either aquatic organisms or organisms higher in the food chain, including humans. One of the main goals of the Toxicity/Chemistry Work Group was the selection of scientifically sound methods for assessing sediment quality. The selected sediment assessment methods were then applied in demonstration studies at several of the Great Lakes Areas of Concern (AOCs).

The sediment assessment methods described in this document include an integration of physical, chemical, and biological information. Decisions regarding the possible need for sediment remediation could therefore be made on the basis of a preponderance of evidence.

The chapters of this guidance document focus on various topics related to the assessment of contaminated sediments. Included is guidance on the necessary elements of a quality assurance and quality control (QA/QC) program, considerations for the conduct of field surveys, screening-level analyses (i.e., relatively rapid, low-cost tests to focus subsequent comprehensive analyses on the more contaminated sediments), chemical analyses, toxicity tests for assessing biological impacts, assessments of benthic invertebrate community structure, surveys of fish tumors and abnormalities, and data presentation and interpretation techniques. In addition to descriptions of the available options within each chapter, recommendations are made to guide the selection of appropriate sediment assessment methods, using the experience gained by the Toxicity/Chemistry Work Group to illustrate key issues. It is intended that the guidance on appropriate sediment assessment methods provided herein may be applied to other Great Lakes AOCs as they undergo investigation by Great Lakes Remedial Action Plan (RAP) personnel at the Federal, State, and local levels.

This report should be cited as follows:

U.S. Environmental Protection Agency. 1994. "ARCS Assessment Guidance Document." EPA-905-B94-002. Great Lakes National Program Office, Chicago, IL.

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