APPENDIX C

STANDARD OPERATING PROCEDURES FOR SEDIMENT EVALUATION IN CONNECTION WITH MAINTENANCE OF THE 9-FOOT NAVIGATION CHANNEL ON THE UPPER MISSISSIPPI RIVER WITHIN THE ST. PAUL DISTRICT, U.S. ARMY CORPS OF ENGINEERS

1.0 INTRODUCTION

1.1 Purpose

There are over 100 dredge cuts on the Upper Mississippi within the St. Paul District with annual dredging frequencies ranging from annual to less than once every 10 years. Because of the number of dredge cuts, the variability of the frequency of dredging, and the short time between the determination of the need for and the actual dredging, a standard operating procedure for contaminant determinations is needed to provide a consistent and expedient decision-making process.

1.2 Existing Data Base

The existing bulk chemical and physical data are summarized in tables in Part III of the Channel Maintenance Plan. These tables will be updated annually and new tables provided to the agencies. This data is also available on a floppy disk. As new data is generated, it would also be input into the computer data base being created by the National Biological Survey and the Water Quality Work Group of the Upper Mississippi River Conservation Committee. Historic data, meeting the criteria for inclusion in this data base, will be added to this data base as budget and schedules allow. In addition, many studies documenting the effects of dredging and disposal on water quality and the toxicity and bioaccumulation potential of dredged material have been completed on the Upper Mississippi River. These will be summarized and included in Part III of the Channel Maintenance Plan.

1.3 Applicability

This Standard Operating Procedure (SOP) is applicable to proposed discharges of dredged material to United States waters associated with the maintenance of the 9-foot channel on the Upper Mississippi River, within the St. Paul District. The testing and evaluation procedures described herein provide only a portion of the information necessary for a complete evaluation of a proposed dredged or fill material discharge, as required by Section 404(b)(1). This protocol only deals with evaluating the potential impacts of contaminants on aquatic biota from open water disposal or effluents from a containment area or from re-exposing contaminants at a disposal site or at a dredge cut area. A variety of other factors, including physical impacts, have to be considered when evaluating a project. In addition, there may be other contaminant concerns associated with a particular project. For instance, if there is a concern that a particular project could cause problems with groundwater quality and potable water supplies, this protocol would only provide a crude

estimate of the potential problems that could arise. Established tests, such as a leachate test, would address this issue better and may be determined necessary for a particular project. Other issues such as potential problems with runoff from or potential uptake by terrestrial organisms at an upland disposal site could be addressed by very specific tests. However, in most instances, the protocol in this document would provide some technical basis to evaluate these concerns. In the case of projects like Reads Landing Dredged Material Transfer, where there is a concern with impacts on potable water supplies, a project-specific detailed monitoring plan would be developed and coordinated with the regulatory agencies.

1.4 Background

The information contained in this document was primarily derived from three sources: 1.) "Evaluating Environmental Effects of Dredged Material Management Alternatives - A Technical Framework" (U.S. Army Corps of Engineers and U.S. Environmental Protection Agency, November, 1992); 2.) "Draft Inland Testing Manual" (U.S. Army Corps of Engineers and U.S. Environmental Protection Agency, Draft - June 1994); and 3.) Great Lakes Dredged Material Testing and Evaluation Manual" (U.S. Environmental Protection Agency - Regions II, III, V and Great Lakes National Program Office and U.S. Army Corps of Engineers - North Central Division, scheduled for public review - Fall of 1994). The latter source contains detailed guidance on sediment sampling and handling; quality assurance; methods for chemical and physical analysis; and protocols for biological-effects testing and has been relied on extensively in preparing this document.. This SOP should be used in conjunction with the national and Great Lakes testing and evaluation guidance.

.0 **TESTING APPROACH**

2.1 Tiered Evaluation

A tiered testing approach consistent with the national manual, with a decision-making process at the end of each tier, is recommended as the standard testing and evaluation protocol. This approach, which uses tests of increasing complexity and sophistication to reach decisions with greater degrees of confidence, provides a defensible and technically sound rationale for decision-making. This approach would allow for economical, early decisions in the planning process, when the conclusions from the early tiers so warrant. More effort, funding, and sophisticated tests would be concentrated on projects of greater concern. The recommended components for the three tiers of evaluation are summarized in figure 1.

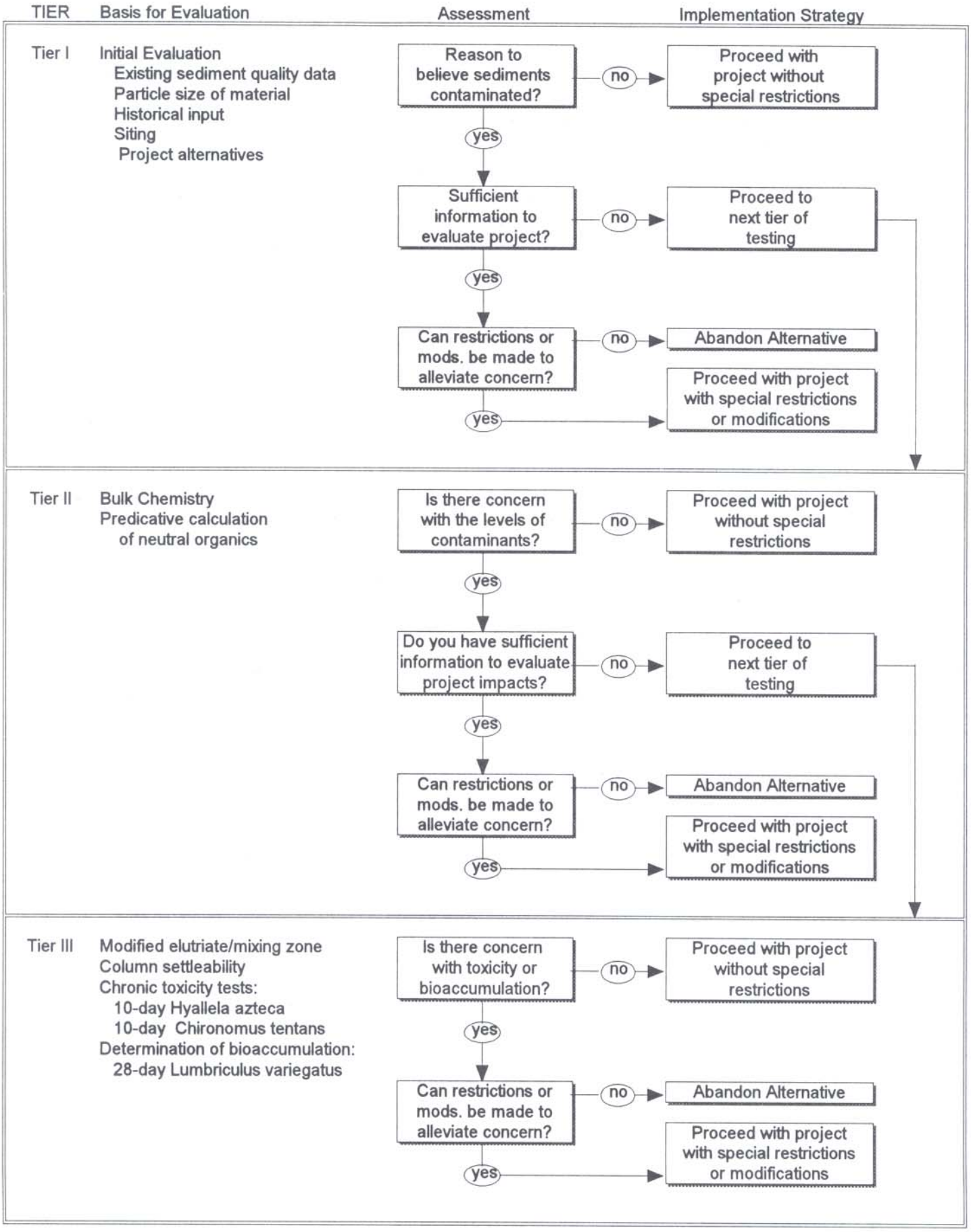
Tier I is an initial evaluation using only existing information, including the following: (1) particle size gradation, which can indicate a potential for contaminant levels; (2) available sediment quality data from within or near the project area; (3) historical input information, including type and proximity to point and non-point discharges, spills, and other sources of pollution; (4) sedimentation history to determine when and how the material to be dredged has accumulated; (5) description of project area, including identification of sensitive areas; and (6) project description, including quantities of dredged or fill material and dredging and disposal methods and sites being considered.

Tier II comprises the standard bulk chemical analysis of sediments and a predictive calculation of neutral organics bioaccumulation potential. Tier III involves more sophisticated tests, including the modified elutriate, column settleability, and biological response tests. The biological response tests concentrate on chronic toxicity and bioaccumulation potential from solid-phase sediments. Acute toxicity testing is not recommended. Based on the contaminant levels that have been found and the results of past acute toxicity testing, it would be extremely rare to find main channel sediments that produce acute toxicity. In addition, some information would be obtained on the potential for acute toxicity from the chronic toxicity tests. Results of acute toxicity testing of sediments would be of limited value for the decision-making. However, ammonia nitrogen levels in some sediments may be an exception, capable of causing acute toxicity. Therefore, the standard ammonia bulk chemistry procedure has been modified to an elutriate procedure, which will allow a direct comparison to water quality criteria and early determination whether ammonia could pose a problem. Appendix F of the National Inland Testing Manual has a detailed discussion of "Specific Considerations for Assessing Ammonia Toxicity in Dredged Material." If it is determined that ammonia concentrations could be toxicologically significant, TIE manipulations as described by Ankley et al. (1992) may be pursued to evaluate the potential toxicity of ammonia in the sediments. There are numerous TIE manipulations and include evaluation of relative species sensitivity (e.g., fish are generally more sensitive than cladocerans), removal of ammonia from the test samples with cation exchange and/or extended air-stripping at elevated pH values prior to toxicity testing, correlation of toxicity with measured ammonia concentrations, and toxicity tests at different pH values with equitoxic concentrations of ammonia. A benthic community analysis of the project area may be desirable for certain projects and could be conducted as part of the tier III evaluation to assist in the interpretation of the chronic toxicity data.

2.2 Coordination/Decision Making Process

From the tier I information, a determination would be made about the potential for contaminants to be present at levels of concern. If there are

Figure 1. Tiered Sediment Testing Protocol for O&M on the Upper Mississippi River



concerns, the specific contaminants and types of problems associated with each of the project alternatives would be identified. In making this determination, the adequacy of the data has to be considered. A lack of adequate information would constitute a reason to be concerned about contaminants. If there is no concern with contaminants, then proceed with the project planning, without special project restrictions. Selection of one of the project alternatives and the project design would be made based on other factors. If there is a concern with contaminants, then the next step is to determine whether there is sufficient information to evaluate the potential effects of the project. If the answer is no, then proceed to the next tier of testing. If the answer is yes, then determine whether economical and engineeringly feasible restrictions can be made to the project to alleviate the contaminants concerns. If the answer is no, then the project or that portion of the project of concern should be abandoned. If the answer is yes, then proceed with the project planning, including the appropriate restrictions. This type of decision-making would be followed after each tier, except that tier III would not have a determination on whether there was adequate information. The reason for this exception is that there has to be some end point in the testing, at which point a final decision on the project has to be reached.

The tiered approach is not intended to be rigid. In all cases, the tier I initial evaluation should be performed. Beyond tier I, decisions to continue with further testing, and the specific tests to be performed, should be done on a project specific basis. In most cases, the tiers should be followed in sequence, with an interagency decision process as outlined in the next paragraph, occurring at the end of each tier. However, the system has to be flexible, and there may be instances when the initial evaluation in tier I may indicate that it is advisable to skip tier II testing and go directly to tier III or perform a combination of tier II and tier III tests. In addition, it is not recommended that all the components within a given tier, especially tier III, be done for all projects in which a decision is made to go to that tier. This has to be decided on a project specific basis based on the results of the earlier tiers and other factors. For example, even if a decision is reached to proceed to tier III testing, if the results from the bulk chemistry and predictive calculations of bioaccumulation potential from tier II do not indicate a concern with bioaccumulation potential, the laboratory determination of bioaccumulation potential in tier III should not be performed. Only those tests in a tier that are necessary to make a technically sound determination should be conducted.

Normal updating of existing sediment data base: Because there are over 100 dredge cuts within the St. Paul District and a very short time between determining the need to dredge and the actual dredging, it is not possible to follow the tiered testing protocol sequentially on a case by case basis. Therefore, a routine updating of the quality of surficial sediments in the historic

dredge cuts is proposed. In addition, contaminant spills and point discharge records supplied by the appropriate agencies will be periodically screened to determine if historically "clean" dredge cuts may have been negatively impacted. This process will provide enough information to provide a tier I and II decision and to determine whether tier III testing might be required for individual dredge cuts. An annual report will be prepared summarizing any data collected that year and the sediment quality data in Part III of the Channel Maintenance Plan would be updated. This information would be provided to the agencies in January of each year. An interagency meeting would subsequently be held to discuss the results of the previous year monitoring and to discuss monitoring requirements for the upcoming year.

Project specific sediment sampling: The ensuing discussion is for larger projects, like the St. Paul Barge Terminal dredge cut in pool 2 or the Reads Landing Dredge Material Transfer project, where a decision is reached that the data provided by the routine updating of sediment quality does not provide adequate information to make a decision. These projects would be handled on a case by case basis, following the tiered testing protocol described above. Interagency coordination will be an integral part of the decision-making process. When the results of a tier are obtained, the Corps of Engineers would evaluate the results and make a preliminary determination. The results and the preliminary determination would then be coordinated with all the agencies having regulatory authority and a mutually agreed upon decision made. The agencies that would be included are the U.S. Environmental Protection Agency and the appropriate State agency having regulatory authority for the particular project. If a decision is reached to proceed to the next tier of testing, the number of samples, the sampling strategy, and the tests to be performed would be discussed with all the agencies and agreed to by the appropriate regulatory agencies for a particular project. Subsequent meetings of the technical experts would be held to discuss the interpretation of the results of the tiers and what, if any, additional testing would be required. A final contaminants determination would be included in the 404(b)(1) Evaluation that is prepared and circulated for public and agency review.

The ensuing discussion and table 1 are only intended to provide some means to put the bulk chemical data collected into perspective and not to establish specific numerical criteria or guidelines. Decisions still have to be made subjectively, considering other factors. Numerical criteria, to determine what bulk chemical levels of contaminants in sediments are of concern, are lacking for the Mississippi River. Attempts have been made for the Great Lakes and are summarized in table 1. Most of these attempts have been made based on an evaluation of background data for the Great Lakes. Table 1 also has summary statistics for the available bulk chemical data for backwater

sediments on the Upper Mississippi River (above and below Lake Pepin), to put the main channel and boat harbor data into perspective. To establish a background concentration range, the statistical concept that in a normal population 95 percent of the measurements lie within plus or minus 2 standard deviations of the mean may be useful and is summarized in table 1. Background concentrations of such parameters as barium, iron, and manganese far exceed the guidelines developed for the Great Lakes and point out the problems of using guidelines developed for the Great Lakes on the Upper Mississippi River.

3.0 SEDIMENT SAMPLING PROTOCOL

3.1 Sampling Design

Normal updating of existing sediment data base: Updating of the sediment quality data base would occur periodically (minimum of every five years). The selection of dredged cuts to be updated would be done based on a concern that a particular dredge cut that historically has had clean sediments may have changed in quality due to spills, new point dischargers or other factors and for areas (i.e., many sites in pool 2 and boat harbors) where the historical data shows elevated concentrations of contaminants of concern. Normally a minimum of two samples would be analyzed from each dredge cut selected for updating.

Project specific sediment sampling: The ensuing discussion is for larger projects where a decision is reached that the data provided by the routine updating of sediment quality does not provide adequate information to make the decision. In designing the sampling protocol for a particular project, two major factors have to be considered; specifically, the anticipated analytical variability and the spatial heterogeneity. Measures to address analytical variability are included in the quality assurance/control section of this report. To handle horizontal heterogeneity, the most frequently used approach is stratified sampling with random sampling within the strata. This is done to reduce cost, while concentrating sampling efforts on the geographic areas of greatest concern. The reasons for stratifying the sampling can include proximity to a potential source of pollution, different sediment textures within the dredge cut(s), existing data indicating potential hot spots, different sedimentation history within the dredge cut(s), or any other reasons that would cause you to suspect and be able to predict spatial heterogeneity. If there is no basis for stratifying the sampling, then a completely randomized sampling is most appropriate. The number of sampling sites should be representative and would have to be decided on a project specific basis considering the degree of areal heterogeneity anticipated, the degree of contamination expected, and the quantities of dredged material and the disposal methods being proposed.

Table 1. Summarization of Great Lakes Sediment Criteria and Upper Mississippi River Backwater Sediment Concentrations

Parameter	Great Lakes Criteria (MOE) Ministry Ontario Environment	Great Lakes Criteria (EPA) Great Lakes Harbors Moderate Class	Great Lakes Criteria (EPA) Great Lakes Harbors Heavy Class	Mississippi River - Above Lake Pepin Background Data for Backwater Sediments Mean	Mean + 1 Standard Deviation	Mean + 2 Standard Deviation	Number Samples	Mississippi River - Below Lake Pepin Background Data for Backwater Sediments Mean	Mean + 1 Standard Deviation	Mean + 2 Standard Deviation	Number Samples
Aluminum								8630	13202	17775	73
Arsenic	8	3	8	11	24	37	30	2.9	5.7	8.5	79
Barium		20	60					108	161	214	68
Beryllium								0.4	0.7	0.9	65
Boron								5	9	12	65
Cadmium	1		6	1.4	2.1	2.8	30	0.9	2.5	4.2	119
Copper	25	25	50	17	23	30	30	12	19	27	121
Chromium	25	25	75	20	31	43	30	17	27	37	121
Cyanide	0.1	0.1	0.25	<2				<2			
Iron	1000	17000	25000					16800	24900	33000	69
Lead	50	40	60	25	34	43	30	14	21	29	118
Magnesium								4350	6811	9273	65
Manganese		300	500	731	963	1195	26	370	657	943	109
Molybdenum								2.1	2.5	2.9	65
Nickel	25	20	50	18	25	33	30	17	31	45	121
Mercury	0.3		1	0.18	0.31	0.44	30	0.09	0.2	0.32	119
Silver								0.7	1.8	2.9	65
Strontium								20	31	42	65
Zinc	100	90	200	81	110	139	30	51	81	112	121
Vanadium								13	23	33	65
COD	50000	40000	80000	29300	68400	107600	12	34600	65000	95300	7
Ammonia	100	75	200								
TKN	2000	1000	2000	1143	2176	3209	12	1117	1868	2620	7
Phosphorus	1000	420	650								
Oil&Grease	1500	1000	2000								
Org. Carbon %				2.9	4.6	6.3	9	4.2	8.3	12.3	17
Vol. Solids %	6	5	8								
PCBs (ng/g)	50		10000	21	50	78	29	5.7	16	26	45

Units are ug/g dry weight unless otherwise specified

(MOE) is Ontario Ministry of the Environment: Guidelines for Inwater Disposal of Dredged Spoils
(EPA) is the U.S. EPA Great Lakes Harbor Pollution Classification Guidelines

Note: Backwater samples are only for period of 1984-1995. The data base was screened to exclude data that had questionable high values. Detection limits varied substantially and samples with poor sensitivities were not included in the analysis. For the samples with appropriate sensitivities, half the detection limits were used in the calculations.

Location	Data Source	Pools	Years	Contact Person	Numbers
Above L. Pepin	U.S. Army Corps of Engineers	2,3,U4	'84,'87,'88,'94	Dennis Anderson	30
Below L. Pepin	U.S. Army Corps of Engineers	4-10	'84,'85,'87,'88,94	Dennis Anderson	42
	Wisconsin DNR	7,9	'84,'87	John Sullivan	11
	U.S. Fish and Wildlife Service	4 - 10	'83,'84,'85	Stan Smith	68

The other source of spatial variability that needs to be considered in designing the sampling effort is vertical heterogeneity. A major concern expressed by the various agencies has been for the potential to re-expose sediments with higher concentrations of contaminants that are presently sequestered within the proposed dredge cut area. This concern is based on the fact that higher levels of persistent chemicals, such as PCB's, were recorded in fish and surficial sediments in the 1960's and 1970's. Stratifying the sampling with depth quickly multiplies the amount of sampling effort and subsequently the cost. It should be done when there are reasonable expectations that vertical heterogeneity exists and when the dredge cut may re-expose a hot layer or the project can be modified to avoid or handle differently any hot layers should they be found. In evaluating whether there is potential for and concern with vertical heterogeneity, the sedimentation history and sediment stratigraphy for the area have to be evaluated. Most O&M dredge cuts on the Upper Mississippi River are dredged on a frequent enough basis that vertical heterogeneity would not be anticipated in most cases. However, some dredge cuts, especially some of the boat harbors, are dredged only infrequently and there may be a concern with vertical heterogeneity. Where there is a potential for the dredge cut to expose a more contaminated layer, at a minimum two composite samples should be taken, one from around 1 foot above and below the dredging depth and the other from the remaining core. If additional stratification is warranted, additional sub-sampling based on a visual examination may be appropriate.

3.2 Sample Collection Methods

For the normal updating of surficial sediment quality, a 9"x9" ponar will be used to collect the samples from the historic dredge cuts. In instances where there is concern with sediment stratigraphy, sediment samples for analytical work should be collected with wide mouth corers (2 inches or greater). Samples for organic analysis should be collected with a stainless steel corer and samples for metal analysis should be collected with a PVC or similarly inert corer. To charecterize the dredged material, depth integrated samples should be collected to the depth of 1 the proposed dredging. In addition, to characterize the exposed layer, a depth integrated sample should be collected from 1 foot above to 1 foot below the proposed dredging depth.

3.3 Sample Storage

Sediment samples should be collected and stored at 4°C in glass containers with teflon-lined caps for analysis of organics and either linear polyethylene containers or glass containers with teflon-lined caps for analysis

of metals.

Sediment samples collected for elutriate analysis should be stored at 4°C in airtight linear polyethylene containers or glass containers with teflon-lined caps. The elutriate procedure should be initiated within 1 week of collection. Water samples resulting from the elutriate procedure should be stored and preserved as specified for normal water samples in EPA (1983) and Plumb (1981).

Samples for biological response testing should be collected and stored in linear polyethylene containers or stainless steel containers. The containers should be filled to the top, leaving no air space. The samples should be maintained on ice and delivered to the laboratory within 48 hours of collection. At the laboratory, the samples should be homogenized with a commercial mixer equipped with stainless steel bowl and paddles and stored at 4°C. All tests should be initiated as soon as practical after collection, but no later than 8 weeks after collection.

4.0 ANALYTICAL PROCEDURE

4.1 Physical and Bulk Chemical Characterization

A standard list of chemical and physical characteristics would be run on all samples collected. Additional parameters would be added to evaluate a specific project, if it is suspected that other contaminants may be present at levels of concern. If an abbreviated list is decided on, at a minimum it should include: elutriate ammonia nitrogen, cadmium, copper, chromium, lead, mercury, particle size, total organic carbon, total volatile solids, zinc, and PCBs (Note for PCBs, congener specific analysis will be proposed for future use. However, because there are over 200 congeners and there is no resolution on which set of congeners should be analyzed on a normal basis, it is not being proposed at this time). The standard parameter list, analytical methods, and approximate limits of detection are listed in Table 2. Appendix F in the Great Lakes Dredged Material Testing and Evaluation Manual is a methods manual for testing and analysis of sediments and water, which will be used in the future when it becomes finalized. When this comes out for public review late this fall, copies will be sent to the agencies for review.

4.2 Modified Elutriate

4.21 Elutriate Preparation

The modified elutriate procedure as described in Environmental Effects of Dredging Technical Notes - EEDP-04-2 (WES 1985) (EM

Table 2. Bulk Chemical Parameter List and Analytical Methods for Sediments.

Parameter	Method	Citation	Practicable Quantification Limit % dry weight
Particle Size	Sieve and hydrometer	Plumb (1981)	0.1
Total Solids	Gravimetric 160.3	EPA (1983)	0.1
Volatile Solids	Ashing Method 160.4	EPA (1983)	0.1
Total Organic Carbon	SW846 - EPA method 9060	EPA (1986)	0.01
Percent Moisture	Method 160.3	EPA (1983)	0.1
			mg/l supernatant
Ammonia Nitrogen	Mod. Elutriate with 350.1	EPA (1983)	0.2
			ug/l dry weight
Cyanide	SW846 - EPA method 9010	EPA (1986)	0.5
Metals			
Arsenic	SW846 - EPA 7060	EPA (1986)	0.2
Cadmium	SW846 - EPA 7131	EPA (1986)	0.2
Chromium	SW846 - EPA 6010	EPA (1986)	5
Copper	SW846 - EPA 6010	EPA (1986)	2
Lead	SW846 - EPA 7421	EPA (1986)	5
Mercury	SW846 - EPA 6010	EPA (1986)	0.01
Nickel	SW846 - EPA 6010	EPA (1986)	5
Zinc	SW846 - EPA 6010	EPA (1986)	1
Manganese	SW846 - EPA 6010	EPA (1986)	10
Chlorinated Hydrocarbons			ug/kg dry weight
alpha BHC	method 8080	EPA (1986)	1
beta BHC	method 8080	EPA (1986)	1
gamma BHC (Lindane)	method 8080	EPA (1986)	1
Chlordane	method 8080	EPA (1986)	1
DDD	method 8080	EPA (1986)	1
DDE	method 8080	EPA (1986)	1
DDT	method 8080	EPA (1986)	1
Dieldrin	method 8080	EPA (1986)	1
Endrin	method 8080	EPA (1986)	1
Heptachlor	method 8080	EPA (1986)	1
PCB's (arochlors 1016 1221, 1232, 1242,1248)	method 8080	EPA (1986)	5
PCB's (arochlors 1254 1260)	method 8080	EPA (1986)	5

NOTES:

1. Samples for ammonia analysis would be extracted following the elutriate procedure. A slurry of water and sediment (concentration of 150 g/l dry weight equivalent) would be prepared and mixed for 5 minutes. This mixture would then be centrifuged at 10,000 times gravity and the supernatant collected and analyzed immediately or within 24 hours, if acidified with H SO to pH <2 and stored at 4 degrees C, following EPA method 350.1 or equivalent.
2. Samples would be extracted by EPA method 3550. Instead of 30 gram samples, 50 grams would be used. The extract would be concentrated to 10 ml and cleaned by GCP using EPA method 3640. The cleaned extract would be further concentrated to 1 ml and solvent exchanged to hexane. The hexane solution would be concentrated to 1 ml before analysis by EPA method 8080. To alleviate problems associated with other contaminants, the extract would be further cleaned by Florosil column using EPA method 3620.

1110-2-5027 would be followed. This procedure involves mixing for 5 minutes with a laboratory mixer in a 1 gallon glass jar a 3-3/4 liter slurry of sediment and dredging site water, with a concentration of 150 g/l (dry-weight basis) sediment. This mixture is then bubble aerated for 1 hour to ensure oxidized conditions in the supernatant during the subsequent settling phase. This is then allowed to settle for 24 hours or the predicted project settling time, and samples of the supernatant are drawn from the cylinder at a point midway between the water surface and the settled sediment interface using syringe and tubing. When trying to similuate the effects of open water disposal of dredged material the standard elutriate procedure should be followed, rather than the modified elutriate procedures.

4.22 Analysis of Supernant

The supernatant samples are then treated and analyzed following the methods for water samples (EPA 1983). The modified elutriate procedure calls for the analysis of the dissolved and total fractions. For analysis of the dissolved constituents, the samples are first filtered (0.45 um filters) and/or centrifuged, depending on the specific parameters to be tested. Samples for analysis of total concentrations would undergo appropriate digestion (EPA 1983) prior to analysis. The volume of receiving water and sediment samples needed depends on the number and types of analyses to be performed.

The parameters tested in the filtered or whole supernatant should be those that were found to be of potential concern from the existing data base or based on the results of the bulk chemistry obtained in the tier II testing. Table 3 summarizes the recommended analytical water sample methods for the appropriate parameters on the standard bulk chemical list. The methods for each of the parameters were selected based on the detection levels needed to compare the results with the water quality criteria developed by EPA (1986, including revisions) and State water quality standards. Detection limits listed in table 3 are methods detection limits. Actual detection limits will vary slightly depending on the nature of the individual samples and the specific equipment of the laboratory and would be reported along with the data.

4.3 Column Settling Test

The column settling test is designed to provide a way to predict the concentration of suspended solids in an effluent and to define the settled behavior of a particular sediment. The protocol is described in EM 1110-2-5027. The tests are conducted in an 8-inch-diameter ported column, usually with a test column depth of 6 feet, although this can be varied to approximate the effective settling depth at the disposal area. A slurry of water and sediment

Table 3. Analytical Methods for Water Samples for the Parameters on the Standard Bulk Chemical Parameter List.

Parameter	EPA (1983) Analytical method	Practical Quantification Limit (ug/l)
Ammonia (N)	Colorimetric Autophenate - EPA 350.1 or Colorimetric , titrimetric, potentiometric distillation - EPA 350.2	50
Cyanide	Colorimetric, Auto UV EPA 335.3	5
Metals		
Arsenic	Sample digestion and spectrophotometric SDDC - EPA 206.4 or Atomic Absorption gaseous hydride - EPA 206.3	19
Cadmium	Atomic Absorption, furnace - EPA 213.2	0.2
Chromium	Atomic Absorption, Chelation extract - EPA 218.	1.1
Copper	Atomic Absorption, direct aspiration - EPA 220.	20
Lead	Atomic Absorption, furnace - EPA 239.2	1
Mercury	Cold vapor, with recorder expans. - EPA 245.1	0.025
Nickel	Atomic Absorption, direct aspiration - EPA 249.	40
Zinc	Atomic Absorption, direct aspiration - EPA 289.	5
Chlorinated Hydrocarbons		
BHC	Gas Chromatography EPA 608	0.003
Lindane	Gas Chromatography EPA 608	0.003
Chlordane	Gas Chromatography EPA 608	0.0043
DDD	Gas Chromatography EPA 608	0.001
DDE	Gas Chromatography EPA 608	0.001
DDT	Gas Chromatography EPA 608	0.001
Dieldrin	Gas Chromatography EPA 608	0.0019
Endrin	Gas Chromatography EPA 608	0.0023
Heptachlor	Gas Chromatography EPA 608	0.004
PCB's	Gas Chromatography EPA 608	0.001

(concentration of 150 g/l dry weight equivalent) is prepared and then allowed to settle. Samples for suspended solids analysis are then taken at prescribed depth intervals above the supernatant/settled solids interface over time. The suspended solids results can then be used to predict, including anticipated resuspension, the effluent quality after various times of settling.

4.4 Theoretical Bioaccumulation of Nonpolar Organic Chemicals

Neutral organics chemicals such as PCB's are distributed within an aquatic ecosystem primarily in the lipids of organisms and in the organic carbon fraction of the sediment. The partition coefficient or preference factor for the neutral organics for organism lipid over sediment organic carbon has been calculated by several investigators. This preference factor has been estimated based on laboratory and field experiments at 4.0 (McFarland, 1987). This relationship then allows for a calculation of the maximum possible concentration that could result in an organism's lipid and subsequently whole-body bioaccumulation potential. This predictive model is relatively simple and is described below.

$$TBP = pf * L * (C_s / FOC)$$

pf = Preference Factor (a constant set to 4.0)
TBP = Maximum whole-body bioaccumulation potential (wet weight - in the same units of concentration as C_s.
L = Decimal fraction of an organism's lipid content (wet weight).
C_s = Concentration of chemical in the sediment (dry weight - any unit of measurement).
FOC = Decimal fraction of organic carbon content of the sediment (wet weight).

This predictive model assumes no metabolic degradation or biotransformation of the chemical and total bioavailability of sediment-associated chemical to the organism. Therefore, estimates of TBP from this model can present a worst-case prediction of bioaccumulation from the sediments. The model does not take into account if a major source of the contaminants is from suspended solids or dissolved in the water or if biomagnification is an important consideration for the particular parameter of interest. The model was developed for sessile organisms living within and obtaining their life prerequisites from the sediments. For mobile species, such as fish, the predictive equation can be complicated by a variety of factors and should be considered a worst-case analysis. This predictive model is still very much state of the art and is based in theory and laboratory experiments, with some field verification (Clarke, McFarland, and

Dorkin, 1988) and (Rubenstein, 1989). As additional research is conducted, slight modifications to this equation, especially for the preference factor constant, may occur.

The TBP for the proposed dredged material should be interpreted by comparison to the TBP of the reference material. If the TBP of the dredged material is not greater than that of the reference sediment, no bioaccumulation testing for non-polar organics may be necessary. For any non-polar organics having a consumption advisory, the TBP for the appropriate species and size/age classes should be evaluated.

The TBP algorithm is not suitable for sediments with FOCs of less than 0.5%. It can be presumed that some level of uptake would occur, if the contaminant concentration is greater and/or the total organic carbon is less in the dredged material versus the reference sediments. When the FOCs are less than 0.5%, the need for going on to Tier 3 bioaccumulation testing will have to be determined on a case-by-case basis. It should be noted that most main channel sediments on the Upper Mississippi River are relatively coarse and contains less than 0.5% FOCs.

In summary, the model will not provide a definitive answer for the bioaccumulation potential of neutral organics, but will provide a rough estimate that can be used to assist in the determination of whether bioaccumualtion of neutral organics is a concern and whether a laboratory determination of bioaccumulation is warranted for a particular project.

5.0 **BIOLOGICAL RESPONSE TESTING**

All the biological response testing described below involves the use of solid-phase sediments. The use of solid-phase sediments is a good approach when evaluating the effects of open water disposal because it simultaneously looks at the water column impacts and the benthic impacts at the disposal site. However, it is a very conservative approach when evaluating the effects of effluents or long-term runoff from containment areas, where the major concern may only be water column effects. Therefore, the results obtained from this testing have to be viewed differently depending on the nature of the project being evaluated. If water column impacts are the only concern, Appendix G of the Great Lakes Dredged Material Testing and Evaluation Manual contains guidance on 21-day *Daphnia magna* and 7-day *Pimephales promelas* water column toxicity tests. The ensuing discussion on chronic toxicity and bioaccumulation is mainly derived from Appendix G of the Great Lakes Dredged Material Testing and Evaluation Manual.

5.1 Chronic Toxicity Testing

10-day *Hyalella azteca* Partial Life Cycle Test: This procedure would determine the chronic toxic effects of chemicals sorbed to sediments using *Hyalella azteca* exposed over a 10-day period. The organisms would be exposed to solid-phase sediments with either an intermittent- or continuous-flow over laying water renewal system, with the endpoint in the toxicity test being survival. The specific details of this work, including animal culture and data analysis, are contained in Appendix G of the Great Lakes Dredged Material Testing and Evaluation Manual. Each treatment would be replicated eight times, using 10 *Hyalella azteca* per replicate, for a total of 80 animals per treatment. *Hyalella azteca* (7-14 days old) would be exposed in 300-ml high-form beakers with 100 ml of control, reference, and test sediments. The exposures would be under intermittent or continuous renewal of overlaying water at 23°C. Food would be added daily and aeration would be accomplished with a glass-tipped air line 4 cm below the surface. At the end of 10 days, survivors would be counted. Dissolved oxygen, pH, and temperature would be monitored daily. In addition, alkalinity, hardness, specific conductance and total ammonia would be monitored at the beginning and at the termination of the exposures.

10-day *Chironomus tentans* Partial Life Cycle Tests: This procedure would determine the chronic toxic effects of chemicals sorbed to sediments using *Chironomus tentans* exposed over a 10-day period. The specific details of this work, including animal culture and data analysis, are contained in Appendix G of the Great Lakes Dredged Material Testing and Evaluation Manual. Each treatment would be replicated eight times, using 10 *C. tentans* per replicate, for a total of 80 animals per treatment. *C. tentans* would be exposed to a control sediment, a reference sediment, and the test sediment over 10 days of their life cycle (second (8-12 days) to fourth instar) in 300-mL glass aquaria with 150-175 mL of water and 100 mL of sediment. Overlaying water would be renewed with a water renewal siphoning cycle. Aeration with a glass-tipped air line 4 cm below the surface would be done. Larvae would be fed daily. At the end of 10 days, the surviving organisms would be counted and weighed (dry weight). Dissolved oxygen, pH, and temperature would be monitored daily. In addition, alkalinity, hardness, specific conductance and total ammonia would be monitored at the beginning and at the termination of the exposures.

5.2 Bioaccumulation Testing

28-day *Lumbriculus variegatus* exposures: This procedure would determine the bioaccumulation of chemicals sorbed to sediments using *Lumbriculus variegatus* exposed over a 28-day period. Laboratory

determination of bioaccumulation potential requires that animals be exposed to a sublethal sediment concentration. Prior to or concurrent with the full 28-day bioaccumulation study, a 10-day toxicity screening test should be performed with each sediment. It is important to screen the sediment for toxicity, evidenced either by mortalities or behavioral effects (i.e., avoidance of sediment by not burrowing), to determine if the full 28-day test should be performed. This screening test would be performed as described for *Hyallela azteca*. Screening tests may not be required if the sediments have been previously screened by performing chronic testing on *Hyallela azteca* and/or *Chironomus tentans*, with no indication of toxicological responses.

Adult *Lumbriculus variegatus* (1-5 grams each depending on the analytes of concern) would be exposed to a control, a reference, and the test sediment for 28-days. The exposures would be run in four replicate tanks, with the number (80 to 1,000) of animals per tank determined by the life requirements of the organisms and by the amount of tissue needed to perform the analytical work. An equal number of animals and replicates would be frozen for background concentration following gut clearance at the time the experiment is started. Exposure to the sediments would be run for 28 days. At the end of 28 days, all remaining organisms would be removed per tank and placed in clean water overnight to allow gut clearance, then frozen. The bioaccumulation exposures would be conducted in a flow-through system (2 volumes per day renewal) consisting of 5.5-liter glass tanks. Prior to the start of the test, approximately 1.6 L of sediment would be added to each test tank. The appropriate amount of water, approximately 6 to 7.5 cm depth, would be added and the mixture would be allowed to settle for 24 hours. Dissolved oxygen, pH, and temperature would be monitored daily. In addition, alkalinity, hardness, specific conductance and total ammonia would be monitored at the beginning and at the termination of the exposures. No food would be provided, because food would alter the organic carbon content of the sediment, which could influence the bioavailability of chemicals in the sediment. The specific tissue analysis method would depend on the contaminants of interest (Appendix F of the Great Lakes Dredged Material Testing and Evaluation Manual contains methods for the analysis). In addition, lipid content of the annelid would be measured and depending on the analyte of concern, total organic carbon and/or acid volatile sulfides would be measured in the sediments.

The above procedure will be sufficient to determine the steady-state bioaccumulation for most analytes. However, for nonionic organic chemicals, the larger the octanol-water partition coefficient the longer it will take to come into equilibrium or steady state in animal tissue. There are two ways to help ensure that steady-state is reached. One is to run tests for longer than 28-days if it is suspected that chemicals of concern will not come to equilibrium tissue concentrations in this time period. The other way is to expand the test to

provide kinetic uptake information. This can only be accomplished by exposing the animals for increasing lengths of time to allow either a direct determination of the steady state concentration. A minimum of 5 time interval exposures should be done (i.e., 1, 3, 7, 14 and 28 days). Calculation of potential maximum bioaccumulation can then be accomplished using a linear regression technique and an iterative process to estimate the steady state value.

This determination method is described in detail in Busacker and Anderson (1989).

6.0 QUALITY ASSURANCE/CONTROL PROCEDURES

6.1 Analytical - General

Potential contractors that would do any of the analytical work would be required to have a comprehensive quality assurance/control program, including documentation following the procedures of U.S. Environmental Protection Agency and U.S. Army Corps of Engineers (in press). A laboratory audit of a potential contractor's laboratory would be performed by a research chemist from the Corps of Engineers prior to any sample analysis. This inspection would cover equipment and facilities, records of maintenance and calibration of equipment, the expertise of the personnel who would be doing the work, the results of any inter-laboratory or intra-laboratory quality control checks, and the laboratory's quality assurance program and documentation. The potential contractor would be required to correct any deficiencies prior to any sample analysis. These audits would be performed every three to five years, unless specific problems were encountered with a particular laboratory, requiring a more frequent audit. A completed laboratory inspection report for a particular contractor would be made available to interested agencies.

6.2 Analytical - Project Specific

In addition to evaluating a potential contractor's quality assurance program, the following quality assurance measures would be run routinely with every batch of samples analyzed by the contractor's laboratory.

Duplicate Samples. Duplicate or split samples would be collected in the field for at least 10 percent of all samples collected, but never less than one duplicate per collection effort. For the first batch of sediment samples collected for bulk chemical analysis by a particular contractor, duplicate samples would be made available to the various Federal and State agencies for their independent analysis. The results of these split samples analyses would be evaluated by the Corps to assess the performance of the contractor's laboratory. Subsequent duplicate samples collected would be analyzed by the contractor's

laboratory as field replicates.

Replicate Analyses. Replicate analyses would be conducted for each parameter on a minimum of 10 percent of the samples collected. The contractor would compute the relative percent differences and/or the coefficient of variation and report it with the data. Samples selected for replicate analysis would be distributed equally among the different types of samples encountered.

Reagent Blanks. The contractor would run a minimum of one reagent blank for every 10 samples and every time samples are analyzed. The reagent blank is to be interspersed with the regular samples; it is not to be analyzed separately. Data for each reagent blank would be reported along with other quality control data for any given analysis.

Spiked Samples. For each parameter possible, at least one sample would be spiked with a known concentration and analyzed during the normal analytical procedure. Surrogate spiking would not be allowed for PCB's and would only be allowed for other parameters if the laboratory can provide sufficient documentation that the surrogate results reflect the normal recovery of the parameters actually being analyzed for. Percent recovery would then be computed and reported with the rest of the data.

Blind Samples. At the discretion of the Corps, blind water samples from the EPA Quality Assurance Laboratory in Cincinnati, Ohio, would be provided to the contractor by the Corps for quality assurance testing of water samples. These samples would be analyzed with a normal run of collected or submitted samples. The results of this testing would be reported with the data from that analytical period.

All contractors would be required to analyze established blind sediment sample as a preliminary screening. At the discretion of the Corps, blind sediment sample would also be provided to the contractor along with a normal run of collected samples for quality assurance testing.

Uninterrupted Parameter Analysis. The Corps requires that a single parameter or set of parameters for a group of samples be analyzed by the contractor during the same analytical session. All analyses for parameters in samples, reagent blanks, spiked samples, and blind samples would be conducted during the same analytical session. To clarify: once the instrument or procedure is set up and running for a given parameter or set of parameters, all samples and their associated controls would be run. The instrument or procedure would not be stopped, except for an emergency, until the analyses for that parameter are completed on all samples. If the analytical sequence is

interrupted or delayed, upon resumption all blanks, spiked samples, and the remaining unknowns would be run.

Performance Criteria. Acceptable accuracy on blind sample and spiked sample analyses is ±2 standard deviations of the mean value. If more than 5 percent of blind sample or spiked sample analyses exceed ±2 standard deviations of the mean value, the Corps may request that quality control be checked or may order another laboratory inspection. In addition, if blind sample or spiked sample analyses exceed ± 3 standard deviations, the data for this set of samples would be rejected by the Corps. The Corps expects the coefficient of variation on replicate analyses to be less than 10 percent for most parameters.

6.3 Biological Response Testing

Detailed quality assurance procedures are described in Appendix G of the Great Lakes Dredged Material Testing and Evaluation Manual, including general laboratory requirements.

As part of the quality assurance for the biological response testing, the following criteria would be used to reject the results of any of the biological response exposures and require repeating the exposures:

1. More than 10 to 30 percent (depending on the particular test) of the organisms in the reference sediment or control sediment die.
2. Temperature deviation exceeds 1°C from prescribed temperature.
3. Dissolved oxygen drops below 40 percent (depending on the particular test) of saturation.
4. pH deviates by more than 1 unit.

Standard reference toxicant bioassays would also be conducted to assess the sensitivity of the laboratory test organisms (Busacker and Anderson 1989).

7.0 **REFERENCES**

Busacker, Greg, and Dennis Anderson. 1989. Bioassessment methodologies for the regulatory testing of freshwater dredged material: phase 2 report. Prepared by Army Corps of Engineers, St. Paul District, St. Paul, Minnesota, for Wisconsin Department of Natural Resources, Madison, Wisconsin.

Clarke, Joan U., Victor A McFarland, and John Dorkin, 1988. Evaluating bioavailability of neutral organic chemicals in sediments -- a confined disposal facility case study. Presented at U.S. Army Corps of Engineers Water Quality '88 Seminar,

February 1988, Charleston, South Carolina.

Mac, Michael J., Carol C. Edsall, Robert J. Hesselberg, and Richard E. Sayers, Jr. 1984. Flow-through bioassay for measuring bioaccumulation of toxic substances from sediment. EPA-905/3-84-007. Great Lakes National Program Office. Environmental Protection Agency, Chicago, Illinois.

McFarland, Victor, and John Clarke. 1987. Simplified approach for evaluating bioavailability of neutral organic chemicals in sediment. Environmental Effects of Dredging Technical Notes EEDP-01-8, U.S. Army Engineer Waterways Experiment Station, Vicksburg, Mississippi.

Mosher, R.G., R.A. Kimerly, and W.J. Adams. 1982. MIC environmental assessment method for conducting 14-day partial life cycle flow-through and static sediment exposure toxicity tests with the midge Chironomus tentans. Monsanto Chemical Company, St. Louis, Missouri, Report No. ES-82-M-10.

Nebeker, A.V., M.A. Cairns, J.H. Gakstatter, V.W. Malueg, G.S. Schuytema, and D.F. Krawczyk. 1984. Biological methods for determining toxicity of contaminated freshwater sediments to invertebrates. Environ. Toxcol. Chem. 3: 617-630.

Palermo, Dr. Michael. 1985. Interim guidance for predicting quality of effluent discharged from confined dredged material disposal areas -- test procedures. Environmental Effects of Dredging Technical Notes EEDP-04-02, U.S. Army Engineer Waterways Experiment Station, Vicksburg, Mississippi.

Plumb, R.H., Jr. 1981. Procedures for Handling and Chemical Analysis of Sediment and Water Samples. Technical Report EPA/CE-81-1. Prepared by Great Lakes Laboratory, State University College at Buffalo, N.Y., for the U.S. Environmental Protection Agency/Corps of Engineers Technical Committee on Criteria for Dredged and Fill Material. Published by the U.S. Army Engineer Waterways Experiment Station, Corps of Engineers, Vicksburg, Mississippi.

U.S. Environmental Protection Agency, 1979. Handbook for analytical quality control in water and wastewater laboratories. EPA-600/4-79/-019. Environmental Monitoring and Support Laboratory, Office of Research and Development, Cincinnati, Ohio.

U.S. Environmental Protection Agency. Federal Register, October 24, 1986. Volume 49, No. 209, pages 43234 - 43442. Guidelines Establishing Testing Procedures for Analysis of Pollutants Under the Clean Water Act; Final, Interim and Proposed Rules.

U.S. Environmental Protection Agency. 1986. Test methods for evaluating solid waste. Volume 1a. EPA 955-001-00000-1.

U.S. Environmental Protection Agency. 1983. Methods for Chemical Analysis of Water and Wastes. EPA/600/14/79/020. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

U.S. Environmental Protection Agency. December 1982. Test methods for inductively coupled plasma - atomic emission spectrometric method for trace element analysis of water and wastes, Method 200.7.