Environmental Effects of Dredging
Technical Notes

A COMPUTERIZED PROCEDURE FOR PREDICTING PLANT UPTAKE OF HEAVY METALS FROM CONTAMINATED FRESHWATER DREDGED MATERIAL

PURPOSE: The Decisionmaking Framework (DMF) developed by Peddicord et al. (in preparation) provides a framework for evaluating sediments before dredging. This framework is made up of several modules, one of which is the plant bioassay for materials proposed for upland or wetland placement. Like the DMF, the plant bioassay module is based on tiered testing. Tier I is a computer simulation based on chemical extraction of test and reference sediments; Tier II is an actual laboratory/greenhouse plant bioassay. The purpose of this note is to briefly describe development and use of the computer simulation on a personal computer (PC).

BACKGROUND: The DMF uses the concept of tiered testing whereby all necessary information, but not more information than necessary, is used to determine regulatory compliance. Mobility of heavy metals into the environment through plant uptake could be significant in some circumstances. A quick screening test to predict potential plant uptake and mobility of heavy metals can be used during the initial sediment evaluation process. Data used in developing and verifying the US Army Engineer Waterways Experiment Station (WES) plant bioassay were collected, compiled, and subjected to predictive modeling techniques. A computer simulation of predicted plant uptake was developed. Methods for generating the required input data are also briefly described.

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Development of the Plant Uptake Program (PUP)

Data collection

Plant bioassay data collected during the past several years were compiled into one data set. The data were separated by sediment redox status (i.e.

flooded and upland) as sediment redox has been shown to strongly affect heavy metal availability to plants (Lee, Folsom, and Engler 1982; Lee, Folsom, and Bates 1983). They showed heavy metals extracted by an organic extract (diethylenetriaminepentaaceticacid) (DTPA) correlated well with plant uptake of heavy metals. The data were further subdivided by plant metal concentration and by total mass of metal taken up (i.e. total metal uptake equals plant tissue metal concentration times plant yield) since small plants may contain high heavy metal concentrations (Folsom, Lee, and Bates 1981). Data separation improved the strength of total plant uptake prediction and resulted in total uptake being independent of plant concentration.

Regression analysis

Regression analysis was used to determine estimators for the concentration and the total plant uptake of each of the heavy metals. Ordinary least-squares regression was used to find the best set of variables for the estimation equations. The estimators are based on linear and nonlinear functions of total and DTPA-extractable heavy metals, percent organic matter, sediment pH, and disposal condition (flooded or upland). The objective was to minimize the sum of the squared deviations of actual concentration or total uptake in the plant from predicted concentration or total uptake. The variables were not restricted. To make the predictions, each of these variables (except for total sediment content) should be determined on both original, flooded- and air-dried, upland sediment.

Installation and Initiation of PUP

The regression model was compiled and converted into a "user friendly" PC software program termed the Plant Uptake Program or PUP. PUP requires a 360-kilobyte low-density floppy disk drive and a 20-megabyte hard drive. The program will not require any other software except MS or PC DOS (3.0 or greater) as the PC operating system. Two 5.25-in. low-density 360-kilobyte floppy disks in a folder on the back page of this note contain PUP. PUP is installed on the hard drive and run using the following steps:

- Insert the PUP floppy disk into drive A.
- Type A:INSTALL C:
  (C: is the designation of the hard drive where
   the program will be installed; substitute your drive
   letter if different from C:).

- The program will now be copied and installed onto the hard drive. (This will not alter any existing files on your computer).
- Put the PUP floppy disks in a safe storage location.
- Type PUP and then press the RETURN key to start the program.

The opening menu (Figure 1) allows the user a choice of five options.

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                    THESE OPTIONS ARE AVAILABLE NOW


   1.   Review the purpose and design of this program.

   2.   Review and possibly modify previously entered sample data.

   3.   Begin the estimation process for a new sample.

   4.   Compare a reference sample and a test sample.

   5.   Exit this program.


            Please enter the number of the option you want:
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Figure 1.   Opening menu for the Plant Uptake Program (PUP)

The user can begin the estimation process by choosing option 3. Option 3 informs the user of required data input. If the data are available, the next PUP screen is the data entry screen. Here the user enters descriptive and chemical information about the sediment sample. PUP will calculate the estimations for whatever heavy metals are entered. Values below this detection limit (DL) are entered as one-half the value of the DL. The data are edited, if necessary, and then the program computes the estimations. At this point, several options (Figure 2) are presented to allow the user to review, analyze, print and store the results for future reference. Choosing option 2 allows the user the view the estimation results on screen. These results can be edited, printed, or stored in the data base by choosing the appropriate option. PUP initially contains several example data sets that the user can use to become familiar with the program. The user can delete them if he or she chooses. The user can then exit the program or continue to analyze other data.

Two measures of the quality of the estimations are provided. The first measure of the quality of estimation is the multiple correlation coefficient

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|                                                                |
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|                                                                |
|                       On Screen Options                        |
|                                                                |
|    1.  Review information on interpreting estimates.           |
|    2.  Review the estimation results.                          |
|    3.  Review field data used to develop estimation equations. |
|                                                                |
|                       Printing Options                         |
|                                                                |
|    4.  Print information on interpreting estimates.            |
|    5.  Print the estimation results.                           |
|    6.  Print field data used to develop estimation equations.  |
|                                                                |
|                  Saving Data and Exiting Options               |
|                                                                |
|    7.  Store the estimation results in the database.           |
|    8.  Return to the main menu to analyze other data or to exit the program. |
|                                                                |
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|          Please enter the number of the option you want:       |
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Figure 2. Available options for estimation results

(R^2). The multiple correlation coefficient is the proportion of the variation of the actual concentration or total plant uptake explained by the estimation equation: a value of 1.0 indicates an excellent fit between the estimation equation and the data used (i.e. data the user has input) in the estimation process; a value of 0.0 indicates the worst possible fit.

A general method in research is to conduct experimentation that allows separation of variables one variable at a time. Correlation coefficients are generally greater than 0.9 when only one pollutant at a time is tested at high concentrations. Most of the existing information used for setting environmental standards is based on this type of research data. Seldom, however, is only one element elevated. Sediments from Black Rock Harbor (Folsom et al. 1988), Indiana Harbor (Environmental Laboratory 1987a, b), and the Detroit River (Folsom, Lee, and Bates 1981) are several examples of multi-element contamination. The inter-active effects encountered when one or more trace elements is in excess include synergisms, antagonisms, competition, protection, sequential additivity, and independence (Wallace 1989). In the absence of this knowledge and using an

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empirical approach (as used in the present study) it is not surprising that frequently encountered regression coefficients are much less than 0.9. Such low regression coefficients may, indeed, be environmentally significant.

The second measure of the quality of estimation is the Standard Error of Prediction (SEP). SEP is the standard deviation of the distribution of the errors between the estimated and actual concentration or total uptake used in the estimation process. Single value estimates are provided for each concentration and total plant uptake. Because ordinary least-squares regression was used to develop the estimation equations, they may produce negative values of estimated heavy metal concentration or total plant uptake. The negative values usually imply that either the estimated value is close to zero or the current input values are sufficiently different from those used in the calibration of the estimation equations so as to make the estimates unreliable. A range of values is provided for each concentration and total uptake. This range is the 90 percent confidence interval which means there is a 90 percent chance that the actual value lies within the range. The development data summary (option 6) is presented to provide the user a frequency distribution of the sediment input data. For example, the user may have a test sediment zinc concentration of 450 µg/g. The user can choose option 6 and see that a zinc concentration of 450 µg/g is in the second quartile of the zinc concentration range. Allowing the user to view these data relationships may help determine whether there is "reason to believe" contamination exists (i.e. the first step in Tier I testing).

Currently, plant uptake of contaminants is appraised in the DMF from sediment extraction (DTPA) and actual plant uptake data. These data are obtained by subjecting the reference and test sediments to the WES plant bioassay. The user has to manually input and laboriously analyze the DTPA extraction and plant bioassay data. PUP frees the user from these tasks and rapidly performs the DTPA extraction comparison calculations. The DTPA comparisons are based on the decision criteria given in paragraph B47 of the DMF summarized below:

1. DTPA-extractable concentrations of all metals from the air-dried sediment are <u>less than or equal to</u> the reference (Case 1a) and <u>less than or equal to</u> the saturated sediment (Case 1b). This leads to a <u>DECISION OF NO RESTRICTIONS</u> to protect against contaminant impacts on plants colonizing the dredged material.

2. DTPA-extractable concentration of <u>any</u> metal from the air-dried sediment is <u>less than or equal to</u> the reference (Case 2a) and <u>greater than</u> the saturated sediment (Case 2b) or

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3. DTPA-extractable concentration of <u>any</u> metal from the air-dried sediment is <u>greater than</u> the reference (Case 3a) and <u>less than or equal to</u> the saturated sediment (Case 3b). Condition b and c lead to a <u>LOCAL AUTHORITY DECISION</u> as discussed in paragraph B49.

4. DTPA-extractable concentraton of <u>any</u> metal from the air-dried sediment is <u>greater than</u> the reference (Case 3a) and <u>greater than</u> the saturated sediment (Case 2b). This leads to a <u>DECISION FOR FURTHER EVALUATION</u> by conducting a plant bioassessment as discussed in paragraph B50.

To indicate the DTPA comparisons the user chooses option 4 (Figure 1) and is prompted to select the reference and test sample data that have already been entered into PUP. PUP then computes the comparisons using the criteria described in paragraph B47 of the DMF. Those heavy metals that exceed the criteria are cause for concern and require further evaluation using the WES plant bioassay (Folsom and Price in preparation). The number of heavy metals exceeding the criteria can then be used for further decisions on plant uptake (criteria given in paragraph B49 of the DMF). A schematic representation of the DTPA comparisons is shown in Figure 3. Figure 3 is an example output of DTPA comparisons made on hypothetical data. If actual data had been used, any metal that exceeded the criteria would appear as red letters labeled EXCD; those that did not exceed the criteria would be in white letters labeled DNEX. Those metals not entered appear as dashes. The reference and test sediments the user chooses to compare are also shown in Figure 3. Culmination of these comparisons completes Tier I testing.

Methods for Generating Required PUP Data

Sediment collection

Sediments to be tested are collected from the area to be dredged using a sampler that can sample the entire vertical profile of the material. A 3.785-ℓ (1-gal glass jar) composite sample of the vertical profile should be sufficient to conduct the testing. The sediment sample contained in the glass jar should be thoroughly mixed before conducting any testing. A 1-ℓ subsample of the material is removed for chemical analyses after mixing. This subsample represents original-flooded material. Another 1-ℓ subsample of the original sediment is placed into an aluminum drying pan and allowed to air dry. This subsample represents upland dredged material if it were placed in an upland disposal site. Total and DTPA-extractable metals, percent organic matter, and pH are determined on both flooded- and air-dried samples of each composited sediment sample. The procedures given below allow the user to obtain required data.

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DTPA COMPARISON CASES

CASE	AS	CD	CR	CU	FE	HG	MN	NI	PB	ZN	No. Exceeded
1a	DNEX	EXCD	DNEX	DNEX	DNEX	EXCD	DNEX	DNEX	DNEX	DNEX	2
1b	DNEX	DNEX	DNEX	DNEX	DNEX	DNEX	DNEX	DNEX	DNEX	DNEX	0
2a	DNEX	DNEX	DNEX	DNEX	DNEX	DNEX	DNEX	DNEX	DNEX	DNEX	0
2b	DNEX	DNEX	DNEX	DNEX	DNEX	EXCD	DNEX	DNEX	DNEX	DNEX	1
3a	DNEX	DNEX	DNEX	DNEX	DNEX	DNEX	DNEX	DNEX	DNEX	DNEX	0
3b	EXCD	EXCD	DNEX	EXCD	DNEX	DNEX	DNEX	DNEX	EXCD	DNEX	4

SAMPLES USED IN COMPARISONS:

Upland or Air Dried Test Sample:
Flooded or Wet Test Sample:
Upland or Air Dried Reference Sample:

DNEX CRITERION

CASE	
1a	DTPA conc of upland test sample <= DTPA conc of upland reference sample
1b	DTPA conc of upland test sample <= DTPA conc of flooded test sample
2a	DTPA conc of upland test sample <= DTPA conc of upland reference sample
2b	DTPA conc of upland test sample > DTPA conc of flooded test sample
3a	DTPA conc of upland test sample > DTPA conc of upland reference sample
3b	DTPA conc of upland test sample <= DTPA conc of flooded test sample

Would you like a printed copy of these results? (Y/N)

Figure 3. Results of reference and test sample comparisons

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Flooded DTPA and flooded pH

A 50.0-g (weighed to the nearest 0.0001 g) oven-dry weight basis (ODW) subsample of the original, flooded sediment is weighed into a 500-ml polycarbonate centrifuge bottle and centrifuged at 4° C and 13,701 × g's* (9,500 rpm) for 30 min. The supernatant is decanted; pH is determined on the supernatant and is the flooded sediment pH. Two hundred fifty millilitres of 0.005 M DTPA + 0.01 M calcium chloride + 0.1 M triethanolamine solution (Lee et al. 1978) buffered at pH 7.3 is added to the sediment in the centrifuge bottle. The bottle is sealed and placed on a shaker for 24 hr and then centrifuged as before. The supernatant is poured into a polyethylene bottle and stored at 4° C until the time of chemical analysis. The supernatant is analyzed for heavy metals using atomic absorption (AA) spectroscopy. Heated graphite furnace analysis (HGA) is generally required to obtain the heavy metal concentration data.

Upland DTPA

The procedure (as in the flooded DTPA extraction above) involves adding 250.0 ml of the DTPA extraction solution to 50.0 g (ODW) of the air-dried sediment in a 500-ml polycarbonate centrifuge bottle which is then shaken for 24 hr. Two hundred fifty millilitres of 0.005 M DTPA + 0.01 M calcium chloride + 0.1 M triethanolamine solution (Lee et al. 1978) buffered at pH 7.3 are added to the sediment in the centrifuge bottle. The bottle is sealed and shaken for 24 hr, then centrifuged as before. The supernatant is poured into a polyethylene bottle and the liquid is stored at 4° C until the time of chemical analysis. Heavy metal concentrations are determined using AA or HGA. Blanks are also subjected to the DTPA extraction procedure. Metal concentrations of the blank solution are subtracted from the DTPA extracting solution metal concentration before performing the calculation shown below.

DTPA-extractable heavy metals (both flooded and upland) are calculated using the following formula:

$$\text{DTPA metal concentration} = \frac{(\text{DTPA extracting solution metal concentration}) \times (\text{extracting solution volume})}{\text{weight of ODW soil actually extracted}}$$

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* The 500-ml centrifuge head loaded with 500-ml centrifuge bottles containing sediment spun at 9,500 rpm for 300 min is equal to 13,700 times the acceleration due to gravity (g).

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$$= \frac{\mu g/m\ell \times 250 \text{ } m\ell}{g \text{ soil}}$$

$$= \frac{\mu g \text{ metal}}{g \text{ soil}}$$

Total heavy metal content

One gram (ODW) (weighed to the nearest 0.0001 g) of upland, air-dried sediment is placed into a 100-mℓ micro-Kjeldahl flask. Ten millilitres of concentrated nitric acid are added to the flask and its contents and allowed to sit overnight. A tertiary acid mixture of a 2:1:5 ratio of perchloric acid ($HClO_4$), sulfuric acid (H_2SO_4), nitric acid (HNO_3) is prepared by adding the following volumes of acid to a 1-ℓ bottle, swirling to mix, and then putting into a repipet:

$$200 \text{ } m\ell \quad \text{conc } HClO_4$$
$$100 \text{ } m\ell \quad \text{conc } H_2SO_4$$
$$500 \text{ } m\ell \quad \text{conc } HNO_3$$

CAUTION: THE FOLLOWING PERCHLORIC ACID ($HClO_4$) DIGESTION SHOULD BE CONDUCTED IN A STAINLESS STEEL ACID-DIGESTION HOOD. Twenty millilitres of the tertiary acid mix are added to the contents of the flask, the flask swirled to wet its contents, and then the flask is placed on a digestion rack. Heat until the mixture starts to boil, and then increase the heat slightly. The nitric acid will distill as a yellowish gas. After the nitric acid is gone, the perchloric acid will distill off as a white gas. When all of the perchloric acid is gone, the digestion is complete and only the sulfuric acid will be left (approximately 2 mℓ). The flask is removed from the burner and allowed to cool to room temperature. Twenty millilitres of distilled water are added to the solution, which is then quantitatively filtered through a Whatman No. 42 filter paper contained in a long-neck funnel in a 50-mℓ volumetric flask. Distilled water should be used to wash (while still on the filter paper in the funnel) any white, gelatinous precipitate that may have formed. This wash water should be allowed to filter into the 50-mℓ volumetric flask as well. Dilute to volume with distilled water and then analyze for heavy metals. Blanks and National Bureau of Standards Standard Reference Material (NBS SRM) 1645 (river sediment) are also subjected to the perchloric acid digestion procedure. Metal concentrations of the blank solutions are subtracted from the solution metal concentration before performing

the calculation shown below. Metals concentrations are then corrected to 100 percent of the NBS SRM. Total heavy metal sediment concentration is calculated using the formula:

$$\text{metal concentration} = \frac{\text{solution metal concentration} \times \text{dilution volume}}{\text{g ODW soil actually digested}}$$

$$= \frac{\mu g/m\ell \times 50 \; m\ell}{\text{g soil actually digested}}$$

$$= \frac{\mu g \; \text{metal}}{\text{g soil}}$$

Organic matter

Organic matter (OM) is determined by weight loss on ignition at 550° C on both flooded and upland sediment. Procedure No. 209E (American Public Health Association 1976) is used for this test. A 5-g subsample (ODW) of the sediment is weighed to the nearest 0.0001 g and dried at 105° ± 2° C until constant weight. Five grams (weighed to the nearest 0.0001 g) of the oven-dried sediment are then combusted at 550° ± 5° C for 24 hr in a muffle furnace. The sample is allowed to cool to room temperature and weighed to the nearest 0.0001 g. Weight loss on ignition is calculated and reported as percent organic matter (%OM). Use the formula below for the calculation of percent organic matter:

$$\%OM = \frac{\text{weight oven-dried sediment} - \text{weight combusted sediment}}{\text{weight oven-dried sediment}} \times 100$$

Upland pH

Ten grams (ODW) (weighed to the nearest 0.0001 g) of upland sediment are weighed into a tall 50-mℓ Pyrex glass beaker. Twenty millilitres of distilled water are added, and the mixture stirred with a polyethylene rod until all dry particles are wetted. The suspension is stirred for 1 min every 15 min for 45 min with a magnetic stirrer. After 45 min with the stirrer off, the pH electrode is placed into the solution above the surface of the sediment and the pH determined.

Summary

Total and DTPA-extractable heavy metals, organic mater, and pH are determined on test and reference sediments prior to dredging and nonaquatic disposal. These data are entered in the Plant Uptake Program (PUP). PUP is Tier I of the Plant Bioassay module of the DMF. Results of Tier I testing (i.e. computer simulation) can be used as a quick screening tool to identify areas of concern. If the results of Tier I testing indicate a reason for concern, then the sediments may be evaluated with the Plant Bioassay module (Tier II) to verify the concern. Procedures for Tier II testing can be found in a companion Technical Note (Folsom and Price in preparation).

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