



Predicting Surface Runoff Water Quality from Upland Disposal of Contaminated Dredged Material

PURPOSE: The U.S. Army Engineer Waterways Experiment Station (WES) Rainfall Simulator/Lysimeter System (RSLs) has been very effective in predicting surface runoff water quality from the upland placement of dredged material. However, this procedure is expensive and lengthy, and requires specialized equipment. The need for a simpler procedure has become evident.

In 1986, WES evaluated potential extraction procedures for use in predicting surface runoff water quality from dredged material. These experiments were conducted in conjunction with RSLs experiments on Indiana Harbor dredged material as reported in Environmental Laboratory (1987). Results of these investigations indicated that a simple laboratory extraction procedure could be used as a tool to provide initial engineering estimates and to screen contaminated sediments prior to conducting the RSLs procedure.

In fiscal year 1996, funding became available from the Long-term Effects of Dredging Operations Program to develop a simplified laboratory runoff procedure (SLRP) using other contaminated sediments and to compare the results with the RSLs procedure. The SLRP and RSLs procedures were conducted on five separate San Francisco Bay, CA, sediments for the U.S. Army Engineer District, San Francisco, and on one sediment from Black Rock Harbor, CT—representing the U.S. west and east coast, respectively. This technical note summarizes the results of this comparison.

BACKGROUND: The surface runoff water quality component of the Decisionmaking Framework for Management of Dredged Material (Lee and others 1991) evaluates the potential water quality problems that may result from discharges of storm water from contaminated dredged material placed in upland environments. Water leaving an upland confined disposal facility (CDF) must meet applicable State water quality standards for discharge into receiving waters. When dredged material is placed in a CDF, contaminant movement from the wet, unoxidized material will be mainly associated with suspended solids. As the material dries and oxidizes, suspended solids concentration may decrease while contaminants such as heavy metals may become more soluble. The RSLs predicts these effects so that restrictions or treatments, such as controlling movement of suspended solids or providing adequate mixing zones, can be incorporated into the CDF design.

The testing protocol for surface runoff water quality, described by Skogerboe, Price, and Brandon (1988), has been applied to dredged material from a number of locations including Black Rock Harbor, Indiana Harbor, Oakland Harbor, Everett Harbor, and New Bedford Harbor. Contaminants have included heavy metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, organotins, and dioxins. The procedure uses a rainfall simulator/lysimeter system in the laboratory (Figure 1).

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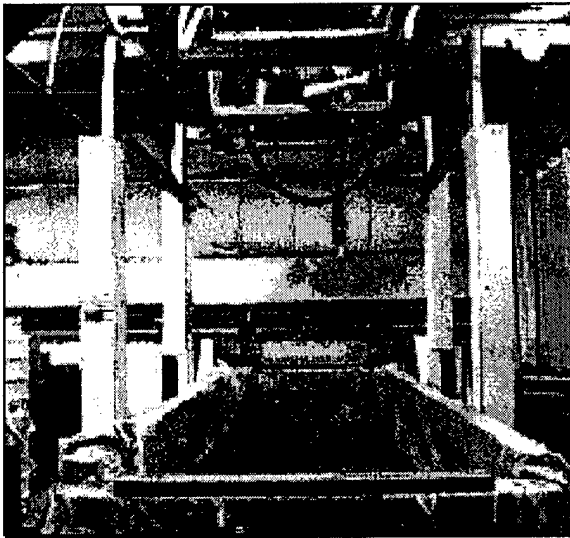


Figure 1. The rainfall simulator/lysimeter system in the laboratory

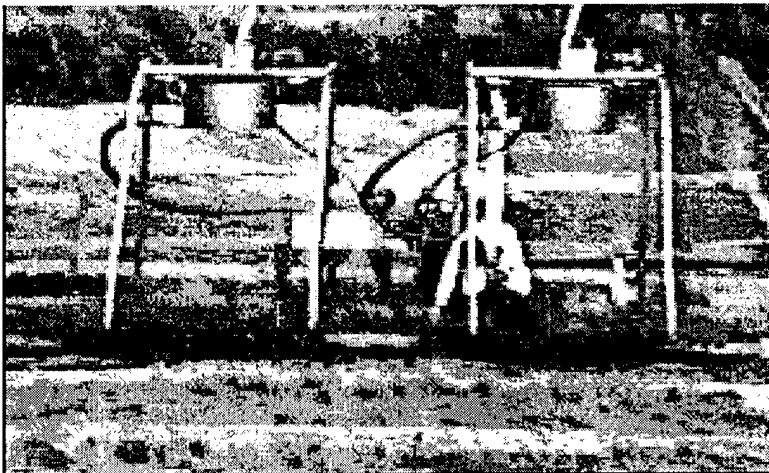


Figure 2. Portable RSLS at field site

The RSLS has been field validated under the Field Verification Program (FVP) at the Black Rock Harbor CDF in Bridgeport, CT, using the portable RSLS (Figure 2).

The RSLS requires a minimum of eleven 208-L drums of sediment, representative of the proposed dredging site. After placing the sediment in a soil lysimeter, surface runoff experiments are conducted on the wet, unoxidized sediment. The lysimeter is then moved outside, covered with a ventilated top, and allowed to dry naturally for 6 months. The runoff experiments are then repeated on the dry, oxidized sediment.

Although the RSLS is a very effective tool for predicting surface runoff water quality from an upland CDF, the procedure is expensive, time consuming, and can only be conducted at the WES. A need for a faster, less expensive response to surface water quality concerns prompted the development of a simple laboratory procedure that could be performed by any qualified laboratory with widely available equipment. The SLRP is designed to provide a less expensive, rapid-response screening evaluation of surface runoff water quality from upland CDFs.

A number of sediment-drying and oxidation procedures were evaluated on Indiana Harbor sediment, and the results obtained were compared with the results from RSLS experiments on the same material (Environmental Laboratory 1987). A procedure using oven-drying and hydrogen peroxide was selected as the best sediment treatment to simulate the long-term effects of drying and oxidation. More recently, the SLRP has been applied to San Francisco Bay and Black Rock Harbor sediments, and the results were compared with RSLS results. The results from these two sediments, the purpose of this technical note, demonstrate the value of the SLRP as a screening procedure to determine the need for the more expensive RSLS procedure. After testing on other sediments and the further development of regression equations, the SLRP may eventually replace the RSLS completely.

METHODS AND MATERIALS:

- **Black Rock Harbor.** Black Rock Harbor (BRH) was the subject of the Field Verification Program conducted at the WES and Bridgeport, CT, from 1982 through 1986. Sediment was collected prior to dredging for chemical and physical characterization. During the actual dredging process, dredged material was placed in an upland and wetland CDF at the FVP site for subsequent testing and evaluation of laboratory methods. Both sediment from the proposed dredging cut and the actual dredged material from the upland CDF were tested using the RSLs. The rainfall simulations were also conducted on the CDF using the field portable RSLs. Rainfall simulations were performed on the wet, unoxidized and the dry, oxidized materials according to procedures described in Skogerboe and others (1987). Surface runoff quality experiments were first conducted on the BRH sediment and dredged material using the RSLs at the WES.

The portable RSLs was used at the CDF to field verify the laboratory results. Experiments were conducted on wet, unoxidized sediment before any significant drying had occurred. The sediment erodibility would be at its maximum level. The dry, oxidized sediment represented the period when heavy metal solubility was at maximum levels and no vegetation had yet been established. Surface runoff samples were collected and analyzed for total and dissolved cadmium (Cd), chromium (Cr), copper (Cu), manganese (Mn), nickel (Ni), zinc (Zn), PCBs, and PAHs.

Dredged material collected from the FVP wetland CDF in 1993 was used to conduct the SLRP experiment. The procedure for wet, unoxidized sediment utilized sediment:water ratios of 1:10, 1:100, and 1:1,000 or 100,000, 10,000, and 1,000 mg L⁻¹ suspended solids, respectively. For the dry, oxidized SLRP experiment, ratios were 1:100, 1:1,000, and 1:10,000 or 10,000, 1,000, and 100 mg L⁻¹ suspended solids. This represented the range of suspended solids previously measured in runoff from BRH sediment using the RSLs. After preparation of three replicate simulated runoff water samples, subsamples were analyzed for filtered and unfiltered (total and soluble) constituents. Results of the SLRP were compared to the RSLs data reported by Skogerboe and others (1987).

- **San Francisco Bay sediments.** Sediment was collected from five proposed dredging locations in San Francisco Bay and brought to the WES for surface runoff quality testing (Lee and others 1992a, 1992b; Lee and others 1993a, 1993b). These sediments included: (1) Inner Oakland Harbor, (2) Oakland Upper Turning Basin (3) Pinole Shoal, (4) West Richmond, and (5) Santa Fe Channel. The sediments were contaminated with varying concentrations of heavy metals, PCBs, PAHs, pesticides, and organotins.

Surface runoff quality experiments were first conducted on each of the five sediments using the RSLs in the laboratory as previously described for Black Rock Harbor. Surface runoff samples were collected and analyzed for total and dissolved heavy metals, and organotins. Next, each of the five sediments was tested using the simplified laboratory procedure. The simplified procedure for wet, unoxidized sediment utilized different ratios than described for Black Rock Harbor: 1:20, 1:200, and 1:2,000 (50,000, 5,000, and 500 mg L⁻¹ suspended solids) for the wet sediment and 1:200, 1:2,000, and 1:20,000 (5,000, 500, and 50 mg L⁻¹

suspended solids) for the dry. The ratios of sediment to water corresponded to the range of suspended solids previously measured in runoff from a number of sediments using the RSLs. The simplified laboratory procedure for dry, oxidized sediment also included oven drying and rapid oxidation with hydrogen peroxide. Samples were analyzed for total and dissolved arsenic (As), Cd, Cr, Cu, lead (Pb), mercury (Hg), Zn, PAHs, PCBs, pesticides, and organotins.

Results of the SLRP for the San Francisco Bay sediments along with sediment particle size and total organic carbon (TOC) concentrations were correlated to results of the RSLs. Multiple linear regression was used to develop equations to predict surface runoff quality from upland dredged material disposal sites (Winer 1971). The independent variables included heavy metal concentrations obtained from the simplified laboratory procedure, sediment percent sand, and sediment total organic carbon (TOC, mg kg^{-1}). Heavy metal concentrations in surface runoff from the RSLs procedure were the dependent variables. Since actual disposal sites did not exist, results from the RSLs procedure were used for the dependent variable. Separate regressions were developed for wet, unoxidized sediment and for dry, oxidized sediment experiments.

RESULTS AND DISCUSSION

- **Black Rock Harbor—comparison of SLRP with RSLs laboratory and field results.** Results of the wet, unoxidized SLRP test were compared with the wet, unoxidized RSLs data as reported in Skogerboe and others (1987). The 10,000- mg L^{-1} SLRP (SLRP 1:100) suspended solids concentration was within the range determined from the three RSLs tests (range: 9,247 to 12,296 mg L^{-1}). The laboratory RSLs test on BRH sediment (RSLs-SED) generally overestimated total concentrations of Cd, Cr, Cu, Ni, and Mn compared with the RSLs results for dredged material in the laboratory (RSLs-DM) and on the CDF (RSLs-CDF), while Mn was not significantly different. The SLRP total metals correlated well with laboratory and field RSLs results on dredged material for all total metals and for soluble Cr, Cu, Ni, and Zn. Figure 3 compares the SLRP 1:100 with the RSLs results for chromium. As with most other metals, chromium was not very soluble in the wet, unoxidized material.

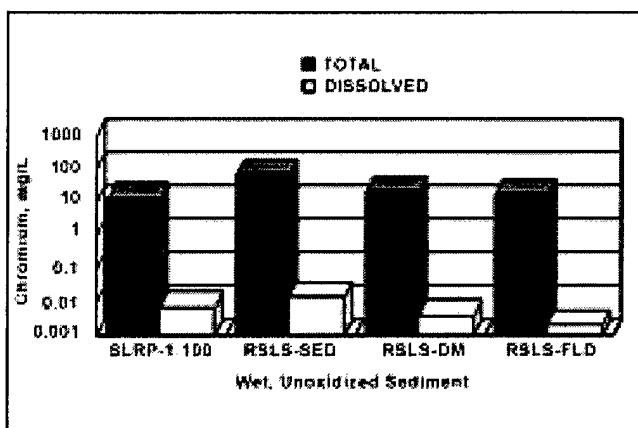


Figure 3. Comparison of SLRP chromium to RSLs tests on wet BRH sediments

On the dry, oxidized material, the SLRP 1:100,000 sediment:water ratio was more closely aligned with the RSLs suspended solids (range 320 to 151 mg L^{-1}). Although suspended solids were reduced nearly 2 orders of magnitude, the soluble fraction of all metals tested increased. Concentrations in the SLRP 1:100,000 ratio were not significantly different from all three RSLs tests for Cr, Cu, and Ni. The SLRP and RSLs laboratory tests underestimated actual Zn and Mn concentrations determined in the CDF. The SLRP estimates for Cd were not significantly different from the

CDF results, although the results were more variable than for the other metals. Results of total and dissolved chromium are shown in Figure 4.

Results of laboratory RSLs tests showed total PCBs and PAHs to be closely associated with suspended solids in the wet material, but near or below detection limits in the dry material. Based on these results, no analysis was conducted for the SLRP.

- **San Francisco Bay sediments —development of prediction equations.**

Heavy metal concentration ranges and means from the wet, unoxidized RSLs test were most closely approximated by the 1:200 SLRP test. Good correlations existed between the simplified laboratory test concentrations of As, Cd, Cr, Cu, Pb, and Zn and their respective RSLs test concentrations for the wet, unoxidized sediment. Heavy metal concentration means from the dry, unoxidized RSLs test were between the means of the 1:200 and the 1:2,000 SLRP tests.

The SLRP 1:200 ratio was also selected for the dry, oxidized sediment because the sediment-to-water ratio, mean concentrations, and concentration ranges were closest to the RSLs test, and the correlation (R^2) values were highest. The process of oxidation and drying did increase metals solubility, and the SLRP simulated that process effectively. Statistically significant correlations existed between SLRP test concentrations and the RSLs test concentrations for Cd, Cr, Cu, Pd, and Zn. Because mercury concentrations were mostly below detection limits, no statistically significant relationships could be determined. The same was true for PAHs, PCBs, pesticides, and organotins.

- **Total organic carbon, percent sand, and suspended solids data.** Soil erosion and resulting suspended solids (SS) concentrations in surface runoff have been shown to be affected by the soil particle size and the organic matter content (Wischmeier, Johnson, and Cross 1971). The percent sands in sediments from this study varied by a factor of 20 (Table 1), and sediment TOC varied by a factor of 2 to 3. Suspended solid concentrations were also highly variable in surface runoff samples from the RSLs tests, although suspended solids were mostly higher in surface runoff samples from wet, unoxidized sediments with low sand and high TOC levels.

- **Prediction equations.** Using the data obtained from the San Francisco Bay sediments, regression equations were developed to predict each heavy metal concentration in surface runoff using the SLRP, the percent sand, and TOC. Heavy metal concentration data from the 1:200 SLRP test were entered into the regression equations, and the predicted concentrations

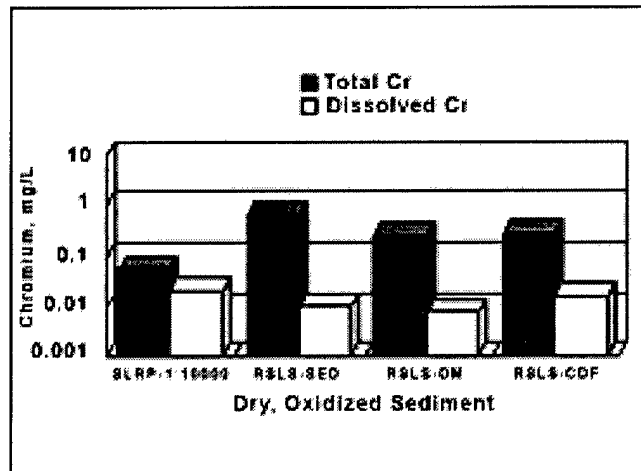


Figure 4. Comparison of SLRP chromium to RSLs tests on dry BRH sediments

were compared with those observed from the RSLs test. Correlations (R^2) and prediction equations for wet, unoxidized sediment are shown in Table 2.

Sediment	Sand, percent dry weight	TOC, mg kg ⁻¹	SS, mg L ⁻¹ wet sediment	SS, mg L ⁻¹ dry sediment
Inner Harbor	66.8	3,364	4,447	1,686
Turning Basin	3.2	6,450	9,140	970
Pinole Shoal	25.0	2,634	1,500	618
West Richmond	55.5	2,292	3,290	2,340
Santa Fe Channel	18.4	4,900	6,240	2,130

Metal	SLRP:RSLs (R^2)	Prediction Equation ¹
Arsenic	0.87	$\ln(As^2) = -1.30268 + 0.87958 * \ln(AS^2) + 0.03072 * (\% \text{ Sand}) + 0.00021 * (\text{TOC})$
Cadmium	0.42	$\ln(Cd) = -3.95989 + 0.85419 * \ln(CD) + 0.04350 * (\% \text{ Sand}) + 0.00062 * (\text{TOC})$
Chromium	0.71	$\ln(Cr) = -2.70912 + 0.87328 * \ln(CR) + 0.01744 * (\% \text{ Sand}) + 0.00040 * (\text{TOC})$
Copper	0.83	$\ln(Cu) = -3.48731 + 1.38320 * \ln(CU) + 0.01230 * (\% \text{ Sand}) + 0.00030 * (\text{TOC})$
Lead	0.96	$\ln(Pb) = -4.02897 + 1.44986 * \ln(PB) + 0.02320 * (\% \text{ Sand}) + 0.00018 * (\text{TOC})$
Zinc	0.93	$\ln(Zn) = -1.63788 + 1.07703 * \ln(ZN) + 0.00533 * (\% \text{ Sand}) + 0.00028 * (\text{TOC})$

¹ Heavy metal concentrations are expressed in micrograms per liter; TOC concentrations are in milligrams per kilogram.

² "As" is the predicted surface runoff concentration, and "AS" is the measured concentration from the simplified laboratory test. Similar forms are used for all parameters.

In the wet sediment, arsenic showed good agreement ($R^2 = 0.87$) between concentrations calculated by the regression model (predicted), and the actual concentrations that resulted from RSLs test.

Predicted Cd concentrations with the poorest R^2 (0.42) tended to overpredict concentrations at lower concentration levels and underpredict at higher levels. Cadmium concentrations were very near or below the detection limits, which caused more variability in the sample analysis. Predicted Cr concentrations mostly showed good agreement with the RSLs test data except for a couple of points at the highest concentration levels observed. Results for chromium are illustrated in Figure 5.

Predicted Cu, Pb, and Zn concentrations showed very good agreement with the concentrations observed from the RSLs data. Concentrations of Hg, PAHs, PCBs, pesticides, and organotins were near or below detection limits, and no statistical comparisons concerning these contaminants could be made.

Correlations and prediction equations for the dry, oxidized sediment are shown in Table 3. Predicted arsenic concentrations showed little agreement with the concentrations observed from the RSLs test. The actual range of values observed was very small (1 to 7 g L⁻¹), so procedural variability was high compared to the data range. However, predicted Cd, Cr, Cu, Pb, and Zn concentrations all showed good agreement with the observed concentrations from the RSLs test. Predicted SLRP chromium and RSLs chromium concentrations for all SFB sediments are illustrated in Figure 6.

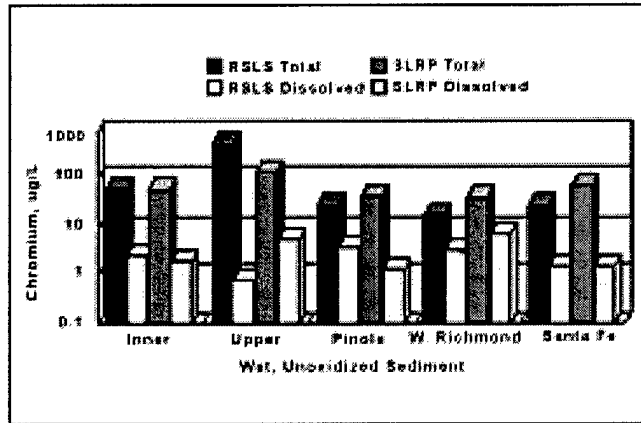


Figure 5. Comparison of SLRP predicted and RSLs measured chromium from wet SFB sediments.

Table 3. Regression Equations for Predicting Heavy Metal Concentrations in Surface Runoff from Dry, Oxidized Sediment Using the Simplified Laboratory Test

Metal	SLRP:RSLs (R ²)	Prediction Equation ¹
Arsenic	0.21	$\ln(As^2) = -0.81497 + 0.09659 * \ln(AS^2) + 0.01848 * (\% \text{ Sand}) + 0.00022 * (\text{TOC})$
Cadmium	0.74	$\ln(Cd) = -2.43298 + 0.99195 * \ln(CD) + 0.04305 * (\% \text{ Sand}) + 0.00017 * (\text{TOC})$
Chromium	0.85	$\ln(Cr) = -7.05319 + 1.55841 * \ln(CR) + 0.04971 * (\% \text{ Sand}) - 0.00017 * (\text{TOC})$
Copper	0.87	$\ln(Cu) = -3.28271 + 0.99471 * \ln(CU) + 0.04454 * (\% \text{ Sand}) + 0.00018 * (\text{TOC})$
Lead	0.89	$\ln(Pb) = -4.57752 + 1.23537 * \ln(PB) + 0.03942 * (\% \text{ Sand}) + 0.00036 * (\text{TOC})$
Zinc	0.82	$\ln(Zn) = 1.44438 + 0.52197 * \ln(ZN) + 0.01106 * (\% \text{ Sand}) + 0.00002 * (\text{TOC})$

¹ Heavy metal concentrations are expressed in micrograms per liter; TOC concentrations are in milligrams per kilogram.

² "As" is the predicted surface runoff concentration, and "AS" is the measured concentration from the simplified laboratory test. Terms of similar form are used for all parameters.

BENEFITS OF THE SLRP: The simplified laboratory test is significantly less expensive than the RSLs test (Table 4). The SLRP can be conducted by almost any competent, certified laboratory in a much shorter period of time than required for the RSLs test. The SLRP provides the Corps with a valuable tool for conducting preliminary engineering estimates to evaluate surface runoff from proposed upland dredged material disposal sites. Sediments can be screened quickly and much more inexpensively for potential surface runoff quality problems. Sediments with obvious runoff quality

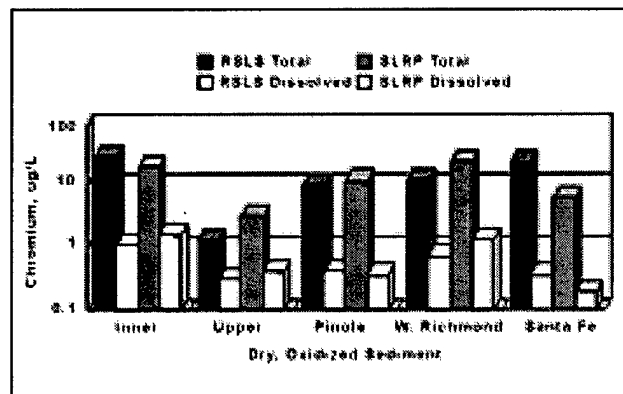


Figure 6. Comparison of SLRP predicted and RSLs measured chromium from dry SFB sediments

problems can be eliminated from further consideration for upland disposal or pinpointed for runoff quality improvement measures.

Expense Item	RSLs		SLRP	
	Cost (\$)	Time (mo)	Cost (\$)	Time (mo)
Sediment collection ¹	11,000	0.5	5,500	0.25
Conduct test/report ²	38,600	12.0	5,600	0.50
Chemical analysis ³	15,400	1.0	15,400	1.0
Disposal of material ¹	5,000		500	
Total	70,000	13.5	27,000	1.75

¹ For the Simplified Laboratory Test, 5 gal (19 L); for the RSLs, eleven 55-gal drums (2,290 L).

² RSLs test conducted by the WES and the SLRP test conducted by any certified laboratory.

³ Twelve samples including extraction at \$1,000/sample plus quality analysis/quality control. Turnaround time by analytical laboratories is highly variable (1 to 6 months).

CONCLUSIONS AND RECOMMENDATIONS: The SLRP developed from this study accurately predicted most heavy metal concentrations in surface runoff from Black Rock Harbor and San Francisco Bay sediments. In cases where the SLRP could not predict the heavy metal concentrations accurately, concentrations were at or below detection limits. Predicted concentrations represent the worst-case scenarios for both the wet, unoxidized sediment stage and the dry, oxidized sediment stage. The conditions that the simplified laboratory test represents are those in which the sediment is most erosive and/or heavy metals are most soluble. The simplified laboratory test is approximately \$40,000/sediment less expensive than the RSLs test and may be completed in one tenth of the time. In addition, the simplified laboratory test requires only 5 gal (19 L) of sediment compared to eleven 55-gal drums (2,290 L) of sediment for the RSLs.

The hydrogen peroxide oxidation does reliably simulate the natural oxidation that occurs when sediment is placed in an upland environment. Comparisons of the results from the simplified laboratory test to selected water quality standards result in the same conclusions as those from the RSLs test.

The SLRP has been applied to San Francisco Bay, Black Rock Harbor, and Indiana Harbor sediments and is currently being applied to New York Harbor sediments. The results from the Black Rock Harbor, Indiana Harbor, and New York Harbor tests will be incorporated into the regression equations to increase the accuracy and nationwide use of the SLRP as a predictive tool. The SLRP requires more testing for general application to sediments throughout the United States as part of a regulatory process. Further testing should be conducted on contaminated marine sediments from the Gulf coast and on contaminated freshwater sediments from lakes and rivers.

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