Results of Studies Correlating Total Organic Chlorine and Dioxin/furans in Selected Oregon Sediments

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Introduction

1. In august 1990 EPA, Region X, requested that USACE, Portland District, test some previously collected sediment samples, which had been analyzed for dioxins, for total organic chlorine (TOCL). Funding of the study came from EPA. The idea was to determine if there was a strong enough correlation between sediment concentrations of organochlorines (TOCL) and dioxins to use the much cheaper TOCL analysis as an indicator of potential dioxin contamination. The cost of a TOCL analysis was $150.00 per sample while that of dioxin analysis was around $1300.00 per sample.

Methods

2. Thirty four sediment samples were now tested for TOCL. These samples came from the Columbia, Chetco and Willamette Rivers and Yaquina Bay (see maps for locations). The samples had been maintained frozen at Battelle, Pacific Northwest Division, Marine Sciences Lab, Sequim, WA. They were sent to the University of Illinois where 10 gram samples were tested for TOCL by neutron activation analysis. The method consists of extracting organochlorines from about 10 grams of wet sediment with hexane and dry sodium sulfate then evaporating the hexane in a plastic vial. Neutron activation analysis involves bombarding the samples with neutrons then measuring the resultant radioisotopes of the chlorine atoms (the bromime content of the samples was also determined).

3. There are three commonly used measures of organochlorines - AOX, EOCL and TOCL. AOX is the adsorbable organic chlorines which attach to fine-grained, colloidal material in water and sediment. EOCL is extractable organic chlorine of molecular weight of 1,000 or less. TOCL is total organic chlorine of molecular weight of 10,000 or less. TOCL was chosen in this study in order to measure as much of the organochlorine as possible. The method used by University of Illinois for measuring TOCL by neutron activation analysis was recommended by Battelle.

4. As a quality assurance measure two standard reference sediments, obtained from the National Research Council of Canada, were included as samples. The reference sediments were certified for their polychlorinated biphenyls (PCBs) content. Quality control was established by measuring the TOCL in four procedural blanks. In this procedure every step was carried out as if there were sediment in the sample. The result is a measure of the TOCL

in the hexane, sodium sulfate and plastic of the vials which is then subtracted from the sample results to obtain the TOCL attributable to the sample sediments.

Results/discussion

Quality control

5. The raw data from the procedural blanks and Canadian reference sediments are shown in the appendix in Table A. The mean chlorine value from the 4 procedural blanks was subtracted from the sediment values to obtain concentrations corrected for blank. The detection limit was determined by using the standard deviation of the procedural blanks. This was done by dividing the standard deviation by 10 to obtain a per gram detection limit if 31.6 ppb. Sediment samples with a TOCL of 30 ppb or less were considered below the detection limit and not used in data analysis.

6. The method accurately reflected the concentrations of chlorine in the reference sediments. The canadian reference sediments were certified for 22 and 112 ppb of PCBs respectively. The method yielded 288 and 668 ppb TOCL for the reference sediments, indicating another source of organochlorines in them, but reflecting the trend towards increased PCBs in reference material.

Data patterns and analysis

7. Table 1 shows the raw data from 15 of the 34 samples. Only 15 sediment samples were included in Table 1 because they had values for TOCL and dioxins that were above detection limits. The raw data for the other 19 samples is in the enclosed appendix. These 19 samples were excluded from Table 1 because they were below TOCL detection limits or were not analyzed for dioxin/furans.

8. Table 1 presents four sediment samples from the Columbia River (CR), nine from the Willamette River (WR) and two from Yaquina Bay (YQ)(see maps). The samples ranged from 0.4 to 92.1 percent fines (silt/clay). The total organic carbon (TOC) content ranged from 0.2 to 7.5 mg/g. Grain size of sediment particles varied from 0.020 to 0.440 mm (medium silt to medium sand).

9. TOCL values were highest in Willamette River sediments followed by Chetco, Yaquina Bay and Columbia River in that order. The Willamette River samples showed TOCL levels ranging from 115 to 2380 ppb. WR-GC-3A&B and WR-GC-4, the two samples with highest TOCL, were taken from areas in Portland Harbor where high levels of contaminants had been found before - the Doan Lake area and downstream from McCormick & Baxters. Willamette River samples were also highest in total dioxin/furans (mean 5.4 ppb, range 0.9 - 19.0 ppb).

10. Most of the Columbia River samples were at or near the detection limit for TOCL (30 ppb). Of 15 Columbia River samples only 4 were above the detection limit for TOCL. These 4 were included in Table 1. Two of the four samples were just above the TOCL detection limit (CR-GC-6A AND CR-GC-25). CR-VC-12A&B (TOCL = 217 ppb) was taken at the mouth of the Westport slough Columbia River mile 43+05 and CR-GC-24 (TOCL = 90 ppb) was taken at St. Helens (RM 85+45) about 3/4 mile from the outfall of the Boise Cascade pulp mill. The TOCL for these two samples was in the range of the low end of TOCL values for Willamette River samples and about equal to the TOCL values for Yaquina Bay samples. The Columbia River samples that were below detection limits for TOCL came from regularly dredged channel areas which are usually coarse sand free of contaminants. A few samples (CR-GC-2,5,6) came from high fines areas near Longview (RM 63-64).

11. Two of three Yaquina Bay samples were above the TOCL detection limit and are included in Table 1. The TOCL and dioxin concentrations were intermediate between Columbia and Willamette River values. The Yaquina Bay samples were from boat harbor areas.

12. Chetco River samples were next highest in TOCL to Willamette River samples (mean 272 ppb, range 58-596 ppb). Unfortunately these samples were not analyzed for dioxins, two samples are archived in cold storage at Battelle.

13. No correlation between bromine and chlorine was observed in the sediment samples. Although bromine is another halide in the same chemical group as chlorine it is not as much a constituent of organic compounds as chlorine. The bromine concentrations found in the Chetco River samples were 2 to 3 times higher than Columbia, Willamette River and Yaquina Bay samples.

14. There are multiple sources of dioxin/furans in the Columbia River, including atmospheric, and no one has yet worked out the contribution of each to the sediment load. Interestingly, the pattern of average concentrations of total dioxin/furan congeners in the Columbia River samples is similar to that of the sediment in Lake Siskiwit, a land-locked wilderness lake on an island in Lake Superior (compare figures A and B in the appendix)(3). The origin of the dioxin/furans in Lake Siskiwit sediment is considered to be totally atmospheric (2).

TOCL - dioxins correlation

15. Figure 1 is a scatter plot showing the relationship between TOCL and dioxins/furans in the 15 sediment samples. There was a significant correlation between the two ($R=0.712$, $p<0.02$, $n=15$). However, the usefulness of this correlation is unclear, especially in the context of using TOCL as a predictor of dioxin contamination in non point source sediment samples. The problem is that only a

very small fraction of the TOCL was contributed by dioxins. This can be calculated assuming that most of the dioxin/furan congeners in the samples were in the OCDD category which contains 8 chlorine atoms per molecule. The contribution of the chlorines to the OCDD molecular weight is about 60 percent. For example, in sample WR-GC-3A&B the sample with the highest total dioxins/furans, the amount of chlorine in the sample is 11.4 ppb (19 ppb dioxin/furans X 60 % Cl). Dividing the 11.4 ppb chlorine from dioxins/furans by the 1665 ppb TOCL gives 0.68% of the TOCL contributed by chlorine from dioxins/furans. In other words, 99.32 % of the TOCL was contributed by sources of organochlorines other than dioxin/furans. The average contribution of chlorine attributed to dioxin/furans to the TOCL in the 15 samples in Table 1 is 0.58% (ie. 99.42 % of Cl from non dioxin sources). Therefore a high TOCL in these sediment samples is not necessarily an indication of dioxin/furan contamination, despite the correlation between TOCL and dioxins/furans, since the dioxin/furans levels might be exceedingly low. Alternatively, one can also envision a situation where a sediment sample contained a environmentally significant concentration of dioxins/furans and a low TOCL. In this case, if TOCL was used as an indicator, dioxin/furan contamination might not be revealed. A high TOCL still could be used as an indicator that further analysis of sediment samples in an area may be needed since the sediments may be contaminated by other organochlorines not attributable to dioxin/furans.

16. Other sources of organochlorine in sediment may be pesticides, PCBs, chlorophenols, plastics or other semivolatiles. These probably make up most of organochlorines in the sediment samples although there may be other unknown organochlorines that contribute to the TOCL. A more exact accounting of the contribution of the above to the TOCL is needed. The data from this study is insufficient for this purpose since we did not measure other sources of organochlorine. A Swedish study of extractable organochlorine (EOCL) suggested that less than 1% of EOCL could be identified as dioxin/furans, DDTs, PCBs, toxaphenes and chlorophenols (2). The rest was unidentified and could be a potential hazard.

17. As mentioned earlier the Chetco River samples were not analyzed for dioxin/furans. However, the data may still be useful because the correlation between TOCL and dioxins would predict that Chetco dioxin/furans are intermediate between Willamette and Columbia River values. The regression line from figure 1 predicts roughly 2.4 ppb dioxin/furans in the Chetco River samples. It would be interesting to test this hypothesis by analyzing the archived Chetco samples.

Usefulness of TOCL

18. The best use of TOCL would be as a tool to help map contamination from a known source of dioxins as was done in a

Swedish study of correlations between extractable organic chlorine (EOCL) and dioxin congeners in coastal sediments outside a pulp mill in the Iggesund area (1). In the Swedish study the dioxin/furans only accounted for a small fraction of the EOCL (about 1/100,00) yet the contamination could be easily mapped seaward from the pulp mill. Our results are similar with the average dioxin/furans contribution to TOCL being about 1/1,000 (ranging from approx. 6/100,000 to 2/100, mean=1/1,000). Interestingly, the Swedish study found concentrations of EOCL at least 40 times higher than the TOCL found in the sediments reported here. The reason for this difference is unknown. At any rate, TOCL could serve as a useful and cheap mapping tool for point source contamination. The cost of a TOCL analysis is approximately $150.00 vs a dioxin analysis of $1,300.00 so the savings in costs of mapping a site would be substantial (about 90 %).

19. As a mapping tool TOCL seems to work in a coastal sediment system, as in the Swedish study, where the sediments are not very mobile. But, its effectiveness in a faster moving riverine environment needs to be proven. Here, the effluent may be composed of dioxin/furans in solution or adsorbed to fine particles or colloidal material which may wash far downstream before settling out into the sediment. In a riverine system, like the Columbia River, where a dam may be downstream from a point source and where sediments tend to collect behind and upstream from the dam, mapping may be useful. A comparison of sediments upstream and downstream from the dam could show the extent to which dioxin/furans are trapped upstream from the dam.

Conclusions

20. There is a positive, significant correlation ($R=0.71$, $p<0.02$, $n=15$) between the concentration of TOCL and dioxins/furans in the samples studied. Even though there is a correlation between TOCL and dioxin/furans the best use of TOCL is as a maping tool for known point source contamination rather than as a tool to look for dioxin/furan contamination in non point source areas. This is because over 99% of the TOCL came from other sources, presumably pesticides, PCBs, Chlorophenols, other chlorinated semivolatiles and plastics or other unknown sources, with dioxin/furans contributing less than 1 %. Thus, a high TOCL may or may not indicate dioxin contamination but may be presumed to signal a potential problem with other organochlorine contaminants. A low TOCL may not reveal an underlying problem with dioxin/furan contamination.

21. TOCL may be a cost effective means of mapping point sources of dioxin/furans, reducing costs by about 90%.

22. The Willamette river sediments in Portland Harbor showed the highest TOCLs and dioxin/furans. Columbia River sediment samples were, for the most part, at or below the TOCL detection limit.

This is probably because most of the samples came from regularly dredged channel areas which are low in contaminants. Only 3 of 15 Columbia River samples were above detection limit levels for TOCL. There was no evident pattern of TOCL or dioxin/furans in Columbia River samples associated with potential sources of organochlorine such as pulp mills. For instance, two Columbia River samples taken downstream from the outfalls of the Wauna and James River mills were near the detection limit for TOCL and low in total dioxin/furans (bottom third of 27 samples where dioxin/furans were measured).

23. Further TOCL/dioxin studies, especially of sediments high in fines and total organic carbon where dioxin/furans concentrate, are needed to determine the usefulness of TOCL in predicting dioxin/furans or other organochlorine contamination. Point sources of dioxins/furans need investigation to see if the TOCL is an effective, cost effective mapping tool. The contribution of other organochlorines, some of which may potentially be hazardous, to the TOCL needs further elucidation.

Table 1. Concentrations of total organic chlorine (TOCL), bromine (Br), and dioxins; percent fines and total organic carbon (TOC) in sediment samples from Columbia (CR) and Willamette Rivers (WR) and Yaquina Bay (YQ).

Sample	TOCl	Br	Dioxins*	Fines	TOC
		ppb		%	mg/g
CR-GC-6A	31	<3.0	0.11	92.1	7.50
CR-GC-24	90	6.8	0.01	0.4	1.10
CR-GC-25	32	3.9	0.05	0.5	<0.20
CR-VC-12A&B	217	<3.0	0.30	79.0	0.84
WR-GC-2	610	5.5	4.10	78.3	2.40
WR-GC-3A&B	1665	12.5	19.00	87.9	4.00
WR-GC-4	2380	13.0	6.30	88.4	2.80
WR-GC-5	424	10.0	7.50	67.0	2.00
WR-GC-6	161	5.2	2.10	63.3	1.40
WR-GC-7	283	15.0	1.90	70.3	2.50
WR-GC-8	137	6.1	0.90	19.6	0.90
WR-GC-9	115	5.8	5.00	55.5	2.60
WR-GC-10	286	13.0	1.80	76.1	3.10
YQEPA-8	230	31.0	0.58	21.7	1.33
YQEPA-9	78	17.0	0.95	69.9	2.40

* Total concentration of dioxin and furan congeners.

Out of 34 samples, the above 15 represent data in which the TOCL was above the detection limit. Eleven Columbia River samples and one Yaquina Bay sample were not included in the table because TOCL was below detection limit. No dioxin/furan analyses were conducted on the six Chetco River samples. The TOCL for sample WR-GC-3A&B is the average of duplicate samples (WR-GC-3A and 3B). The raw data for all 34 samples is in the appendix.

REFERENCES

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3. Smith R., O'Keefe P., Aldous K., Valente H., Connor S., and Donnelly R. Chlorinated dibenzofurans and dioxins in atmospheric samples from cities in New York. Environ. Sci. Tecnol., 24, 1502-1506, 1990.

Table A.

CONCENTRATIONS OF ORGANIC CHLORINE AND ORGANIC BROMINE IN SEDIMENT

MSL Code	Sample No.	μg/Kg (dry weight) Cl	Br	PCB	Dioxin	
18	CR-GC-2B, Rep. 1	< 30	< 3	--	0.15	
22	CR-GC-2B, Rep. 2	< 30	< 3	--	--	
28	CR-GC-4	< 30	5.0	--	0.04	
7	CR-GC-5	< 30	< 3	--	0.02	
45	CR-GC-6A	31	< 3	--	0.11	composite 6A + 6B
37	CR-GC-6B	< 30	< 3	--	0.11	composite 6A + 6B
10	CR-GC-15	< 30	11	--	0.04	
38	CR-GC-16	< 30	17	--	0.04	
5	CR-GC-17	< 30	7.4	--	0.07	composite 17 + 18
13	CR-GC-18	< 30	7.6	--	0.07	composite 17 + 18
12	CR-GC-23	< 30	7.1	--	0.01	composite 23 + 24
9	CR-GC-24	90	6.8	--	0.01	composite 23 + 24
46	CR-GC-25	32	3.9	--	0.05	composite 25 + 26
40	CR-GC-26	< 30	6.2	--	0.05	composite 25 + 26
33	CR-VC-12A&B	217	< 3	< 50	0.3	
8	WR-GC-2	610	5.5	--	4.1	
11	WR-GC-3A	1780	12	--	19	composite 3A + 3B
47	WR-GC-3B	1550	13	--	19	composite 3A + 3B
17	WR-GC-4	2380	13	--	6.3	
4	WR-GC-5	424	10	--	7.5	
3	WR-GC-6	161	5.2	--	2.1	
6	WR-GC-7	283	15	--	1.9	
31	WR-GC-8	137	6.1	--	0.9	
15	WR-GC-9	115	5.8	--	5.0	
35	WR-GC-10	286	13	--	1.8	
44	YQEPA-6	< 30	5.7	< 80	0.27	
20	YQEPA-8	230	31	< 80	0.58	
43	YQEPA-9	78	17	< 120	0.95	
19	CHR-P-1	596	46	--	--	
26	CHR-P-2	58	59	--	--	
41	CHR-P-3	127	16	--	--	
4	CHR-P-4	352	8.5	--	--	
42	CHR-P-5	227	26	--	--	
16	CHR-P-8	< 30	7.9	--	--	

-- = data not available

Table A cont'd.

CONCENTRATION OF ORGANIC CHLORINE
AND ORGANIC BROMINE IN SEDIMENT (continued)

MSL Code	Sample No.	Cl	Br	
		ng/Vial		
1	Proc. Blank 1	897	26	
30	Proc. Blank 2	1230	26	
34	Proc. Blank 3	1598	40	
36	Proc. Blank 4	1510	31	
Mean ± SD		1309 ± 316	31 ± 7	
		µg/Kg		
25	CRM HS-1	288	81	Certified 22 µg/kg PCB
21	CRM HS-2	668	91	Certified 112 µg/kg PCB

National Research Council Canada | Conseil national de recherches Canada

Marine Analytical Chemistry Standards Program | Programme de standards de chimie analytique marine

CS-1, HS-1, HS-2

Marine Sediment Reference Materials for Polychlorinated Biphenyls

CS-1, HS-1 and HS-2 are natural marine sediment research materials for determinations of polychlorinated biphenyls (PCB). CS-1 is a coastal sediment collected in the Laurentian Channel midway between Nova Scotia and Newfoundland, and the two sediments, HS-1 and HS-2, were collected from Nova Scotian harbours.

This suite of samples provides a range of PCB levels from below 2 ppb in CS-1 to 112 ppb in HS-2. The matrix varies from a clean carbonaceous clay to an organic and sulfur rich material from a commercially active harbour.

The materials have been freeze dried, homogenized in a modified cement mixer and sub-sampled into solvent-rinsed pint-sized steel cans. Each can contains about 200 grams of material.

To order these materials, or for further technical information, contact:

Marine Analytical Chemistry Standards Program
National Research Council of Canada
Atlantic Research Laboratory
1411 Oxford Street
Halifax, Nova Scotia, Canada B3H 3Z1

Telephone (902) 426-8280
Facsimile (902) 426-9413
Telex 019-21653

Determinations have been carried out on CS-1, HS-1 and HS-2 using packed column gas chromatography and electron capture detection. Aroclor 1254 has been used as the standard PCB mixture. The results (μg PCB/kg dried sediment) are summarized below:

CS-1	1.15	$\pm$ 0.60 μg/kg
HS-1	21.8	$\pm$ 1.1 μg/kg
HS-2	111.8	$\pm$ 2.5 μg/kg

Uncertainties are expressed as $\pm$ one standard deviation for results based on a minimum of 32 extractions of each sediment.

Homogeneity tests and determinations of PCB in CS-1, HS-1 and HS-2 were carried out using 35 gram samples of sediments.

Typical data from capillary column gas chromatography using electron capture detection for HS-1 and HS-2, will be supplied with the marine sediments. Quantitative data for individual PCB compounds are as follows:

HS-1 and HS-2, will be supplied with the marine sediments. Quantitative data for individual PCB compounds are as follows:

Polychlorinated Biphenyl Concentrations
(micrograms/kilogram of dry sediment)

IUPAC#	HS-1	HS-2
101	1.62 ± 0.21	5.42 ± 0.34
138	1.98 ± 0.28	6.92 ± 0.52
151	0.48 ± 0.08	1.37 ± 0.07
153	2.27 ± 0.28	6.15 ± 0.67
170	0.27 ± 0.05	1.07 ± 0.15
180	1.17 ± 0.15	3.70 ± 0.33
194	0.23 ± 0.04	0.61 ± 0.07
196	0.45 ± 0.04	1.13 ± 0.12
201	0.57 ± 0.07	1.39 ± 0..09
209	0.33 ± 0.10	0.90 ± 0.14

Figure A. Average dioxin/furan concentration in lower Columbia River sediment. The values are the averages, for all the sediment samples, of total concentrations in each congener class.

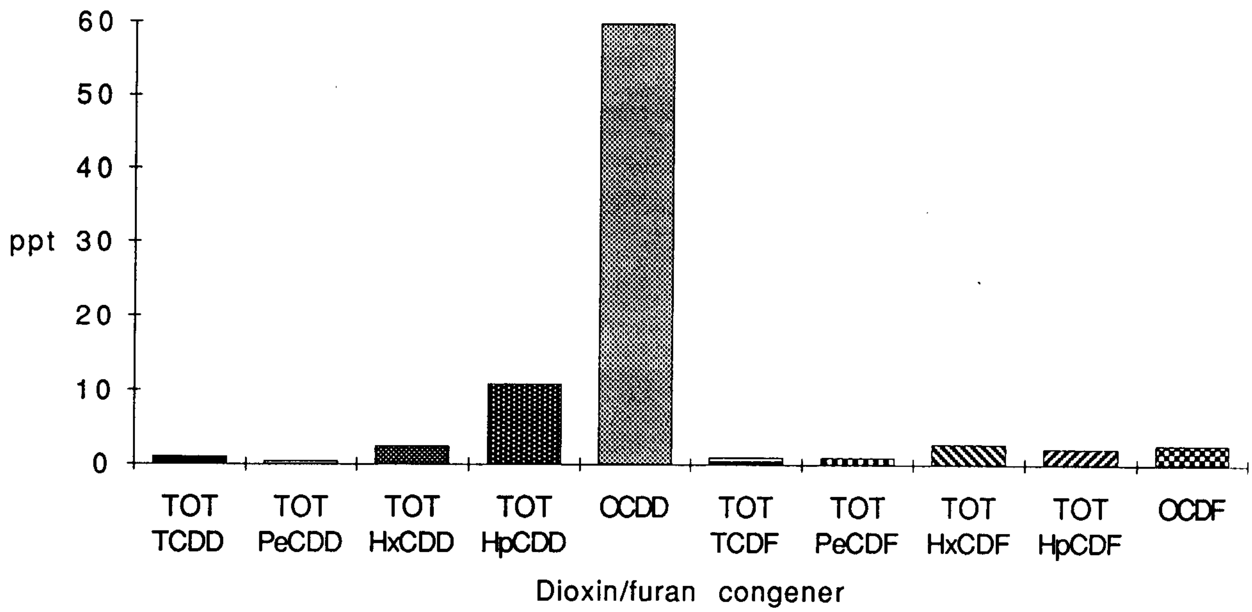
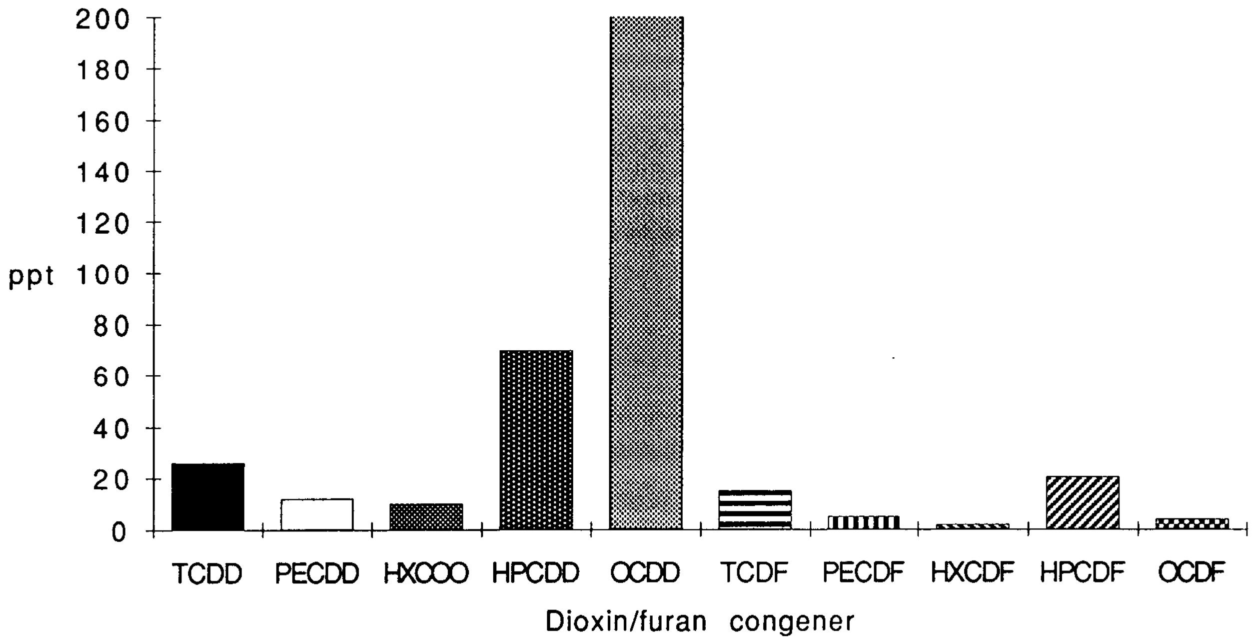


Figure B. Dioxin/furan concentrations in Lake Siskiwit sediment. Explanation is same as for figure A.



US Army Corps
of Engineers
Portland District

Sediment Physical and Chemical Analyses

on the Cowlitz and Columbia Rivers

Subsequent to the 18 May 1980

Mt St. Helens Eruption

SEDIMENT PHYSICAL AND CHEMICAL ANALYSES ON THE COWLITZ AND COLUMBIA RIVERS SUBSEQUENT TO THE 18 MAY 1980 MT. ST. HELENS ERUPTION

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ABSTRACT

Water quality chemical analyses, elutriate analyses, and physical analyses were performed on sediments deposited by the 18 May 1980 mudflows in the Cowlitz and Columbia Rivers. Water and sediment samples were obtained from 20 May through 25 November 1980.

In-situ water quality testing indicated that dissolved oxygen, pH, temperature, and oxidation reduction potential were within the ranges suitable for survival of salmonids. Water quality in Spirit Lake was the exception. Turbidity was determined to be very high in the Cowlitz and Toutle Rivers.

Water quality and sediment chemical data indicated that the majority of the sediments sampled were within the sand and gravel grain size range, contained approximately 20% ash, and did not contain excessive levels of the contaminants analyzed. An exception was elutriate, total phenolic compound numbers which were higher than would normally be expected given the other sediment and water quality findings. These high levels were determined by this study and others to be from non-point source discharges and widespread in the drainage basin.

Physical analyses indicate the mudflow material is angular to subangular in shape, very dense and mixed with pebble to rubble size pieces of pumice. The sediment is also graded coarse to fine from upstream to downstream and from mid-channel to the bank.

SEDIMENT PHYSICAL AND CHEMICAL ANALYSES

INTRODUCTION

The U.S. Army Corps of Engineers is responsible for maintaining adequate depths for waterborne traffic in authorized Federal navigation projects. It also plans and constructs flood control structures in areas of high flooding potential. Following the 18 May 1981, Mount St. Helens mudflows in the Toutle, Cowlitz, and Columbia Rivers, the Corps was faced with an emergency situation in regards to both its navigation and flood control responsibilities. Both the Columbia and Cowlitz River channels were blocked to navigation and additional flooding of several municipalities along the Toutle and Cowlitz watersheds was likely. Physical and chemical data regarding the sediments in the channels were needed to determine (1) best management techniques for materials removed from the channels; (2) potential contaminants of concern in the sediments; (3) the need for further in-depth studies during the dredging and flood-control operations; and (4) potential physical and chemical impacts from proposed operations pursuant to the evaluation requirements of Section 404 of Public Law 92-500.[1] This section of the law requires that impacts of a sediment disposal operation in navigable waters be evaluated following a set of specific testing guidelines.

Accordingly, a series of reconnaissance surveys were performed which involved sampling and testing water and sediment for various chemical and physical characteristics.

TESTING PROGRAM

The tests performed consisted of (1) a standard agricultural sediment analysis to assess impacts of upland disposal of sediment and determine if soil amendments should be added (table 1, figure 1); (2) elutriate and receiving water tests to assess potential water quality chemical impacts from open water disposal of sediments (table 2); (3) bulk sediment analyses to determine the presence of contaminants of concern which could cause long-term impacts at the sediment disposal sites (table 3, figure 1); (4) physical sediment analyses including various density measurements, void ratios, water content, and roundness gradation (table 4); and (5) In-situ water quality analyses to help evaluate sediment/water interactions and impacts from Corps' operations.

The testing program consisted of nine separate sampling and testing episodes beginning on 20 May 1980 and ending November 1980.

ANALYTICAL METHODS

The majority of the elutriate and all of the bulk sediment analyses were performed by U.S. Geological Survey (USGS) following the procedures discussed in the USGS publication, "Native Water, Bottom Material and Elutriate Analyses of Selected Estuaries and Rivers in Western Oregon and Washington".[2] The exceptions to this are cyanide, phenolics, orthophosphate and phosphate elutriate analyses. These were performed by the Corps' North Pacific Division Materials Laboratory on eluate provided by USGS using methods described in the 14th Edition of <u>Standard Methods for Examination of Water and Wastewater</u>.[3]

Physical analyses of sediments were performed by the Corps' North Pacific Division Materials Laboratory using both standardized and in-house methods. Either a Mark V or Hydrolab 8000 water quality testing system was used to measure dissolved oxygen, pH, oxidation reduction potential (ORP), conductivity, and temperature. Turbidity was measured with a YSI turbidimeter.

The 20 and 21 May sediment samples were obtained by hand. Ponar, pipe, or coring apparati were used to obtain subsequent sediment samples.[4] An eight-liter Van Dorn water sampler was used to collect water samples. Sediment and water containers were prepared using standard methods for acid rinsing.[3]

RESULTS

Chemical Analyses

An agricultural analysis was performed on sediments collected from the Cowlitz River's mouth on 20 May. The sediments contained sufficient trace elements to support vegetation but would require additional organic amendments and nutrients for significant plant growth.

Elutriate analyses were performed with sediments collected on the following locations and dates:

1. Mouth of Cowlitz River on 21 May 1980;
2. Cowlitz river miles (RM) .2, 2.0, and 3.5; Carroll Channel, midway between the Cowlitz and Columbia; and Columbia RM 71.4 on 28 May 1980; and
3. Cowlitz RM 12.8 on 4 June 1980.

Water samples were collected for use in elutriate tests and laboratory analyses at Columbia RM 67.01 on 21 May, and Columbia RM 71.4 on 28 May and 4 June.

Bulk sediment analyses for 20 parameters were performed on sediments collected from the mouth of the Cowlitz River on 21 May (table 3, figure 1). Sediments collected in the river mouth on 28 May and Cowlitz RM 12.8 on 4 June underwent bulk analyses for nitrogen and phosphorus.

No contaminants of concern except for phenols were detected during the elutriate, water, and bulk chemical tests (figure 2). Phenols were found to be excessive when compared to 1976 EPA criteria (1 ug/l)[5]; but the new EPA criteria promulgated in November 1980[6] indicated the parameter was probably not of concern in terms of Corps operations. However, eleven phenolic compounds of concern were identified in the new criteria and have yet to be identified in the Cowlitz-Toutle system.

The phenols chemical analysis groups a large number of phenolic compounds, some of which can be highly toxic. Further research is being coordinated with USGS and the National Marine Fisheries Service (NMFS) to assess the types of phenolics present and their potential impact. Also, on 12 August, additional sampling in Spirit Lake and Toutle River was performed to identify the source. High levels (675 ug/l) were found in Spirit Lake, whereas the Toutle contained levels (1 to 10 ug/l) which were an order of magnitude lower.

The tests performed on Toutle River indicated that the water there was of much better quality than that of Spirit Lake except for turbidity. The high levels of this parameter are attributed to high suspended solids levels in the river.

In-situ Water Quality Analyses

Hydrolab or Mark V data was obtained at Cowlitz RM .2 and 1.3, Carrolls Channel, and Columbia RM 70.55 and 67.75 on 29 May; on North Toutle River immediately upstream of the Weyerhauser Green Mountain Mill and downstream of Camp Baker, on South Fork Toutle River off the Highway 4 bridge, and on the main stem of Toutle River at the Tower Road bridge on 14 July; on Johnsons, Brownell, Thirteen, and Eighteen Creeks, and South Fork Toutle River on 16 July 1980; and on South Fork Toutle River and Spirit Lake on 12 August.

Turbidity measurements were made in Columbia River at various locations upstream and downstream of the mouth of Cowlitz on 18 June; in the Toutle River on 14 July; and in the Toutle River and Spirit Lake on 12 August (figure 3). It ranged from 4.4 to 21 NTU in the Columbia; 60 to 735 NTU in the Toutle, and 100 to 130 NTU in Spirit Lake.

The dissolved oxygen, pH and temperature levels were suitable for survival of the fish at all locations except Spirit Lake. The water in the lake was very poor in quality. The dissolved oxygen was too low to support fish and the conductivity was higher than is generally found in the ocean. The pH was within EPA criteria (6.5 to 9.0).

Since turbidity appears to be the parameter of greatest concern in terms of fisheries as well as Corps operations, the National Marine Fisheries Service (NMFS) is performing extensive turbidity monitoring in the Cowlitz, Toutle, and Columbia Rivers. This research has been coordinated with the Corps so that information can help determine impacts of dredging and disposal operations.

Physical Analyses

Sediment physical analyses included density of material in place, density of median solids, void ratio, percent volatile solids, percent organic material, water content in place, and roundness gradation. Sediments were collected for physical analysis from the Cowlitz River mouth on 20 May and from the mouth, RM .2, 2.0, 3.5, and 8.5 on 27 and 28 May 1980 (figure 4). They were collected from the mudflows on the banks at RM 9.5, 11, 12.1, 12.9, 13.5, 14, and 15 on 3 June and from the river at RM 9, 10, 11, 12, 12.8, 14, 16, 19.5, and at the Highway 4 intersection of the Toutle River on 4 June. On 18 June, sediments were collected from Columbia River at RM 64, 64.57, 65.75, 66.47, 67.07, 67.75, 68.19, 68.75, 67.95, 69.75, 70.75, 71.38, 71.75, and 72.19 and opposite lights 29A and 31.

Sediments contained up to 20 percent fine ash at the mouth of the Cowlitz. A significant percentage of large sized material from gravel to boulder in size were in both the Toutle and Columbia Rivers with lesser amounts present in the Cowlitz.

The 27 to 29 May and 3 to 4 June physical samples indicated that sediments tended to become progressively coarser from the mouth of Cowlitz River upstream (figure 5).

Sediments which settled on shore were finer grained than those found in the main channel of the river and resembled that which shoaled at the mouth of the river. The bank material was well-drained in some areas but in others it was still plastic. If left unamended, it will be a poor media for plant growth as its organic and nutrient content is low and it forms a surface crust which may inhibit aeration of the subsurface sediments.

The erodibility of the rivers would normally be decreased by the substantial percentage of gravel, rubble, boulders, and logs which were discovered in the sediments. As the fine sediments are removed, the percentage of rock in the surface of the sediments would increase, eventually forming an armored bed which would offer more resistance to erosion. Dredging the river will help restore project depths and remove the embedded stones thus allowing shoals of finer material to move downstream.

CONCLUSIONS

The parameter of most concern discovered in the foregoing studies was turbidity. The suspended sediments which cause this problem are expected to continue at high levels for years and possibly decades due to continuing erosion of ash and mudflow material in the blast area of Mount St. Helens. Phenolics are also of some concern though the 1980 EPA water quality criteria indicated that significant impacts were unlikely.

The eleven phenolic compounds listed in the 1980 criteria are to be further studied by NMFS and USGS to assure that significant levels are not present. The results of their studies will be used to help determine impacts from any release of this parameter which is attributable to Corps operations.

The physical data on sediments indicated that the majority were composed of sand with significant percentages of ash, silt and larger grain sized materials up to boulder in size. However, the continuing influx of newly eroded material from the blast area may input varying sediment types in the future.

Detailed information concerning the Corps testing program is contained in the Corps publication "Mount St. Helens Eruption; Impacts on the Toutle, Cowlitz and Columbia River Systems." This publication is intended primarily as an in-house document and as such, it is continually updated to include new data which is produced by both Corps and other research groups.

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1. U.S. Environmental Protection Agency, (Wednesday, December 24, 1980), "Guidelines for Specification of Disposal Sites for Dredged or Fill Material," Federal Register, Vol. 40, Part 230.

2. Rinella, Frank A., and Greg Fuhrer, n.d., "Native Water, Bottom Material and Elutriate Analyses of Selected Estuaries and Rivers in Western Oregon," U.S. Geological Survey, Open File Report 81 - ________ (in review).

3. American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1976. Standard Methods for the Examination of Water and Wastewater, 14th Edition, American Public Health Association, Washington, D.C.

4. U.S. Army Engineer District, February 1980. "Supplemental, Interim Procedures for Evaluating and Testing Discharges of Dredged Materials," Portland District, OR.

5. U.S. Environmental Protection Agency, Quality Criteria for Water, 1976. USAEPA 440/9-76-023 Washington, D.C.

6. U.S. Environmental Protection Agency, (Friday, November 28, 1980) "Quality Criteria Documents; Availability," Federal Register, Vol. 45, No. 231.

Figure 1
ANALYSIS OF SEDIMENTS FROM COWLITZ RIVER AFTER MUD FLOW COMPARED TO AVERAGE CRUSTAL ABUNDANCES AVERAGE SURFACE SOILS

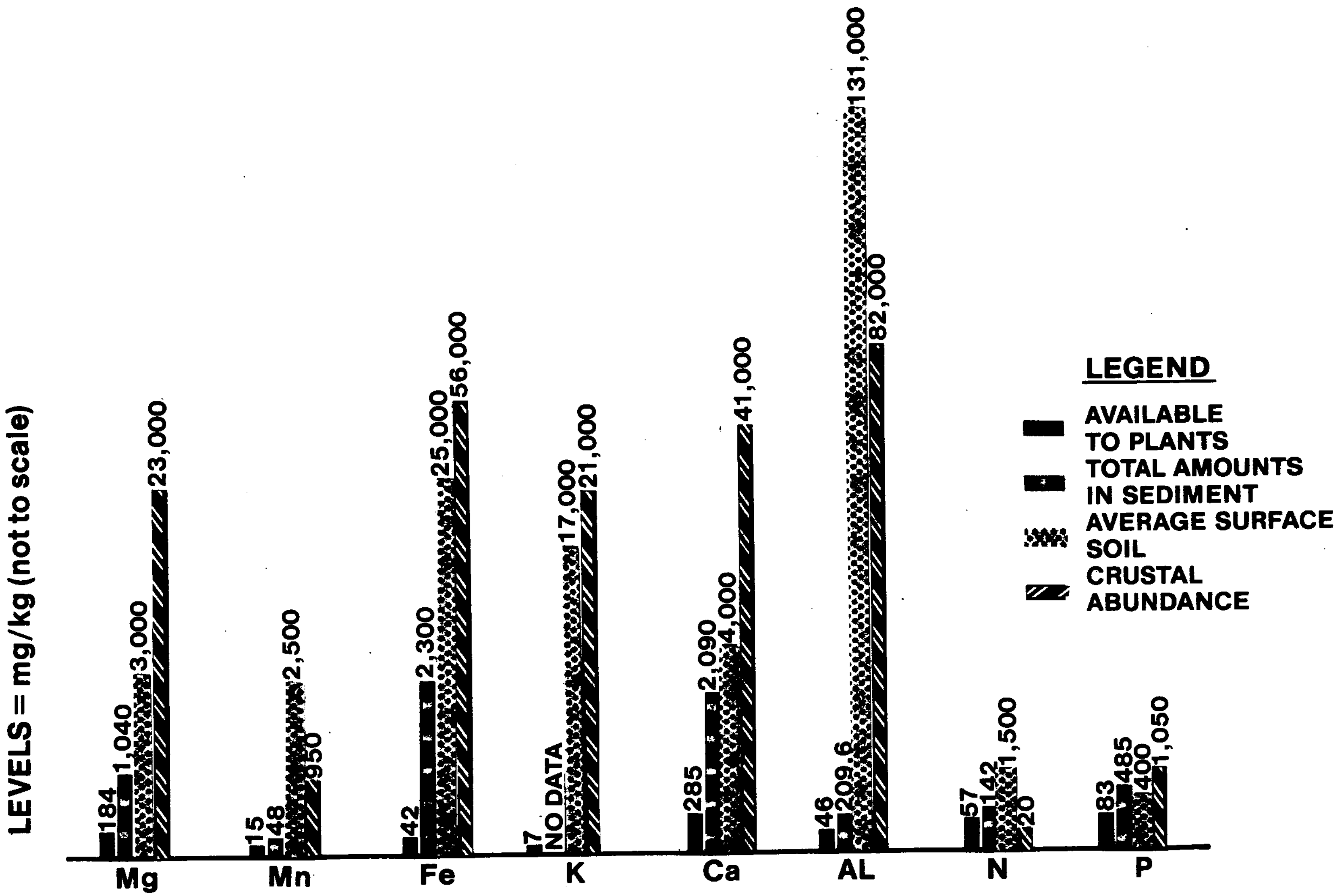


Figure 2
PHENOL LEVELS

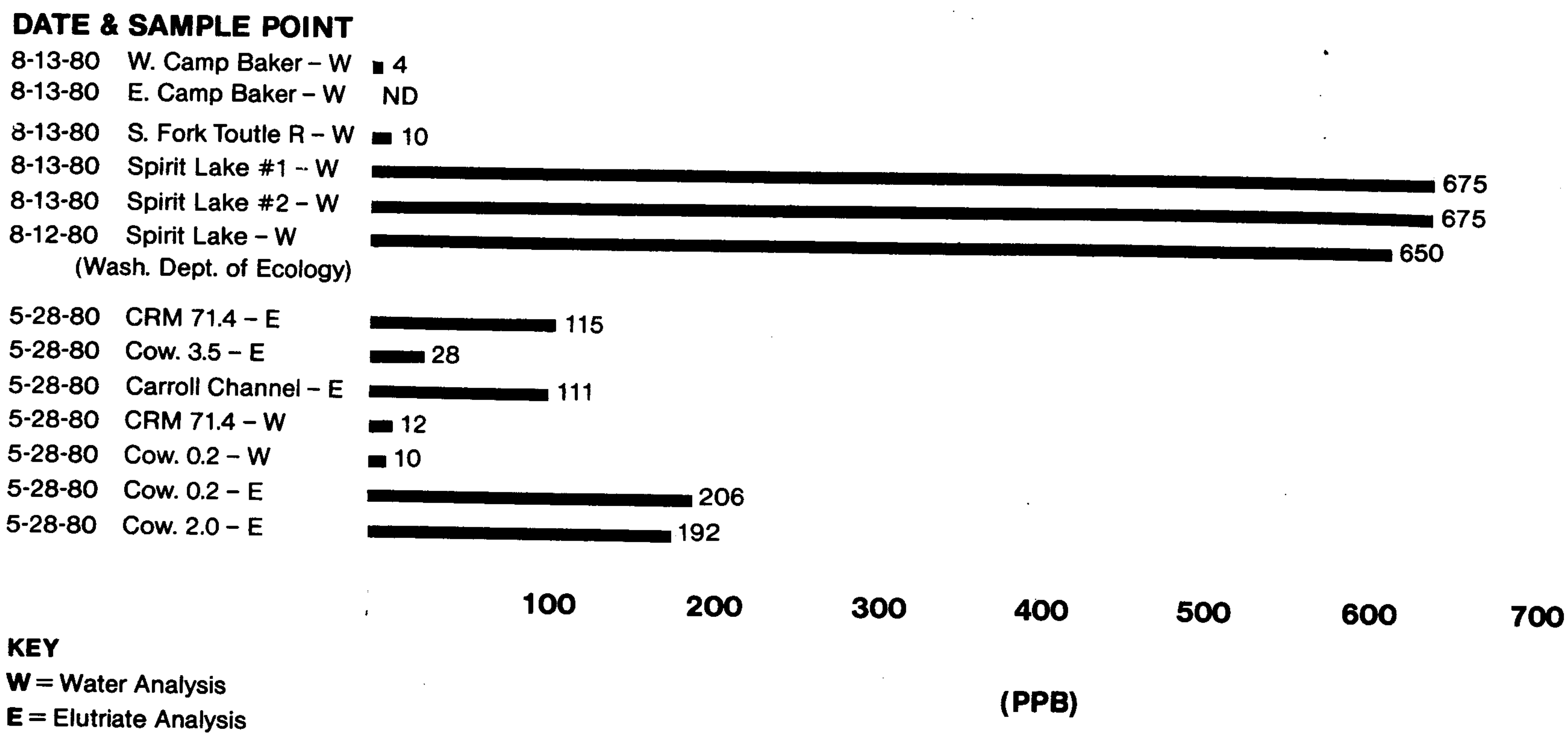
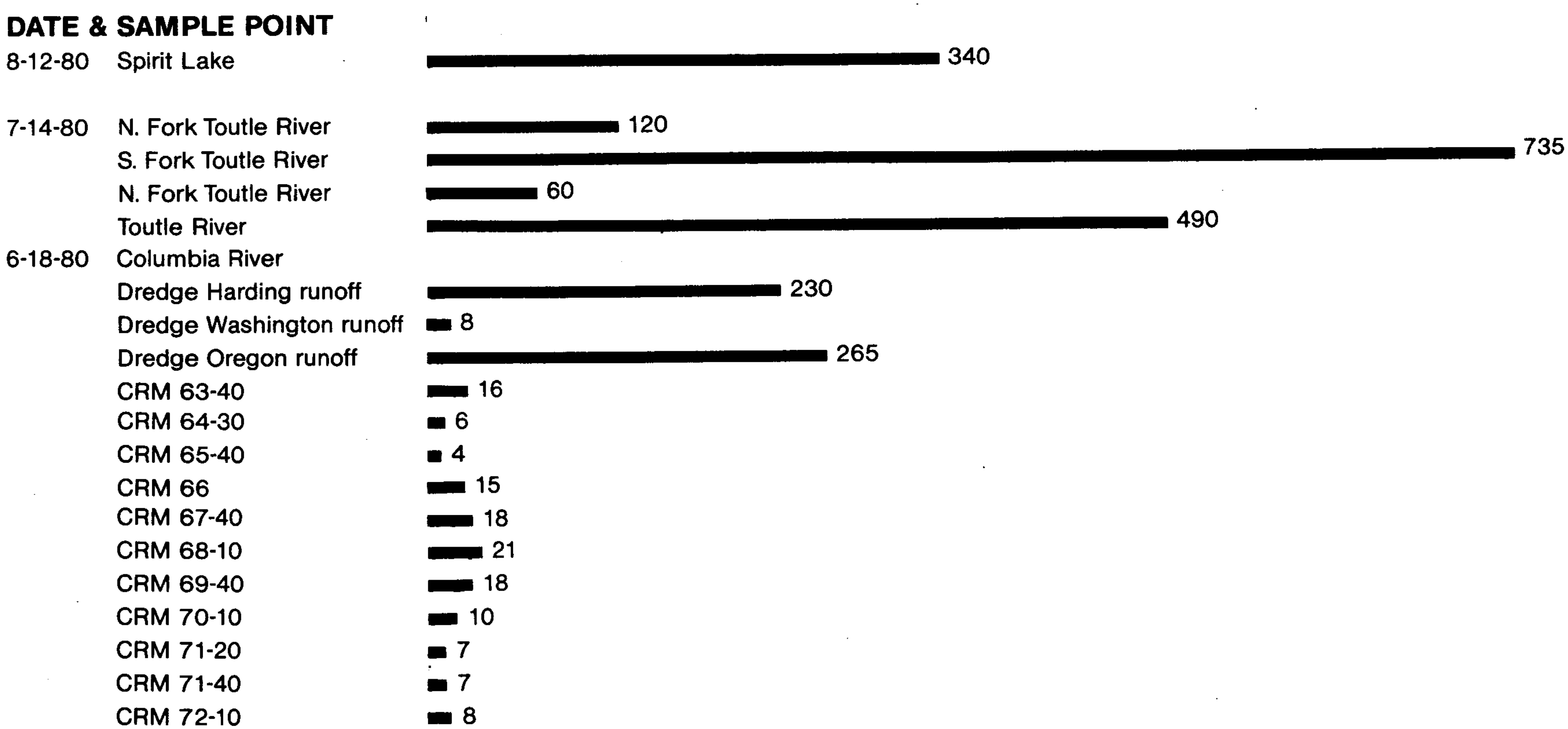
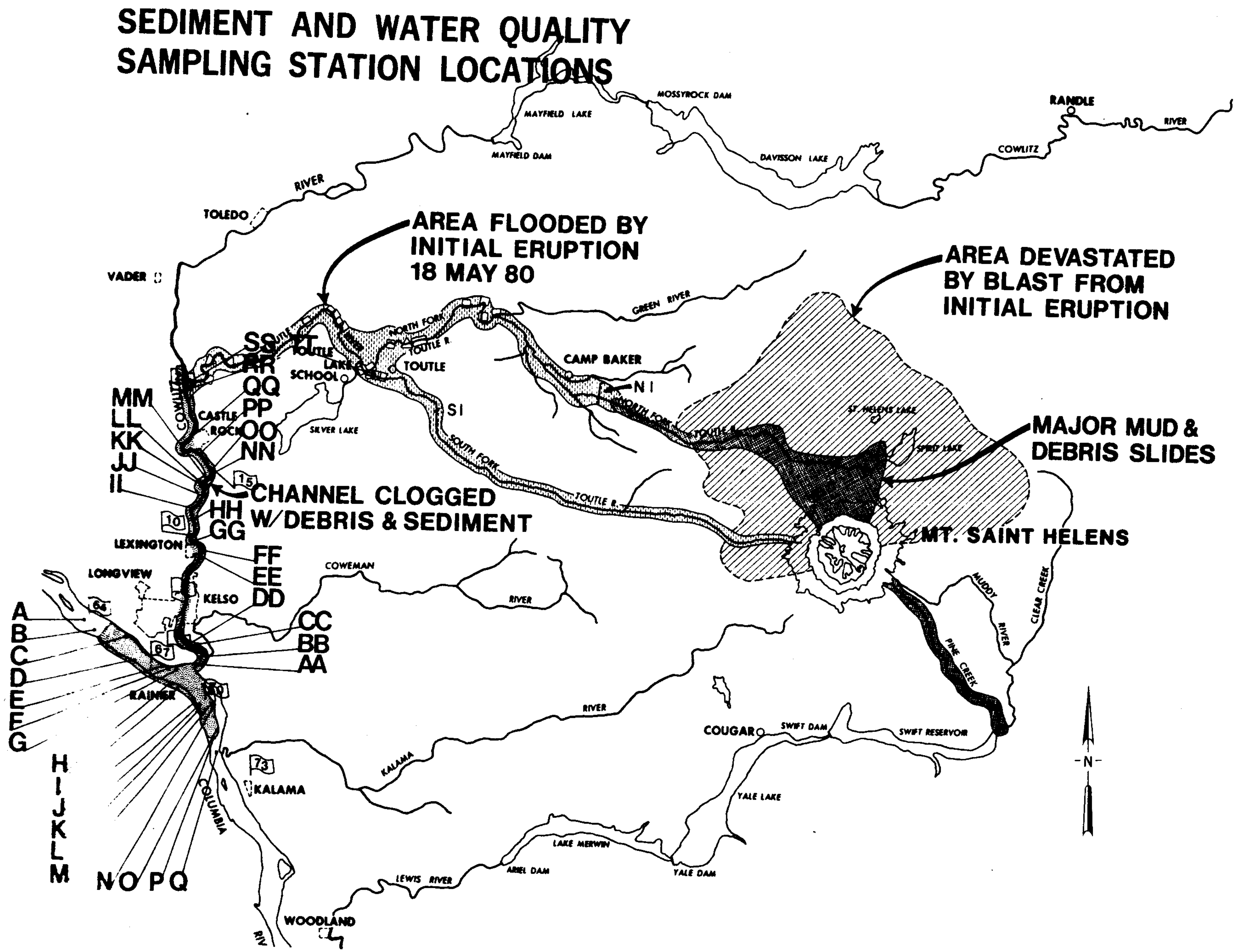


Figure 3
(NTU)
TURBIDITY LEVELS




SEDIMENT AND WATER QUALITY
SAMPLING STATION LOCATIONS
MOSSYROCK DAM
MAYFIELD LAKE
MAYFIELD DAM
DAVISSON LAKE
RANDLE
RIVER
COWLITZ
RIVER
TOLEDO
VADER
AREA FLOODED BY
INITIAL ERUPTION
18 MAY 80
AREA DEVASTATED
BY BLAST FROM
INITIAL ERUPTION
GREEN RIVER
NORTH FORK
TOUTLE R.
TOUTLE
CAMP BAKER
N I
SS
TT
RR
QQ
PP
OO
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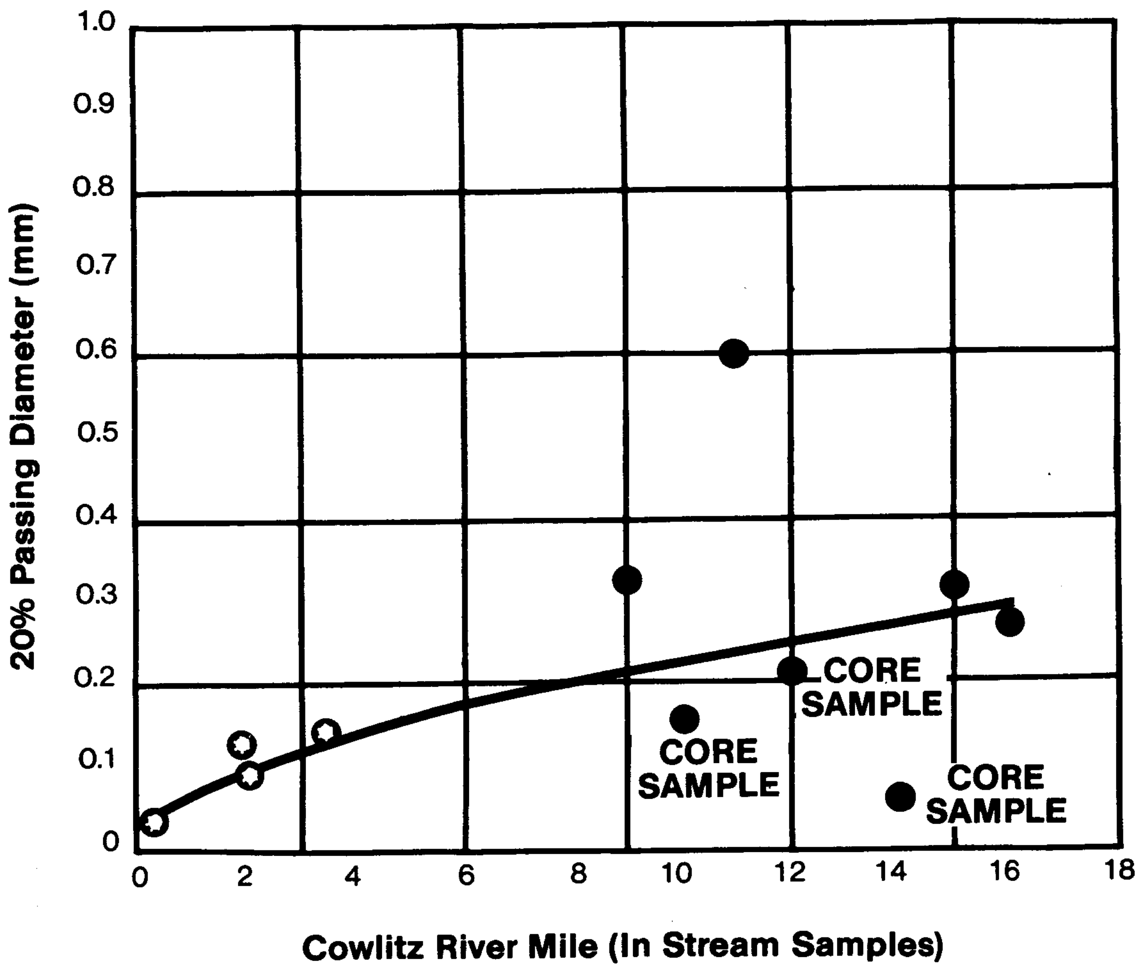
MM
LL
KK
JJ
II
HH
GG
FF
EE
DD
CC
BB
AA
TOUTLE
LAKE
SCHOOL
CASTLE
ROCK
SILVER LAKE
COWLITZ
S I
SOUTH FORK
TOUTLE R.
ST. HELENS LAKE
SPIRIT LAKE
MAJOR MUD &
DEBRIS SLIDES
CHANNEL CLOGGED
W/DEBRIS & SEDIMENT
MT. SAINT HELENS
LEXINGTON
LONGVIEW
KELSO
COWEMAN
RIVER
MUDDY
RIVER
CLEAR CREEK
PINE CREEK
A
B
C
D
E
F
G
H
I
J
K
L
M
N O P Q
RAINIER
RIVER
KALAMA
KALAMA
COLUMBIA
COUGAR
SWIFT DAM
SWIFT RESERVOIR
YALE LAKE
LAKE MERWIN
ARIEL DAM
YALE DAM
LEWIS RIVER
WOODLAND
RIV
N

FIGURE 4

Figure 5
COWLITZ RIVER SEDIMENT STRATIFICATION OF MT. ST. HELENS MUDFLOW



LEGEND

● Sample taken 4 June, 1980

○ Sample taken 27-28 May, 1980

Unless otherwise marked, the samples were obtained with a Ponar or Ellard Sampler.

TABLE 1
AGRICULTURAL ANALYSIS OF SEDIMENTS FROM COWLITZ RIVER*

Collected 20 May 1980

	pm dry weight (mg/kg)
Kjeldahl Nitrogen	52.5
Manganese	15.1
Magnesium	184
Iron	41.8
pH	6.4
Potassium	37.5
Nitrate Nitrogen	4.3
Total Phosphorus	83.6
Ortho-Phosphate Phosphorus	29.2
Calcium	285
Aluminum	48.5
Sulfate	89.9
Chlorides	118.8

*- Sample shaken with acetic acid. Filtered through 0.45mm membrane filter. Testing was done to evaluate potential for use of sediment in agricultural applications.

Sediment sample was taken from a shoal at the mouth of Cowlitz River. The shoal was a result of mudflows caused by the 18 May 1980 eruption of Mt. St. Helens.

TABLE 2
WATER AND SEDIMENT CHEMICAL DATA

PARAMETERS	Elutriate Analyses						Receiving Water 5/29/80		
	Cowlitz RM .2E	Cowlitz RM 2.0	Cowlitz RM 2.0E	Cowlitz RM 3.5	Carroll Channel	Columbia* RM 71.4E	Cowlitz RM .2W	Columbia RM 67+75	Columbia RM 71.4
Field Water Quality Measurements									
Dissolved Oxygen, mg/l		10.85			10.5		10.86	10.56	10.12
Nitrogen, Ammonia mg/l					.09	.01			
ORP		243			245		259	263	260
Conductance, UMHO/CM	112		121	130	190	180	83		128.5
Temperature, C		11.5			13.5		13.6	14.1	14.1
pH	7.3	7.33	7.8	7.1	7.86	7.1	7.5	7.73	7.73
Laboratory Chemical Analyses									
Arsenic, ug/l	1		1				1		1
Barium, ug/l	5		2				2		10
Beryllium, ug/l	1		1				1		1
Cadmium, ug/l	8.6		3	.47	.07	.04	.69		.18
Carbon, Organic mg/l	1.3		2.6	4.8	6.9	4.9	2.2		3.2
Chromium, ug/l	0		0	0	0	0	0		0
Copper, ug/l	8		2	8	03	3	5		3
Cyanide, ug/l	4		1						
Iron, ug/l	270		10	230	80	20	70		20
Lead, ug/l	3		1	2	1	3	3		2
Manganese, ug/l	150		160	100	420	540	130		5
Mercury, ug/l	0		0	0	0	0	0		0
Nickel, ug/l	3		6				3		1
Nitrogen, Ammonia mg/l	.01		0	.01	.09	.01	.01		.03
Nitrogen, Organic mg/l	.31		.21				.13		.41

TABLE 2 (CONTINUED)
WATER AND SEDIMENT CHEMICAL DATA

PARAMETERS	Elutriate Analyses						Receiving Water 5/29/80		
	Cowlitz RM .2E	Cowlitz RM 2.0	Cowlitz RM 2.0E	Cowlitz RM 3.5	Carroll Channel	Columbia* RM 71.4E	Cowlitz RM .2W	Columbia RM 67+75	Columbia RM 71.4
Phenol, ug/l	206		192	28	111	115	10		12
Phosphorus, Total ug/l	34		27						34
Orthophosphate, ug/l	16		19	18		17	10		21
Sulfate, mg/l	11		10						10
Zinc, ug/l	30		3.4	22	2.2	4.2	6.6		2.3
Ametryne, ug/l			0						0
Atrazone, ug/l			0						
Atrazine, ug/l			0						0
Cyanazine, ug/l			0						0
Cyprazine, ug/l			0						0
Prometone, ug/l			0						0
Prometryne			0						0
Propazine, ug/l			0						0
Simazine, ug/l			0						0
Simetone, ug/l			0						0
Simetryne, ug/l			0						0
Bulk Sediment Analyses, mg/kg									
Nitrogen, Ammonia	3.7								
Nitrogen, Total Kjeldahl	37								
Phosporus	460								

*Was elutriated with water from Columbia RM 71.4 obtained on 6-4-80.

TABLE 3
BULK SEDIMENT CHEMICAL ANALYSIS OF THE COWLITZ RIVER SEDIMENTS[1]

21 May 1980

Parameter	Value	Corps' Guidelines[2]
Nitrogen, Kjeldahl-N, mg/kg	116	1,000
Nitrogen, NH_4-N, mg/kg	26	———
Phosphorus, total -P, mg/kg	485	420
Carbon, Organic, g/kg	2.3	60
Carbon, Inorganic, g/kg	0	———
Carbon, Total, g/kg	2.3	———
Arsenic, Total, ug/g	1	3
Barium, Total, ug/g	0	———
Beryllium, Total, ug/g	0	———
Cadmium, Total, ug/g	0	———
Chromium, Total, ug/g	0	———
Chromium, Total, ug/g	0	———
Copper, Total, ug/g	26	25
Cyanide, Total, ug/g	0.55	———
Iron, Total, ug/g	2,300	17,000
Lead, Total, ug/g	0	40
Manganese, Total, ug/g	48	300
Mercury, Total, ug/g	0.01	1
Nickel, Total, ug/g	0	20
Zinc, Total, ug/g	8	90

TABLE 3 (CONTINUED) BULK SEDIMENT CHEMICAL ANALYSIS OF THE COWLITZ RIVER SEDIMENTS[1]

Parameter	Value	Corps' Guidelines[2]
Aluminum* ug/g	209	----
Antimony ug/g	10	----
Bismuth* ug/g	21	----
Boron* ug/g	6	750
Gallium* ug/g	6	----
Germanium* ug/g	15	----
Silica* mg/g	2	----
Silver* ug/g	.2	----
Tin* ug/g	15	----
Titanium* ug/g	63	----
Zirconium* ug/g	.2	----

Moisture Loss	=	22.20%
Gross Ignition Loss	=	23.24%
Net Ignition Loss	=	1.04%

1. Sediment was a composite sample from Columbia River stations CR-902 and 903.

2. The Corps' guidelines were established by Portland District for comparison purposes only and possess no legal standing. The levels given in the guidelines are at the low end of the levels commonly found in moderately polluted sediments.

*- Digested and filtered sediment sample. Data is semi-quantitative only. Was corrected for size and moisture loss.

TABLE 4
SEDIMENT ANALYSIS, COLUMBIA RIVER
Sediments after 18 May 1980 Mount St. Helens Eruption

Sample	River Mile	Date Collected	Void Ratio	Density of Mat'l in place gms/liter	Density of Median Solids gms/liter	Percent Volatile Solids	Percent Water Content in Place	Roundness Grade	D20/mm[1]
A	CRM 64	18 Jun 80	0.860	1908	2689	0.69	32.0	Angular to subangular	0.18
B	CRM 64.57	18 Jun 80	0.905	1938	2787	0.18	32.5	"	0.15
C	CRM 65.75	18 Jun 80	0.838	1981	2804	0.17	29.9	"	0.13
D	CRM 66.47	18 Jun 80	1.049	1824	2687	0.35	39.0	"	0.14
E	CRM 67.07	18 Jun 80	0.931	1903	2743	0.57	34.0	"	0.17
F	CRM 67.75	18 Jun 80	0.901	1896	2703	0.22	33.3	"	0.43
G	CRM 67.95 (#1)	—	0.838	1914	2679	0.20	23.8	"	0.4
H	CRM 67.95 (#2)	—	0.904	1890	2695	0.19	33.6	"	0.4
I	CRM 68.19	18 Jun 80	0.738	1982	2705	0.21	27.3	"	0.83
J	Light 29A[2]	18 Jun 80	0.659	2032	2711	0.24	24.3	"	0.37
K	Light 31[3]	18 Jun 80	0.751	1988	2730	0.19	27.5	"	0.39
L	CRM 68.75	18 Jun 80	0.738	1987	2715	0.22	27.2	"	0.54
M	CRM 69.75	18 Jun 80	0.811	1952	2723	0.19	29.8	"	0.29
N	CRM 70.75	18 Jun 80	0.688	2069	2805	0.16	24.5	"	0.21
O	CRM 71.38	18 Jun 80	0.753	1993	2741	0.24	27.5	"	0.18
P	CRM 71.75	18 Jun 80	0.871	1936	2751	0.21	31.7	"	0.18
Q	CRM 72.19	18 Jun 80	0.903	1887	2688	0.37	33.6	"	0.29

[1] 80 percent of material is coarser than reported grain size.

[2] At dredge WASHINGTON disposal site on Cottonwood Island.

[3] At dredge OREGON disposal site on Cottonwood Island.

Sample	River Mile	Date Collected	Void Ratio	Density of Mat'l in place gms/liter	Density of Median Solids gms/liter	Percent Volatile Solids	Percent Organic Mat'l	Percent Water Content in Place	Roundness Grade	Grain Size
AA	River Mouth	27 May 80	0.711	1981	2678	0.57	0.62	26.6	Subangular to Subrounded	Silty Sand
BB	R.M. 0.2	28 May 80	1.107	1801	2688	0.38	0.41	41.2	Angular to Subangular	Sandy Silt
DD	R.M. 3.5	28 May 80	0.835	2087	2994	0.05	0.11	27.9	"	Sand
EE	R.M. 8.5	27 May 80	0.713	2026	2758	0.17	0.22	25.9	"	Sand
CC	R.M. 2.0	28 May 80	0.822	2083	2973	0.08	0.12	27.7	"	Silty Sand
GG	Cowlitz R.M. 9.6 East Bank Horseshoe Curve	3 Jun 80	0.977	1830	2640	0.78	0.82	37.0	"	Silt
II	Cowlitz R.M. 11.1 East Bank Horseshoe Curve	3 Jun 80	1.148	1746	2603	1.16	1.41	44.1	"	Sandy Silt
KK	Cowlitz R.M. 12.1 Horseshoe Curve	3 Jun 80	1.287	1694	2586	2.96	3.08	49.8	Angular	Sandy Silt
LL	Cowlitz R.M. 12.9 S. End Horseshoe Curve	3 Jun 80	0.813	1931	2687	0.57	0.64	30.2	Angular to Subangular	Silty Sand
MM	Cowlitz R.M. 13.5 N. End Horseshoe Curve	3 Jun 80	1.209	1744	2643	0.73	0.80	45.7	Angular to Subangular	Sandy Silt
NN	Cowlitz R.M. 14 N. End Horseshoe Curve	3 Jun 80	0.750	1959	2679	0.49	0.74	28.0	"	Silty Sand
NN	Cowlitz R.M. 14 East Side Horseshoe Curve	3 Jun 80	0.555	2090	2695	0.31	0.49	20.6	"	Gravelly Silty Sand
FF	Cowlitz R.M. 9	4 Jun 80	0.736	1978	2698	0.12	0.14	27.3	"	Sand
HH	Cowlitz R.M. 10	4 Jun 80	0.998	1825	2669	1.79	3.07	37.4	"	Sand
JJ	Cowlitz R.M. 12	4 Jun 80	0.861	1953	2774	0.21	0.24	31.0	"	Sand
KK	Cowlitz R.M. 12.8	4 Jun 80	1.066	1805	2663	0.44	–	40.0	"	Sand
OO	Cowlitz R.M. 14 Core	4 Jun 80	0.848	1953	2761	0.20	0.21	30.7	"	Sand
QQ	Cowlitz R.M. 16	4 Jun 80	0.905	1884	2684	0.46	0.54	33.7	"	Sand