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TO: Steve Saunders

FROM: Art Johnson and Brad Hopkins

SUBJECT: Metal and Fecal Coliform Concentrations in the Lower Columbia River

We recently completed a water quality survey in the Lower Columbia River, conducted at your request. These are Class A waters, with a special condition that temperature shall not exceed 20°C due to human activities. The impetus for the survey was Ecology's decision to classify this reach of the Columbia as water quality impaired. Ed Rashin had the major responsibility for this assessment, and summarized the basis for the decision as follows:

"For the 1988 Statewide Water Quality Assessment (305(b) Report), the Lower Columbia River is considered to be water quality impaired. That is, the designated uses are not supported based on existing water quality information. This assessment is based primarily on water quality monitoring data collected at the USGS station at Warrendale, Oregon (river mile 141.0) through 1987, and the USGS station at Bradwood, Oregon (river mile 38.9) through 1980, as well as recent (EPA) data on 2,3,7,8-TCDD (dioxin) in fish tissues and pulp mill discharges. Uses which are not fully supported include primary and secondary contact recreation (as indicated by exceedances of bacteria criteria) and aquatic life uses (as indicated by exceedances of metals criteria for the protection of aquatic life and dioxin criteria for protection of human health)."

"Analysis of monthly data collected from October 1976 to October 1980[1] at Bradwood indicates exceedances of Class A criteria for fecal coliform bacteria in 37% of the samples (15 of 40 samples exceeded 100 organisms/100 ml). At this same location, the chronic criteria was exceeded 61% of the time for Pb, 75% of the time for Cu, 16% of the time for Hg, 42% of the time for Cd, and 8% of the time for Zn, assuming a hardness of 50 mg/L. Analysis of monthly data collected during this same time period at Warrendale indicates no exceedances of the criteria for fecal coliform bacteria. However, the chronic criteria was exceeded 80% of the time for Pb, 83% of the time for Cu, 10% of the time for Hg, 55% of the time for Cd, and 16% of the time for Zn at Warrendale. High levels of these metals are also occurring at other stations on the Columbia River, upstream of Bonneville Dam."

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[1]Station discontinued in 1980

Because these conclusions were based, in part, on old information and because of concerns about the accuracy of the metals data, additional data were desired to confirm what appeared to be serious water quality problems in the lower river. Our survey focused on metals and fecal coliform bacteria. The full suite of variables routinely measured as part of Ecology's ambient monitoring program was also analyzed. As you know, the significance of dioxin contamination in the Lower Columbia River was recently evaluated in a study by the Northwest Pulp & Paper Association (Keenan *et al.*, 1990) and is currently being examined through surveys being conducted by the Oregon Department of Environmental Quality and U.S. Fish and Wildlife Service. The metals analyses for the present survey were funded by EPA Region 10.

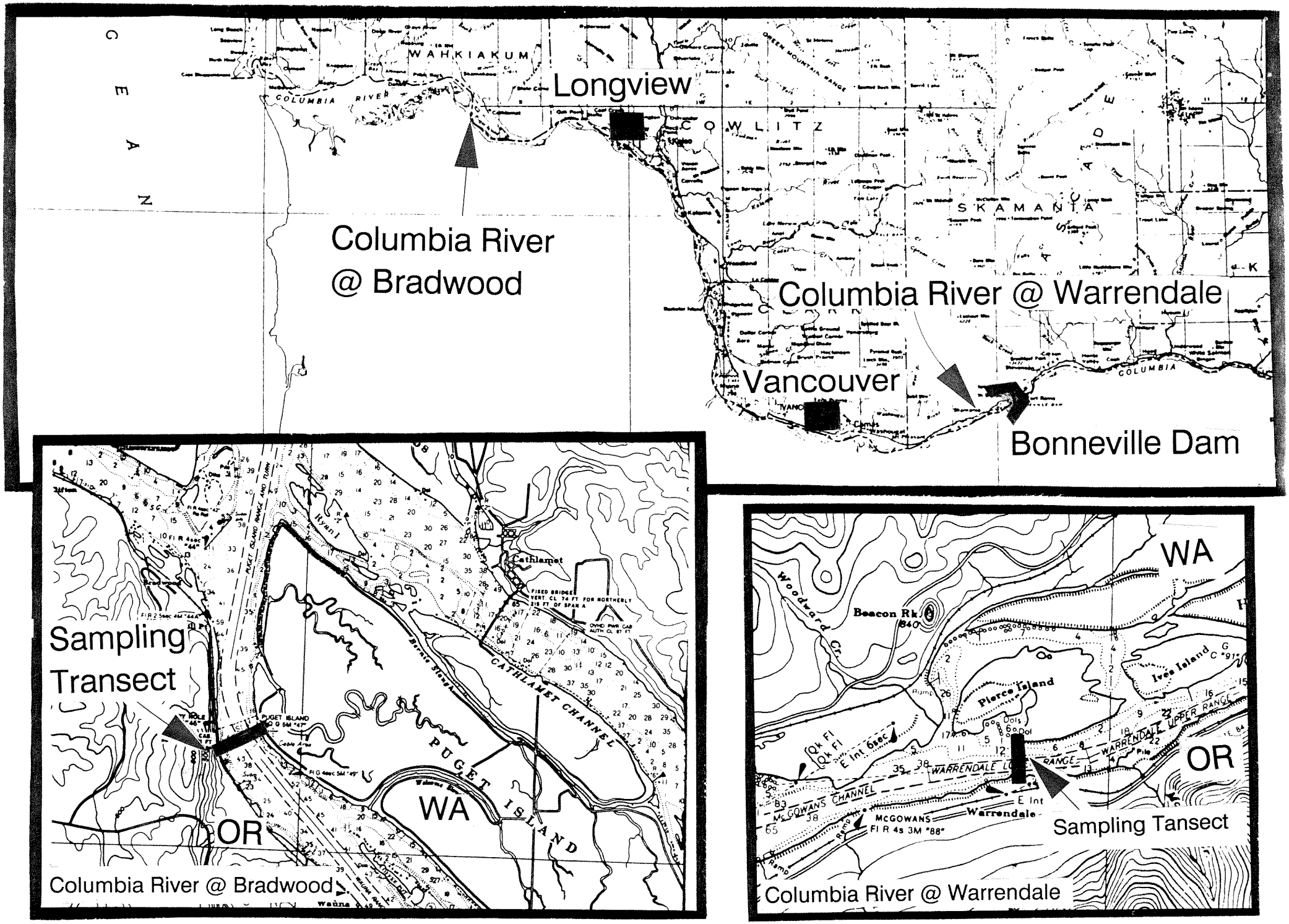
METHODS

Water samples were collected at Warrendale and Bradwood on January 9, May 30, and September 25, 1990 (see Figure 1). Collection periods were chosen to cover a range of hydrologic conditions. All samples were surface grabs collected on a quarter-point transect and analyzed individually. We assumed the water column was well-mixed vertically.

Containers for metals samples were 1-liter teflon bottles previously cleaned by heating in concentrated reagent grade HNO_3 for 48 hours at 90°C, then rinsed five times in deionized water and dried in a laminar flow clean-air bench. Samples were collected from the bow of a small boat facing the current by submerging the teflon bottle to a depth of approximately one foot. For all Warrendale collections, replicates of each grab were filtered in the field (0.45 μm cellulose nitrate filter) for determination of dissolved metals. The filters and filter apparatus (Nalgene 450-0045 CN) were cleaned with 5% HNO_3 by contacting the sample funnel and filter for five minutes and the reservoir for ten minutes upright and ten minutes inverted with lid on, then rinsed five times in deionized water and dried in a laminar flow clean-air bench. All samples were preserved in the field with 8% HC1 and stored on ice for transport to the laboratory.

Metals were analyzed at the Battelle Marine Research Laboratory in Sequim, Washington. The samples were extracted with ammonium pyrrolidine dithiocarbamate for Cu, Pb, and Cd, then quantified by graphite furnace AA (Bloom and Crecelius, 1984). Zinc was run directly by GFAA (EPA Method 200.9). Mercury was analyzed by cold vapor AA (Bloom and Crecelius, 1983). The data were blank corrected. The results are for total metal.

Sampling and analytical methods for fecal coliform bacteria and other water quality variables followed routine practice of the ambient monitoring program as described in the 1990 Ambient Monitoring Annual Freshwater Data Report (in prep). Fecal coliform samples were analyzed by the membrane filter procedure (Standard Methods No. 909c). The samples were collected by hand in pre-sterilized bottles. The stopper was removed, bottle inverted, then submerged below the surface. The bottle was tipped upright to collect the water sample. This method limits surface contamination.


Longview
Columbia River
@ Bradwood
Columbia River @ Warrendale
Vancouver
Bonneville Dam
WAHKIAKUM
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Transect
Cathlamet
PUGET ISLAND
CATHLAMET CHANNEL
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Columbia River @ Bradwood
Beacon Rk
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Ives Island
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DATA QUALITY

The accuracy of the metals data was assessed through analysis of standard reference materials (SRMs), laboratory duplicates, and field blanks.

SRM results are in Table 1. Battelle achieved excellent agreement with certified values for Cu, Zn, Pb, and Hg. Cadmium results were below certified values by approximately 25%.

Precision was assessed from duplicate analysis of three field samples, one from each collection. The standard deviations of these results were as follows: Zn - ± 0.09 μg/L; Cu - $\pm$ 0.07 μg/L; Pb - $\pm$ 0.02 μg/L and Cd - $\pm$ 0.002 μg/L. Mercury was not detected.

Transport (bottle) and filter blanks were also analyzed. The results (Table 2) showed there was no significant contribution of metals from sample containers or the filtration process.

Data quality for fecal colifrom bacteria and other variables was assessed using standard procedures of the ambient monitoring program (see annual report). All data reported here were acceptable for use without further qualification.

RESULTS AND DISCUSSION

Hydrologic Conditions

River flow and rainfall data pertinent to the water sample collections are summarized in the following table.

Sampling Dates (1990)	Mean Daily Discharge @ Bonneville Dam (cfs)	Precipitation (inches) for Week Prior to Sample Collection	
		@ Vancouver	@ Longview
January 9	139,000	2.78	3.20
May 30	253,000	0.96	0.63
September 25	126,000	0.01	0

The flow data were obtained through USGS. Flow is regulated by discharge at Bonneville Dam; there are no gaging stations on the mainstem below Bonneville. Local runoff, as indicated by NOAA precipitation records for Vancouver and Longview, was high during the January sample collection and accompanied by widespread flooding in Western Washington. Runoff was moderate for samples taken in May. Conditions had been dry for the week preceding the sampling done in September.

Table 1. Lower Columbia River - Analysis of Standard Reference Materials (mean ± S.D., n=3; μg/L)

SRM No. and Description		Copper	Zinc	Lead	Cadmium	Mercury
SLRS-1 St. Lawrence River Water (0.2 μm filtered) National Research Council Canada Ottawa	Battelle Analysis	3.58 ± 0.40	1.41 ± 0.15	0.107 ± 0.005	0.020 ± 0.002	---
	Certified Value	3.58 ± 0.30	1.34 ± 0.20	0.107 ± 0.06	0.015 ± 0.002	---
1641 b Mercury in Water National Bureau of Standards Gaithersburg, Maryland	Battelle Analysis	---	---	---	---	1) 0.062 2) 0.00172 3) 0.00158
	Certified Value	---	---	---	---	1) 0.060 2) 0.00152 ± 0.00004 3) 0.00152 ± 0.00004

Table 2. Lower Columbia River - Analysis of Field Blanks (μg/L).

Collection Date (1990)	Copper	Zinc	Lead	Cadmium	Mercury
		Transport Blanks			
January 9	0.24	<0.33	0.033	<0.004	0.0006
May 30	<0.022	<0.16	0.011	<0.001	<0.001
September 25	0.01	0.22	0.050	0.002	<0.0004
		Filter Blanks			
January 9	0.30	<0.33	<0.007	<0.004	0.0004
May 30	<0.022	<0.16	0.007	<0.001	<0.001
September 25	<0.01	<0.17	<0.015	<0.001	<0.0005

Metals Concentrations

The metals concentrations measured in Lower Columbia River water are shown in Table 3. Concentrations of all metals were consistently low at both sampling sites. The following concentration ranges were observed for total metal in whole (unfiltered) water samples: Cu - 1.2 to 2.2 μg/L; Zn - <0.33 to 1.7 μg/L; Pb - 0.18 to 0.50 μg/L and Cd - 0.025 to 0.044 μg/L. None of the samples had detectable concentrations of Hg; detection limits for Hg were 0.001 to 0.002 μg/L.

Metals concentrations did not change appreciably between Warrendale and Bradwood. Statistically significant differences (student's t; $p \leq .05$) were limited to the January runoff event where Zn and Pb concentrations at Bradwood were roughly twice that of upstream concentrations. Substantial seasonal differences were also not apparent, except, again, for January where Zn concentrations were low relative to those in May and September.

Table 4 compares these results with EPA aquatic life criteria and Washington State drinking water standards. Our measurements indicate Cu, Zn, Pb, Cd, and Hg concentrations in this reach of the Columbia were well within levels considered protective of freshwater organisms[2]. Additionally, none of these concentrations would be significant drinking water concerns.

Dissolved metals were measured at Warrendale for purposes of comparison with USGS results which are limited to the dissolved fraction. USGS made three collections at Warrendale during 1990 (obtained through STORET, courtesy of John Tooley). These data are compared to Ecology results in Table 5.

The Zn and Cu concentrations reported by USGS were an order of magnitude higher than the concentrations measured by Ecology. The detection limits associated with USGS' analyses of Pb, Cd, and Hg were much higher than in Ecology's samples. In the one instance where Pb and Cd were quantified, concentrations were two orders of magnitude above Ecology measurements. Mercury was not detected by USGS at detection limits of 0.1 μg/L. As flagged in Table 5, USGS results for Cu, Pb, and Cd in June and Cu in August approach or exceed EPA water quality criteria.

We contacted Gil Bortleson of the USGS Water Resources Division in Tacoma to discuss these results. No blanks or other QA data were available from USGS that were applicable to the present problem. USGS is aware, however, that their depth integrating samplers (P61 and P63) are potential sources of Zn and Cu contamination because they contain metal parts.

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[2]EPA recommends the water quality criteria be compared to total recoverable metals. Because total metals was analyzed for the present survey the above comparison with criteria is conservative.

Table 3. Lower Columbia River - Metal Concentrations in Whole Water Samples (unfiltered) (mean ± S.D., n=3; total metal in μg/L).

Collection Date (1990)	Station	Copper	Zinc	Lead	Cadmium	Mercury
January 9	Warrendale	1.8 ± 0.2	<0.33	0.33 ± 0.04	0.030 ± 0.002	<0.002
	Bradwood	2.2 ± 0.2	0.77 ± 0.07	0.50 ± 0.12	0.028 ± 0.003	<0.002
May 30	Warrendale	1.2 ± 0.2	1.4 ± 0	0.35 ± 0.01	0.044 ± 0.001	<0.001
	Bradwood	1.5 ± 0.4	1.7 ± 0.6	0.35 ± 0.06	0.034 ± 0.004	<0.001
September 25	Warrendale	1.3 ± 0.1	1.1 ± 0.2	0.18 ± 0.01	0.025 ± 0.002	<0.001
	Bradwood	1.3 ± 0.3	1.6 ± 0.6	0.20 ± 0.04	0.025 ± 0.002	<0.001

Table 4. Metals Concentrations Measured in the Lower Columbia River During 1990 Compared to Water Quality Criteria (μg/L)

	Copper	Zinc	Lead	Cadmium	Mercury
Concentration Range in Whole (unfiltered) Water	1.0-2.4	<0.33-2.4	0.18-0.64	0.023-0.044	<0.001-<0.002
EPA Water Quality Criteria* to Protect Freshwater Aquatic Life (for 50 mg/L hardness)			Acute Criteria		
	9.2	65	34	1.8	2.4
			Chronic Criteria		
	6.5	59	1.3	0.66	0.012
Washington State Drinking Water Standards**	(1,000)	(5,000)	50	10	2

* From EPA. 1986. Quality Criteria for Water, 1986. EPA 440/5-86-001

** From Department of Health (1989) State Board of Health Drinking Water Regulations

( ) Secondary standard for taste and odor.

Table 5. Comparison of Ecology and USGS Data on Dissolved Metal Concentrations in the Columbia River at Warrendale During 1990 (mean ± S.D., n=3; μg/L).

Collection Date (1990)	Copper		Zinc		Lead		Cadmium		Mercury	
	Ecology	USGS	Ecology	USGS	Ecology	USGS	Ecology	USGS	Ecology	USGS
January 9	0.94 ± 0.15	---	<0.33	---	0.040 ± 0.031	---	0.014 ± 0.001	---	<0.002	---
March 6	---	3	---	4	---	<1	---	<1	---	<0.1
May 30	0.76 ± 0.26	---	0.26 ± 0.06	---	0.049 ± 0.006	---	0.012 ± 0.002	---	<0.001	---
June 27	---	8*	---	5	---	1*	---	3*	---	<0.1
August 14	---	22*	---	4	---	<1	---	<1	---	<0.1
September 25	0.81 ± 0.06	---	0.20 ± 0.03	---	<0.015	---	0.012 ± 0.002	---	<0.001	---

* Approaches or exceeds EPA water quality criteria to protect freshwater aquatic life (at 50 mg/L hardness)

Table 6. Lower Columbia River - Fecal Coliform Bacteria in Water Samples (col/100ml).

Collection Date (1990)	Station	Left Bank	Mid-channel	Right Bank
January 9	Warrendale	13	8	10
	Bradwood	300	160	230
May 30	Warrendale	1	2	1
	Bradwood	8	3	18
Sept. 25	Warrendale	1	4	1
	Bradwood	19 X	14 X	28 X

X = many background organisms

According to Gil, the USGS Pacific Northwest District has initiated a study to assess differences between dissolved Zn and Cu concentrations obtained by depth/width integrated samples collected with suspended sediment samplers and near surface grab samples using polyethylene bottles. Duplicate samples will be taken at 19 NASQAN sites in Washington and Oregon in water year 1991.

Fecal Coliforms

The results of analysis for fecal coliform bacteria are in Table 6. The Class A standard for fecal coliforms in freshwater is that fecal coliform organisms shall not exceed a geometric mean value of 100 organisms/100 ml, with no more than 10 percent of samples exceeding 200 organisms/100 ml. Although a consistent downstream increase in fecal coliform bacteria concentrations was observed between Warrendale and Bradwood, all Bradwood samples were within Class A standards except those collected in January. These elevated counts (160, 230, and 300 organisms/100ml) may be related to runoff. Low counts were observed in the samples collected under drier conditions in May and September, suggesting the source was primarily non-point.

General Water Quality

Other water quality data (Appendix A) showed the river to be within Class A standards for D.O., pH, and turbidity. Temperatures were also within the Class A standard, although the measurements in September showed the river to be at the limit of the 20°C special temperature condition applied to the Lower Columbia (the usual Class A standard is 18°C). Review of USGS historical data for Warrendale shows violation of the Class A temperature standard in this part of the river is a chronic problem during July through September. This is a long recognized problem due to upstream impoundments. Additionally, a small increase in TSS and nutrient concentrations was generally observed between Warrendale and Bradwood.

CONCLUSIONS AND RECOMMENDATIONS

Contrary to USGS historical data, our survey showed no evidence that Cu, Zn, Pb, Cd, or Hg are a present water quality concern in the Lower Columbia River. Results for fecal coliform bacteria did not indicate a severe or chronic problem exists in the river. It should be recognized that this effort was limited in scope and that an accurate assessment of water quality in the Lower Columbia River will require both intensive studies and routine monitoring. Based on existing information, a major water quality concern in the Lower Columbia is temperature.

The quality of USGS data on metals concentrations in ambient surface waters is suspect. Current designations of state water bodies as limited for aquatic life should be viewed with skepticism where based solely on USGS metals data - particularly when dealing with attainment of the low EPA chronic metals criteria. Until the accuracy of USGS metals data can be demonstrated, they should be used cautiously.

AJ/BH:blt

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Bloom, N.S. and E.A. Crecelius. Determination of silver in seawater by co-precipitation with cobalt pyrrolidine dithiocarbamate and Zeeman graphite-furnace atomic absorption spectrometry. Acta Chimica Acta 156:139 - 145, 1984.

Keenan, R. E., A.H. Parsons, E.S. Ebert, P.D. Boardman, S.L. Huntley, and M.M. Sauer. Assessment of the human health risks related to the presence of dioxins in Columbia River fish. ChemRisk, Portland, ME prep for N.W. Pulp & Paper Assoc., Bellevue, WA, 1990.

Appendix A. Ecology Ambient Monitoring Data for Lower Columbia River during 1990

Station	Time	Date	Depth (Ft)	Temp (°C)	D.O. (mg/L)	D.O. (%Sat)	pH	Field Cond. (@25°C umho)	Lab Cond. (@25°C umho)	Barom. in. of Hg	Tot. H. (mg/L) as CaCO3	Turb (NTU)	TSS (mg/L)	NH3 +NH4-N (mg/L)	NO2-N (mg/L)	NO2+NO3-N (mg/L)	T-PO4 (mg/L)	Ortho-P (mg/L)
Warrendale Left Bank	1115	1/09/90	51	5.8	12.2	97.2	8.4	160	155	29.98	75	5.2	13	0.01	<0.01	0.26	0.05	0.02
Warrendale Mid Channel	1135	1/09/90	39	5.8	12.2	97.2	8.3	163	156	29.98	68	5.4	14	0.01	<0.01	0.26	0.04	0.03
Warrendale Mid Channel Duplicate	1135	1/09/90	39	5.8	12.2	97.2	8.2	162	158	29.98	68	6.1	14	0.01	<0.01	0.27	0.05	0.02
Warrendale Right Bank	1150	1/09/90	12	5.8	12.3	97.9	8.2	166	155	29.99	68	6.0	15	0.01	<0.01	0.26	0.06	0.03
Bradwood Left Bank	1555	1/09/90	104	6.5	11.9	96.0	7.9	133	129	30.11	55	7.8	30	0.04	<0.01	0.48	0.07	0.05
Bradwood Mid Channel	1600	1/09/90	68	6.6	12	97.1	7.9	135	128	30.10	49	8.4	26	0.04	<0.01	0.42	0.08	0.04
Bradwood Right Bank	1610	1/09/90	58	6.7	11.6	94.0	8.0	132	129	30.12	53	9.0	36	0.04	<0.01	0.42	0.07	0.04

Appendix A. (continued)

Station	Time	Date	Depth (Ft)	Temp (°C)	D.O. (mg/L)	D.O. (%Sat)	pH	Field Cond. (@25°C umho)	Lab Cond. (@25°C umho)	Barom. In. of Hg	Tot. H. (mg/L) as CaCO3	Turb NTU	TSS (mg/L)	NH3 +NH4-N (mg/L)	NO2-N (mg/L)	NO2+NO3-N (mg/L)	T-PO4 (mg/L)	Ortho-P (mg/L)
Warrendale Left Bank	1045	5/30/90	41	14.0	11.0	106.4	8.1	NM	138	NM	56	3.9	1	0.01	<0.01	0.05	0.03	<0.01
Warrendale Mid Channel	1050	5/30/90	19	14.0	11.4	110.3	8.1	NM	127	NM	56	3.9	7	0.01	<0.01	0.05	0.03	<0.01
Warrendale Mid Channel Duplicate	1050	5/30/90	19	14.0	11.4	110.3	8.1	NM	128	NM	57	3.6	5	0.02	<0.01	0.04	0.03	<0.01
Warrendale Right Bank	1100	5/30/90	11	14.0	11.5	111.3	8.2	NM	128	NM	55	3.5	7	0.02	<0.01	0.05	0.03	<0.01
Bradwood Left Bank	1500	5/30/90	90	14.1	10.5	101.6	8.1	NM	130	NM	52	4.2	13	0.01	<0.01	0.11	0.05	0.02
Bradwood Mid Channel	1505	5/30/90	57	13.9	10.7	103.1	8.2	NM	128	NM	54	4.1	8	0.01	<0.01	0.09	0.04	0.01
Bradwood Right Bank	1510	5/30/90	47	13.9	10.7	103.1	8.0	NM	130	NM	55	3.4	10	0.01	<0.01	0.08	0.04	0.01

NM = No measurement taken

Appendix A. (continued)

Station	Time	Date	Depth (Ft)	Temp (°C)	D.O. (mg/L)	D.O. (%Sat)	pH	Field Cond. (@25°C umhos)	Lab Cond. (@25°C umhos)	Barom. In. of Hg	Tot. H. (mg/L) as CaCO3	Turb NTU	TSS (mg/L)	NH3 +NH4-N (mg/L)	NO2-N (mg/L)	NO2+NO3-4 (mg/L)	T-PO4 (mg/L)	Ortho-P (mg/L)
Warrendale Left Bank	1420	9/25/90	41	20.1	8.6	93.5	8.1	162	161	30.08	64	1.6	5	0.056	<0.01	0.06	0.03	0.02
Warrendale Mid Channel	1425	9/25/90	30	20.1	8.7	94.5	8.0	156	157	30.08	64	1.6	4	0.049	<0.01	0.05	0.02	0.02
Warrendale Mid Channel Duplicate	1425	9/25/90	30	20.1	8.6	93.4	8.1	154	154	30.08	63	1.5	8	0.042	<0.01	0.05	0.03	0.02
Warrendale Right Bank	1440	9/25/90	7	19.7	8.7	93.8	8.1	150	159	30.08	63	1.7	4	0.05	<0.01	0.06	0.03	0.05
Bradwood Left Bank	1200	9/25/90	95	19.4	8.6	91.7	8.1	147	161	30.23	60	1.8	6	0.04	<0.01	0.07	0.05	0.02
Bradwood Mid Channel	1210	9/25/90	60	19.4	8.7	92.8	8.1	148	153	30.23	61	2.2	9	0.029	<0.01	0.06	0.03	0.02
Bradwood Right Bank	1210	9/25/90	55	19.2	8.8	93.8	8.1	149	150	30.23	60	1.7	8	0.029	<0.01	0.06	0.04	0.02