

Chemistry and Toxicity of Three Wastewaters

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CHEMISTRY AND TOXICITY OF THREE WASTEWATERS

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Prepared for

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EXECUTIVE SUMMARY

As a first step toward developing a toxicity testing program tailored to the Fraser River Basin, the Fraser Pollution Abatement Office (FPAO) initiated a pilot wastewater characterization study in April and May 1992. Three representative effluent types were sampled: (1) primary treated domestic sewage from greater Vancouver (Annacis Island Wastewater Treatment Plant); (2) final effluent from a bleached Kraft pulp mill (Northwood Pulp and Timber Ltd., Prince George); and (3) urban runoff from a Vancouver storm sewer. A flow-weighted composite sample from each site was subjected to duplicate chemical analysis to identify the main components and toxicological testing with an array of acute and chronic bioassays.

Interpretation of the effluent chemical profiles was hindered by a serious discrepancy between results from the two analytical laboratories, possibly arising from the sample compositing procedure. Annacis Island effluent contained high concentrations, relative to environmentally significant levels, of suspended solids, ammonia, nitrogen and the metals aluminum, copper and zinc. Northwood's effluent contained suspended solids (bacterial floes), resin acids, dissolved salts, nitrogen and phosphorus, aluminum and zinc. A long list of chlorinated organic compounds were identified in the pulp mill effluent, all in extremely low concentrations, but the total adsorbable organic halides (AOX) concentration exceeded 10 mg/L. Storm sewer water was relatively low in dissolved salts, but contained significant concentrations of metals: aluminum, copper, zinc and nickel. Concentrations of dioxins and furans were extremely low in all effluents and PCBS were never detected.

Annacis Island effluent was acutely toxic to rainbow trout (LC50 55%) and bacterial bioluminescence (Microtox). Undiluted effluent was lethal to *Daphnia* The effluent also inhibited reproduction in *Ceriodaphnia* Ammonia and metals are the probable sources of the acute toxicity. Northwood Pulp effluent was slightly toxic to trout at full strength, probably from resin acids, and inhibited reproduction in *Ceriodaphnia*.

This effluent was extremely repressive of algal growth (threshold of effect below 0.3%) from unknown sources, possibly chlorinated organics. The strength of the response in the algal growth test is unusual and requires confirmation. Storm sewer water produced no acute toxicity, and only slightly inhibited *Ceriodaphnia* reproduction, again probably through heavy metals. All three effluents produced strong evidence of genotoxicity in the SOS-Chromotest, with effect thresholds of 1-4% of undiluted effluent. Many constituents could potentially have produced the genotoxic response. Generally, toxicity testing agreed with expectations based on chemical analysis but was more revealing. In terms of severity of potential environmental effects, Annacis Island effluent would rank first, Northwood Pulp second, and the storm sewer distant third.

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1.0 INTRODUCTION

Under the auspices of the Fraser River Action Plan, the Fraser River Pollution Abatement Office (FPAO) is charged with identifying sources of pollution, characterizing wastewater discharges, and finding ways to reduce pollution entering the Fraser River drainage. The FPAO has a goal of reducing discharges of "environmentally disruptive" effluents to the Fraser River Basin by 30% in five years. To accomplish this task, and to keep interested parties and the general public apprised of progress toward reducing pollutant loads, the FPAO has need of a reliable toxicity testing program to compare wastewater discharges and to assign priorities for abatement. Laboratory toxicity testing would be used to quantify and rank effluents with respect to their "environmentally disruptive" character, and to monitor the progress of pollution abatement actions.

As a first step in the development of a toxicity testing framework for the Basin, the FPAO carried out a pilot wastewater characterization study in April and May, 1992, using three effluent sources that are both common in the Basin and representative of the range of major effluent types. Single, flow-weighted, composite samples were taken from:

- (1) municipal wastewater (primary treatment effluent)
- (2) pulp mill effluent (bleached Kraft, secondary treatment)
- (3) urban runoff.

All three samples were subjected to duplicate chemical analysis to identify their major components, and toxicological testing, involving a broad spectrum of acute and chronic bioassays.

The present report provides analysis and interpretation of the data from the pilot study with respect to generality of the results and their implications for the Fraser River. This end required, first, an examination of the chemical profiles of each effluent to see if they are typical of their respective sources and to resolve any analytical problems or inconsistencies. Then, the toxicity data were evaluated to identify dose-response relationships between constituents of the effluent and toxicity test results. Finally, the toxicity and chemistry data were interpreted in the larger context of the potential effects of each effluent on the Fraser River ecosystem. This step addressed a central objective of the pilot study, which was to determine the relevance of toxicological testing to assessing environmentally disruptive effects of wastewater effluent.

2.0 METHODS

2.1 SAMPLING SITES

Three effluents were selected as representative of the range of common wastewater types entering the Fraser River basin. The effluents were: (1) primary treated domestic sewage from greater Vancouver (Annacis Island Wastewater Treatment Plant); (2) final effluent from a bleached Kraft pulp mill (Northwood Pulp and Timber Ltd., Prince George); and (3) urban runoff from a Vancouver storm sewer. Domestic sewage is one of the most conspicuous wastes entering the Fraser River basin, particularly in the lower Fraser River valley, where most of the human population is concentrated. Pulp mills are located throughout the upper and middle basin, and produce copious quantities of chemically complex, organically rich effluent. The third effluent type, urban runoff, represents a separate class of wastewater: intermittent in flow, exceedingly variable in chemical composition, but still significant to the river by virtue of its cumulative volume and sometimes heavy load of contaminants.

Annacis Island, the second largest of four wastewater treatment plants in the Greater Vancouver Regional District (GVRD), discharges primary treated municipal sewage into the main arm (Annieville Channel) of the Fraser River between North Delta and New Westminster. Thirteen percent of the average, dry-weather flow to the treatment plant is from major industrial sources, although the proportion of industrial wastes is decreasing (FREMP 1990). Influent sewage is screened to remove large detritus, aerated, and settled to remove grit and about 60% of the organic solids. Surface scums are skimmed off, and during the summer months (May-September) the effluent is chlorinated (and dechlorinated) before being released to the Fraser River through a channel-bottom diffuser. The effluent was not being chlorinated when samples were taken on 1 and 2 April 1992 (Thomas and Dwernychuk 1992).

The Northwood Pulp and Timber Ltd. mill produces bleached. Kraft pulp and discharges wastewater to the Fraser River about 10 km upstream from Prince George. The Kraft process separates cellulose fibres from lignin in wood by digesting chips at high temperature (170°C) and pressure (>160 psi) in the presence of sodium sulphite and sodium hydroxide. After cooking and washing, the fresh pulp is bleached, usually in five or six stages, using chlorine, sodium hydroxide and chlorine dioxide as brightening agents (AEC 1987). At the time of sampling, 6 and 7 April 1992, Northwood was bleaching using a six-stage process with 70% chlorine dioxide substitution. The digestion stage produces a concentrated, highly toxic, spent liquor, which requires substantial treatment before it may be discharged, and the chlorination stage contributes chlorinated organic compounds to the effluent. At Northwood, the raw effluent undergoes primary clarification (scum removal and settling to remove particulate), followed by secondary treatment in aerated lagoons with nutrient additions (Thomas and Dwernychuk, 1992, Appendix 1).

Street runoff was sampled from a GVRD storm sewer located in the upper basin of Still Creek, near the eastern boundary of Vancouver (Collingwood Trunk, 5358 Cecil Street, Manhole No. 16). The sewer receives runoff from both commercial and residential areas and eventually drains into the North Arm of the Fraser River.

2.2 SAMPLE COLLECTION AND ANALYSIS

A full description of sampling techniques is contained in a previous data report (Thomas and Dwernychuk 1992). Briefly, each of the three sites was sampled at three-hour (Annacis Island, Northwood) or two-hour (storm sewer) intervals for up to twenty-four hours. The storm sewer samples were taken during a rainstorm following at least four days of dry weather. Sampling there finished after 18 hours because the rain had ended and sewer discharge had returned to base flow. Simultaneous flow measurements were taken at each site and used to calculate 24-hr

discharge (Annacis Island, Northwood) or 18-hr discharge (storm sewer) (Thomas and Dwernychuk 1992).

Wastewater samples, collected using appropriate containers by personnel experienced in sampling of ultra-trace contaminants, were sent immediately to two independent laboratories for chemical analysis: Envirotest Laboratories Ltd., Edmonton, Alberta, and Analytical Services Laboratories Ltd. (ASL), Vancouver, B.C. The wastewaters from Annacis Island and the GVRD storm sewer were sent to the laboratories as a set of discrete samples; the laboratories produced flow-proportionate composite samples by combining discrete aliquots in proportion to flow measurements for each sampling interval. Discharge from the Northwood pulp mill was constant over the sampling period and unweighed composites were mixed in the field. Analysis of oil and grease used discrete samples from three selected intervals over the sampling period (Thomas and Dwernychuk 1992).

Chemical profiles of each effluent were produced by analysing the composite samples for physical parameters (pH, suspended solids), nutrients, oil and grease, biochemical oxygen demand (BOD), metals, and organics. The last class included volatiles, phenols, base-neutral extractable, polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and dioxins and furans. Pulp mill effluent was also analyzed for resin and fatty acids and adsorbable organic halides (AOX); water from the storm sewer was analyzed for pesticides. The chemical analyses included most parameters on the Canadian Environmental Protection Act (CEPA) priority substances list, as well as those listed under Ontario's MISA program. The laboratories each submitted complete quality control and quality assurance (QC/QA) information along with the results of their analyses (see Thomas and Dwernychuk, Appendices 3 and 4).

Split samples from each effluent source were also sent to two biological laboratories for toxicity testing. Composite samples of >100 L volume were prepared in the

field by mixing aliquots from each sampling interval in proportions commensurate with discharge. Portions of the well-mixed composite sample were then sent to Environment Canada's laboratory "in North Vancouver for acute toxicity tests and to Analex Inc., Laval, Quebec, for other assays.

Environment Canada tested each effluent with the following assays, following standard protocols:

- (1) Rainbow trout 96-h LC50 (acute)
- (2) Daphnia magna, 48-h LC50 (acute)
- (4) Bacterial luminescence (Microtox assay (5 and 15 rein).

Analex tested the effluents using Microtox plus three other chronic assays:

- (3) Ceriodaphnia dubia survival and reproduction assay
- (5) Algal growth test with Selenastrum capricornutum
- (6) SOS chromotest with Escheria coli.

Analex also aerated the samples for five days, with nutrient additions to stimulate biodegradation (and volatilization) and re-tested toxicity afterward. The Analex bioassays are intended to provide data for an index of toxicity (the PEEP index), the utility of which is reviewed elsewhere (EMA 1993). In the present work the toxicity test results alone are used to construct a profile of toxicity from each of the three wastewater effluents.

3.0 RESULTS AND DISCUSSION

3.1 COMPARISON OF SPLIT SAMPLES

Chemical profiles for each of the three effluents are presented in Tables 1-3; a more exhaustive compilation, including QA/QC reports and loading rates, may be found in the data report (Thomas and Dwernychuk 1992). Before attempting to interpret these data, a persistent problem of inter-laboratory variation must be addressed. Even a quick glance at Tables 1-3 reveals that values reported by Envirotest and ASL often disagree, and the differences are sometimes quite substantial. The discrepancies extend across all three sites and all classes of compounds, including those analyzed by subcontractors to the main laboratories. This variability confounds interpretation of the data, especially for compounds present in trace amounts.

To define the extent and magnitude of variation between laboratories, we computed the ratio between the datum for Envirotest over that for ASL for each applicable parameter. Only parameters detected by at least one laboratory were included and no ratio could be calculated where the detection limit for one laboratory was greater than the value listed by the other. Where the detection limit was lower than the value reported by the other laboratory, the detection limit was used in the ratio.

Results are summarized in Table 4 (see the Appendix for a complete list). Across all three sites, the maximum ratio (where Envirotest reported the higher value) was about an order of magnitude greater than 1, which value would indicate perfect concordance. Hence, at worst, Envirotest data are about 10 times greater than ASL data. However, the minimum ratios (where ASL reported the higher value) are also about 10 times smaller than 1, so while there is a disappointing range of variability in the data, there is no evidence of a systematic bias in one direction or the other. The number of ratios exceeding 1 is also not very different from 50% of the total

TABLE 1

CHEMICAL PROFILE OF EFFLUENT FROM ANNACIS ISLAND WASTEWATER TREATMENT PLANT

	LABORATORY	
PARAMETER	ENVIROTEST	ASL
PHYSICAL		
pH (units)	6.9	6.74
Total Suspended Solids (mg/L)	47	50
Volatile Suspended Solids (mg/L)	47	48
DISSOLVED IONS (mg/L)		
Calcium	17.0	
Sodium*		
Fluoride		0.14
NUTRIENTS (mg/L)		
Ammonia-N	26.0	22.3
Total Kjeldahl N	29.7	85.9
Nitrate-N	< 0.05	0.010
Nitrite-N	0.12	0.014
Total Phosphorus	4.45	4.47
METALS (mg/L)		
Aluminum	0.5	0.43
Antimony ^z	0.0008	0.0003
Arsenic*	0.0005	0.0012
Cadmium	< 0.003	0.0002
Copper	0.17	0.199
Lead	< 0.04	0.015
Mercury	0.0008	0.0001
Molybdenum	< 0.02	0.008

TABLE 1
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	LABORATORY			
PARAMETER	ENVIROTEST	ASL		
Nickel	0.04	< 0.020		
Selenium ²	0.0005	< 0.0005		
Titanium	0.003	< 0.03		
Vanadium	0.007	< 0.005		
Zinc	0.195	0.117		
GENERAL ORGANICS (mg/L)				
Oil and Grease'	31 (26-35)	19.7 (14-27)		
BOD,	4			
Total Phenols	< 0.003	0.006		
VOLATILE ORGANICS (μg/L) ⁵	VOLATILE ORGANICS (µg/L) ⁵			
Chloroform	< 1.0	8.2		
1, 4-dichlorobenzene	2.5	2.1		
Tetrachloroethylene	4.3	7.4		
Trichloroethylene	< 1.0	1.9		
Ethylbenzene	5.5	10.5		
Toluene	8.0	19.5		
	40	67.4		
BASE-NEUTRAL EXTRACTABLE (µg/L) ⁵				
Di-n-Octylphthalate	5.3	< 1.0		
PAHs ⁵ (µg/L)				
Phenanthrene	0.63	< 0.3		
DIOXIN CONGENERS (pg/L)				
1, 2, 3, 6, 7, 8- HCDD	< 4.6	11		
1, 2, 3, 7, 8, 9- HCDD	c 4.7	(6.5) ⁸		

TABLE 1
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	LABORATORY			
PARAMETER	ENVIROTEST	ASL		
1, 2, 3, 4, 6, 7, 8- HCDD	79	43		
FURAN CONGENERS (pg/L)				
2, 3, 7, 8- TCDF	10	(4.5)		
1, 2, 3, 4, 6, 7, 8- HCDF	< 3.2	28		
TOTAL DIOXINS AND FURANS (pg/L)				
H₄CDD	< 4.8	36		
H,CDD	100	88		
O ₈ CDD'	(580)	260		
H,CDF	< 9.1	46		
O ₈ CDF°	< 14	(35)		
TEQ¹⁰	0.89	2.1		

- 8.64 mg/L in Hatfield Table 10A is a typo.
- ² Envirotest: dissolved; ASL: Total (all other metals are totals)
- Mean (and range) of three replicates
- Not analyzed. 1.3 mg/L in Hatfield Table 8A is a typo.
- ⁵ ASL data are means of duplicates.
- Sum of ortho, metaandpara forms.
- ⁷ 76.2 μg/L in Hatfield Table 4Ais a miscalculation.
- ⁸ Values in brackets are reported as quantitatively unreliable.
- Reported as congeners 0,8 in Hatfield Table 3A.
- Toxic equivalents in pg/L.

TABLE 2

CHEMICAL PROFILE OF EFFLUENT FROM NORTHWOOD PULP AND TIMBER

	LABORATORY	
PARAMETER	ENVIROTEST	ASL
PHYSICAL		
pH (units)	7.6	7.65
Total Suspended Solids (mg/L)	62	59
Volatile Suspended Solids (mg/L)	38	45
DISSOLVED IONS (mg/L)		
Calcium	117	
Sodium	474	470
Chloride	293	229
Fluoride		0.04
NUTRIENTS (mg/L)		
Ammonia-N	0.45	0.76
Total Kjeldahl N	3.81	2.77
Nitrate-N	< 0.05	< 0.005
Nitrite-N	< 0.05	< 0.001
Total Phosphorus	0.98	1.41
METALS (mg/L)		
Aluminum	2.30	1.75
Antimony ¹	0.006	0.0003
Arsenic ¹	0.0008	0.0015
Copper	c 0.01	0.013
Titanium	0.021	< 0.03
Vanadium	0.022	< 0.005
Zinc	0.102	0.046

TABLE 2
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	LABORATORY			
PARAMETER	ENVIROTEST	ASL		
GENERAL ORGANICS (mg/L)				
Oil and Grease ²	9 (4-18)	2 (cl-3)		
BOD ₅	23	75		
Total Phenols	0.098	0.24		
VOLATILE ORGANICS (µg/L)				
Chloroform	16	9.9		
Trichlorobenzene	0.0984	< 0.01 ⁴		
Hexachlorobenzene	0.062			
ADSORBABLE ORGANOHALIDES (AOX) (mg/L)	12	17.8		
FATTY ACIDS (mg/L)				
Arachidic	0.023	0.029		
Benenic		0.123		
Lignoceric		0.088		
Linoliec	0.021	0.0235		
Linolenic	< 0.01	0.040		
Oleic	< 0.01	0.023 ⁵		
Palmitic	0.016	0.012		
Stearic	0.011	0.021		
RESIN ACIDS (mg/L)				
Abietic	0.19	0.138		
Dehydroabietic	0.11	0.141		
Chlorodehydrobietic	0.087	0.076		
Isopimaric	0.0615	0.114		

TABLE 2
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	LABORATORY	
PARAMETER	ENVIROTEST	ASL
Levopimaric	0.0615	0.067
Neoabietic	0.032	0.011
Pimaric	0.041	0.069
S	< 0.010	0.010
Palustric	0.043	
PHENOLS ³ (µg/L)		
2,4-dichlorophenol	1.3	< 1.7
2,3,5 -trichlorophenol	3.8	< 1.1
2,4,6-trichlorophenol	1.9	1.0
4-chlorocatechol	0.3	
3,5-dichlorocatechol	1.5	
4,5-dichlorocatechol	20	
3,4,5 -trichlorocatechol	19	<1
3,4,6-trichlorocatechol	0.9	
Tetrachlorocatechol	1.9	<1
4,5-dichloroquaiacol	4.0	
4,6-dichloroquaiacol	0.48	
3,4,5 -trichloroquaiacol	6.0	6.0
3,4,6 -trichloroquaiacol	0.39	
4,5,6 -trichloroquaiacol	1.9	
Tetrachloroquaiacol	1.6	1.5
4,5-dichloroveratrole	1.1	
3,4,5-trichloroveratrole	2.3	
Tetrachloroveratrole	1.8	

TABLE 2

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	LABORATORY			
PARAMETER	ENVIROTEST	ASL		
DIOXIN CONGENERS ⁶ (pg/L)				
1,23,467,8- HCDD	< 10	60		
FURAN CONGENERS ⁶ (pg/L)	FURAN CONGENERS ⁶ (pg/L)			
2,3,7,8- TCDF	(23)'	18		
1,2,3,4,6,7,8- HCDF	< 3.2	8.2		
TOTAL DIOXINS AND FURANS ⁶ (pg/L)				
H ₆ CDD	< 3.1	22		
H₁CDD	< 10	115		
O ₈ CDD ⁷	< 14	205		
T ₄ CDF	39	45		
P₅CDF	16	< 3		
H, CDF	< 3.9	8.2		
TEQ ⁸	0	2.7		

- Envirotest: dissolved; ASL: Total. (All other metals are totals). Mean (and range) of three replicates.

 Data from both laboratories are means of duplicates.
- 2
- 3
- 4
- Envirotest: all isomers; ASL: 1,2,4 form only. Coeluted; value listed is for both acids combined. 5
- Data from ASL are means of duplicates.
- 7 Reported as congener 0,8 in Hatfield Table 3A.
- 8 Toxic equivalents in pg/L.
- Values in brackets are reported as quantitatively unreliable.

TABLE 3

CHEMICAL PROFILE OF EFFLUENT FROM GVRD STORM SEWER

	LABORATORY	
PARAMETER	ENVIROTEST	ASL
PHYSICAL		
pH (units)	7.1	6.88
Total Suspended Solids (mg/L)	17	3
Volatile Suspended Solids (mg/L)		2
DISSOLVED IONS ¹ (mg/L)		
Calcium	10	
Sodium	8.6	
Chloride	'7.5	
Fluoride		0.07
Nutrients (mg/L)		
Ammonia-N	0.145	0.067
Total Kjeldahl N	0.50	0.39
Nitrate-N	0.19	0.583
Nitrite-N	< 0.05	0.04
Total Phosphorus	< 0.05	0.029
METALS ¹ (mg/L)		
Aluminum	1.43	0.53
Antimony	< 0.0005	0.0003
Arsenic	0.0060	0.0009
Cadmium	< 0.003	0.0002
Copper	0.02	0.021
Lead	< 0.04	0.002

TABLE 3
PAGE 2 OF 3

	LABORATORY			
PARAMETER -	ENVIROTEST	ASL		
Nickel	0.05	< 0.020		
Selenium	0.0002	< 0.0005		
Titanium	0.012	< 0.030		
Vanadium	< 0.003	0.005		
Zinc	0.021	0.064		
GENERAL ORGANICS (mg/L)				
Oil and Grease ²	5 (4-7)	4 (3-5)		
BOD ₅	1.3	-		
Total Phenols	0.009			
PAHs (μg/L)				
Phenanthrene	c 0.4	0.3		
Pyrene	< 0.4	0.3		
PESTICIDES (µg/L)				
2,4-D	0.26	<5		
DIOXIN CONGENERS (pg/L)				
1,2,3,4,6,7,8- HCDD	(100) ³	25		
FURAN CONGENERS (pg/L)				
1,2,3,4,6,7,8- HCDF	24	8.8		
TOTAL DIOXINS AND FURANS (pg/l)				
H ₆ CDD	< 3.1	6.1		
H₁CDD	< 8.2	46		
O ₈ CDD ⁴	(310)	80		
H ₆ CDF	< 3.5	10		

TABLE 3 PAGE 3 OF 3

	LABORATORY	
PARAMETER	ENVIROTEST	ASL
H ₇ CDF	< 10	19
O ₈ CDF⁴	67	< 20
TEQ ⁵	0.31	0.4

1

2

ASL data are means of duplicates.

Mean (and range) of three replicates.

Values in brackets are reported as quantitatively unreliable.

Reported as congeners 0,8 in Hatfield Table 3A.

5 Toxic equivalents in pg/L. (Table 4), except possibly for Northwood Pulp, again negating a systematic bias. A more detailed examination showed that there was no bias for any one group of analytes, such as dioxins, metals or volatile organics. The troublesome variability, however, remains; on average, results from the two laboratories differ by about a factor of two.

Analytical techniques and instrumentation, as well as QA/AC procedures, are well enough advanced that analyses of split samples following the same procedures should yield reasonably reproducible results. As a rough approximation, duplicate organic analyses are expected to agree within about 20-50%. Relaxing that standard somewhat in the present study, because of the large number of analyses of ultra-trace parameters such as dioxins, a difference greater than 100% might be a reasonable bound beyond which data should be considered suspect. The numbers of analytes exceeding the 100% limit for each of the three sites are tabulated in Table 4 as those having ratios exceeding 2 or below 0.5. Considering errors in both directions, some 47% of the parameter estimates on Annacis Island effluent, 43% on Northwood Pulp effluent, and 67% on storm sewer wastewater are of dubious accuracy.

The large number of variable data is perplexing given that the laboratories were analysing painstakingly collected split samples following identical or similar methods, and with strict attention to QA/QC Furthermore, the variability extends throughout the parameter list, even to substances present in conspicuous quantities that do not require sophisticated equipment to quantify. For example, chloride was reported at 293 and 229 mg/L in Northwood Pulp effluent (Table 2), a difference of 64 mg/L in an ion measurable at < 0.5 mg/L. That same effluent generated estimated total phosphorus concentrations of 0.98 mg/L and 1.4 mg/L. Most surprising, total suspended solids from the GVRD storm sewer, one of the most straightforward parameters to measure, was estimated at 17 mg/L by one laboratory and only 3 mg/L by the other (Table 3).

TABLE 4

COMPARISON OF RATIOS OF CHEMICAL CONCENTRATIONS DETERMINED BY ENVIROTEST OVER THOSE DETERMINED BY ASL FOR THREE WASTEWATER EFFLUENTS (See Appendix Tables Al to A3 for data)

	ANNACIS ISLAND	NORTHWOOD PULP	GVRD STORM SEWER
Max. Ratio	8.6	20	6.7
Min. Ratio	0.11	0.07	0.18
Number > 1	16	18	9
Number > 2	8	9	7
Number ≤ 0.5	8	11	5
Total Number of Ratios Compared	34	46	18

What is the source of these errors? The pervasiveness of the variability across sites, parameter groups and laboratories, along with the success of standards analyses at meeting quality control criteria (Thomas and Dwernychuk 1992, Appendices 3 and 4) argue strongly that it is not the fault of inaccurate determinations by either laboratory. For a few of the parameters, viz., volatile organics and oil and grease, the laboratories were not operating on true split samples, because the special sampling bottles required were filled sequentially directly from the effluent flow. Higher variability is also to be expected for ultra-trace contaminants like dioxins and furans, which crowd the limit of our analytical capabilities, and for many of the other parameters (metals, volatile organics, phenols) whose concentrations were typically very low relative to detection limits in all three effluents. But the poor reproducibility of chemical determinations at higher analyte concentrations demands a better explanation.

By elimination, the most likely source of the error is the preparation of composite samples. Samples from Annacis Island and the storm sewer were mixed in the laboratories in proportions according with flow information provided by the field crews. The accuracy of those proportions, and how well samples were mixed before compositing, could be major sources of variation, especially if individual samples varied widely in contaminant concentrations. Effluent samples from Northwood Pulp were mixed in equal proportions in the field on behalf of both laboratories, yet there is no indication that results were any more or less reproducible at this site (Table 4). Whatever its cause, the variability of the chemical data limits the resolution of the pilot study. Steps should be taken to find the source of the problem, and rectify it, before full-scale sampling begins.

3.2 CHEMICAL PROFILES

Despite the problem of poor reproducibility, the general character of effluents from the three sources is evident. Effluent from the Annacis Island Wastewater Treatment Plant is high in suspended material (Table 1), the vast majority of it organic, representing the unsettled fraction of sewage. The wastewater is also rich in nitrogen, of which the largest part, in excess of 20 mg/L, is ammonia derived from decomposition of nitrogenous organic matter. Typical of primary sewage, nitrite and nitrate are present in only very low concentrations (Table 1) reflecting the incomplete oxidation of the ammonia. The effluent also carries an extremely high concentration of phosphorus (4.5 mg/L), which, although not a direct contributor to toxicity, represents a major source of nutrient enrichment to the river.

Most metals are present in the sewage effluent at levels of a few micrograms per litre, with the exceptions of aluminum, copper and zinc (Table 1). Metals are a normal component of human excrement, but industrial sources are also important to municipal wastewaters. The three metals mentioned above are among the most common in many wastewaters.

Annacis Island effluent is high in oil and grease, from any of a number of domestic sources, but phenols are virtually absent, again illustrating the incomplete stage of decomposition of the organic matter. Phenols are manufactured during the decay of polycyclic structural compounds such as lignin, and are therefore more abundant after secondary wastewater treatment.' It is unfortunate that BOD was not measured on this wastewater because the high oxygen demand expected from decay of putrescible matter may be a significant disruptive influence in the river.

In contrast to the major components listed above, the list of environmentally problematic trace organics in Annacis Island effluent is quite brief (Table 1). There is no obvious source of chloroform, although one analyst did suggest it may be a laboratory contaminant (Thomas and Dwernychuk 1992, Appendix 3). Since the effluent was not being chlorinated when the samples were taken the usual mechanism for formation of chlorinated organics in municipal sewage was not operating. Dry cleaning fluids and other industrial solvents are the probable source

of the other chlorinated compounds detected. All of the volatile organics were near detection limits except for toluene and xylene (Table 1). There were no substituted phenolic compounds at all in the Annacis Island effluent, and PCBS were never detected at any site.

Dioxins and furans are not unknown in sewage effluent, but only a few compounds were detected at Annacis Island. Here the problem of inter-laboratory variability is particularly acute, and only one congener (1,2,3,4,6,7,8 -HCDD) can unequivocally be recorded as present (Table 1). Concentrations of dioxins and furans can be adjusted for differences in toxicity by reporting the total as toxic equivalents (TEQ) to the most potent congener (2,3,7,8 -TCDD). Dioxins are mostly of concern because of their potential to bioaccumulate, and the level in Annacis Island effluent is far too small to be acutely toxic.

The Northwood pulp mill effluent was also high in suspended solids (Table 2); most of this material would be so-called biosolids, i.e., floes formed by aggregation of microbes and organic matter during secondary treatment. The dominant contribution of organic matter to TSS is reflected in the proportion of volatile suspended solids (Table 2).

Pulp mill effluent is characteristically saline from the salts added as part of the pulping process, and from ions released from the wood (Wong 1983). The Northwood effluent contains sodium (470 mg/L), chloride (200-300 mg/L) and calcium (>100 mg/L) at least, and undoubtedly also sulphate, although this was not measured. Based on the ions necessary to achieve charge balance, the total dissolved solids concentration of this effluent probably approaches 1500 mg/L. Salinity in that range, or more particularly the calcium concentration (hardness) associated with it, will reduce the potency of many toxicants (CCREM 1987, Mance 1987), but the total salts concentration itself approaches threshold levels that may be detrimental to sensitive freshwater species (Bierhuizen and Prepas 1985,

AOSERP 1977, Haynes and Hammer 1978). Itisunfortunate, therefore, that major ions were not measured more fully.

Excess nutrients in secondary treated pulp mill effluent are derived from the feedstock and from fertilizers added to the lagoons to accelerate decomposition of carbon-rich woody wastes. This is undoubtedly the source of most of the N and P observed in Northwood's effluent (Table 2). The relatively large proportion of organic nitrogen demonstrates that added N is quickly taken up by the microbial community. Again, the effluent is a significant source of nutrient enrichment to the river

Of the few metals in Northwood's effluent (Table 2), only aluminum, and possibly zinc, are of environmental significance. The aluminum could be derived from alum used in the treatment of intake water from the Fraser River. Some aluminum could have come from the mill furnish, especially if bark was included in the feedstock (Harder and Einspahr 1980).

The pulp mill effluent retains a substantial oxygen demand even after secondary treatment (Table 2). Although the concentration of total phenols appears low, there is a long list of chlorinated phenolic compounds, as is typical of Kraft mills employing chlorine bleach. However, most of these compounds were present only in minute quantities (several orders of magnitude below acutely toxic levels (CCREM 1987)) and were only detected by one laboratory. Chlorinated benzenes, and chloroform, if it is not an artifact, were also found (Table 2). The presence of AOX compounds in milligrams per litre demonstrates that most of the chlorinated compounds in this effluent remain unidentified.

Fatty acids are very labile to biological degradation, and only minute quantities survived secondary treatment (Table 2). The effluent also contains the eight resin acids common in coniferous wood (Taylor et al. 1988), along with a chlorinated

form. Despite recent reports of dioxins and furans in pulp mill wastes, only a few congeners were detected in Northwood's effluent, and none of these were quantitatively measurable by both laboratories (Table 2). The high degree of chlorine dioxide substitution used in Northwood's bleaching process may in part account for the low concentrations of dioxins in the effluent.

GVRD stormwater was chemically the simplest effluent of the three compared (Table 3). The total suspended solids load of stormwater is difficult to gauge because of the variability between laboratories, but it appeared to be largely inorganic, probably consisting mostly of grit and soil suspended by current. Unlike the other effluents, the ionic content of stormwater was quite low: rainwater is very soft, and the contact time between water and soil or other salt sources in surface runoff would be brief at best. Concentrations of N and P in stormwater were too low to be of consequence either as toxicants or as nutrients.

The stormwater did carry significant loads of metals, in particular aluminum, copper, zinc and possibly nickel. Metals are typically the major contaminant in street runoff; a variety of metals, including all of the above, are components of automobiles or automobile tires, which tend to be the predominant contributors to metals in drainage water. In contrast, the stormwater contained little organic matter, as reflected by the low BOD (Table 3), and only a few target organic compounds were detected. The two PAHs measured were barely above detection limits and could easily be derived from natural sources. Although pesticides tend to see heavy use on lawns and gardens, only 2,4-D was found in stormwater, and that again at the limits of analytical resolution (Table 3). The stormwater contained dioxins and furans, although only two congeners of each were present, and the total amounted to < 0.5 TEQ.

3.3 TOXICITY PROFILES

Results of acute toxicity tests on whole effluents are reported as the LC50, the concentration, in percent (v/v) that is lethal to 50% of the test population; where a response other than mortality is of interest, an EC50 (for effective concentration) is reported. Chronic tests can be used to derive several other end-points: the No Observed Effect Concentration, or NOEC, is the highest concentration of the effluent that has no measurable adverse effect on the test organisms; the Lowest Observed Effect Concentration (LOEC) is the lowest concentration of the effluent to produce an adverse effect, and is always the next greatest concentration after the NOEC in the effluent dilution series. The Threshold Effect Concentration (TEC) is the geometric mean of the LOEC and NOEC and estimates the concentration at which toxic effects begin. Results of the chronic tests here are given as LOEC and TEC because EC50s were not reported by Analex (1992).

Acute toxicity was assayed with trout, *Daphnia*, and Microtox, the latter by both Analex and Environment Canada. The *Ceriodaphnia* test also measured lethality, although this is not strictly an acute test (7 d). Of the three effluents, only Annacis Island exhibited strong acute toxicity (Table 5). The median lethal concentration for trout was 55%, and undiluted effluent was lethal to *Daphnia* (Table 5). The effluent also severely depressed light production in the Microtox assay. There is a noteworthy discrepancy, however, between Microtox results from Environment Canada and Analex: while the former reported an EC50 of only 7% effluent, the latter estimated no toxicity below 18%. There is no apparent explanation for the discrepancy, unless labile compounds were degraded during shipping to Quebec

Northwood pulp mill effluent was lethal to some trout only at full strength, but had no acute effect on *Daphnia*. Again there is a disagreement between the two laboratories with respect to Microtox toxicity; Environment Canada found no inhibition, while Analex found a toxic response above 50% effluent. On' balance the

TABLE 5

RESULTS OF TOXICITY ASSAYS ON THREE WASTEWATERS,
IN PER CENT OF FULL STRENGTH EFFLUENT

TECT	LADODATODVI	TND	ANNIACIC	NORTHWOOD	CVDD
TEST	LABORATORYI	END- POINT	ANNACIS ISLAND	PULP	GVRD STORM
					SEWER
Trout	EC	LC50	54.6	$> 100^{2}$	> 100
Daphnia	EC	LC50	100	> 100 ³	> 100 ³
Ceriodaphnia					
Survival	Analex⁴	LOEC	> 1005	> 100	> 100
Reproduction		LOEC	25	25	100
		TEC	17.5	17.5	71.4
Algal Growth	Analex⁴	LOEC	> 100 ⁵	0.33	> 100
		TEC	> 100	0.22	> 100
SOS Chromotest	Analex4				
-s9		LOEC	10	1.56	10
		TEC	4.4	1.11	4.4
+ \$9		LOEC	10	3.1	> 50
		TEC	4.4	2.2	> 50
Microtox	EC	EC50	7	> 100	> 100
	Analex4	LOEC	25	50	> 50
		TEC	17.5	35.7	> 50

EC, Environment Canada, Vancouver, BC; Analex, Analex Inc., Laval Quebec

^{20%} mortality in 100% effluent.

Zero mortality in 100% effluent.

LOEC and TEC back-calculated from toxic units reported by Analex (1992).

No observed adverse effect in 100% effluent. Therefore LOEC and TEC given as > 100%.

tests suggest mild acute toxicity from the pulp mill effluent. GVRD stormwater exhibited no acute toxicity to either trout or *Daphnia*, and did not inhibit bacterial light production at the highest concentrations tested. None of the effluents was lethal to *Ceriodaphnia* (Table 5).

Chronic toxicity results contrast sharply with those for acute toxicity. Effluents from both Annacis Island and Northwood Pulp depressed reproduction in *Ceriodaphnia*, with identical LOECs of 25'%. Storm sewer water was inhibitory only near full strength (Table 5). In the algal growth test, in contrast, while sewage effluent and stormwater were harmless, effluent from the pulp mill was severely inhibitory, with an effect threshold below 0.5%. Clearly, some constituent unique to pulp mill effluents is severely phytotoxic.

The SOS-chromotest genotoxicity assay is repeated with and without a preparation of rat liver enzymes (S9) that metabolize constituents of the test solution and thereby reveal potential carcinogens that require metabolic activation. In the present study, assays with S9 were always equally or less toxic than those without, so only the latter results are considered. All three effluents displayed substantial genotoxicity (Table 5). Thresholds of effect were near 4% for domestic sewage and stormwater, but approached 1% for pulp mill effluent. Again, pulp mill effluent stands out from the other effluents by the strength of its chronic toxicity.

3.4 SOURCES OF TOXICITY

There are a number of potentially toxic constituents in the Annacis Island effluent, but only two, metals and ammonia, are present in sufficiently high concentrations to produce the observed acute toxicity. (Xylene, a powerful "bactericide, would have contributed to the strong inhibition of bacterial light production.) Fish are especially sensitive to ammonia, but at the pH (7) and temperature (15°C) at which the trout assays were carried out, the concentration of total ammonia in undiluted

effluent (roughly 25 mg/L; Table 1) barely exceeded the British Columbia criterion for acute protection of aquatic life (20 mg/L; Pommen 1991). Hence, ammonia would only make a small contribution to the acute toxicity of the effluent.

Among the metals, aluminum, copper and zinc are present at relatively high concentrations (Table 1) and are almost certainly the chief toxicants beside While aluminum concentrations appear high in absolute terms ammonia. (0.4-0.5 mg/L) toxicity of this metal is mitigated at neutral pH (CCREM 1987), and the other metals, especially copper, would be more potent. Copper can be toxic at concentrations of a few micrograms per litre, especially to crustaceans (Mance 1987), so the presence of approximately 200 μ g/L in the sewage effluent would be expected to exert considerable effect. In fact, the relatively high LC50 to Daphnia from this effluent, and the moderate inhibition of Ceriodaphnia reproduction, normally a very sensitive endpoint (Table 5), is unexpected given the metals levels present. The chemical form of a metal is important to its toxicity, and a number of factors would have acted to reduce the toxicity of copper in the effluent, including the presence of organic matter, interactions among metals, and possibly water hardness. Given the importance of alkalinity and hardness to toxicity of many contaminants, it is unfortunate that these parameters were not measured.

It is more difficult to attribute the genotoxicity (SOS-chromotest, Table 5) to any specific compound. Metals, chlorinated organics, substituted benzenes, and uncharacterized components of the 50 mg/L organic matter load could all be responsible. Dioxins are powerful mutagens, but the concentrations in sewage effluent were low. In a complex effluent of this nature, some apparent genotoxicity in bacterial screening tests is inevitable.

Northwood pulp effluent was moderately toxic to trout at full strength, and in one test slightly inhibited bacterial light production (Table 5). That level of toxicity accords neatly with levels of resin acids in the effluent. Resin acids, natural defense

compounds in the bark of coniferous trees, are toxic to salmonids at concentrations around 0.5-1.5 mg/L at neutral pH (Taylor et al. 1988). The variation in potency among individual acids is small enough that the total concentration is more important in the prediction of toxicity. Northwood pulp effluent contains about 0.5-0.6 mg/L total resin acids (Table 2), including the more toxic chlorinated form of dehydroabietic acid. Hence, some acute toxicity would be expected in undiluted effluent, as was observed, but not at lower concentrations.

None of the other constituents of this complex effluent are sufficient to cause significant acute toxicity. The sum of all chloropenols as determined by Envirotest $(70.2 \ \mu g/L)$ is high enough that toxicity to a few sensitive species is conceivable, based on tests with individual compounds (CCREM 1987), but the total from ASL is ten times lower (Table 2). While the total aluminum concentration appears high, it would be almost entirely particulate and would therefore have very low biological activity. The high calcium concentration of the effluent (Table 2) would also provide considerable protection against toxic effects.

The severe repression of algal growth by pulp mill effluent presents a quandary. Treated pulp mill effluents frequently exhibit chronic toxicity in the algal growth test, but the apparent strength of the response here is unique; growth stimulation from added nutrients, rather than inhibition, is the more usual response at low concentrations (Bothwell et al. 1992). The magnitude of the response could have been exaggerated by the dark colour of the effluent if a light absorbency technique was used to estimate cell number (Environment Canada, 1992); but this reservation does not apply here because algal cells were counted directly (N. Birmingham, Personal Communication). In either case the reported phytotoxicity of Northwood's effluent begs confirmation, through both repeated sampling and comparison with other pulp mill effluents.

The source of the algal growth suppression is unknown. The salt content of this effluent alone would suppress growth of freshwater algae somewhat at full strength, but of course that would not be significant at the LOEC concentration of 0.33%. The AOX fraction, which constitutes a large and incompletely characterized assortment of chlorine-substituted organics, is one possible source of the algal toxicity. Without further work it would be impossible to attribute toxicity to one or a few compounds.

A similar situation appears for the SOS-chromotest. Potential genotoxicants include dioxins and furans, chlorinated phenols, chlorinated benzenes and even neobietic acid (Taylor et al. 1988). Again, however, the largest source is almost certainly AOX. Chlorinated organics, especially those with one or more phenyl rings, are often powerful mutagens, and the relatively much larger size of the AOX fraction (10-20 mg/L) virtually assures it of being the dominant toxicant pool.

The storm sewer runoff had the simplest effluent profile and also displayed the least toxicity. Storm sewer drainage was slightly inhibitory to reproduction in *Ceriodaphnia* and expressed genotoxicity similar to that of treated sewage (Table 5). The *Ceriodaphnia* toxicity would be expected from the levels of metals, particularly copper, zinc and aluminum in this wastewater. Cladocerans are unusually susceptible to metals toxicity (Mance 1987), and the storm drainage is much softer than the other effluents. Again there are a number of compounds capable of causing the genotoxic response, among which PAHs and dioxins are prominent.

The three effluents responded differentially to the five-day biodegradation test (Table 6). Total organic content of Annacis Island effluent declined sharply, with commensurate increases in effect thresholds for Microtox and the SOS-chromotest, but toxicity to algae increased slightly, evidently through the formation of toxic breakdown products. A similar increase occurred with Northwood pulp mill effluent (Table 6), although toxicity was relieved at least a little in the other assays. TOC

TABLE 6

EFFECT OF 5-D AERATION ON TOXICITY AND TOC CONTENT OF THREE WASTEWATER EFFLUENTS. TOXICITY VALUES ARE THRESHOLD EFFECT concentrations (TEC) As PERCENTA GE OF UNDIL UTED EFFLUENT

TEST	ANNACI	ISLAND	NORTH	IWOOD	STORM	SEWER
	BEFORE	AFTER	BEFORE	AFTER	BEFORE	AFTER
Algal Growth	>100	9.1	0,22	0.11	> 100	> 100
SOS Chromotest	I					
-s9	I 4.4	22.2	1.1	2	4.4	> 50
+89	4.4	22.2	2.2	2	>50	>50
Microtox	l 17.5	35.7	35.7	> 50	> 50	> 50
TOC (mg/L)	67.6	17.8	104.1	99.7		-

declined only marginally in that test. reflecting the recalcitrant nature of lignin-rich woody wastes that had already received 11 days of aerobic treatment. Biodegradation completely removed the genotoxicity observed in storm sewer water, which suggests that it was caused by a more labile component than those listed earlier.

In summary, sewage effluent from Annacis Island was acutely toxic to trout and *Daphnia*, and chronically toxic to *Ceriodaphnia*, probably because of ammonia and metals. Pulp mill effluent showed weak acute toxicity to fish, probably from resin acids, and severe suppression of algal growth from unknown sources, possibly chlorinated organics. Storm sewer runoff slightly inhibited reproduction in *Ceriodaphnia*, for which metals are again seen as probably responsible. All three effluents exhibited genotoxicity to bacteria, but that in pulp mill effluent was especially severe; a variety of compounds or elements could be causing the genotoxicity.

Generally, toxicity agreed with expectations based on the chemical composition of each effluent, but toxicity testing revealed details of the biological activity of each effluent that could not be derived from chemical data alone, for example the powerful effect of pulp mill effluent on algae. The effluents differed both in the strength and the nature of their toxicities: sewage expressed largely acute toxicity while that in pulp mill effluent was mostly chronic! On the basis of these data, the Annacis Island effluent would be ranked first in terms of overall potential for environmental disruption, Northwood second, and GVRD storm drainage third.

3.5 IMPLICATIONS FOR THE FRASER RIVER BASIN

Toxicity bioassays can only measure the potential for harm to organisms in the field from wastewaters because of the obvious differences between laboratory and field conditions, and because it is impossible to test for toxicity to every organism in any ecosystem. Environmental conditions in the river (e.g., hardness, temperature, turbidity, as well as biological interactions) can strongly modify laboratory results. Acute toxicity, or at least acute lethality, will seldom be realized beyond the initial mixing zone because of dilution. Therefore, acute toxicity data must invariably be translated into potential chronic, sublethal effects. A subtle, sublethal effect like reduced fecundity in *Ceriodaphnia* indicates an organism under stress and translates into a probable reduction in health, disease resistance and reproductive capacity in cladocerans and other small plankters generally. These, in turn, through food-web interactions, impinge on the success of other species, including fishes, and hence on ecosystem function generally. Toxic effects on one test species, therefore, should be taken to indicate a potential stress on the receiving-water ecosystem. Experience has shown that contaminant concentrations sufficient to produce chronic toxic responses in laboratory tests may lead to loss of species in nature, and a disruption of normal ecosystem function (USEPA 1991). Toxicant additions to the Fraser River, therefore, are best interpreted as forces that disrupt the ecosystem away from its normal level of function.

The magnitude of in-river effects depends on (1) the strength of toxicity (2) its persistence and (3) the volume of effluent relative to the flow of the river. The Annacis Island effluent is acutely toxic to salmonids, an important component of the Fraser River, but the ammonia responsible would be lost through volatilization within a short distance of the outfall. Still, the presence of acutely toxic substances within the mixing zone represents a new source of mortality for aquatic organisms and creates a considerable loss of habitat, given the very large volume of effluent (>400000 m³/d), and thus forms a new stress on the populations.

The effluent from Northwood, although it bore only marginal acute toxicity, could potentially have nearly as great an effect on the river because of the persistence of the toxic components and the large discharge (125 000 m³/d) being diluted by a smaller river at Prince George. Resin acids, considered the chief acute toxicant in

the effluent, are degraded rapidly in the water column and would not be expected to cause long-term problems. Many of the chronic toxicants, however, may be more persistent, so the chronic effects demonstrated in the laboratory may apply directly to the field. The effluent appeared to be particularly toxic to algal growth. The volume of effluent and the strength of this toxic response would suggest that a large volume of the river may suffer impaired primary production, although the quantitative reliability of this single measurement is uncertain.

The GVRD storm sewer had the weakest toxicity and by far the smallest discharge (9500 m³/d); it would contribute metals and some trace organics to the river. The seeming insignificance of storm sewer inflows must be tempered by several considerations. First, both quality and quantity of storm sewer discharges vary immensely depending on the amount and timing of rainfall. Runoff from a heavy rain following a long dry period, as is typical of autumn in Vancouver, can contain very high concentrations of sediments, metals, oil and trace organics that have accumulated since the last rain. Second, the effect of the tested sewer must be multiplied by the large number of urban storm drains in the GVRD and other municipalities in the basin. Third, effluents from storm sewers all enter the river at once as a pulse following rainfall. Their cumulative effects, especially to, nearshore areas, could be substantial.

4.0 CONCLUSIONS AND RECOMMENDATIONS

- 1. The three effluents sampled in the pilot toxicity study are chemically normal for their respective sources.
- 2. Usefulness of the chemical analyses was weakened by large and pervasive inter-laboratory variability.
- 3. Toxicity of' the three effluents varied in strength and character and was generally explicable based on chemical data. However, toxicity tests revealed strong chronic toxicity in pulp mill effluent and genotoxicity in all three effluents that would not be apparent from extant chemical data.
- 4. Future chemical analyses should include some measure of ionic strength and ion balance; electrical conductance is the minimum requirement, but total dissolved solids plus hardness, alkalinity and major ions should ideally be included.
- 5. Future sampling should include field measurement of effluent dissolved oxygen because toxicity of many chemicals is more severe under low oxygen tensions.
- 6. Some measure of colour should be added to chemical analyses because toxicity testing can be confused or complicated by highly coloured effluents.
- 7. It is imperative that the source of poor reproducibility of chemistry results be found and rectified, possibly through a comparison of spiked, split samples. Reproducibility of toxicity test results must also be verified.

8. Further algal toxicity testing on Fraser Basin pulp mill effluents is recommended to verify the severe growth suppression observed in this study.

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APPENDIX I

COMPARISON OF LABORATORY RESULTS FOR EFFLUENT CHEMISTRY

TABLE A1

COMPARISON OF LABORATORY RESULTS FOR ANNACIS ISLAND WASTEWATER TREATMENT PLANT

		LABORA	TORY	
PARAMETER	ENVIROTEST (a)	ASL (b)	RATIO (a/b)	WQ ¹⁵ CRITERION
PHYSICAL				
pH (units)	6.9	6.74	1.0	6.5-9.0
Total Suspended Solids (mg/L)	47	50	0.94	10% ¹¹ increase
Volatile Suspended Solids (mg/L)	47	48	1.0	
DISSOLVED IONS (mg/L)				
Calcium	17.0	•	-	-
Sodium ¹	-	-	-	-
Fluoride	-	0.14	-	0.311
NUTRIENTS (mg/L)				
Ammonia-N	26.0	22.3	1.2	19.712
Total Kjeldahl N	29.7	85.9	0.35	·
Nitrate-N	< 0.05	0.010	-	20011
Nitrite-N	0.12	0.014	8.6	0.06
Total Phosphorus	4.45	4.47	1.0	,
METALS (mg/L)				
Aluminum	0.5	0.43	1.2	0.1
Antimony ²	0.0008	0.0003	2.7	0.0511
Arsenic ²	0.0005	0.0012	0.42	0.05
Cadmium	< 0.003	0.0002		0.0008
Copper	0.17	0.199	0.85	0.002
Lead	< 0.04	0.015	-	0.002

TABLE A1
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		LABORA	TORY	
PARAMETER	ENVIROTEST (a)	ASL (b)	RATIO (a/b)	WQ¹⁵ CRITERION
Mercury	0.0008	0.0001	8.0	0.0001
Molybdenum	< 0.02	0.008	-	211
Nickel	0.04	< 0.020	2.0	0.065
Selenium ²	0.0005	< 0.0005	1.0	0.001
Titanium	0.003	< 0.03	1.0	0.111
['] Vanadium	0.007	< 0.005	1.4	
Zinc	0.195	0.117	1.7	0.03
GENERAL ORGANICS (mg/L)				
Oil and Grease ³	31 (26-35)	19.7 (14-27)	1.6	
BOD,	_4	-	-	
Total Phenols	< 0.003	0.006	2.0	0.00113
VOLATILE ORGANICS (μg/L)	5			
Chloroform	< 1.0	8.2	0.12	1
1, 4-dichlorobenzene	2.5	2.1	1.2	4.014
Tetrachloroethylene	4.3	7.4	0.58	260
Trichloroethylene	< 1.0	1.9	1.9	
Ethylbenzene	5.5	10.5	1.9	700
Toluene	8.0	19.5	0.41	300
Xylene ⁶	40	67.4 ⁷	0.59	
BASE-NEUTRAL EXTRACTAB	LES (μg/L) ⁵			
Di-n-Octylphthalate	5.3	< 1.0	5.3	0.2
PAHs ⁵ (µg/L)				

TABLE A1
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		LABORA	ATORY	
PARAMETER	ENVIROTEST (a)	ASL (b)	RATIO (a/b)	WQ ¹⁵ CRITERION
Phenanthrene	0.63	< 0.3	2.1	
DIOXIN CONGENERS (pg/L)				
1, 2, 3, 6, 7, 8 - HCDD	< 4.6	11	0.42	
1, 2, 3, 7, 8, 9 - HCDD	< 4.7	$(6.5)^8$	-	
1, 2, 3, 4, 6, 7, 8 - HCDD	79	43	1.8	
FURAN CONGENERS (pg/L)				
2, 3, 7, 8 - TCDF	10	(4.5)	-	
1, 2, 3, 4, 6, 7, 8 - HCDF	< 3.2	28	0.11	
TOTAL DIOXINS AND FURAN	NS (pg/L)			
H ₆ CDD	< 4.8	36	0.13	
H ₇ CDD	100	88	1.1	
O ₈ CDD ⁹	(580)	260	*	
H ₇ CDF	< 9.1	46	0.20	
O ₈ CDF ⁹	< 14	(35)		
TEQ ¹⁰	0.89	2.1	-	

TABLE A1

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- 8.64 mg/L in Hatfield Table 10A is a typo.
- Envirotest: dissolved; ASL: Total (all other metals are totals)
- Mean (and range) of three replicates
- Not analyzed. 1.3 mg/L in Hatfield Table 8A is a typo.
- 5 ASL data are means of duplicates.
- Sum of ortho, meta and para forms.
- ⁷ 76.2 μ g/L in Hatfield Table 4A is a miscalculation.
- ⁸ Values in brackets are reported as quantitatively unreliable.
- ⁹ Reported as congeners 0,8 in Hatfield Table 3A.
- Toxic equivalents in pg/L.
- ¹¹ BC Ministry of Environment criterion (Pommen 1991).
- BC MOE criterion for 15°C, pH 7
- To prevent fish tainting. Toxic effects begin near 0.01 mg/L.
- Recommended criterion from McCarty et al. (1984).
- Aquatic life criterion from CCREM (1987) unless indicated otherwise.

TABLE A2

COMPARISON OF LABORATORY RESULTS FOR NORTHWOOD PULP AND TIMBER

		LABORA	TORY	
PARAMETER	ENVIROTEST (a)	ASL (b)	RATIO (a/b)	WQ ¹⁵ CRITERION
PHYSICAL				
pH (units)	7.6	7.65	1.0	6.5-9.0
Total Suspended Solids (mg/L)	62	59	1.1	10% ¹⁰ increase
Volatile Suspended Solids (mg/L)	38	45	0.84	
DISSOLVED IONS (mg/L)				
Calcium	117	- .	-	
Sodium	474	470	1.0	
Chloride	293	229	1.3	
Fluoride	-	0.04	<u>.</u>	0.310
NUTRIENTS (mg/L)				
Ammonia-N	0.45	0.76	0.59	19.711
Total Kjeldahl N	3.81	2.77	1.4	
Nitrate-N	< 0.05	< 0.005	-	20010
Nitrite-N	< 0.05	< 0.001	-	0.06
Total Phosphorus	0.98	1.41	0.70	
METALS (mg/L)				
Aluminum	2.30	1.75	1.3	0.1
Antimony ¹	0.006	0.0003	20	0.0510
Arsenic ¹	0.0008	0.0015	0.53	0.05
Copper	< 0.01	0.013	0.77	0.002
Titanium	0.021	< 0.03	-	0.110

TABLE A2

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DANALTTO		LABORA	TORY	
PARAMETER	ENVIROTEST (a)	ASL (b)	RATIO (a/b)	WQ ¹⁵ CRITERION
Vanadium	0.022	< 0.005	4.4	
Zinc	0.102	0.046	2.2	0.03
GENERAL ORGANICS (n	ng/L)			
Oil and Grease ²	9 (4-18)	2 (<1-3)	4.5	
BOD ₅	23	75	0.31	
Total Phenols	0.098	0.24	0.41	0.001^{12}
VOLATILE ORGANICS (ıg/L)			
Chloroform ³	16	9.9	1.6	
Trichlorobenzene	0.0984	< 0.014	<u>-</u>	
Hexachlorobenzene	0.062	-	-	
ADSORBABLE ORGANOHALIDES (AOX) (mg/L)	12	17.8	0.87	
FATTY ACIDS (mg/L)		<u> </u>		
Arachidic	0.023	0.029	0.79	
Behenic	-	0.123	-	
Lignoceric	-	0.088	-	
Linoleic	0.021	0.0235	0.91	
Linolenic	< 0.01	0.040	0.25	
Oleic	< 0.01	0.0235	-	
Palmitic	0.016	0.012	1.3	
Stearic	0.011	0.021	0.52	
RESIN ACIDS (mg/L)	- 			
Abietic	0.19	0.138	1.4	0.025^{13}

TABLE A2
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	LABORATORY			
PARAMETER	ENVIROTEST (a)	ASL (b)	RATIO (a/b)	WQ ¹⁵ CRITERION
Dehydroabietic	0.11	0.141	0.78	0.00810
Chlorodehydroabietic	0.087	0.076	1.1	
Isopimaric	0.0615	0.114	0.54	0.02513
Levopimaric	0.0615	0.067	0.91	0.02513
Neoabietic	0.032	0.011	2.9	0.02513
Pimaric	0.041	0.069	0.59	0.02513
Sandaracopimaric	< 0.010	0.010	1.0	0.02513
Palustric	. 0.043	-	-	0.02513
PHENOLS ³ (μg/L)				
2,4-dichlorophenol	1.3	< 1.7	-	0.210
2,3,5-trichlorophenol	3.8	< 1.1	3.5	1814
2,4,6-trichlorophenol	1.9	1.0	1.9	1814
4-chlorocatechol	0.3	. -	•	
3,5-dichlorocatechol	1.5	-	-	
4,5-dichlorocatechol	20	-	•	
3,4,5-trichlorocatechol	19	<1	19	
3,4,6-trichlorocatechol	0.9	-	-	
Tetrachlorocatechol	1.9	<1	1.9	
4,5-dichloroquaiacol	4.0	-	-	
4,6-dichloroquaiacol	0.48	-	-	
3,4,5-trichloroquaiacol	6.0	6.0	1.0	
3,4,6-trichloroquaiacol	0.39	-	_	
4,5,6-trichloroquaiacol	1.9	-	-	

TABLE A2
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		LABORA	TORY			
PARAMETER	ENVIROTEST (a)	ASL (b)	RATIO (a/b)	WQ ¹⁵ CRITERION		
Tetrachloroquaiacol	1.6	1.5	1.1			
4,5-dichloroveratrole	. 1.1	-	-			
3,4,5-trichloroveratrole	2.3	-	-			
Tetrachloroveratrole	1.8	-	-			
DIOXIN CONGENERS ⁶ (pg/L)						
.1,2,3,4,6,7,8 - HCDD	< 10	60	0.17			
FURAN CONGENERS ⁶ (pg/L)						
2,3,7,8 - TCDF	(23) ⁹	18	-			
1,2,3,4,6,7,8 - HCDF	< 3.2	8.2	0.39			
TOTAL DIOXINS AND FU	RANS ⁶ (pg/L)					
H ₆ CDD	< 3.1	22	0.14			
H ₇ CDD	< 10	115	12			
O ₈ CDD ⁷	< 14	205	0.07			
T ₄ CDF	39	45	0.86			
P ₅ CDF	16	< 3	5.3			
H ₇ CDF	< 3.9	8.2	0.48			
TEQ ⁸	0	2.7	-			

TABLE A2

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- Envirotest: dissolved; ASL: Total. (All other metals are totals).
- Mean (and range) of three replicates.
- Data from both laboratories are means of duplicates.
- Envirotest: all isomers; ASL: 1,2,4 form only.
- ⁵ Coeluted; value listed is for both acids combined.
- Data from ASL are means of duplicates.
- Reported as congener 0,8 in Hatfield Table 3A.
- ⁸ Toxic equivalents in pg/L.
- ⁹ Values in brackets are reported as quantitatively unreliable.
- ¹⁰ BC Ministry of Environment Criterion (Pommen 1991).
- BC MOE criterion for 15°C, pH 7
- To prevent fish tainting. Toxic effects begin near 0.01 mg/L.
- BC MOE criterion for total resin acids at pH 7.
- ¹⁴. BC MOE criterion for total trichlorophenols.
- Aquatic life criterion from CCREM (1987) unless indicated otherwise.

TABLE A3

COMPARISON OF LABORATORY RESULTS FOR EFFLUENT FROM GVRD STORM SEWER

		LABORA	TORY	
PARAMETER	ENVIROTEST	ASL (b)	RATIO (a/b)	WQ° CRITERION
PHYSICAL	(a)	(0)	(a/b)	CRITERION
pH (units)	7.1	6.88	1.0	6.5-9.0
Total Suspended Solids (mg/L)	17	3	5.7	10% increase
Volatile Suspended Solids (mg/L)		2		
DISSOLVED IONS* (mg/L)				
Calcium	10			
Sodium	8.6			
Chloride	7.5			
Fluoride		0.07	-	0.3^{11}
NUTRIENTS ¹ (mg/L)				
Ammonia-N	0.145	0.067	2.2	19.7 ⁷
Total Kjeldahl N	0.50	0.39	1.3	
Nitrate-N	0.19	0.583	0.33	200,
Nitrite-N	< 0.05	0.04	-	0.06
Total Phosphorus	c 0.05	0.029	-	
METALS' (mg/L)				
Aluminum	1.43	0.53	2.7	0.1
Antimony	< 0.0005	0.0003	-	0.05'
Arsenic	0.0060	0.0009	6.7	0.05
Cadmium	< 0.003	0.0002	-	0.0008
Copper	0.02	0.021	0.95	0.002

TABLE A3

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	LABORATORY				
PARAMETER	ENVIROTEST (a)	ASL (b)	RATIO (a/b)	WQ' CRITERION	
Lead	< 0.04	0.002	-	0.002	
Nickel	0.05	< 0.020	2.5	0.065	
Selenium	0.0002	< 0.0005	-	0.001	
Titanium	0.012	< 0.030	-	0.016	
Vanadium	< 0.003	0.005	0.60		
Zinc	0.021	0.064	0.33	0.03	
GENERAL ORGANICS (mg/L	.)				
Oil and Grease ²	5 (4-7)	4 (3-5)	1.3		
BOD ₅	1.3	-	-		
Total Phenols	0.009	-	•	0.0018	
PAHs (μg/L)					
Phenanthrene	< 0.4	0.3	-		
Pyrene	< 0.4	0.3	•		
PESTICIDES (μg/L)					
2,4-D	0.26	<5	-	4.0	
DIOXIN CONGENERS (pg/L)					
1,2,3,4,6,7,8 - HCDD	$(100)^3$	25	_		
FURAN CONGENERS (pg/L)					
1,2,3,4,6,7,8 - HCDF	24	8.8	2.7		
TOTAL DIOXINS AND FURA	NS (pg/l)				
H,CDD	< 3.1	6.1	0.51		
H,CDD	< 8.2	46	0.18		
O ₈ CDD ⁴	(310)	80	-		

TABLE A3

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DAD AMERICA	LABORATORY				
PARAMETER	ENVIROTEST (a)	ASL (b)	RATIO (a/b)	WQ° CRITERION	
H ₆ CDF	< 3.5	10	0.35		
H ₇ CDF	< 10	19	0.53		
O ₈ CDF⁴	67	< 20	3.4		
TEQ ⁵	0.31	0.4			

- ASL data are means of duplicates.
- Mean (and range) of three' replicates.
- Values in brackets are reported as quantitatively unreliable.
- Reported as congeners 0,8 in Hatfield Table 3A.
- Toxic equivalents in pg/L.
- BC Ministry of Environment Criterion
- BC MOE Criterion for 150 C, pH 7
- To prevent fish tainting. Toxic effects begin near 0.01 mg/L.
- Aquatic life criterion from CCREM (1987) unless indicated otherwise.