WASHINGTON STATE DEPARTMENT OF ECOLOGY
ENVIRONMENTAL INVESTIGATIONS AND LABORATORY SERVICES

M E M O R A N D U M

TO: Mike Templeton, SWRO

FROM: Joe Joy, SWIS

SUBJECT: Quality Assurance Results from Samples Split with CH2M Hill and Cowlitz Conservation District from Ditch 10, Longview

DATE: January 17, 1989

## INTRODUCTION

As a result of legal action by Ecology, the Reynolds Metals Company was required by the Washington Pollution Control Hearings Board to study the water quality of Ditches 5 and 10 in Longview. Reynolds contracted the consulting firm CH2M Hill, Inc. (CH2M) to perform the work during three storm events in the winter of 1987-88. The Cowlitz Conservation District (the District) had also targeted Ditch 5 and 10 for water quality investigations. Funds from Ecology through the Washington Conservation Commission had been made available to the District for the investigation. The District, with Ecology's approval, decided not to duplicate Reynolds' effort and focused their resources on two other watersheds, the Arkansas and Coweeman, instead (Somers, 1988a).

The Ecology Southwest Regional Office (SWRO) requested the Ecology Surface Water Investigations Section (SWIS) to assure and evaluate the quality of the data being collected by CH2M and the District. No other quality assurance task was included in the CH2M or District work plan. Determan (1987) proposed that side-by-side samples be taken by the three participants during one or more of CH2M's monitoring events as a quality assurance evaluation.

## METHODS

On February 29, 1988, SWIS met with the District and CH2M at the Longview Ditches study area during CH2M's last monitoring event. Earlier attempts to coordinate a quality assurance (QA) sampling event had failed, primarily because of fewer-than-normal rainfall events and miscommunications between CH2M and SWIS. More than one QA sampling would have been desirable.

Samples were collected from Ditch 10 upstream of Industrial Way from the left bank at the mouth of the culvert (Figure 1). This was Site 6 in the CH2M study. SWIS also carried transport and transfer blanks for metals and semivolatile analyses, and performed a duplicate sampling of some conventional parameters.

Field analysis of pH, temperature and specific conductivity were performed by CH2M and SWIS staff. SWIS, CH2M, and District staff used sample containers provided by their respective analytical laboratories. Sample bottles were filled from the ditch in rotating order.

SWIS samples were stored in the dark on ice and received by the Ecology Environmental Laboratories in Manchester within 24 hours. Conventional and metals analyses were performed by the Manchester Lab; semivolatiles were analyzed by Laucks Testing Laboratories under contract with the Manchester Lab. Samples were analyzed using approved procedures (Huntamer, 1986). The laboratory quality assurance report for the semivolatile analyses identified one unacceptable result: the 4-nitrophenol matrix spike recovery was higher than the upper allowable limit (Araki, 1988). All other data were acceptable, and the nitrophenol recovery was not considered to seriously impair the data because no acid compounds had been detected (Araki, 1988).

CH2M samples were received within 48 hours by CH2M Hill Environmental Laboratory in Corvallis, and were analyzed by them (CH2M, 1988). The District used the Cowlitz-Wahkiakum Counties Health Dept. laboratory for its fecal coliform analysis, and Columbia Analytical Services of Longview for the total suspended solids analysis (Somers, 1988b).

**RESULTS & DISCUSSION**

Results of the three labs' conventional analyses, and two labs' metals analyses are shown in Table 1. The two sets of semivolatile analytical along with transfer and transport blank results are shown in Table 2.

Of the two analyses performed by all three parties, the fecal coliform results had the widest variability. The variability in the total suspended solids results between laboratories was similar to that reported by the Standard Methods (APHA, 1985) statement of precision for this method, i.e. $\pm$ 5.2 mg/L at 15 mg/L TSS. All three labs used the multiple-tube fermentation method for fecal coliform analysis. The 95% confidence limits for each lab's result are listed as follows (APHA, 1985):

| Lab MPN Count/100 mL | Lower Limit | Upper Limit |
|---|---|---|
| 80 | 30 | 250 |
| 8 | 3 | 24 |
| 22 | 9 | 56 |
| 50 | 20 | 170 |

The confidence limits illustrate the large degree of error in the fecal coliform method--confidence limits for one MPN count included one or more other MPN counts or their limits. However, the difference between the 80 and 8 MPN counts may indicate an analytical problem. Several more collections would be necessary to determine if significant differences in fecal coliform results are due at all to technique errors by the labs.

Results from most of the other conventional parameters analyzed by CH2M and SWIS labs were similar to each other (Table 1). However, pH and conductivity results measured in the field should have been closer. Laboratory pH values matched well.

The CH2M lab detected more metals than the Manchester lab (Table 1). The metals reported by CH2M were in a range that should have been detected by Manchester since the latter had lower limits of detection. In some cases, CH2M and SWIS metal results were very different from one another. One example is the reported zinc concentrations. The SWIS transport blank indicated some minor blank water or sample container contamination of lead and zinc, and the transfer blank also contained a low concentration of zinc (26 ug/L). The SWIS Ditch 10 sample contained zinc, but at a similar concentration to the blanks. However, the CH2M zinc concentration was an order of magnitude greater than any of the SWIS zinc values, e.g. sample, transfer and transport blank values. CH2M did not have transfer or transport blank data, so we cannot know if the CH2M sample container was contaminated, if one of the laboratories made an analytical error, or if this is environmental variability in Ditch 10.

These metals data differences are serious considering the fact that the aquatic toxicity criteria involved are established at the same order of magnitude as these data (USEPA, 1986). For example, at a hardness value of 50 mg/L the CH2M data would exceed USEPA 4-day criteria for cadmium, lead and zinc. The SWIS transport blank lead concentration would even exceed the lead 4-day criterion.

CH2M and SWIS cyanide results also differed (Table 1). The Ecology result suggests a possibility for the presence of cyanide exceeding USEPA criteria (USEPA, 1986). Cyanide was not detected by CH2M.

Semivolatile organics were not detected by either laboratory (Table 2). The transport and transfer blanks were clean for the most part. The small concentration of bis(2-ethylhexyl)phthalate detected in the SWIS sample was also detected in the transport blank. The compound is a persistent and ubiquitous contaminant in most laboratory samples. Since no other semivolatile compounds were detected, the true analytical differences between the two labs were not rigorously tested. Therefore, not much can be stated from a quality assurance standpoint. Spiked samples and certified test materials may be a better method of evaluating labs when there is a good possibility that no compounds will be detected in environmental samples.

**CONCLUSIONS AND RECOMMENDATIONS**

The side-by-side sampling method of quality assurance evaluation indicated there were some differences between the Cowlitz Conservation District, CH2M Hill, and Ecology (SWIS) results. Some of the differences were to be expected because of the natural variability of the parameter in the environment, or the nature of the analytical method, e.g. fecal coliform by the MPN method. Other differences indicated that some types of data may be more reliable than others. For example, the two laboratory pH values were closer than the two field pH values. But, some differences were serious enough to question the results outright. For example, metals and cyanide results from the two participating laboratories were very different and could result in very different conclusions about the water quality of Ditch 10.

A primary weakness of this quality assurance data is that only one set of samples was collected. Therefore, there can be no certain determination if the differences observed between some sample results was random environmental variation, or interlaboratory variation. Some of the environmental variability could have been removed had all samples been collected from a single homogenized container. Other methods of quality assurance such as spiked samples and certified materials testing would have better addressed the question of interlaboratory variation. Also, these other methods may have better assessed the analytical accuracy of the two labs in areas where the particular samples collected showed no detectable result. For example, semivolatile organics were not detected in either the CH2M or SWIS sample, but were detected by CH2M during a different monitoring event at the same location. How accurate their results are over various ranges of a compound's concentration remains untested.

The following recommendations are presented:

- o The CH2M Hill data collected for the Reynolds Metals Company will not have the field or lab QA data to back-up anything more than general statements on the water quality of the Longview Ditches. If definitive answers were expected, another survey will be necessary.
- o If future sampling is ordered or planned, a more extensive QA plan should be included, e.g. a plan with replicate sampling, interlaboratory comparisons with reference or spiked samples, and adequate field blanks.

JJ:sk

cc: Kathy Cupps, Ecology/SWRO

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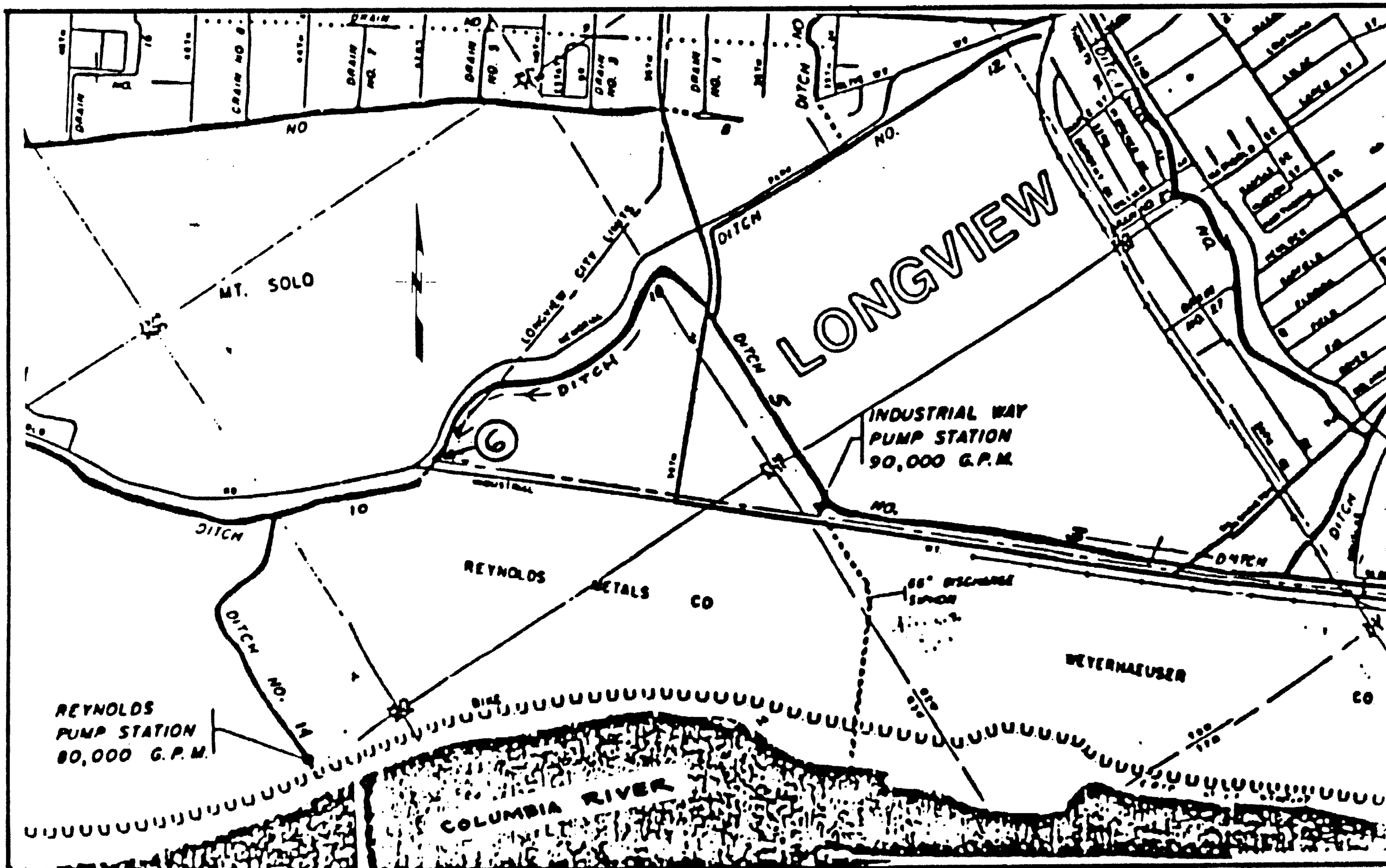


Figure 1. Dept. of Ecology, $CH_2M$ Hill, and Cowlitz County Conservation District sampling site, ⑥, on Ditch 10, Longview. February 29, 1988.

Table 1. A comparison of analytical results for samples collected by CH2M Hill, Cowlitz County Conservation Dist.. and the Dept. of Ecology from Ditch 10 at Industrial Way, February 29, 1988. All values mg/L unless otherwise indicated.

| | CH2M Hill | Cowlitz Con. Dist. | Ecology Sample | Ecology Duplicate | Transfer Blank | Transport Blank |
|---|---|---|---|---|---|---|
| Time | 1335 | | 1335 | 1415 | | |
| Flow (cfs) | 10 | | | | | |
| Temperature | 14.5 | | 14.5 | 13.3 | | |
| pH (s.u.) Field | 5.8 | | | 6.8 | | |
| pH (s.u.) Laboratory | 6.6 | | 6.8 | 6.6 | | |
| Sp. Cond. (umhos/cm) Fld. | 300 | | | 250 | | |
| Sp. Cond. (umhos/cm) Lab | | | 238 | 245 | | |
| Dissolved Oxygen | 5.4 | | | | | |
| Turbidity (NTU) | 47 | | 29 | 32 | | |
| Total Suspended Solids | 18 | 16 | 11 | 12 | | |
| Biochemical Oxygen Demand | 3 | | | | | |
| Fecal Coliform | 80 | 8 | 22 | 50 | | |
| Oil and Grease | 4 | | 1 | | | |
| Cyanide (Total) | <0.005 | | 0.012 | | <0.005 | |
| Cadmium | 0.0007 | | <0.0002 | | <0.0002 | <0.0002 |
| Copper | <0.05 | | 0.001 | | <0.001 | <0.001 |
| Lead | 0.007 | | <0.001 | | <0.001 | 0.003 |
| Nickel | 0.080 | | <0.001 | | <0.001 | <0.001 |
| Zinc | 0.295 | | 0.010 | | 0.026 | 0.002 |
| Mercury | -- | | <0.00005 | | <0.00005 | <0.00005 |

Table 2. A comparison of analytical results for samples collected by CH2M Hill, and the Dept. of Ecology from Ditch 10 at Industrial Way, Longview, on February 29, 1988. All values ug/L.

| COMPOUND | CH2M Hill Sample | Ecology Sample | Ecology Duplicate | Transfer Blank | Transport Blank |
|---|---|---|---|---|---|
| Phenol | 10 u | 3 u | 2 u | 2 u | 2 u |
| 2-chlorophenol | 10 u | 3 u | 4 u | 2 u | 2 u |
| 2-nitrophenol | 10 u | 5 u | 8 u | 4 u | 4 u |
| 2,4-dimethylphenol | 10 u | 3 u | 4 u | 2 u | 2 u |
| 2,4-dichlorophenol | 10 u | 5 u | 8 u | 4 u | 4 u |
| 4-chloro-3-methylphenol | 10 u | 5 u | 8 u | 4 u | 4 u |
| 2,4,6-trichlorophenol | 10 u | 5 u | 8 u | 4 u | 4 u |
| 2,4,5-trichlorophenol | 50 u | 5 u | 8 u | 4 u | 4 u |
| 2,4-dinitrophenol | 50 u | 27 u | 40 u | 20 u | 20 u |
| 4-nitrophenol | 50 u | 27 u | 40 u | 20 u | 20 u |
| 4,6-dinitro-o-cresol | 50 u | 27 u | 40 u | 20 u | 20 u |
| Pentachlorophenol | 50 u | 27 u | 40 u | 20 u | 20 u |
| bis(2-chloroethyl)ether | 10 u | 3 u | 4 u | 2 u | 2 u |
| bis(2-chloroisopropyl)ether | 10 u | 3 u | 4 u | 2 u | 2 u |
| bis(2-chloroethoxy)methane | 10 u | 3 u | 4 u | 2 u | 2 u |
| 4-chlorophenyl phenyl ether | 10 u | 3 u | 4 u | 2 u | 2 u |
| 1,3-dichlorobenzene | 10 u | 3 u | 4 u | 2 u | 2 u |
| 1,4-dichlorobenzene | 10 u | 3 u | 4 u | 2 u | 2 u |
| 1,2-dichlorobenzene | 10 u | 3 u | 4 u | 2 u | 2 u |
| 1,2,4-trichlorobenzene | 10 u | 3 u | 4 u | 2 u | 2 u |
| Hexachloroethane | 10 u | 5 u | 8 u | 4 u | 4 u |
| Nitrobenzene | 10 u | 3 u | 4 u | 2 u | 2 u |
| Hexachlorobenzene | 10 u | 3 u | 4 u | 2 u | 2 u |
| 2,6-dinitrotoluene | 10 u | 5 u | 8 u | 4 u | 4 u |
| 2,4-dinitrotoluene | 10 u | 5 u | 8 u | 4 u | 4 u |
| Isophorone | 10 u | 3 u | 4 u | 2 u | 2 u |
| Nitrosodiphenylamine | 10 u | 3 u | 4 u | 2 u | 2 u |
| Hexachlorobutadiene | 10 u | 3 u | 4 u | 2 u | 2 u |
| Hexachlorocyclopentadiene | 10 u | 5 u | 8 u | 4 u | 4 u |
| 2-chloronaphthalene | 10 u | 3 u | 4 u | 2 u | 2 u |
| Acenapthene | 10 u | 3 u | 4 u | 2 u | 2 u |
| Acenaphthylene | 10 u | 3 u | 4 u | 2 u | 2 u |
| Fluorene | 10 u | 3 u | 4 u | 2 u | 2 u |
| Naphthalene | 10 u | 5 u | 8 u | 4 u | 4 u |
| Phenanthrene | 10 u | 3 u | 4 u | 2 u | 2 u |
| Anthracene | 10 u | 3 u | 4 u | 2 u | 2 u |
| Fluoranthene | 10 u | 3 u | 4 u | 2 u | 2 u |
| Pyrene | 10 u | 3 u | 4 u | 2 u | 2 u |
| Benzo(a)anthracene | 10 u | 3 u | 4 u | 2 u | 2 u |
| Chrysene | 10 u | 3 u | 4 u | 2 u | 2 u |
| Benzo(b)fluoranthene | 10 u | 5 u | 8 u | 4 u | 4 u |
| Benzo(k)fluoranthene | 10 u | 5 u | 8 u | 4 u | 4 u |
| Benzo(a)pyrene | 10 u | 5 u | 8 u | 4 u | 4 u |
| Dibenzo(a,h)anthracene | 10 u | 5 u | 8 u | 4 u | 4 u |
| Indeno-1,2,3-c,d-pyrene | 10 u | 5 u | 8 u | 4 u | 4 u |
| Benzo(g,h,i)perylene | 10 u | 5 u | 8 u | 4 u | 4 u |
| Diethylphthalate | 10 u | 3 u | 4 u | 2 u | 2 u |
| Di-n-butylphthalate | 10 u | 3 u | 4 u | 2 u | 2 u |
| Benzyl butylphthalate | 10 u | 3 u | 4 u | 2 u | 2 u |
| bis(2-ethylhexyl)phthalate | 10 u | 4 | 5 | 2 u | 2 |
| Di-n-octyl phthlate | 10 u | 3 u | 4 u | 2 u | 2 u |
| Dimethylphthalate | 10 u | 3 u | 4 u | 2 u | 2 u |
| | | | | | |
| Benzoic acid | 50 u | 67 u | 100 u | 50 u | 50 u |
| 2-nitroaniline | 10 u | 5 u | 8 u | 4 u | 4 u |
| 3-nitroaniline | 10 u | 13 u | 20 u | 10 u | 10 u |
| 4-nitroaniline | 50 u | 5 u | 8 u | 4 u | 4 u |
| 4-chloroaniline | 10 u | 3 u | 4 u | 2 u | 2 u |
| 2-methylnaphthalene | 10 u | 3 u | 4 u | 2 u | 2 u |
| 3,3-dichlorobenzidine | 20 u | 27 u | 40 u | 20 u | 20 u |
| 2-methylphenol | 10 u | 3 u | 4 u | 2 u | 2 u |
| 4-methylphenol | 10 u | 3 u | 4 u | 2 u | 2 u |
| Dibenzofuran | 10 u | 3 u | 4 u | 2 u | 2 u |
| n-nitroso-di-n-propylamine | 10 u | 3 u | 4 u | 2 u | 2 u |
| 4-bromophenyl phenyl ether | 10 u | 5 u | 9 u | 4 u | 4 u |
| Benzyl alcohol | 10 u | 3 u | 4 u | 2 u | 2 u |
| n-nitroso-dimethylamine | 10 u | | | | u |
| aniline | 10 u | 13 u | 20 u | 10 u | 10 u |
| benzidine | 10 u | 67 u | 100 u | 50 u | 50 u |
| 1,2-diphenylhydrazine | | 5 u | 8 u | 2 u | 2 u |

u = less than stated detection limit.