

B.C. Environment  
Province of British Columbia

Canada-British Columbia Water Quality  
Monitoring Agreement

**Comparing Field and Laboratory Filtration  
for Low-Level Dissolved  
Ortho-Phosphorus Samples**

T.N. Webber  
J. J. Tilly (Co-op Student)  
Water Quality Branch  
Water Management Division  
Victoria, B.C.  
April, 1992

## SUMMARY

Field replicate and blank samples were collected from the Kootenay River near Creston and filtered in the laboratory or in the field prior to low-level, dissolved ortho-phosphorus analysis. There was no significant difference between the field and laboratory filtered results for samples collected at Kootenay River at Creston, where dissolved ortho-phosphorus averaged just over 1  $\mu\text{g/L}$ . The system detection limit determined from the field blanks was the same as the laboratory method detection limit of 1  $\mu\text{g/L}$ . Laboratory filtration is recommended for low-level, dissolved ortho-phosphorus to simplify field operations and eliminate the risk of field contamination during the field filtration process.

## TABLE of CONTENTS

	Page:
Summary -----	i
Table of Contents -----	ii
1.0 Introduction -----	1
2.0 <b>Methods</b>	
2.1 Equipment and Supplies -----	2
2.2 Procedure -----	2
3.0 <b>Results and Discussion</b>	
3.1 Results -----	3
3.2 Discussion -----	3
4.0 <b>Conclusions and Recommendations</b> -----	4
Literature Cited -----	5
Table 1 Results of Dissolved Ortho-Phosphorus Low-Level Replicate Sampling -----	6
Table 2 Results of Dissolved Ortho-Phosphorus Low-Level Quality Assurance Replicate Sampling -----	8
Table 3 Results of Dissolved Ortho-Phosphorus Low-Level Field Blanks -----	9
<b>Appendix 1</b>	
Dissolved Ortho-Phosphorus Low-Level Routine Sampling Results from the Thompson River at Spences Bridge -----	10

## 1.0 INTRODUCTION

Routine water sampling under the Canada-B.C. Water Quality Monitoring Agreement included the requirement for field filtration for trace metals and low-level dissolved ortho-phosphorus at a number of jointly operated sites within the province of B.C. The requirement for field filtering of low-level phosphorus samples was suspended as of May 19, 1989 (Memorandum to Environmental Section Heads from Mr. N.R. McQuaker, Manager, Data Standards Group, B.C. Ministry of Environment).

The B.C. Water Quality Branch conducted a study to determine if there was a significant difference between field-filtered and lab-filtered Dissolved Ortho-Phosphorus Low-Level (DOP-LL) results. It had been suggested by staff of Environment Canada, that field filtering immediately after collecting the sample would provide more accurate results due to the potential for change in the sample enroute to the analysing laboratory.

It is well known that field filtration has the potential for introducing errors due to contamination introduced by the filtration unit and/or during the field-filtering process. Water Quality Branch has conducted a number of experiments to examine the potential for metals and phosphorus contamination during filtration. Please refer to the 'Field Filtration Testing' report for total dissolved and dissolved ortho-phosphorus low-level blanks prepared by Water Quality Branch (formerly Water Management Branch) dated September, 1989.

DOP-LL is routinely collected at two sites managed under the Canada-B.C. Water Quality Monitoring Agreement; Kootenay River at Creston and Thompson River at Spences Bridge. Water Quality Branch selected the Creston site to evaluate the potential for significant differences between field-filtered and lab-filtered samples. Paired, routine samples collected by the sample collector (hired under the Agreement) were filtered in the field or the lab, analysed, and evaluated for significant differences. Paired field blanks filled with laboratory-supplied deionized (DI) water and processed through the normal field sampling routine were also filtered in the field or the lab, analysed, and evaluated for significant differences and contamination due to laboratory supplied and prepared equipment, the sampling technique, and the filtering technique.

## 2.0 METHODS

### 2.1 Equipment and Supplies

- 125 mL brown glass DOP Low-Level sample bottles, laboratory cleaned and supplied.
- 50 mL disposable 'luer-lok' syringes.
- 25 mm Sartorius disposable in-line filter units (complete with 'luer-lok' ports and 0.45  $\mu\text{m}$  cellulose acetate filter paper).
- 500 mL polyethylene (PE) 'metals only' collection bottles; laboratory cleaned and supplied.
- 500 mL PE 'metals only' collection bottles; laboratory cleaned and filled with deionized (DI) water (for blanks).

### 2.2 Procedure

#### (a) Paired Replicate Samples

Two sets of paired samples were collected from the Creston site. Lawrence Schalla, (sampler collector hired under the Agreement) collected 28 routine paired samples from September 26, 1989 to November 5, 1990. The second set of six paired samples were collected by Tom Webber (Water Quality Branch Biologist) on the 13th of June 1990. Both sets of samples were collected in the same manner using the provincial 'multi sampler' attached to a 23-m length of braided poly rope extending from the center of the upstream side of the Kootenay River bridge near the town of Creston. The lab-filtered samples were obtained by filling a 125 mL bottle from the 500 mL collection bottle for subsequent filtering in the lab. The field-filtered samples were obtained by filtering approximately 100 mL (2 full syringes) from the 500 mL collection bottle into a 125 mL sample bottle. Syringes were flushed with a small amount of sample water before filling each syringe and filtering the contents. All samples were carefully packed in Ministry coolers with an ice pack before shipping directly to the Zenon Environmental Laboratory in Burnaby, B.C. via Loomis courier service. Transit time from the Creston site to the Lab is estimated at 24 hours.

#### (b) Paired Field Blanks

Six 500 mL 'metals' bottles were filled with deionized (DI) water in the Zenon Environmental Laboratory and transported to the Creston site in coolers using a Federal government vehicle. These six collection bottles were fitted in the provincial 'multi sampler' and carefully lowered to within about 0.5 m of the river water surface. The 500 mL bottles containing the lab supplied DI water did not come in contact with ambient water although every other aspect of the sample collection and transfer of water was identical to that of the routine samples.

This includes the sampling location, sampling method and time suspended above the river water surface. A portion of the contents of each 500 mL collection bottle was poured directly into a 125 mL sample bottle for subsequent lab filtration and analysis.

The remainder was poured into the open end of a 50 mL disposable syringe fitted with an in-line filter unit to obtain a field-filtered sample. In all cases, both the syringe and filter unit were prerinsed with DI water before any water was released into the 125 mL sample bottles. Two syringes full of sample (approximately 100 mL) was required to obtain a nearly full sample bottle. All field samples were carefully packed in Ministry coolers with an ice pack before shipping directly to the Zenon Environmental Laboratory in Burnaby, B.C. via Loomis courier service. Transit time from the Creston site to the Lab is estimated at 24 hours.

### 2.3 Results

The results of the dissolved ortho-phosphorus low-level replicate samples collected by Lawrence Schalla are tabulated in Table 1. The results of the dissolved ortho-phosphorus low-level replicate samples, collected by T. Webber, are tabulated in Table 2. The results of the dissolved ortho-phosphorus low-level field blanks are tabulated in Table 3.

### 2.4 Discussion

By reviewing the replicate data in Table 1, we find that of the 28 pairs of samples, 19 pairs were identical, 3 pairs had values higher for lab filtration and 6 pairs had values higher for field filtration.

i.e.: 67.9 % = identical values.  
10.7 % = higher for lab filtration.  
21.4 % = higher for field filtration.

Also, the 9 non-identical pairs had values that are within 1 µg/L of each other which is the smallest value to which measurements for this variable can be resolved. Given the typical low precision near the Method Detection Limit (MDL) (i.e., ± 100 %, Taylor, 1987), the pairs should be considered virtually identical. A similar review of the Quality Assurance replicate data in Table 2 reveals that only 1 of the 6 pairs is identical with 2 pairs having higher values for lab filtration and 3 pairs having higher values for field filtration. Note that 5 out of the 6 pairs have values that are within 1 µg/L of each other, the smallest value to which measurements for this variable can be resolved.

Given the typical low precision near MDL (i.e.,  $\pm 100\%$ , Taylor, 1987), only the replicate pair that is  $2\ \mu\text{g/L}$  different may be considered significantly different. Reviewing the data in Table 3, we find that all 6 pairs of field blanks are identical with only one pair showing detectable levels at  $1\ \mu\text{g/L}$  for Dissolved Ortho-Phosphorus Low Level. The system detection limit derived from these field blanks is the same as the laboratory method detection limit of  $1\ \mu\text{g/L}$ .

### 3.0 CONCLUSIONS and RECOMMENDATIONS

We conclude that there is no significant difference between field-filtered and laboratory-filtered dissolved ortho-phosphorus low-level results because only one pair of 34 pairs of results could be considered to be significantly different. The results of the low-level paired field blanks indicate that contamination due to sampling technique, sample transportation, collection and sample bottles was insignificant. The System Detection Limit remains at  $1\ \mu\text{g/L}$  for this variable.

The routine sample data for the Thompson River at Spences Bridge (see Appendix 1) has been included for general interest and comparison. With the exception of a very few of the results, the majority of these data are also very close to MDL. It would be interesting to compare field and laboratory filtered dissolved ortho-phosphorus data that are not distributed as close to MDL as was found with the Creston site data.

Laboratory filtration of low-level, dissolved ortho-phosphorus is recommended to simplify field operations and eliminate the risk of contamination during field filtration.

## REFERENCES

Taylor, J.K. 1987. Quality Assurance of Chemical Measurements.

Lewis Publishers Inc., Chelsea, Michigan. 328 pp.

Webber, T.N., Pommen, L.W., 1989. Field Filtration Testing for Total Dissolved Phosphorus and Dissolved Ortho-Phosphorus Low-Level Blanks.

Ministry of Environment and Parks, Water Management Branch, Victoria, British Columbia.

12 pp.



TABLE 1

## Results of Dissolved Ortho-Phosphorus Low-Level Routine Replicate Sampling

SITE: Kootenay River at Creston

SEAM: E206587

SAMPLER: Lawrence Schalla

SAMPLE DATE: YY MM DD	TIME: 2400	LAB FILTERED (CLSP 12/01) mg/L	FIELD FILTERED (LL PHOS : O) mg/L
89 09 26	1100	<0.001	<0.001
89 10 10	?	<0.001	<0.001
89 10 24	1100	<0.001	<0.001
89 11 06	1100	<0.001	<0.001
89 11 21	1100	<0.001	<0.001
89 12 05	1445	0.002	0.001
89 12 18	1100	<0.001	0.001
90 01 02	1110	<0.001	0.001
90 01 15	1145	0.003	0.004
90 02 12	1030	0.001	0.002
90 02 26	0930	<0.001	0.001
90 03 13	1140	<0.001	<0.001
90 03 27	1100	<0.001	<0.001
90 04 10	1100	<0.001	<0.001
90 04 23	1100	<0.001	0.001
90 05 08	1015	<0.001	<0.001
90 05 22	0930	<0.001	<0.001
90 06 04	1010	0.001	0.001
90 06 19	0900	0.001	<0.001
90 07 03	1000	<0.001	<0.001
90 07 17	0910	0.001	<0.001
90 07 31	1115	<0.001	<0.001
90 08 28	0850	<0.001	<0.001
90 09 10	0915	0.001	0.001
90 09 25	0915	<0.001	<0.001
90 10 09	0930	<0.001	<0.001
90 10 23	1045	<0.001	<0.001
90 11 05	0630	<0.001	<0.001

TABLE 1 (continued)

SAMPLE DATE: YY MM DD	TIME: 2400	LAB FILTERED (CLSP 12/01) mg/L	FIELD FILTERED (LL PHOS : O) mg/L
MEAN VALUE		0.0011	0.00115
MDL *		0.0010	0.0010
S.D. **		0.0004	0.0006
%R.S.D ***		36.4	52.2

\* MDL = Method Detection Limit (Laboratory).

\*\* S.D. = Standard Deviation.

\*\*\* %R.S.D. = Relative Standard Deviation = S.D. / Mean X 100.

Statistics include less than MDL values in bold face, with <MDL assumed to be equal to MDL.

? - Sample times not recorded by sample collector; unavailable from Environment Canada.

Samples were collected in a 500 mL metals bottle and poured or filtered into brown, 125 mL DOP-Low Level bottles and shipped in coolers with ice packs by ground freight to Zenon Environmental Laboratory within 24 hours.

TABLE 2

## Results of Dissolved Ortho-Phosphorus Low-Level Quality Assurance Replicate Sampling.

SITE: Kootenay River at Creston  
 SEAM: E206587  
 SAMPLE DATE: June 13, 1990  
 SAMPLER: Tom N. Webber

TIME:	LAB FILTERED CLSP 12/01 mg/L	FIELD FILTERED L1118 12/22 mg/L
2400		
1040	<0.001	<0.001
1044	<0.001	<b>0.001</b>
1048	0.001	<0.001
1052	0.001	<0.001
1056	0.001	0.002
1100	0.006	0.008

MEAN VALUE	0.00183	0.00233
MDL *	0.0010	0.0010
S.D. **	0.0020	0.0028
%R.S.D. ***	109	122

\* MDL = Method Detection Limit (Laboratory).

\*\* S.D. = Standard Deviation.

\*\*\* %R.S.D. = Relative Standard Deviation = S.D. / Mean X 100.

Statistics include less than MDL values in bold face, with <MDL assumed equal to MDL.

Samples were poured or filtered into paired, brown 125 mL DOP-Low Level sample bottles and shipped in coolers with ice packs by ground freight to Zenon Environmental Laboratory within 24 hours.

TABLE 3

## Results of Dissolved Ortho-Phosphorus Low-Level Paired Field Blanks.

SITE: Kootenay River at Creston.  
 SEAM: E206587  
 SAMPLE DATE: June 13, 1990.  
 SAMPLER: Tom Webber

Field Blank Number	TIME: 2400	LAB FILTERED CLSP 12/01 $\mu\text{g/L}$	FIELD FILTERED L1118 12/22 $\mu\text{g/L}$
1	1126	<1	<1
2	1130	<1	<1
3	1134	<1	<1
4	1138	1	1
5	1142	<1	<1
6	1146	<1	<1

MEAN VALUE		1.00	1.00
MDL *		1 $\mu\text{g/L}$	1 $\mu\text{g/L}$
S.D. **		0.00	0.00
S.D.L. ***		1.00	1.00

\* MDL = Method Detection Limit (Laboratory).

\*\* S.D. = Standard Deviation

\*\*\* S.D.L. = System Detection Limit = mean value plus 3 S.D.  
 (rounded to the next highest measurable unit).

Statistics include less than MDL values in bold face, with <MDL assumed equal to MDL.

Field blanks were poured or filtered into paired, brown 125 mL DOP-Low Level sample bottles and shipped in coolers with ice packs by ground freight to Zenon Environmental Laboratory within 24 hours.

## APPENDIX 1

## Results of Dissolved Ortho-Phosphorus Low-Level Routine Sampling

SITE: Thompson River at Spences Bridge.

SEAM: E206586

SAMPLER: Lloyd Fredericks

SAMPLE DATE: YY MM DD	TIME: 2400	LAB FILTERED (CLSP 12/01) mg/L
90 04 01	1830	<b>&lt;0.001</b>
90 04 15	1830	0.001
90 05 02	1830	0.002
90 05 13	1900	0.001
90 05 27	1930	0.002
90 06 10	1930	<b>&lt;0.001</b>
90 06 25	0630	0.002
90 07 09	0600	0.012
90 07 23	0730	0.001
90 08 07	0800	0.001
90 08 20	0900	0.001
90 09 03	1830	0.001
90 09 16	1830	<b>&lt;0.001</b>
90 10 01	0645	<b>&lt;0.001</b>
90 10 15	1000	<b>&lt;0.001</b>
90 10 29	0830	<b>&lt;0.001</b>
90 11 12	1630	0.005
90 11 25	1630	0.004
90 12 09	1600	0.003
90 12 23	1630	0.003
91 01 06	1600	0.003
91 01 21	0900	0.004
91 02 04	0830	0.015
91 02 17	1730	0.005
91 03 04	0930	0.003
91 03 17	1830	0.002

Values in bold face are less than laboratory MDL (Method Detection Limit).

Routine samples were collected in a 500 mL 'metals' bottle and poured into a lab cleaned, 125 mL borosilicate glass sample bottle and filtered in the Zenon Laboratory.

Estimated shipping time via Loomis Courier Service to Zenon Lab in Burnaby is 24 hours.



Province of  
British Columbia

Ministry of  
Environment  
WATER MANAGEMENT  
BRANCH

# MEMORANDUM

To: Distribution List

Date: July 14, 1992  
File: Wqu 64.123103

**Re: Comparing Field and Laboratory Filtration for Low-Level  
Dissolved Ortho-Phosphorus Samples**

Attached for your information is a study that shows that there was no significant difference between field and lab filtered low-level dissolved ortho-phosphorus results for the Kootenay River at Creston at concentrations close to the detection limit (1  $\mu\text{g/L}$ ).

L.W. Pommen, MSc, PEng  
Water Quality Branch

Attachment

DISTRIBUTION:

M.J.R. Clark, Environmental Protection, Victoria  
P.H. Whitfield, Environment Canada  
A. Ryan, Environment Canada  
N. Wade, Environment Canada  
H. Quon, C & P Laboratory  
D. Jeffery, Zenon Environmental Laboratories  
L. Erickson, EP, Nanaimo  
M. Gow, EP, Surrey  
P. Ross, EP, Smithers  
V. Jensen, EP, Penticton  
R. Crozier, EP, Nelson  
D. Holmes, EP, Kamloops  
D. Sutherland, EP, Prince George  
N. Zirnhelt, EP, Williams Lake  
L. McDonald, EP, Cranbrook  
R. Grace, EP, Kamloops  
B. Carmichael, EP, Prince George  
B. Moore, EP, Surrey  
K. Andrews, EP, Williams Lake  
J. Deniseger, EP, Nanaimo  
R. Rocchini, Water Quality Branch  
R. Nordin, Water Quality Branch  
L. Swain, Water Quality Branch  
L. Pommen, Water Quality Branch  
Circulation - Water Quality Branch Library  
K. Neer, BC Environment Library (2)