

**PRESERVATION OF ORGANICS. PART II
STABILITY OF CHLOROPHENOLS IN PRESERVED
NATURAL WATER SAMPLES**

by

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PERSPECTIVES DE GESTION

Vu la centralisation des Laboratoires de la qualité de l'eau au Canada, c'est le Laboratoire national de la qualité de l'eau de Burlington qui reçoit les échantillons à analyser, expédiés du Pacifique et du Yukon, du nord et de l'ouest du Québec, de la région Atlantique et de l'Ontario. Souvent, les échantillons doivent être conservés pendant un certain temps avant que l'extraction et l'analyse puissent être effectuées. Pour obtenir des résultats significatifs à partir de ces échantillons, leur intégrité doit être conservée à partir de la date du prélèvement jusqu'au moment de l'analyse. Dans beaucoup de cas, l'information relative à la stabilité des paramètres organiques dans les échantillons d'eau et de sédiments est absente ou incomplète. Une série d'études a donc été nécessaire pour mettre au point des techniques pour la préservation des matières organiques analysées régulièrement dans les échantillons naturels.

Dans le cadre d'un programme permanent, la présente étude a consisté à évaluer diverses techniques pour préserver 20 chlorophénols dans les échantillons d'eau naturelle dopée. La technique de préservation choisie a été vérifiée par suivi de la stabilité des chlorophénols pendant une période de 15 semaines dans certaines conditions en laboratoire. Tous les chlorophénols présents dans les échantillons d'eau préservée demeuraient stables pendant au moins 15 semaines.

RÉSUMÉ

Dans cette étude, on a suivi la stabilité de 20 chlorophénols (CP), y compris les monochlorophénols dans des échantillons d'eau dopée provenant de cinq régions. Avant la mise en oeuvre de l'étude à l'échelle réelle, une étude pilote a été conçue pour évaluer l'efficacité de trois produits chimiques, soit le chloroforme, le sulfate de cuivre et l'acide sulfurique, pour la préservation des CP dans l'eau. Avec l'eau du lac Ontario comme échantillon type, les résultats ont montré que le sulfate de cuivre aussi bien que l'acide sulfurique étaient des préservatifs efficaces. Cependant, c'est l'acide sulfurique qui a été choisi en dernier lieu pour l'étude à l'échelle réelle, car il est également utilisé pour préserver les échantillons d'eau lors des analyses d'herbicides pour les métaux à l'état de trace et les acides. La stabilité des CP dans les échantillons d'eau dopés et préservés à l'acide sulfurique a été suivie par analyses répétées des échantillons immédiatement après le dopage, et après 3, 6, 10 et 15 semaines de stockage à 4°C à l'obscurité. Dans ces conditions, les résultats de l'étude à l'échelle réelle ne révélaient aucun signe de dégradation pour aucun des CP des échantillons sur toute la période d'étude de 15 semaines.

MANAGEMENT PERSPECTIVE

Since the occurrence of centralization of Water Quality Laboratories across Canada, test samples are being shipped from the Pacific and Yukon, Western and Northern, Quebec, Atlantic and Ontario regions to the Water Quality National Laboratory in Burlington for analysis. Frequently, samples will have to be stored for a period of time before extraction and analysis can be performed. In order to obtain meaningful results from the samples, their integrity must be maintained from the time of collection until the time of analysis. In many instances, the information regarding the stability of organic parameters in water and sediment samples is lacking or incomplete. A series of studies was thus required to develop techniques for the preservation of the routinely analyzed organics in natural samples.

As a part of a continuing program, the present study evaluated the techniques to preserve 20 chlorophenols in spiked natural water samples. Further validation of the chosen preservation technique was provided by monitoring the stability of chlorophenols over a 15 week period under controlled laboratory conditions. All chlorophenols in the preserved water samples were stable for at least 15 weeks.

ABSTRACT

This study monitored the stability of 20 chlorophenols (CP) including the monochlorophenols in spiked water samples from five regions. Before the full-scale study was implemented, a pilot study was designed to evaluate the efficiency of three chemicals, namely, chloroform, copper sulfate and sulfuric acid, for the preservation of CP in water. Using Lake Ontario water as a typical sample, results indicated that both copper sulfate and sulfuric acid were effective preservatives. However, sulfuric acid was later chosen in the full-scale study since it was also used to preserve water samples for trace metal and acid herbicide analyses. The stability of CP in the spiked and sulfuric acid-preserved water samples was monitored by repetitive analysis of the samples immediately after spiking, as well as after 3, 6, 10, and 15 weeks of storage at 4°C in the dark. Under such conditions, the results in the full-scale study indicated no evidence of degradation for any CP in all samples over the 15-week study period.

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1.0 INTRODUCTION

Since the occurrence of centralization of Water Quality Laboratories across Canada, test samples are being shipped from the Pacific and Yukon, Western and Northern, Quebec, Atlantic and Ontario regions to the Water Quality National Laboratory (WQNL), Burlington, for analysis. Compared to most trace metals and major ions, organics and pesticides are usually less stable in environmental matrices. Also, organic analytical procedures are frequently lengthy so that it is impractical for a laboratory to analyze the samples as soon as they arrive. This implies that samples will have to be stored for a period of time until extraction and analysis can be performed. In order to obtain meaningful results, the integrity of samples must be maintained from the time of collection until they are analyzed.

Since a large number of parameters are involved in the preservation of organics, the studies were organized so that a group of compounds with similar analytical properties were examined at one time. We have previously reported the results of the preservation of natural water samples for the analysis of chlorinated insecticides (1). In Part II of this continuing program, we studied the stability of chlorophenols in water. Chlorophenols are an important class of industrial and environmental pollutant. Five out of the 20 chloro-phenols included in this study are listed as priority pollutants by USEPA (2). Indeed, pentachlorophenol in water has been routinely analyzed by Water Quality laboratories since the 1970's. Also, water, sediment, and biota samples from "Areas of Concern" such as Niagara River in Ontario and Fraser River in British Columbia are regularly monitored for many chlorophenols. Although water samples for phenol analysis were previously preserved by different chemicals such as copper sulfate, potassium or sodium hydroxide, and others, those methods were only examined for a few selected phenols and the stability of other phenols was unknown. In this work, we evaluated several techniques to preserve 20 chlorophenols in water samples and

reported the stability of all these phenols over a period of up to 15 weeks under controlled conditions.

2.0 STUDY DESIGN

The following 20 chlorophenols were included into the present preservation study: 2-chlorophenol (MCP), 3-MCP, 4-MCP, 2-chloro-5-methylphenol, 4-chloro-3-methylphenol, 2,6-dichlorophenol (DCP), 2,4-DCP, 3,5-DCP, 2,3-DCP, 3,4-DCP, 2,4,6-trichlorophenol (TCP), 2,3,6-TCP, 2,3,5-TCP, 2,4,5-TCP, 2,3,4-TCP, 3,4,5-TCP, 2,3,5,6-tetrachlorophenol (TECP), 2,3,4,6-TECP, 2,3,4,5-TECP, and pentachlorophenol (PCP). It should be noted that 2,5-DCP was not included into this study because the derivatives of 2,4- and 2,5-DCP were not resolvable on the columns which we have tried. Therefore, 2,5-DCP was omitted since 2,4-DCP is the more important phenol in environmental analysis.

The locations of the five regional water samples used in this work are given in Table 1. For simplicity in identification, the region of origin (i.e., Pacific, Western, Ontario, Quebec and Atlantic) instead of the exact location of collection was used in this report. Only one type of water from each region was evaluated because of limitation of resources, however, up to three levels of fortification (i.e., 50, 5, and 0.5 $\mu\text{g/L}$) were studied in some samples. The levels of chlorophenols in the fortified samples were higher than those found in open lake natural water samples. In this case, the results of test samples are more indicative of the stability of the chlorophenols rather than analytical uncertainties. Preliminary analysis of the unspiked waters indicated that all of them had less than detectable amounts of chlorophenols in the blanks. Therefore, no correction was required for the calculation of recoveries.

This chlorophenol preservation study was divided into two parts:

- (a) a pilot study to examine the efficacy of several preservatives (i.e., chloroform, copper sulfate, and sulfuric acid), and
- (b) a full-scale study to monitor the stability of the 20 chlorophenols in the above five regional waters using the most effective preservative determined in the pilot study for a period of up to 15 weeks.

3.0 EXPERIMENTAL

3.1 Standard Solutions

Stock solutions of individual chlorophenols were prepared in toluene. A spiking solution of the 20 chlorophenols in acetone at 50 µg/mL for each phenol was also prepared. For the lowest level of fortification (i.e., 0.5 µg/L), a 1:10 dilution of the above solution was made in acetone.

3.2 Subsampling, Fortification and Preservation

Bulk water samples from the five regions were mechanically stirred in their original 100 L containers and subsampled into glass bottles of either 100 mL or 1 L size. Each bottle was then spiked with 100 µL of an appropriate spiking solution using a syringe, followed by the addition of the chosen preservative. In the pilot study, 12 100 mL aliquots of Lake Ontario water were fortified to 50 µg/L for each phenol and were then preserved with 0.2 g copper sulfate per sample. Another 15 100 mL aliquots were similarly fortified but they were preserved with 10 mL of chloroform per sample. Finally, another 15 100 mL aliquots were fortified and preserved with 1 + 1 sulfuric acid (pH < 1). In all cases, test samples were stirred for 10 minutes after spiking and the addition of a preservative. A set of samples were immediately analyzed to generate the 0-time results, while the rest of the samples were kept at 4°C in the dark and analyzed after the storage period. See Table 2 for more information about the test samples.

3.3 Extraction, Derivatization, and Cleanup

(1) Short procedure:

This method was used for all 100 mL samples. The sample was adjusted to about pH 7 with 1 M KOH. Then 1.0 g of anhydrous K_2CO_3 was added and sample was stirred until the base was completely dissolved. This was followed by the addition of 25 mL petroleum ether (b.p. 30-60°C) and 300 mg chloroacetic anhydride. The sample was stirred for exactly 1 minute and the organic layer was immediately separated from the aqueous layer using a separatory funnel. Another 25 mL petroleum ether and 300 mg chloroacetic anhydride were added to the water sample to repeat the extractive chloroacetylation for a second 1 minute period. After phase separation, a third extractive chloroacetylation was performed for 18 minutes. The combined organic layer was dried through a column of anhydrous sodium sulfate and the solvent was evaporated down to ca 3 mL in the presence of isooctane as a keeper.

(2) Long procedure:

For samples of 1 L size, pre-extraction of chlorophenols from water was required. The sample was adjusted to pH < 1 before it was extracted with 50 mL methylene chloride for 30 minutes. The extraction procedure was repeated twice and the chlorophenols in the combined organic extract was back extracted into 40 mL 1% K_2CO_3 . The back extraction was again repeated twice with two 30 mL aliquots of 1% K_2CO_3 . Then the short procedure described above was followed for the chloroacetylation of chlorophenols. The derivatized extract was cleaned up on a 5% deactivated silica gel column. The toluene fraction was collected and analyzed for the phenols. For a calibration standard, a known amount (e.g., 100 μ L) of the spiking solution was derivatized using the short procedure. See ref. 5 for details.

3.4 GC Analysis

All GC analyses were done by a Hewlett-Packard 5880A gas chromatograph equipped with a Ni-63 electron capture detector, splitless injection port, a model 7671A autosampler and Level 4 terminals. A 12 m x 0.2 mm id OV-1 fused silica capillary column was used. A two-ramp oven temperature program was used: initial temperature 70°C with a 0.5 minute hold, programming rate 1, 25°C/minute (from 70°C to 140°C), programming rate 2, 2°C/minute (from 140°C to 180°C) and a 5 minute hold at 180°C. Temperature for the injection port and detector were 250°C and 300°C, respectively. Carrier gas was helium with a column head pressure of 10 psi. Makeup gas was argon/ methane (95 + 5) with a 30 mL/minute flow rate. Splitless injection (valve time 0.5 minute) of ca. 2 µL of samples were made by the autosampler.

4.0 RESULTS AND DISCUSSION

Although there is a need to determine most chlorophenols in environmental samples, only PCP and a few other chlorophenols are routinely analyzed by Water Quality laboratories. In the past three years, we have developed four chemical derivatization methods for the isomer-specific analysis of all chlorophenols in water and sediment samples at ppb and sub-ppb levels (3 - 6). The chloroacetylation procedure (5) was used in this study since the chloroacetates of monochloro- to pentachloro- phenols are sensitive to electron-capture detection at low levels. In this case, the stability of all chlorophenols included in USEPA Method 604 could be evaluated in the present study. The other advantage of chloroacetylation procedure is that for smaller water samples (i.e. 100 mL), derivatization of chlorophenols can be done in situ. This eliminates the lengthy solvent extraction steps and also reduces recovery losses due to high solubility of some chlorophenols in water. In this study, the short

procedure was applied to all 100 mL samples except for those preserved by copper sulfate. For water samples of lower chlorophenol concentration (i.e. less than 1 $\mu\text{g/L}$), 1 L size samples and the long procedure were used. See Table 2 for more details.

4.1 Pilot Study

Before the full-scale study began, the efficacy of several preservatives including chloroform, copper sulfate, and sulfuric acid was evaluated for the preservation of chlorophenols in natural waters. Results for the chloroform preserved samples (Table 3) showed that the recoveries of both PCP and 2,3,5,6-TECP were continuously decreasing during the 15 week study period. After 15 weeks of storage at 4°C in the dark, PCP was only ca. 4% recovered while 2,3,5,6-TECP was ca. 56% recovered. Recovery for 2,3,4,5-TECP was also low (60%) at week 15. Chloroform was therefore considered ineffective for the preservation of chlorophenols since it failed to stabilize PCP, one of the most important chlorophenols in environmental analysis, in natural water samples. On the other hand, all of copper sulfate (Table 4) and sulfuric acid (Table 5) preserved samples did not show any significant decrease in recovery for the 20 chlorophenols over the entire study period. However, sulfuric acid was used in the full-scale study instead of copper sulfate since the former was also used to preserve water samples for some trace metals (7) as well as acidic herbicides (study in progress).

4.2 Full-Scale Study

The results in the full-scale study were presented in Tables 6 through 14. In this part of the study, the stability of chlorophenols in regional water samples of up to 3 levels of fortification (50, 5, and 0.5 $\mu\text{g/L}$ for each phenol) preserved with H_2SO_4 (pH < 1)

was monitored for 15 weeks. Other than a few minor exceptions, the recovery of all chlorophenols was better than 90% for all samples fortified at 50 and 5 µg/L. See Tables 6, 7, 9, 10, 12 and 13. The precision of chlorophenol recovery in duplicate analyses was excellent (standard deviation less than 5%) in those cases. At the 0.5 µg/L level of fortification, recoveries for 3-, 4-, 2-chloro-5-methyl-, and 4-chloro-3-methyl- phenols were mostly between 40 and 70%, while the recoveries of the rest of the chlorophenols were mostly between 80 and 90% throughout the 15 week study period. See Tables 8, 11, and 14 for details. Lower recoveries for the above monochlorophenols were probably due to their higher water solubilities and thus lower solvent extractability rather than due to degradation of these phenols in the water samples. This hypothesis was supported by the fact that similarly low recoveries were also observed at 0-time for all three natural waters studied at the 0.5 µg/L level. Low recoveries of monochlorophenols were not observed for the 50 and 5 µg/L samples since solvent extraction of phenols was not involved in those cases.

In summary, the results tabulated in Tables 6 through 14 indicated that all chlorophenols in this study were stable for at least 15 weeks when water samples were preserved with sulfuric acid (sample pH < 1) and stored at 4°C in the dark. Other than exceptions due to random analytical errors and extraction recoveries explained above, quantitative recoveries of chlorophenols from all fortified regional water samples were obtained throughout the entire study period.

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TABLE 1

List of Natural Water Samples Used in the Preservation Study
for Chlorophenols

REGION	SITE
Atlantic	Mersey River at Jakes Landing, N.S.
Ontario	Station 23, Lake Ontario
Pacific	Fraser River, B.C.
Quebec	R. Outaouais, NAQUADAT Station 05QU022LV9001
Western	East Proper River, Saskatchewan NAQUADAT Station 00SA11AE008

TABLE 2

Test Samples Prepared In This Study

Study	Water	Preservative	Level of Fortification ($\mu\text{g/L}$)	Sample Size (L)	Procedure*	No. of Samples**
Pilot	Ontario	chloroform	50	0.1	A	3 x 5
Pilot	Ontario	copper sulfate	50	0.1	B	4 x 3
Pilot	Ontario	sulfuric acid	50	0.1	A	3 x 5
Full-scale	Pacific	sulfuric acid	50	0.1	A	4 x 6
Full-scale	Pacific	sulfuric acid	5	0.1	A	4 x 6
Full-scale	Western	sulfuric acid	0.5	1	B	4 x 5
Full-scale	Ontario	sulfuric acid	50	0.1	A	4 x 6
Full-scale	Ontario	sulfuric acid	5	0.1	A	4 x 6
Full-scale	Ontario	sulfuric acid	0.5	1	B	4 x 5
Full-scale	Quebec	sulfuric acid	50	0.1	A	4 x 6
Full-scale	Quebec	sulfuric acid	5	0.1	A	4 x 6
Full-scale	Atlantic	sulfuric acid	0.5	1	B	4 x 5

* A = short procedure

B = long procedure

**3 x 5 means 3 replicate samples analyzed at 5 different times, and so on.

TABLE 3

Mean recoveries of chlorophenols in fortified Lake Ontario water
preserved by chloroform - pilot study.

(Replicate = 3)

PHENOL	Week 0	Week 3	Week 6	Week 10	Week 15
2-MCP	81	101	86	88	86
3-MCP	100	95	88	97	86
4-MCP	98	93	88	97	88
2-CL-5-ME	91	86	81	86	84
26-DCP	97	91	84	87	85
4-CL-3-ME	95	80	69	81	79
24-DCP	97	94	86	91	85
35-DCP	96	94	91	102	85
23-DCP	97	92	86	93	84
34-DCP	96	101	88	99	84
246-TCP	96	93	95	87	86
236-TCP	100	87	94	83	84
235-TCP	95	90	93	96	81
245-TCP	89	89	95	99	83
234-TCP	87	90	90	99	82
345-TCP	91	91	95	103	83
2356-TECP	99	76	60	57	56
2346-TECP	105	88	86	82	78
2345-TECP	93	76	82	82	61
PCP	102	31	10	6	4

TABLE 4

Mean recoveries of chlorophenols in fortified Lake Ontario water
preserved by copper sulfate - pilot study.

(Replicate = 4)

PHENOL	Week 0	Week 5	Week 10
2-MCP	87	87	85
3-MCP	76	84	82
4-MCP	68	73	72
2-CL-5-ME	77	63	64
26-DCP	96	93	87
4-CL-3-ME	63	--	--
24-DCP	86	86	83
35-DCP	87	87	87
23-DCP	90	89	84
34-DCP	79	76	76
246-TCP	95	95	85
236-TCP	94	96	88
235-TCP	89	96	92
245-TCP	85	92	91
234-TCP	81	88	89
345-TCP	78	86	84
2356-TECP	97	91	86
2346-TECP	95	91	88
2345-TECP	90	93	89
PCP	91	86	81

TABLE 5

Mean recoveries of chlorophenols in fortified Lake Ontario water
preserved by sulfuric acid - pilot study.

(Replicate = 4)

PHENOL	Week 0	Week 3	Week 6	Week 10	Week 15
2-MCP	75	76	92	82	82
3-MCP	93	89	93	80	83
4-MCP	91	85	93	80	82
2-CL-5-ME	94	95	92	79	81
26-DCP	99	102	91	85	85
4-CL-3-ME	93	89	89	84	84
24-DCP	96	94	90	79	91
35-DCP	87	82	91	77	81
23-DCP	96	92	89	78	81
34-DCP	96	85	91	75	80
246-TCP	90	103	91	86	86
236-TCP	97	105	89	88	86
235-TCP	92	85	92	77	77
245-TCP	87	82	92	78	78
234-TCP	85	82	90	76	79
345-TCP	77	66	91	74	77
2356-TECP	95	106	83	96	87
2346-TECP	98	101	84	92	88
2345-TECP	72	65	96	76	72
PCP	90	95	94	96	88

TABLE 6

Mean recoveries of chlorophenols in fortified (50 µg/L)

Pacific Region water - full-scale study.

(Replicate = 4)

PHENOL	Week 0	Week 1	Week 3	Week 6	Week 10	Week 15
2-MCP	94	94	97	98	93	95
3-MCP	92	93	97	97	93	94
4-MCP	94	93	96	98	92	94
2-CL-5-ME	91	91	98	99	88	92
26-DCP	96	96	96	97	94	97
4-CL-3-ME	95	94	100	95	87	94
24-DCP	92	92	96	95	90	91
35-DCP	91	91	97	91	93	91
23-DCP	93	92	99	95	90	90
34-DCP	90	94	95	91	93	88
246-TCP	98	97	95	98	94	96
236-TCP	99	96	94	100	94	95
235-TCP	93	95	91	100	103	91
245-TCP	94	91	92	100	100	91
234-TCP	92	92	94	93	94	89
345-TCP	93	92	90	92	96	89
2356-TECP	98	94	95	96	93	98
2346-TECP	99	93	94	99	95	93
2345-TECP	92	95	88	96	106	95
PCP	100	97	96	97	93	97

TABLE 7

Mean recoveries of chlorophenols in fortified (5 µg/L)
Pacific Region Water - full-scale study.
(Replicate = 4)

PHENOL	Week 0	Week 1	Week 3	Week 6	Week 10	Week 15
2-MCP	100	95	97	97	92	91
3-MCP	97	93	98	97	91	92
4-MCP	97	97	98	97	91	95
2-CL-5-ME	102	97	92	94	97	91
26-DCP	100	94	100	98	91	92
4-CL-3-ME	96	93	102	94	93	100
24-DCP	98	97	96	94	91	90
35-DCP	95	95	100	95	88	90
23-DCP	96	95	94	94	91	90
34-DCP	94	97	96	95	90	93
246-TCP	99	100	101	99	93	93
236-TCP	99	102	98	99	92	94
235-TCP	93	89	101	97	84	88
245-TCP	94	92	100	97	86	90
234-TCP	94	94	94	92	89	93
345-TCP	92	95	100	90	81	93
2356-TECP	95	101	87	101	95	97
2346-TECP	98	98	96	101	95	96
2345-TECP	92	85	93	87	77	89
PCP	97	98	89	102	97	99

TABLE 8

Mean recoveries of chlorophenols in fortified (0.5 µg/L)
Western Region water - full-scale study.
(Replicate = 4)

PHENOL	Week 0	Week 3	Week 6	Week 10	Week 15
2-MCP	83	81	85	83	96
3-MCP	56	57	59	58	64
4-MCP	44	47	51	42	59
2-CL-5-ME	50	54	66	60	68
26-DCP	87	90	91	91	102
4-CL-3-ME	28	25	50	63	39
24-DCP	84	90	86	76	98
35-DCP	84	89	81	83	93
23-DCP	89	89	86	86	97
34-DCP	84	78	74	65	86
246-TCP	85	90	89	92	104
236-TCP	90	90	91	90	94
235-TCP	88	83	82	83	90
245-TCP	89	86	85	81	93
234-TCP	96	89	86	78	98
345-TCP	89	83	81	79	85
2356-TECP	94	94	94	96	82
2346-TECP	91	89	90	93	89
2345-TECP	87	81	79	82	84
PCP	92	84	92	95	85

TABLE 9**Mean recoveries of chlorophenols in fortified (50 µg/L)****Ontario Region Water - full-scale study.****(Replicate = 4)**

PHENOL	Week 0	Week 1	Week 3	Week 6	Week 10	Week 15
2-MCP	93	94	101	94	92	96
3-MCP	89	93	101	93	93	96
4-MCP	90	95	101	94	93	95
2-CL-5-ME	91	98	100	100	90	94
26-DCP	93	95	99	94	92	99
4-CL-3-ME	91	97	103	96	86	96
24-DCP	89	97	101	89	92	93
35-DCP	89	96	101	88	98	89
23-DCP	90	97	102	92	93	92
34-DCP	86	95	98	90	94	92
246-TCP	96	96	98	95	94	99
236-TCP	96	97	98	98	93	99
235-TCP	90	92	99	86	91	87
245-TCP	88	94	100	86	90	86
234-TCP	90	94	99	86	90	88
345-TCP	88	83	96	88	88	89
2356-TECP	90	101	89	104	90	101
2346-TECP	92	94	99	101	93	98
2345-TECP	91	85	102	87	91	86
PCP	99	103	91	106	91	99

TABLE 10

Mean recoveries of chlorophenols in fortified (5 µg/L)

Ontario Region Water - full-scale study.

(Replicate = 4)

PHENOL	Week 0	Week 1	Week 3	Week 6	Week 10	Week 15
2-MCP	101	98	97	96	95	91
3-MCP	98	98	95	93	98	92
4-MCP	93	99	96	94	98	96
2-CL-5-ME	100	100	92	93	98	87
26-DCP	98	100	100	99	93	91
4-CL-3-ME	93	101	100	98	96	94
24-DCP	97	99	93	89	94	90
35-DCP	98	96	93	83	95	93
23-DCP	97	97	89	88	95	91
34-DCP	97	98	90	83	97	89
246-TCP	96	97	100	99	98	94
236-TCP	92	99	98	101	94	93
235-TCP	96	94	91	83	90	94
245-TCP	96	95	91	83	91	94
234-TCP	96	94	88	81	96	94
345-TCP	101	98	96	76	92	98
2356-TECP	92	97	98	105	99	96
2346-TECP	97	97	99	99	97	95
2345-TECP	97	92	102	100	88	96
PCP	95	97	98	103	101	98

TABLE 11

Mean recoveries of chlorophenols in fortified (0.5 µg/L)

Ontario Region water - full-scale study.

(Replicate = 4)

PHENOL	Week 0	Week 3	Week 6	Week 10	Week 15
2-MCP	89	91	91	76	95
3-MCP	61	57	63	55	64
4-MCP	52	51	54	49	58
2-CL-5-ME	63	57	63	60	74
26-DCP	93	93	100	90	100
4-CL-3-ME	32	33	54	52	45
24-DCP	94	93	90	91	98
35-DCP	94	91	83	83	95
23-DCP	97	92	90	85	98
34-DCP	88	77	80	72	90
246-TCP	97	101	107	96	105
236-TCP	82	91	105	89	95
235-TCP	95	89	85	77	92
245-TCP	104	91	87	83	83
234-TCP	107	89	88	81	92
345-TCP	108	85	77	81	92
2356-TECP	67	92	111	92	95
2346-TECP	80	92	108	91	98
2345-TECP	98	91	70	73	89
PCP	76	91	106	92	97

TABLE 12**Mean recoveries of chlorophenols in fortified (50 µg/L)****Quebec Region Water - full-scale study.****(Replicate = 4)**

PHENOL	Week 0	Week 1	Week 3	Week 6	Week 10	Week 15
2-MCP	97	98	94	96	92	94
3-MCP	93	95	93	95	93	95
4-MCP	93	94	93	95	92	93
2-CL-5-ME	91	98	91	99	88	91
26-DCP	101	101	97	95	94	97
4-CL-3-ME	93	96	96	99	90	99
24-DCP	93	94	89	93	91	92
35-DCP	91	91	88	93	95	93
23-DCP	93	95	90	93	92	92
34-DCP	90	93	86	90	91	94
246-TCP	103	102	97	95	95	97
236-TCP	107	96	98	98	95	99
235-TCP	99	94	90	90	99	94
245-TCP	95	93	88	91	97	94
234-TCP	92	93	85	90	93	94
345-TCP	87	89	83	87	95	93
2356-TECP	99	80	111	105	93	104
2346-TECP	90	94	101	99	95	100
2345-TECP	92	89	85	95	93	94
PCP	92	90	113	107	95	104

TABLE 13

Mean recoveries of chlorophenols in fortified (5 µg/L)

Quebec Region Water - full-scale study.

(Replicate = 4)

PHENOL	Week 0	Week 1	Week 3	Week 6	Week 10	Week 15
2-MCP	99	95	101	98	97	94
3-MCP	98	94	100	95	100	96
4-MCP	99	97	101	96	99	98
2-CL-5-ME	96	94	97	94	97	90
26-DCP	99	95	102	100	96	94
4-CL-3-ME	97	93	104	98	98	99
24-DCP	97	97	98	93	96	92
35-DCP	95	97	93	90	98	92
23-DCP	96	95	95	92	96	91
34-DCP	95	95	96	89	101	93
246-TCP	99	98	102	102	94	95
236-TCP	98	98	102	103	96	96
235-TCP	93	95	85	90	94	91
245-TCP	94	93	87	91	94	91
234-TCP	91	96	85	87	99	95
345-TCP	88	87	81	83	99	97
2356-TECP	102	87	92	107	101	102
2346-TECP	100	96	97	102	98	98
2345-TECP	88	96	82	87	91	93
PCP	103	92	93	104	101	103

TABLE 14

Mean recoveries of chlorophenols in fortified (0.5 µg/L)

Atlantic Region water - full-scale study.

(Replicate = 4)

PHENOL	Week 0	Week 3	Week 6	Week 10	Week 15
2-MCP	91	84	88	85	96
3-MCP	54	59	60	56	66
4-MCP	59	48	57	42	58
2-CL-5-ME	58	57	79	60	79
26-DCP	81	90	91	82	93
4-CL-3-ME	39	29	52	63	46
24-DCP	81	93	87	80	89
35-DCP	83	91	81	80	95
23-DCP	90	90	85	81	95
34-DCP	78	84	78	69	97
246-TCP	81	93	83	86	91
236-TCP	79	94	81	84	85
235-TCP	76	86	76	77	98
245-TCP	79	89	79	75	103
234-TCP	83	89	83	78	99
345-TCP	78	89	77	74	101
2356-TECP	79	97	81	93	75
2346-TECP	80	94	82	89	82
2345-TECP	74	85	70	75	98
PCP	78	91	85	93	71