



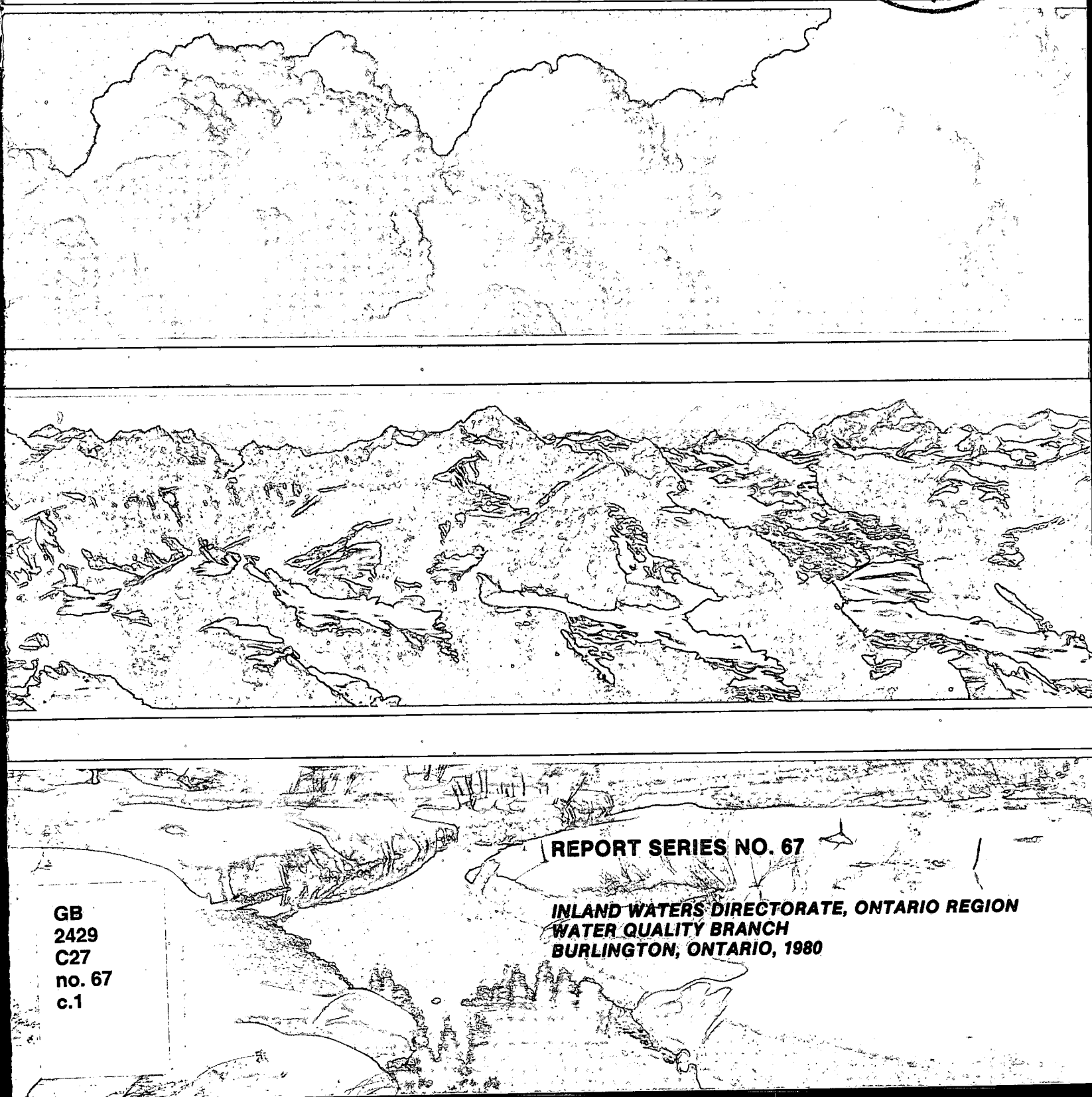
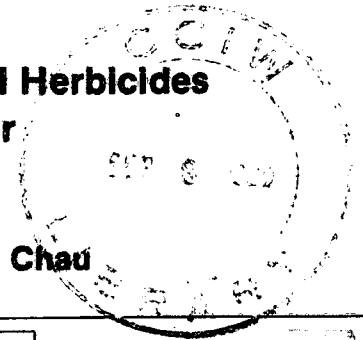
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# Interlaboratory Quality Control Study No. 24

## Analysis of Eight Acid Herbicides in Natural Fresh Water

Haig Agemian and A.S.Y. Chau



REPORT SERIES NO. 67

INLAND WATERS DIRECTORATE, ONTARIO REGION  
WATER QUALITY BRANCH  
BURLINGTON, ONTARIO, 1980

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## **Abstract**

A national interlaboratory quality control study for Canadian laboratories on the determination of eight acid herbicides (MCPA; 2,4-DP; 2,4-D; silvex; MCPB; 2,4,5-T; 2,4-DB; and picloram) in natural fresh water is described. The data show that most laboratories have acceptable expertise for the analysis of silvex; 2,4,5-T; and 2,4-D. No data were reported for MCPB by any laboratory, while only a few participants reported results on MCPA; 2,4-DP; 2,4-DB; and picloram. The overall results indicate that most participants in this study had not attempted the analysis of all eight herbicides. This may reflect the limited expertise in multi-residue analysis of these herbicides in water at the designed concentrations.

## **Résumé**

Le rapport renferme les résultats d'une étude interlaboratoire nationale, menée dans des laboratoires canadiens, pour contrôler la qualité des dosages de huit herbicides acides (MCPA; 2,4-DP; 2,4-D; silvex; MCPB; 2,4,5-T; 2,4-DB et piclorame), dans les eaux douces. Dans la plupart des laboratoires, les résultats du dosage du silvex, du 2,4,5-T et du 2,4-D ont été acceptables. Aucun laboratoire n'a communiqué de données sur le MCPB, et seulement quelques-uns ont communiqué des résultats sur le MCPA, le 2,4-DP, le 2,4-DB et le piclorame. Il ressort de l'ensemble des résultats que la majorité des participants n'ont pas tenté de doser les huit herbicides. Aux concentrations préparées, il se pourrait donc que les possibilités de doser plusieurs résidus de ces herbicides soient limitées.

## List of Symbols

N.V. No value reported

R Identification of results which have been rejected in calculating  $\bar{x}$  and S.D. (using S.D. method twice)

n Number of results used in calculating the group mean ( $\bar{x}$ )

$\bar{x}$  Mean value  $\bar{x} = \frac{\sum_{i=1}^n x_i}{n}$

S.D. Standard deviation, S.D. =  $\sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{(n - 1)}}$

R.S.D. Relative standard deviation or the coefficient of

variation, R.S.D. =  $\frac{\text{S.D.}}{\bar{x}} \times 100$

% Rec. Percent recovery relative to design value

# Interlaboratory Quality Control Study No. 24 Analysis of Eight Acid Herbicides in Natural Fresh Water

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## INTRODUCTION

The use of various acid herbicides has prompted many laboratories to develop new analytical methodologies or to adopt existing ones for their determination in different substrates. Natural water is one key substrate which is of interest to Water Quality Branch laboratories throughout Canada. They have conventionally used the traditional methyl ester derivatization method for the determination of four herbicides, namely MCPA; 2,4-D; silvex; and 2,4,5-T (Environment Canada, 1974; Goerlitz and Lamar, 1967; Yip, 1971). Recently, relevant work has been undertaken in the Quality Assurance and Methods Section in Burlington to develop methods for the multi-residue determination of additional herbicidal acids. Chau and Terry (1975, 1976) have reported reaction conditions for the preparation of 2-chloroethyl and pentafluorobenzyl ester derivatives of ten phenoxy acid herbicides. Later, Agemian and Chau described methods for the multi-residue determination of MCPA and MCPB (Agemian and Chau, 1976) as well as for eight herbicidal acids (Agemian and Chau, 1977) (namely MCPA; 2,4-DP; 2,4-D; silvex; MCPB; 2,4,5-T; 2,4-DB; and picloram) in natural waters. Knowledge of these reported methods as well as the preservation conditions of these compounds in water (Chau and Thomson, 1978) makes it possible for an analyst to perform the analysis of water samples confidently.

The objectives of this study are to explore whether any problems exist in the analysis of herbicides in water, to identify the interlaboratory compatibility of analytical standards, and to provide an idea of the capability of laboratories in multi-residue analysis for these acid herbicides in water. Furthermore, if the laboratories are capable of performing such analyses, this study will provide some information on the compatibility of the analytical data, which in turn will assist the future design of quality control studies for acid herbicides.

Samples were distributed to participating laboratories in November 1978 and most of the data were received by February 1979.

## EXPERIMENTAL

### *Design*

To obtain information on the objectives outlined earlier for this study, it was felt that it was sufficient to have a minimum design of sending two spiked water samples and one ampul of standard solution. Without knowledge of the overall capability of the laboratories in multi-residue analysis of herbicide acids in water, it would have been ineffective for this first study to have a more elaborate design such as a multi-sample approach to rank laboratories in terms of performance to estimate the precision of each laboratory. A more elaborate study will be justified when an idea of the overall capability of the laboratories is obtained.

For study No. 24, the following samples and standard were sent to the participating laboratories: two Lake Ontario water samples in 40-oz whiskey bottles, spiked with an appropriate amount of the compounds of interest (as the acid), and one ampul containing a more concentrated standard used in the Water Quality Branch Laboratory in Burlington, which was intended to be used as an unknown by the participants.

### *Water Samples*

A bulk water sample was obtained in a 100-L polyethylene barrel from the middle of Lake Ontario. The barrel was stored at 4°C soon after sampling until ready for use. No preservative was used in the 100-L barrel to avoid any contaminants that might have leached off the plastic by the preservative.

First, the water sample was sampled directly from the polyethylene barrel by means of an all-glass siphon to minimize any possible contamination of the bulk sample. Replicate analysis of the water sample in the polyethylene barrel stored at 4°C produced a clear chromatogram with no contamination or interfering peaks. Then spiking

experiments were performed with the eight herbicides to determine the extraction efficiency of the compounds in this type of water. The efficiencies were well within the levels given by Agemian and Chau (1977).

The chemical preservative of 1 mL H<sub>2</sub>SO<sub>4</sub> per litre water sample recommended by Chau and Thomson (1978) was tested for this water sample. Preservation studies were initiated for 1-L Lake Ontario samples stored in 40-oz glass whiskey bottles at room temperature in the dark and preserved with 1 mL H<sub>2</sub>SO<sub>4</sub> per litre of sample. These samples were monitored during up to four months of storage to check sample stability to confirm the effectiveness of the literature preservation procedure (Chau and Thomson, 1978). The preservation conditions were found satisfactory. Replicate analyses of spiked samples showed variability of data within the precision of the method and therefore acceptable homogeneity of the Lake Ontario samples.

Table 1 shows the concentrations of the eight herbicides spiked into the Lake Ontario water. A standard herbicide acid mix was prepared using relative ratios to give roughly equivalent peak height sensitivities based on the electron capture sensitivities of the 2-chloroethyl esters of these compounds. This acid mix was used to spike the appropriate amount in the 1-L water samples to give the levels indicated in Table 1.

Table 1. Concentrations of Herbicides Spiked into Lake Ontario Water

Herbicide	Design levels in quality control samples		
	Standard in ampul (mg/L or ng/ $\mu$ L)	Water sample 1 ( $\mu$ g/L)	Water sample 2 ( $\mu$ g/L)
MCPA	62.5	5	2.5
2,4-DP	5	0.4	0.2
2,4-D	7.25	0.6	0.3
Silvex	2.5	0.2	0.1
MCPB	625	50	25
2,4,5-T	5	0.2	0.1
2,4-DB	25	2	1
Picloram	12.5	1	0.5

#### Herbicide Acid Standard

About 2 mL of the same herbicide acid mix solution used for spiking the water samples was sealed in 10-mL pre-scored ampuls. Because the solvent used for the standard (ethyl acetate) had a high boiling point, there were no problems during the sealing of the ampuls. Ampuls were randomly analyzed to provide a check on reproducibility from one ampul to another. The precision of replicate analyses was within that of the method.

In case laboratories did not have a routine method, a copy of a reprint on multi-herbicide analysis (Agemian and Chau, 1977) was sent to each participating laboratory as background information.

#### Herbicide Acids

The following analytical grade acids were provided free by the manufacturers; dicamba (2-methoxy-3,6-dichlorobenzoic acid) from Velsicol Chemical Corp.; MCPA (4-chloro-2-methylphenoxyacetic acid), MCPB (4-(4-chloro-2-methylphenoxy) butyric acid), and 2,4-DB (4-(2,4-dichlorophenoxy) butyric acid) from May and Baker (Canada) Ltd.; and picloram (4-amino-3,5,6-trichloropicolinic acid) from Dow Chemical Co., Brockville, Ontario. The following acids were purchased commercially: 2,4-D (2,4-dichlorophenoxyacetic acid); 2,4,5-T (2,4,5-trichlorophenoxyacetic acid); silvex (2-(2,4,5-trichlorophenoxy) propionic acid); and 2,4-DP (2,4-dichlorophenoxypropionic acid).

## RESULTS AND DISCUSSION

Tables 2 to 4 present the raw data submitted by participants for the standard in the ampul and the two water samples, respectively. A quick inspection of these tables shows that all seven laboratories supplied data only for 2,4-D; silvex; and 2,4,5-T. No data were submitted for MCPB by any laboratories, while four or fewer laboratories supplied data for MCPA; 2,4-DP; 2,4-DB; and picloram. Therefore statistical data were only calculated for 2,4-D; silvex; and 2,4,5-T herbicides. Table 5 gives a summary of methods used by participants. Only one laboratory used the 2-chloroethyl esters, while the rest employed the conventional methyl ester for gas chromatographic analysis. Laboratories 8, 10, 14 and 48, which used the methyl ester for derivatization, supplied data on only four or fewer herbicides. Since there are limited data for each of the two methods of chemical derivatization, it is not possible to make a statistical comparison on methodology.

The data in Tables 3 and 4 for water samples 1 and 2 give the interlaboratory recovery and precision of the complete methods from the initial step of solvent extraction to chemical derivatization and determination. The data in Table 2 for the ampul reflect the interlaboratory precision and accuracy of only the chemical derivatization and determination part of the method. If there is a significant difference between these two sets of data, it means that the solvent extraction concentration step used by the laboratories is inefficient. The effect of the standards could not be isolated completely, since the data in Table 2 also contained bias and imprecision owing to the chemical



Table 2. Raw Data Submitted by Participants for Standard in Ampul (ng/ $\mu$ L)

Laboratory number	MCPA	2,4-DP	2,4-D	Silvex	MCPB	2,4,5-T	2,4-DB	Picloram
1	129.0	5.75	8.70	2.75	N.V.	5.97	28.4	N.V.
2	N.V.	3.28	3.13	2.83	N.V.	6.16	N.V.	9.74
4	90.9	4.09	5.58	1.79	N.V.	3.81	24.72	7.52
8	N.V.	N.V.	13.6	11.6 R	N.V.	11.5 R	41.2	N.V.
10	N.V.	N.V.	7.4	2.6	N.V.	4.7	N.V.	12.5
14	N.V.	N.V.	8.37	2.70	N.V.	6.04	26.6	N.V.
48	N.V.	N.V.	7.73	2.67	N.V.	6.65	N.V.	N.V.
Design level (ng/ $\mu$ L)	62.5	5	7.25	2.5	625	5	25	12.5
Mean value $\bar{x}$ (ng/ $\mu$ L)			7.8	2.6		5.6		
S.D. (ng/ $\mu$ L)			3.2	0.4		1.1		
R.S.D. (%)			41	15		20		
% Rec.			107	104		112		

Table 3. Raw Data Submitted by Participants for Water Sample 1 ( $\mu$ g/L)

Laboratory number	MCPA	2,4-DP	2,4-D	Silvex	MCPB	2,4,5-T	2,4-DB	Picloram
1	8.18	0.372	0.558	0.215	N.V.	0.446	2.14	N.V.
2	N.V.	0.29	0.32	0.20	N.V.	0.45	N.V.	1.92
4	7.86	0.91	0.82	0.20	N.V.	0.51	5.45	1.13
8	N.V.	N.V.	0.22	0.09 R	N.V.	0.195	0.904	N.V.
10	N.V.	N.V.	0.41	0.18	N.V.	0.32	N.V.	0.46
14	N.V.	N.V.	0.614	0.209	N.V.	0.565	2.18	N.V.
48	N.V.	N.V.	0.493	0.214	N.V.	0.421	N.V.	N.V.
Design level ( $\mu$ g/L)	5	0.4	0.6	0.2	50	0.2	2	1
Mean value $\bar{x}$ ( $\mu$ g/L)			0.49	0.20		0.42		
S.D. ( $\mu$ g/L)			0.20	0.01		0.12		
R.S.D. (%)			41	5		29		
% Rec.			82	100		210		

Table 4. Raw Data Submitted by Participants for Water Sample 2 ( $\mu$ g/L)

Laboratory number	MCPA	2,4-DP	2,4-D	Silvex	MCPB	2,4,5-T	2,4-DB	Picloram
1	4.97	0.211	0.300	0.100	N.V.	0.225	1.06	N.V.
2	N.V.	0.14	0.16	0.09	N.V.	0.19	N.V.	0.69
4	3.01	1.12	1.53 R	N.V.	N.V.	0.33	0.54	0.42
8	N.V.	N.V.	0.16	0.04 R	N.V.	0.11	0.498	N.V.
10	N.V.	N.V.	0.22	0.093	N.V.	0.18	N.V.	0.28
14	N.V.	N.V.	0.313	0.100	N.V.	0.272	1.05	N.V.
48	N.V.	N.V.	0.292	0.107	N.V.	0.230	N.V.	N.V.
Design level ( $\mu$ g/L)	2.5	0.2	0.3	0.1	25	0.1	1	0.5
Mean value $\bar{x}$ ( $\mu$ g/L)			0.24	0.1		0.22		
S.D. ( $\mu$ g/L)			0.07	0.01		0.07		
R.S.D. (%)			29	10		32		
% Rec.			80	100		220		

Table 5. Summary of Methods Used in Study No. 24

Laboratory number	Extraction method	Chemical derivatization method
1	100 mL dichloromethane (twice)	BF <sub>3</sub> -methanol
2	(a) 200 mL + 50 mL (twice) ethyl acetate (b) Back extract into 2% KHCO <sub>3</sub> (c) Reextract - 50 mL dichloromethane three times	BCl <sub>3</sub> /2-chloroethanol
4	(a) Add 350 g Na <sub>2</sub> SO <sub>4</sub> and extract with 50 mL ether (three times) (b) Back extract into 20 mL 5% NaOH (three times) (c) Reextract into 50 mL chloroform (three times)	Diazomethane methylation
8	120 mL + 60 mL (twice) methylene chloride	BF <sub>3</sub> -methanol
10	40 mL benzene (twice)	Diazomethane methylation
14	100 mL (twice) + 50 mL methylene chloride	BF <sub>3</sub> -methanol
48	50 mL chloroform (three times)	BF <sub>3</sub> -methanol

derivatization step. For this reason the data in Tables 3 and 4 could not be corrected with those in Table 2. It is, however, possible without correction to obtain some insight into the behaviour of methods, as is shown below.

Inspection of the silvex data in Tables 2 to 4 shows that the average mean recoveries were 104%, 100% and 100% and that the R.S.D.'s were 15%, 5% and 10% for the ampul standard, and water samples 1 and 2, respectively. Both recovery and precision are in the same close range, indicating that no major inconsistencies exist owing to bias or errors in the standards, the derivatization step or the solvent extraction step. The one-operator precision and recovery data of a typical method for silvex were shown to be 7% and 109%, respectively (Agemian and Chau, 1976). These agree well with the interlaboratory data discussed above. The agreement of the ampul standard data with the design value of silvex is good (Fig. 1), except for one outlier which was rejected.

Data for 2,4-D (Tables 2 to 4) show average mean recoveries of 107%, 82% and 80% and R.S.D.'s of 41%, 41% and 29% for the ampul standard, and water samples 1 and 2, respectively. Although the recovery in the ampul standard (107%) is higher than that for the water samples (82% and 80%), it is not clear from this population whether a low efficiency in solvent extraction exists, since the range of variabilities is larger than the difference in recoveries. Agemian and Chau (1976), however, showed for their published method that the one-operator precision for 2,4-D (10%) is similar to that for silvex (7%) and that the recovery of the method is 102%. Inspection of Table 2 and Figure 1 for the 2,4-D ampul data reveals that four laboratories (Nos. 1, 10, 14 and 48) reported values very close to

the design value, while the values of the other three (Nos. 2, 4 and 8) were considerably different. These three laboratories, however, could not be rejected by accepted statistical treatment. Yet if the 2,4-D data (Table 2) for laboratories Nos. 1, 10, 14 and 48 are isolated and treated as a separate population, it can be seen that the mean recovery relative to the design value becomes 111% with an R.S.D. of 7%. Evidently, the recovery is not changed substantially but the precision (R.S.D.) is improved from

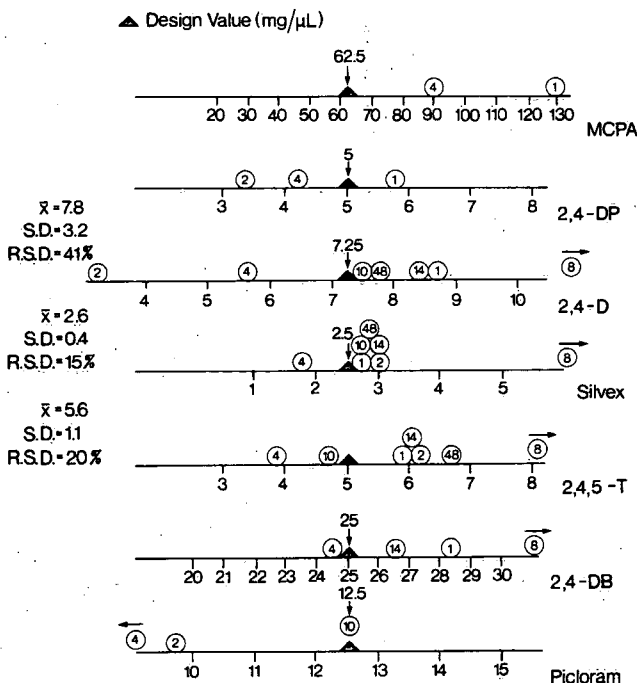


Figure 1. Distribution of levels of herbicides in ampul standard.

41% to 7%. It is important to point out that laboratories Nos. 2, 4 and 8 which showed large discrepancies from this mean used three different chemical derivatization techniques that were also used by the other laboratories. This indicated that the disagreements in the 2,4-D data in Table 2 are not dependent on the nature of the chemical reaction and may well be due to the standards used by the laboratories. Similar treatment of the data for water sample 1 (Table 3) for the selected group gives an 86% mean recovery for 2,4-D with an R.S.D. of 17% as compared with the original mean recovery of 82% and an R.S.D. of 41%. Again substantial improvement of the data for water sample 2 is obtained with a mean recovery of 94% and an R.S.D. of 15% as compared with the original mean recovery of 80% and an R.S.D. of 29%. The data in Tables 2 to 4 considered with the discussion above indicate that some large inconsistencies may exist in the purity of 2,4-D standards. It is also apparent that for a limited population of participants, the methodology gives satisfactory data with quality approaching that for silvex.

As indicated in Table 2, 2,4,5-T had a mean recovery of 112% with an R.S.D. of 20% in the ampul standard. These data approach those for silvex and show no major inconsistency among the laboratory standards or the chemical derivatization step. This could indicate that the quality of available standards is nearly equal to that for silvex and definitely superior to that for 2,4-D. The data for the two water samples, however, show mean recoveries of 210% and 220% with an R.S.D. of 29% and 32% for samples 1 and 2, respectively. It is evident that some consistent bias exists in the data. Since the same herbicide acid mix was used in the ampul standard as well as in the water spikes and because the 2,4,5-T data for the ampul (recovery = 112%) are not in error, it follows that the bias is not due to an error in our 2,4,5-T standard used. Furthermore, since the concentration ratio of the herbicide in the spiking acid mix was fixed and the silvex data were satisfactory, the possibility of an error owing to fortification is removed. An error in 2,4,5-T data should also reflect an error in silvex data by the same ratio.

As indicated in the "Experimental," the lake water used in this study had been analyzed previously, and no interfering peaks were found in using the published method (Agemian and Chau, 1976). Furthermore, inspection of the 2,4,5-T data in Tables 2, 3 and 4 shows that the high recovery is not method dependent, that is, the  $\text{BCl}_3$ /2-chloroethanol (laboratory 2),  $\text{BF}_3$ -methanol (laboratories 1, 8, 14 and 48) or the diazomethane methylation (laboratories 4 and 10) methods all gave about 200% recovery in the two water samples. Therefore the explanation for the 2,4,5-T behaviour is not clear from the experimental data and further investigation is necessary.

Figure 1 is a schematic presentation of the distribution of the data for the ampul standard, which can be used to determine the compatibility of analytical standards used by the laboratories. Again, since there are not enough data for the other compounds, it is only possible to comment on 2,4-D; silvex; and 2,4,5-T. Figure 1 serves as a visual aid in assessing compatibility of the standards in use. Silvex standards are definitely the most consistent, as witnessed by the good precision and agreement with the design level (+4% deviation). The 2,4,5-T standards follow, but between-laboratory precision and agreement with design level are not as good (+12%). As discussed earlier, 2,4-D standards vary considerably for some laboratories, while others agree well. It appears that some sources of 2,4-D standards may not be pure.

Although there are not enough data for an evaluation of the other compounds, it is evident from the data that there are gross inconsistencies in the standards used by the few laboratories that attempted their analysis. Visual inspection indicates that there are variations in the MCPA standards and also in recoveries from water samples. Similar situations could have occurred in the case of picloram.

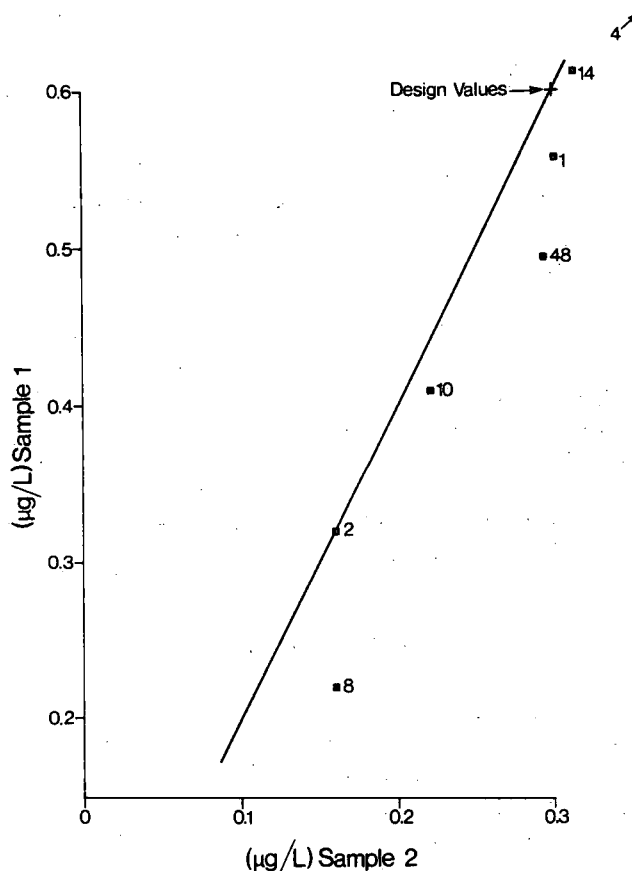


Figure 2. Pair sample plot of water sample 1 as a function of water sample 2 for 2,4-D.

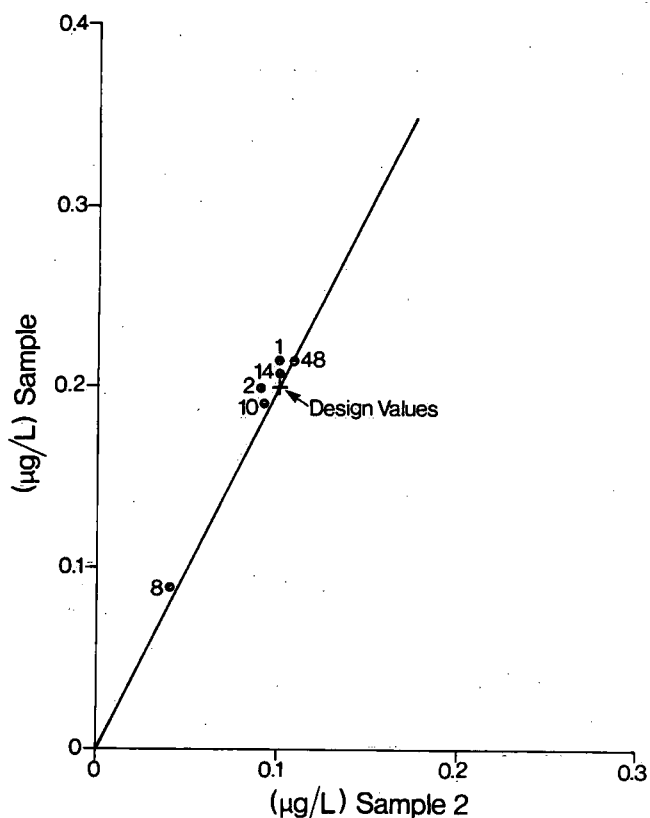


Figure 3. Pair sample plot of water sample 1 as a function of water sample 2 for silvex.

Furthermore, it is also suspected that the derivatization conditions used by the participants for picloram might not have been all optimized for quantitative esterification, since it is less reactive compared with other acid herbicides.

Figures 2 to 4 show pair sample plots of the data of water sample 1 vs. 2 for 2,4-D; silvex; and 2,4,5-T, respectively. The accuracy and precision for silvex are better than those for 2,4-D and 2,4,5-T, as indicated by the proximity of the plotted points to the straight line. The bias of the laboratories, as measured by the spread of points along the straight line, is definitely inferior in the case of these two herbicides compared with silvex.

### CONCLUSION

It has been shown that interlaboratory data on the analysis of silvex in two natural water samples and a one-ampul standard are superior to those for the other herbicides with respect to precision and accuracy. Based on the data, analytical standards for silvex used by the various laboratories have similar purities.

The data for 2,4-D and 2,4,5-T are inferior to those for silvex with respect to both precision and recovery.

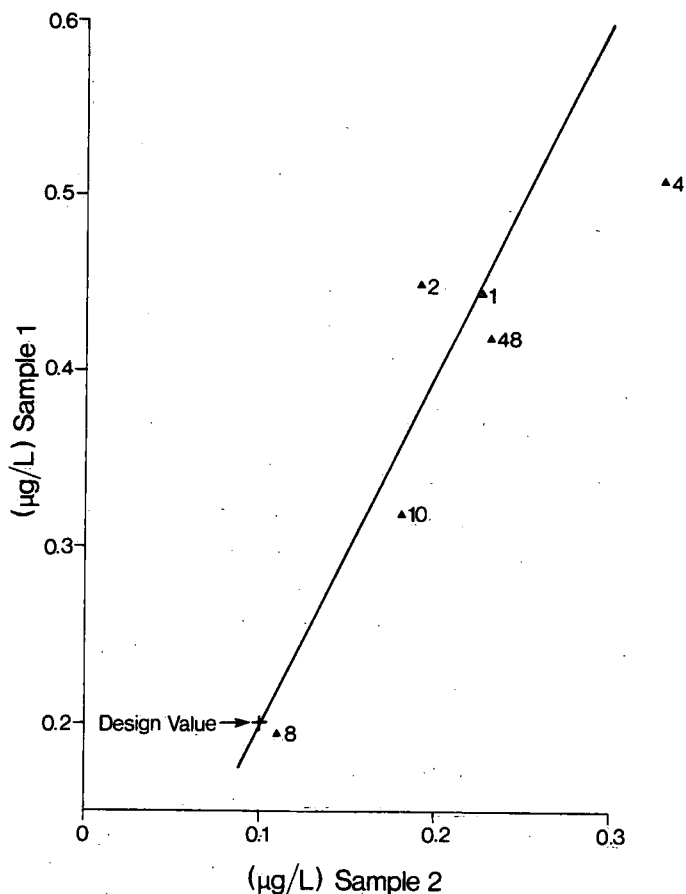


Figure 4. Pair sample plot of water sample 1 as a function of water sample 2 for 2,4,5-T.

Some evidence indicates that inconsistencies of standards for 2,4-D are causes of imprecision. Although 2,4,5-T standards show better agreement in between-laboratory data, an unidentified positive interference was suspected in the water samples analyzed.

This initial study has revealed that either the laboratories do not have sufficient capability to do multi-residue analysis of phenoxy acid herbicides or they do not attempt to do a complete analysis. It also substantiates the observation on the quality of commercial acid herbicide analytical reference standards that with the exception of the silvex data, the between-laboratory compatibility in the analysis of these herbicides (Fig. 1) is somewhat disappointing.

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- Lee, H.B. and A.S.Y. Chau. Interlaboratory quality control study No. 25: polychlorinated biphenyls in wet sediments.

- Cheam, V. and K.I. Aspila. Interlaboratory quality control study No. 26: arsenic and selenium in waters.
- Lee, H.B. and A.S.Y. Chau. Interlaboratory quality control study No. 27: polychlorinated biphenyls in naturally contaminated dry sediments.
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## APPENDIX

### LIST OF PARTICIPANTS

*Environment Canada, Environmental Management Service*  
Atlantic Region, Water Quality Branch Laboratory  
(Moncton)  
Quebec Region, Water Quality Branch Laboratory  
(Longueuil)  
Western Region, Water Quality Branch Laboratory  
(Calgary)  
Pacific Region, Water Quality Branch Laboratory  
(Vancouver)

*Environment Canada, Environmental Protection Service*  
Atlantic Region, Environmental Services Branch  
(Halifax)

*Provincial Government Laboratories*

Alberta Environment, Pollution Control Laboratory  
(Edmonton)  
Department of Mines, Natural Resources and the  
Environment (Winnipeg)

Environment Canada Library, Burlington



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