United States
Environmental Protection
Agency

Region III
Annapolis Field Office
Annapolis Science Center
Annapolis, MD 21401

EPA-903/9-81-003
November 1980

EPA

SURVEY OF THE HUNTINGTON AND PHILADELPHIA RIVER WATER SUPPLIES FOR PURGEABLE ORGANIC CONTAMINANTS

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FOREWORD

In response to the growing concern for better information on public water supplies the CRL undertook a long term survey of two surface water supplies during 1979 and 1980. The objective was to determine the frequency of occurrence of a specific class of organic compounds, namely volatile organics such as chloroform, and to determine the variation in concentrations of these compounds over a period of time.

The quality of our public water supplies has become a critical environmental issue. This essential resource that we too often take for granted must be protected to insure public health. Information such as that contained in this report will help to determine the true quality of these resources and evaluate any potential health risk to the public users.

Orterio Villa
Director
Central Regional Laboratory

ABSTRACT

Raw river water from the Schuylkill and Ohio Rivers was analyzed for purgeable organic halogenated and non-halogenated compounds. The Schuylkill River water contained chloroform ranging from zero to 13.5 µg/l (ppb). Eleven (11) additional compounds occurred at <1 ppb values. The Ohio River water contained nine (9) identifiable compounds with all the compounds present below 1 ppb with the exception of chloroform which ranged from zero to 3.0 ppb. No non-halogenated compounds were found in either river with the exception of toluene in one Schuylkill River sample. Among the more prominent compounds found in both rivers were: (1) chloroform, (2) carbon tetrachloride, (3) trichloroethylene, (4) tetrachloroethylene, and (5) 1,1,1-trichloroethane.

TABLE OF CONTENTS

TABLES

FIGURES

ACKNOWLEDGEMENT

We would like to thank Tom Holbrook and his staff at Huntington Water Corp. along with Geoffrey Brock and his staff at the Belmont Water Treatment facility for the city of Philadelphia, Pennsylvania for enabling us to carry out the river water study. Also, we would like to thank the following members of the Central Regional Laboratory without whose assistance we would not have been able to keep up with the work: Evelyn McPherson, Colleen Walling, Scott Morrow, Janet Roberson and Ann Donaldson.

Finally, we wish to thank Gerry Donovan for his fine work in drafting the figures included in this report.

INTRODUCTION

For purposes of this report, the compounds discussed are compounds recoverable by the Purge and Trap device. In some instances they are referred to as purgeable organics and in others as volatile organic compounds (VOAs).

The following report presents data collected during the study of volatile organic compounds in the Ohio River at Huntington, West Virginia and the Schuylkill River at Philadelphia, Pennsylvania during the period December 4, 1978 through January 29, 1979 for Huntington, and November 27, 1978 through February 24, 1979 for Philadelphia. The purpose of this study was to determine present baseline values of VOAs and to determine whether the concentrations of these chemicals found indicated the occurrance of unreported chemical mishaps on these waterways.

MATERIALS AND METHODS

The following sampling procedure was employed:

- Sample vials (25 ml) were cleaned and prepared by Central Regional Laboratory (CRL) staff members and sent to the various locations. Pierce Vials - #13075 were used.
- Aliquots of organic free water obtained by passing water from a Millipore Super Q System through a cannister of granular charcoal accompanied sealed empty sample vials as blanks.
- One box contained 36 vials. Of those vials, 12 were blanks. One carton contained 3 boxes.
- Quadruplicate sample sets of raw river water were taken every 12 hours (1 sampling period) at the two locations by Water Works personnel.
- When sufficient numbers of samples were taken, generally 1 carton (18 sampling periods), they were shipped by U.S. Mail to CRL for analysis.
- Samples were stored at CRL and the monitoring stations in refrigerators at 4°C. No preservatives were employed in this study. Samples were shipped at ambient temperatures.
- The VOAs were detected using the Purge and Trap Methodology described by Bellar and Lichtenberg[1].
- The samples were grouped into sets covering five sampling periods and composited to generate sets of composite samples representing periods of 2 1/2 days.

- The Hall Electrolytic Conductivity Detector was utilized in detecting halogenated compounds while the Flame Ionization Detector (FID) was employed for the determination of non-halogenated compounds. Dual column identification techniques were used to identify the compounds found.
- Sample size purged was 5 ml.
- Table 1 illustrates the composite numbers and the periods covered.
- Table 2 gives the optimum detection limits obtained during the study for the Hall Detector.
- The analytical conditions were as follows:

  Hall Detector:

    Quantitative column -

      carrier gas N_2 @ 40 ml/min.

      0.2% Carbowax 1500/Carbopack C 80/100 mesh

      2.4 m x 6.35 mm OD x 4 mm ID glass column

      60°C for 4 min., 8°/min. to 160°C, Run Time 30 min.

    Qualitative column -

      carrier gas N_2 @ 30-40 ml/min.

      n - Octane/Porasil C 100/120 mesh

      1.8 m x 6.35 mm OD x 4 mm ID

      50°C for 4 min., 5°/min. to 160°C, Run Time 32 min.

  FID - Flame Ionization Detector:

    1% SP-1000/Carbopack B 60/80 mesh

    3.0 m x 6.35 mm OD x 2 mm ID

    50°C for 4 min., 10°/min. to 200°C, Hold for 18 min.

    Carrier gas N_2 @ 30 ml/min.

DISCUSSION

Chloroform was the most prevalent compound found both in quantity and in the number of occurrences at both Philadelphia and Huntington. Generally, the values for all the componds at Huntington were considerably lower (by a factor of 10) than those values for the same compounds found in the Schuylkill River. From the Ohio River, eleven (11) compounds were identified (Table 3) in addition to the occurrence of a compound thought to be trichlorofluoromethane and/or 1,1-dichloroethylene. The ambiguity arises from the presence of a small broad peak within the time window where these two compounds occur on the chromatogram. The confirmatory column could not clarify the situation due to its inherently poor peak shape compared to the quantitative column, thus resulting in an even broader peak, very near the detection limit. The values reported for these two peaks are arbitrarily high due to the reference quantitation to chloroform, which responds to the Hall Dector much better than either of these compounds. The Schuylkill River profile (Table 4) yielded 12 identifiable compounds of which nine (9) were found in the Huntington samples.

Some of the materials found were in such low concentrations that the relative retention time error increases with the type of peak generated by those materials. Thus the "most probable compound identification (*)" is an indication of a peak within the relative retention time window of the compound suggested (Tables 3 and 4). The compound is of course very near the detection limit of the system. The baseline figures for these two rivers were dramatically different as noted above. The Ohio River, from the standpoint of halogenated hydrocarbons, was cleaner than the Schuylkill.

Chloroform was the only compound that occurred sufficiently above the detection limit to exhibit fluctuation trends both in concentration and occurrences for the Ohio River samples (Figure 1). However, trends in the Schuylkill are apparent not only with chloroform (Figure 2) but additionally with 1,1,1-trichloroethane, trichloroethylene, tetrachlorethylene (Figure 3) and 1,1,2,2-tetrachloroethane. For instance, one apparent trend was that whenever chloroform increases so does tetrachloroethylene. Also, chloroform rose sharply and then slowly dissipates until it rises again. Tetrachloroethylene, 1,1,1-trichloroethane, and trichloroethylene also seem to be cyclical but not with the same intensity between peaks and valleys.

Flame ionization analysis revealed no major peaks throughout the entire program. The suspected presence of toluene at a low level for one Philadelphia composite was the lone exception. Several possibilities could account for the absence of these compounds, including the following: (1) they were not present at all, (2) holding times were long enough to allow degradation by biological, chemical, or photo-chemical action to levels below the detection limits, and (3) the poor purging efficiencies of some of the more polar compounds increased the detection limit above the concentration found in the sample.

Our preliminary studies of purging efficiencies of some of the more polar compounds, e.g. methanol, acetone, isopropanol, displayed approximately 30% efficiencies. With a general detection limit (FID) of approximately 0.5 ppb for non-halogenated compounds, the actual detection limit would increase to the 1.5 to 2.0 ppb range for the polar compounds.

Other investigators have found that, in samples stored at 4°C for more than a week, low levels of many purgeable compounds will biologically degrade nearly completely for most water types. The actual decay rate was highly dependant on the type of water sampled.[2]

Conversely, in the past we have analyzed samples held for periods much longer than one week and have found those compounds. Therefore, we truly have no way of knowing how the degradation may have affected the results. If 90% of the materials were lost by the time of analysis, the detection limits would be from 5-20 ppb dependant on the individual purging efficiencies. Additionally, if 99% of the material were removed by some process, the effective detection limit would be within the 50-200 ppb range.

[1]"The Analysis of Trihalomethanes in Finished Waters by the Purge and Trap Method", U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio (September 9, 1977)

[2]David Munch - Personal Communication November 26, 1980

CONCLUSION AND RECOMMENDATIONS

While we realize the extent of the study's limitations such as the relatively short time period covered, samples not being run individually, and the inherent uncertainties introduced by the long time lag between sample collection and analysis, we feel that the results do yield some useful information. The rivers tend to be contaminated by halogenated species at lower levels than were anticipated based upon earlier studies.[3] Also, cyclical patterns can be seen which indicate some contamination whose source has yet to be determined. The study shows that the Schuylkill River exhibits greater contamination than the Ohio River at the points measured.

Further studies on this subject should attempt to isolate compounds at sub-part-per-billion values. At those levels significant (measurable) variations of contaminates may be seen. Our studies indicate that those levels must be obtained before any additional comments can be made on the subject of isolating sources of contamination.

Finally, the investigation gave an indication of the extent of volatile contamination of two river systems within the Region.

[3]"Monitoring to Detect Previously Unrecognized Pollutants in Surface Waters and Appendix", B. B. Erving, E. S. K. Chian, et al., July 1977, U.S. Department of Commerce National Technical Information Service, PB-273 349 and PB-273 350.

TABLE 1

Composite Identification Numbers and Dates
For Organics Monitoring Program At
Huntington, W. Va. & Philadelphia, Pa.

November 1978 - January 1979

Huntington, W. Va. Composite ID#	Period Covered			
H1	12/4	AM	12/6	AM
H2	12/6	PM	12/8	PM
H3	12/9	AM	12/11	AM
H4	12/11	PM	12/13	PM
H5	12/14	AM	12/16	AM
H6	12/16	PM	12/18	PM
H7	12/19	AM	12/21	AM
H8	12/21	PM	12/23	PM
H9	12/24	AM	12/26	AM
H10	12/26	PM	12/28	PM
H11	12/29	AM	1/2	AM
H12	1/2	PM	1/4	PM
H13	1/5	AM	1/7	AM
H14	1/7	PM	1/9	PM
H15	1/10	AM	1/12	AM
H16	1/12	PM	1/14	PM
H17	1/15	AM	1/17	AM
H18	1/17	PM	1/19	PM
H19	1/20	AM	1/22	AM
H20	1/22	PM	1/24	PM
H21	1/25	AM	1/27	AM
H22	1/27	PM	1/29	PM

Philadelphia, Pa.-Belmont Plant Composite ID#	Period Covered			
P1	11/27	AM	11/29	AM
P2	11/29	PM	12/1	PM
P3	12/2	AM	12/4	AM
P4	12/4	PM	12/6	PM
P5	12/7	AM	12/9	AM
P6	12/9	PM	12/11	PM
P7	12/12	AM	12/14	AM
P8	12/14	PM	12/16	PM
P9	12/17	AM	12/19	AM
P10	12/19	PM	12/21	PM
P11	12/22	AM	12/24	AM
P12	12/24	PM	12/26	PM
P13	12/27	AM	12/29	AM
P14	12/29	PM	12/31	PM
P15	1/1	AM	1/3	AM
P16	1/3, 1/4, 1/8			
P17	1/9	AM	1/11	AM
P18	1/11	PM	1/13	PM
P19	1/14	AM	1/16	AM
P20	1/16	PM	1/18	PM
P21	1/19	AM	1/21	AM
P22	1/21	PM	1/26	AM
P23	1/27	AM	1/30	AM
P24	1/30	PM	2/1	PM
P25	2/2	AM	2/4	AM
P26	2/4	PM	2/6	PM
P27	2/7	PM	2/10	PM
P28	2/11	AM	2/13	AM
P29	2/13	PM	2/15	PM
P30	2/16	AM	2/16	AM
P31	2/18	PM	2/20	PM
P32	2/21	AM	2/23	AM
P33	2/23	PM	2/24	AM

TABLE 2

Hall Detector Detection Limits For Compounds Identification In Huntington/Philadelphia Organics Monitoring Program

Compounds	ppb
Methylene chloride	0.01
1,1-Dichloroethane	0.01
Chloroform	0.004
Carbon tetrachloride	0.005
1,2-Dichloropropane	0.005
Trichloroethylene	0.003
1,1,2-Trichloroethane	0.01
Tetrachloroethylene	0.006
Trans-1,3-Dichloropropane	0.008
Bromodichloromethane	0.008
1,1,2,2-Tetrachloroethane	0.007

TABLE 3

Results For Volatile Organics Analysis of
Huntington Waster Supply (µg/l)

	Composite ID#										
	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10	H11
Chloroform	--	--	0.14	0.13	0.18	0.04	--	--	--	--	0.34
Carbon tetrachloride	*T	*T	*T	--	*T	0.09	0.07	0.06	0.05	0.04	0.03
1,2-Dichloropropane	0.06	--	--	--	--	--	*T	--	--	--	--
Trichloroethylene	0.03	0.06	0.05	--	--	--	*T	*T	0.03	0.04	0.02
Tetrachloroethylene	0.10	0.20	--	--	--	*T	0.07	0.09*	0.08	0.06	0.05
1,1,1-Trichloroethane	*T	0.57	--	--	*T	--	*T	0.08*	0.06	0.05	0.07
Bromodichloromethane	--	--	--	--	--	--	*T	--	--	--	0.05
1,1,2-Trichloroethane	--	--	--	--	--	--	--	--	*T	--	--
1,1-Dichloroethane	--	--	--	--	--	--	*T	*T	--	--	--

	H12	H13	H14	H15	H16	H17	H18	H19	H20	H21	H22
Chloroform	0.9	0.3	1.7	2.1	1.8	1.0	1.8	3.0	.72	?	1.9
1,2-Dichloroethane	T	--	--	--	--	--	--	--	--	--	--
1,1,1-Trichloroethane	T	T	T	0.2	0.1	--	--	--	--	--	--
Carbon tetrachloride	T	T	T	0.01	0.06	0.06	--	--	--	--	--
Bromodichloromethane	--	--	T	T		T	--	--	--	--	?
Trichloroethylene	T	T	T	0.06	0.04	0.06	--	--	--	--	--
Tetrachloroethylene	T	T	--	0.06	0.03	0.1	--	--	--	--	--
Trichlorofluoromethane[1] and/or 1,1-Dichloroethylene	--	--	--	1.0	1.4	--	--	--	--	--	--
1,1,2,2-Tetrachloroethane	--	--	--	--	T	T	--	--	--	--	--
1,2-Dichloropropane	--	--	--	--	--	T	--	--	--	--	--
1,1-Dichloroethane	--	--	T	---	--	--	--	--	--	--	?

[1] calculated based upon chloroform response
? possibly present, not confirmed (low level)
T trace at or near detector level generally $\leq$ 0.1 ppb
* most probable compound identification - see narrative in report

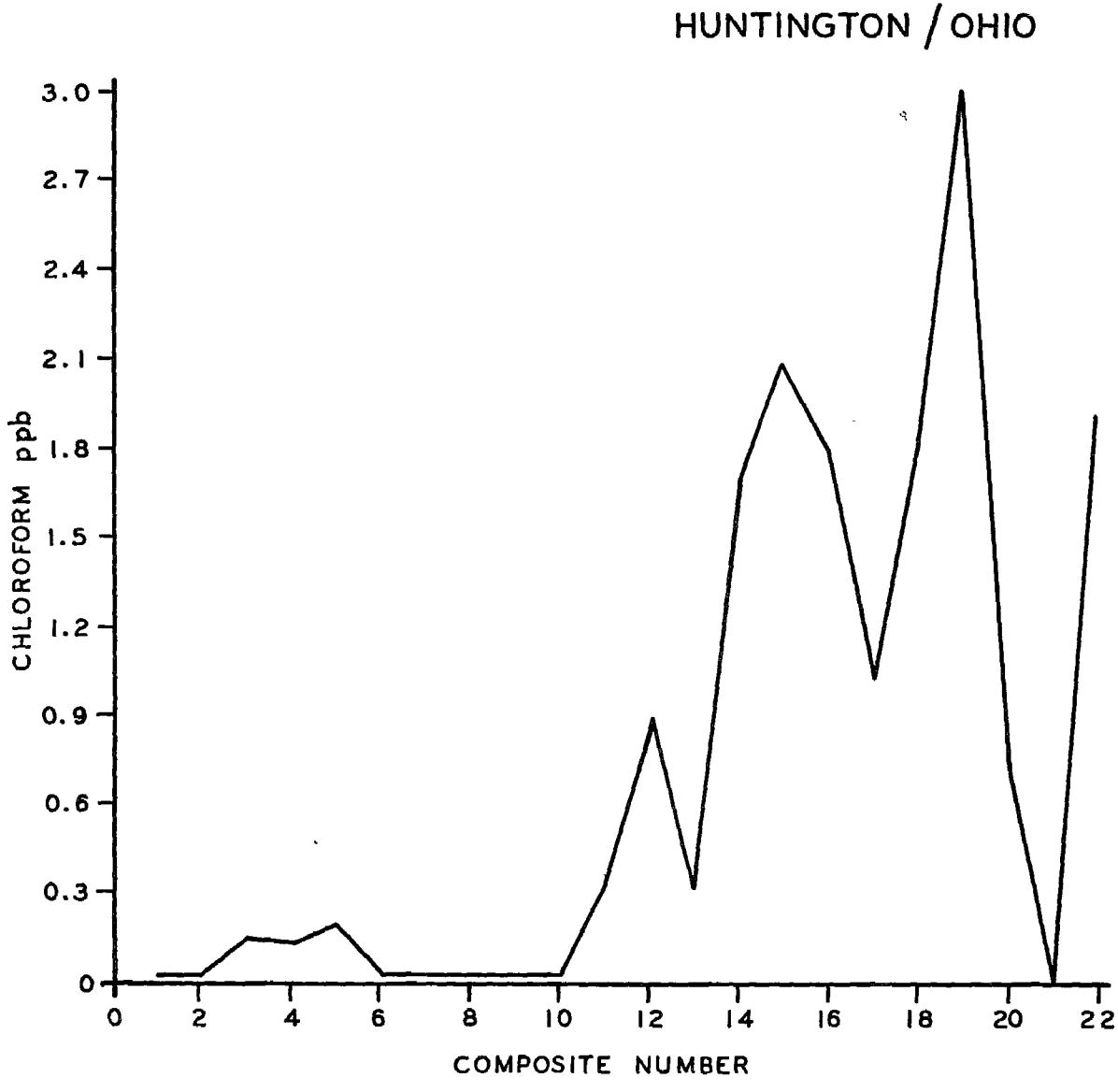
TABLE 4

Results For Volatile Organics Analysis of
Philadelphia Water Supply (µg/l)

Compounds Found	Composite ID# P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	P13	P14	P15	P16	P17
Chloroform	--	0.34	7.5	10.0	6.8	1.2	9.5	3.2	3.2	1.9	2.1	1.4	1.6	0.6	5.3	4.7	3.4
Carbon tetrachloride	--	T	T	0.16	--	--	--	T	0.17*	0.19*	0.23*	--	--	--	--	--	--
1,2-Dichloropropane	--	--	--	--	0.06	--	0.01	--	--	--	--	--	--	--	--	--	--
Trichloroethylene	0.06	0.08	0.12	0.11	0.09	0.12	0.09	0.13	0.11	0.12	0.20	0.1	0.1	0.2	0.2	0.2	0.3
Tetrachloroethylene	0.07	0.07	0.16	0.15	0.14	0.20	0.12	0.12	0.13	0.14	0.30	T	T	--	0.1	0.3	0.2
1,1,1-Trichloroethane	0.14	0.18	0.19	0.19	0.28	0.22	0.24	T	0.20*	0.22*	0.28*	0.05	--	--	0.2	0.3	0.3
Bromodichloromethane	T	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Trans-1,3,-Dichloropropane	--	--	--	--	*	--	--	--	--	--	--	--	--	--	--	--	--
1,1,2,2-Tetrachloroethane	0.23	0.23	0.13	0.13	0.12	0.13	--	0.32	0.18	0.19	0.33	T	0.3	0.1	0.5	1.9	0.2
Methylene chloride	*T	*T	*T	*T	*T	*T	*T	*T	*T	*T	0.87	--	--	--	--	--	--
1,1-Dichloroethane	*T	*T	*T	*T	*T	*T	*T	*T	*T	*T	0.47*	--	--	--	--	--	--
Toluene	--	--	--	--	--	--	--	--	--	--	--	?	--	--	--	--	--

	P18	P19	P20	P21	P22	P23	P24	P25	P26	P27	P28	P29	P30	P31	P32	P33
Chloroform	3.2	1.6	3.3	?	13.5	4.3	2.8	2.0	0.95	?	3.2	3.5	2.5	0.90	0.38	0.90
1,1,1-Trichloroethane	--	--	0.11	0.15	0.13	--	0.13	0.13	--	?	?	--	?	0.15	0.10	0.21
Trichloroethylene	--	0.22	0.22	0.34	0.31	--	--	?	--	?	?	--	?	?	0.29	0.50
Tetrachloroethylene	--	0.22	0.22	0.51	0.57	--	T	0.28	0.28	?	0.54	--	0.44	--	0.54	0.82
Bromodichloromethane	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
1,1,2,2-Tetrachloroethane	--	--	--	--	--	--	?	?	?	--	--	--	--	--	--	--
1,1-Dichloroethane	--	--	--	--	--	--	--	?	?	--	?	--	--	--	--	--

* most probable compound identification - see narrative in report
T trace at or near detection level
? unsure of the true identity or quantity


HUNTINGTON / OHIO
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8
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12
14
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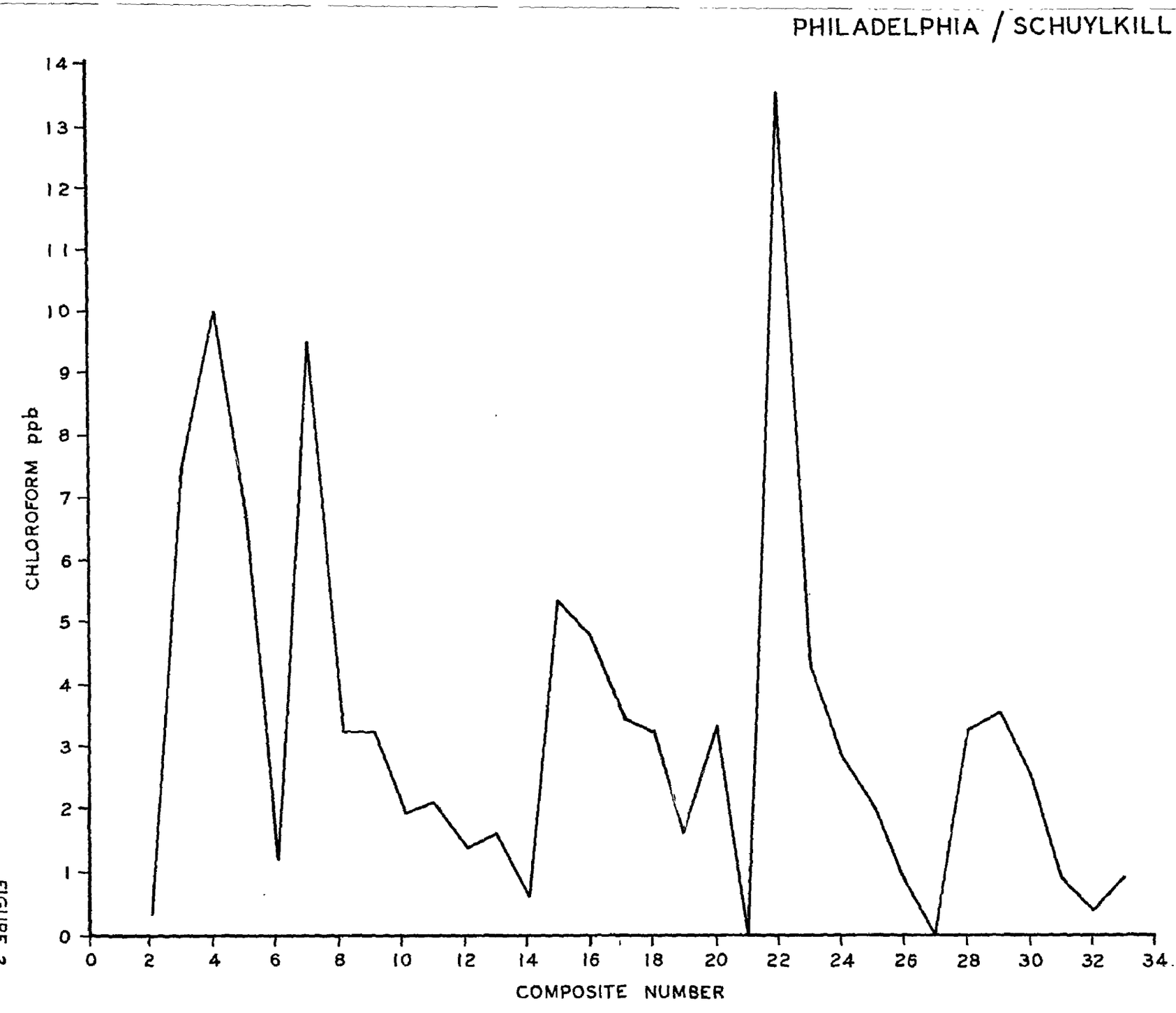
18
20
22
COMPOSITE NUMBER

FIGURE 1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COMPOSITE NUMBER

FIGURE 2

PHILADELPHIA / SCHUYLKILL

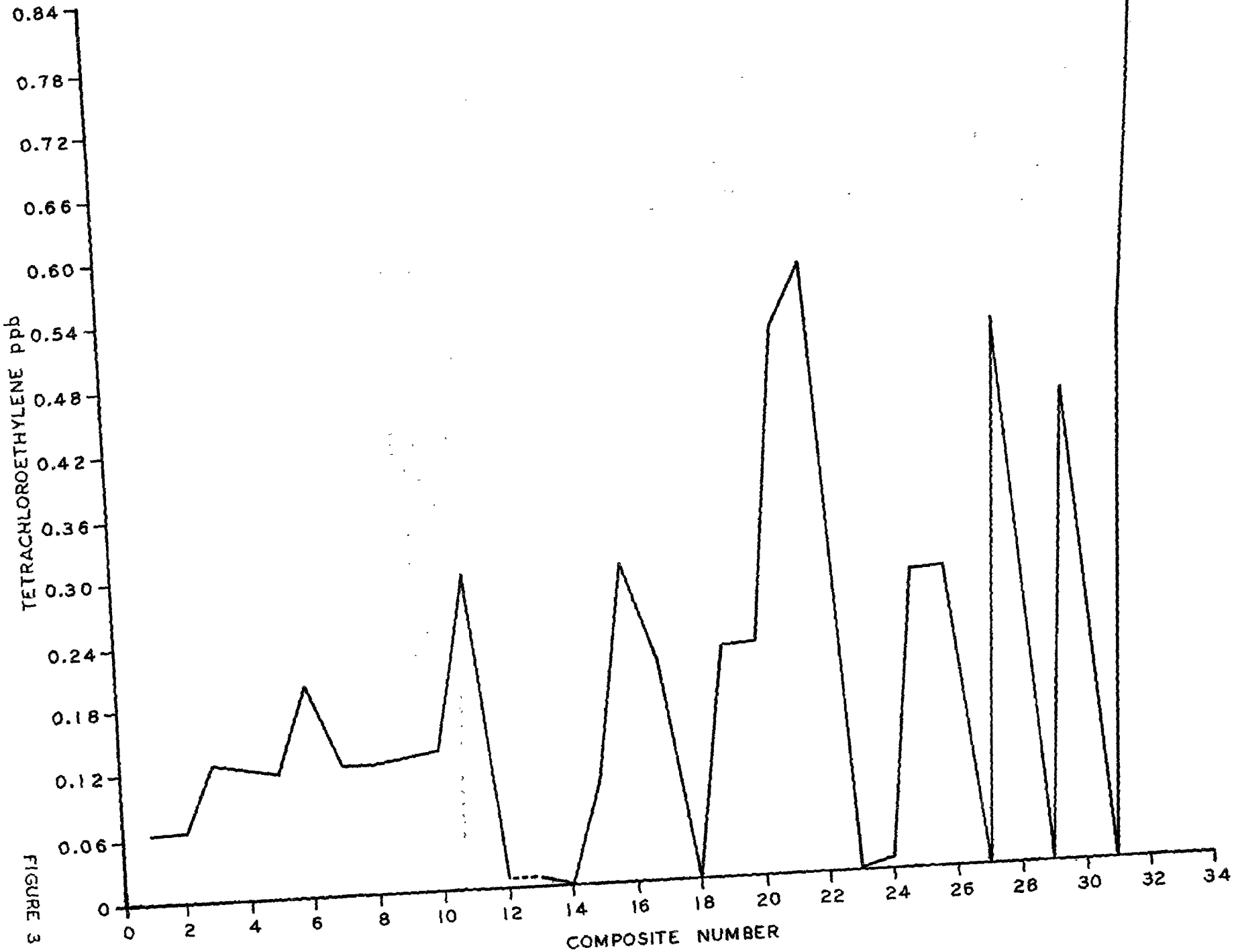

FIGURE 3

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-903/9-81-003		

4. TITLE AND SUBTITLE	5. REPORT DATE
Survey of the Huntington and Philadelphia River Water Supplies for Purgeable Organic Contaminants	November 1980
	6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Frederick A. Dreisch, Marilyn Gower, and Thomas O. Munson	

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
U.S. Environmental Protection Agency, Region III Central Regional Laboratory 839 Bestgate Road Annapolis, Maryland 21401	11. CONTRACT/GRANT NO. N/A

12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Same	14. SPONSORING AGENCY CODE EPA/903/00

15. SUPPLEMENTARY NOTES

16. ABSTRACT

Raw river water from the Schuylkill and Ohio Rivers was analyzed for purgeable organic halogenated and non-halogenated compounds. The Schuylkill River water contained chloroform ranging from zero to 13.5 µg/l (ppb). Eleven (11) additional compounds occurred at <1 ppb values. The Ohio River water contained nine (9) identifiable compounds with all the compounds present below 1 ppb with the exception of chloroform which ranged from zero to 3.0 ppb. No non-halogenated compounds were found in either river with the exception of toluene in one Schuylkill River sample. Among the more prominent compounds found in both rivers were: (1) chloroform, (2) carbontetrachloride, (3) trichloroethylene, (4) tetrachloroethylene, and (5) 1,1,1-trichloroethane.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Water Supply Survey Purgeable Hydrocarbons Huntington, W. Va./Ohio River Philadelphia, Pa./Schuylkill River	Water Supply Purgeable Hydrocarbons Chloroform Trichloroethylene	

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release to Public	UNCLASSIFIED	21
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (9-73)