Analysis of Trace Organics in the Aquatic Environment

Editors

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PREFACE

The importance of environment assessment pollution control to protect and upgrade environmental quality, has led to the necessity and demand in the study and monitoring of the pollutants in the aquatic environment. All research and surveillance activities to assess the quality of the environment depend upon the availability of analytical data, since scientific conclusions and political decisions on environmental issues are based on their interpretation. Questionable data result in questionable conclusions.

One of the key elements of effective quality assurance to ensure reliable data generation is the availability of reliable analytical methods and their appropriate application. Many books have been published which cover measurement techniques for chemical constituents. The present book is part of a multi-volume work which is designed to provide, in a single source, theories and important analytical techniques and methodologies necessary for understanding and determining the trace organic contaminants in various compartments of the aquatic environment.

The first three volumes dealt with the analysis of pesticide residues and their toxic degradation products in the aquatic environment. This final volume covers the toxaphene, organometallic compounds, humic acids, and related substances and industrial chemicals such as PCBs, phenols, chlorinated dioxins, and volatile organics.

The book is intended to serve as a general reference for university and college students as well as a practical reference for environmental chemists and technologists. It provides sufficient theoretical and practical detail to ensure that a reader would be able to determine trace constituents in an accurate manner. Each chapter covers practical applications of techniques, and provides state-of-the-art methodologies in current use with special reference to sampling, concentration, cleanup, quantitative and confirmatory analysis, etc. The detail provided is such that it should not be necessary to refer to other protocols or manuals to set up a particular method.

The authors of the chapters have attempted to emphasize the practical aspects, and with the amount of information provided, it should be possible to make critical comparisons of the available methods in order to satisfy specific needs.

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THE EDITORS

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Dr. Afghan has conducted independent research for over 20 years and has also directed research activities related to analytical chemistry, radiochemistry, and application of electron microscopy to biological studies.

He has published and/or co-authored over 50 technical papers and reports. The work has included the development of new and/or improved methods for analysis of inorganic and organic trace constituents in environmental samples. The techniques utilized included polarographic and related electroanalytical techniques, spectrophotometry, spectrofluorometry, and luminescence, high pressure liquid chromatography, gas chromatography, and gas chromatography/mass spectrometry. He has also written chapters for books and has co-edited books and symposium proceedings.

Dr. Afghan has contributed significantly to the promotion of analytical chemistry and international cooperation in scientific matters. He has served as a member and/or chairperson of various working groups devoted to standardization of chemical and biochemical water quality parameters. He has served in an official capacity to professional societies such as the Chemical Institute of Canada, the American Society for Testing and Materials, and the International Standards Organization.

Dr. Afghan has lectured widely in Canada, the U.S., Europe, and Australia on advances in analytical chemistry.

Alfred S. Y. Chau, M.Sc., is Chief, Quality Assurance Program at the Research and Application Branch National Water Research Institute, Canada Centre for Inland Waters. He obtained his B.Sc. degree from the University of British Columbia in 1961 and his M.Sc. degree from Carleton University, Ottawa, Ontario, Canada.

From 1965 to 1970 he held the position of pesticide analyst in the Department of Agriculture. At the Department of the Environment he was Head of the Organic Laboratories Section and then Head of the Special Services Section. He has held his current position since 1987.

Mr. Chau was the General Referee and is a member of the Association of Official Analytical Chemists, a Fellow of the Chemical Institute of Canada, a Life Fellow of the International Association, U.K., and Fellow of the American Biographical Institute, and is currently on the Advisory Board, National Division of the American Biographical Institute, Chairman of several binational and multiagency quality assurance committees and a member of the Canadian Advisory Committee on Quality Assurance Management, and International Standards Organizations. Mr. Chau is listed in 23 international books of recognition including *Who's Who in the World, Who's Who in America, Personalities of America, International Who's Who of Contemporary Achievement, and International Who's Who of Intellectuals.* He has published over 100 scientific papers in the areas of analytical methodologies, research, and development of certified reference materials for organic and inorganic contaminants in lake sediments.

Further, Alfred Chau is well known as an accomplished nature artist having work admitted to regional and national juried exhibitions such as the Ontario Society for Artists Touring Exhibition (Collectors' Choice Awards, 1981), Ontario Jury Exhibition, 1985; Etobicoke Civic Centre Art Competition (CCAC Award, 1984), World Wildlife Fund Art Auction, 1982, Canada Nature Art National Tour 1982-84. His works are in many private and permanent collections including the Dofasco Canadian Art Collection, Hiram-Walker Art Collection, the Beckett Collection, and IBM.

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Chapter 1

ANALYSIS OF VOLATILE HALOGENATED AND PURGEABLE ORGANICS

Barry G. Oliver

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I. INTRODUCTION

A. Production and Uses

Interest in the presence of volatile halogenated compounds in water has been high for several years because of the discovery of the ubiquitous presence of trihalomethanes, THMs, in chlorinated drinking water in several countries.[1-4] The THMs, chloroform, bromodichloromethane, chlorodibromomethane, and bromoform, are formed from the reaction of chlorine with naturally occurring organics such as fulvic acid,[5-8] algae,[9-11] etc., during water disinfection. There is also concern about other volatile halogenated compounds that are *not* water chlorination byproducts such as tetrachloroethylene[12] and carbon tetrachloride[4] because they have been found at high concentrations in some drinking waters from groundwater sources.

The purgeable halogenated compounds on the U.S. Environmental Protection Agency's priority pollutant list are shown in Table 1 together with some of their physical properties.[13] In general the compounds have low boiling points (<200°C), high vapor pressures (≥1 torr), low water solubilities, and fairly low octanol/water partition coefficients.

U.S. production figures for some of the compounds are shown in Table 2.[14] It can be seen that massive quantities of these materials are produced in the U.S. which is only a fraction (1/2 to 1/5) of world production. Some of the compounds are used as chemical intermediates, for example, 1,2-dichloroethane in the production of vinyl chloride which in turn is used to produce polyvinyl chloride; chloroform and carbon tetrachloride in the manufacture of fluorohydrocarbons. Many of the compounds are used as solvents in such applications as paint, extraction or reaction media solvents, and in dry cleaning, vapor degreasing, metal cleaning, and textile processing. Metal cleaning and dry cleaning are the first and second largest solvent applications.[14]

The chlorinated hydrocarbons are produced by a variety of chlorination reactions involving hydrocarbon feedstocks such as methane (natural gas), ethane, ethylene, propylene, and propane.[14] Chlorination of benzene in the presence of a catalyst such as ferric chloride is used to produce the chlorinated benzenes. Industrial solvents are to a large extent recovered and total production represents handling losses to the environment. On the other hand, the quantity of chemical intermediates that enter the environment is only a small fraction of the annual production. It should be noted that all THMs produced during water chlorination (drinking or cooling water) will be lost to the environment.[15] In addition to anthropogenic sources, compounds such as CH_3Cl and CH_3Br are thought to have large natural sources mainly in the oceans.[16]

B. Environmental Distribution

1. Ambient Water, Sediments, and Biota

The concentration of volatiles in ambient waters is usually quite low in the ng/L or ppt range. Pearson and McConnell[17] reported C_2HCl_3, C_2CL_4, and CCl_4 concentrations in the 100 to 300 ng/l range for Liverpool Bay, England seawater. Hammer et al.[18] showed that the CCl_3F concentration averaged 20 ng/l in the Gulf of Maine, U.S. Kaiser and Valdmanis[19] report concentrations from 11 to 76 ng/l for CCl_2F_2, $CHCl_3$, CCl_4, and C_2HCl_3 in Lake Erie, Canada. Concentrations of dichlorobenzenes ranged from 2 to 64 ng/l for Lakes Huron and Ontario, Canada.[20] Somewhat higher concentrations in the μg/l or ppb range are found in wastewater effluents[20,21] or in rivers close to outfalls.[22,23,24]

A mass balance study on Lake Zurich, Switzerland on the least volatile purgeable compound in Table 1, 1,4-dichlorobenzene, showed that the major environmental pathway of this compound was volatilization to the atmosphere.[25] Using laboratory studies, Dilling et al.[26] showed that the time required for 50% evaporation from water of many of the chemicals in Table 1 was less than 1 h. Mesocosm experiments[27] also showed that the major process removing these compounds from water is volatilization. The removal of these purge-

Table 1
PURGEABLE HALOCARBONS IN THE U.S. ENVIRONMENTAL PROTECTION AGENCY'S PRIORITY POLLUTANT LIST AND SOME OF THEIR PHYSICAL PROPERTIES[13]

Chemical	Formula	Boiling Point at 760 mm (°C)	Vapor pressure at 20°C (torr)	Water solubility at 20°C(mg/l)	Log octanol/water partition coefficient
Chloromethane	CH_3Cl	−24.2	3765	6450—7250	0.91
Bromomethane	CH_3Br	4.6	1420	900	1.1
Dichlorodifluoromethane	CCl_2F_2	−29.6	4310	280	2.2
Vinyl chloride	C_2H_3Cl	−13.4	2660	60	0.6
Chloroethane	C_2H_5Cl	12.3	1000	5740	1.5
Methylene chloride	CH_2Cl_2	39.8	362	17000	1.3
Trichlorofluoromethane	CCl_3F	23.8	667	1100	2.5
1,1-Dichloroethylene	$C_2H_2Cl_2$	37	591	400	1.5
1,1-Dichloroethane	$C_2H_4Cl_2$	57.3	180	5500	1.8
Trans-1,2-dichloroethylene	$C_2H_2Cl_2$	47.5	200	600	1.5
Chloroform	$CHCl_3$	61.7	151	8200	2.0
1,2-Dichloroethane	$C_2H_4Cl_2$	83.5	61	8690	1.5
1,1,1-Trichloroethane	$C_2H_3Cl_3$	74.1	96	480—4400	2.2
Carbon tetrachloride	CCl_4	76.5	90	785	2.6
Bromodichloromethane	$CHBrCl_2$	90	50	—	1.9
1,2-Dichloropropane	$C_3H_6CL_2$	96.8	42	2700	2.3
Trans-1,3-dichloropropene	$C_3H_4Cl_2$	112	25	2800	2.0
Trichloroethylene	C_2HCl_3	87	57.9	1100	2.3
Dibromochloromethane	$CHClBr_2$	120	15	—	2.1
1,1,2-Trichloroethane	$C_2H_3Cl_3$	133.8	19	4500	2.2
Cis-1,3-dichloropropene	$C_3H_4Cl_2$	104.3	25	2700	2.0
2-Chloroethylvinyl ether	C_4H_7OCl	108	26.8	15000	1.3
Bromoform	$CHBr_3$	149.5	10	3100	2.3
1,1,2,2-Tetrachloroethane	$C_2H_2Cl_4$	146.2	5	2900	2.6
Tetrachloroethylene	C_2Cl_4	121	14	150—200	2.9
Chlorobenzene	C_6H_5Cl	132	8.8	500	2.8
1,3-Dichlorobenzene	$C_6H_4Cl_2$	173	2.3	123	3.4
1,2-Dichlorobenzene	$C_6H_4Cl_2$	180.5	1.5	145	3.4
1,4-Dichlorobenzene	$C_6H_4Cl_2$	174	0.6	79	3.4

Table 2
U.S. PRODUCTION FOR SOME VOLATILE CHLORINATED HYDROCARBONS[14]

Compound	Thousands of metric tons 1970	1976
Vinyl chloride	1534	2289
1,1-Dichloroethylene	54	70
1,2-Dichloroethane	3773	4773
Chloromethane	192	168
Methylene chloride	182	227
Chloroform	109	125
Carbon tetrachloride	459	385
1,1,1-trichloroethane	166	234
Trichloroethylene	274	127
Tetrachloroethylene	320	304
Chlorobenzene	—	163
1,2-Dichlorobenzene	—	68
1,4-Dichlorobenzene		

able compounds during wastewater treatment occurs mainly by volatilization; biodegradation or adsorption to solids are minor processes.[28] When effluents containing volatile chemicals are discharged at depth (below the waterbody surface) or beneath an ice cover,[29] volatilization is restricted and the compounds make excellent tracers for industrial plumes in lakes[22] and in the ocean.[30] Some exchange of these materials between water and the atmosphere does occur,[31] and some recycling takes place since measurable concentrations of these compounds are found in rainwater.[17] But the ultimate fate of these compounds appears to be destruction in the troposphere by reaction with hydroxyl radicals or photodecomposition or reaction with ozone in the stratosphere.[32] The destruction in the stratospheric ozone layer by reactions with freons and other halocarbons is still a matter of controversy.[33,34]

The concentrations of purgeable halocarbons in ambient lake and river sediments should be low because partitioning onto solids is not a favored process for these chemicals.[35,36] Sediments in Liverpool Bay were in the low μg/Kg or ppb range for CCl_4, $CHCl_3$, C_2Cl_4, and C_2HCl_3.[17] Great Lakes sediments[20] and southern Californian coastal sediments[21] contained similar concentrations (low ppb) for dichlorobenzenes. Exceptionally high sediment perchloroethylene concentrations up to percent levels have been reported in the St. Clair River, Canada, but this was due to direct spillage of the solvent into the river.[37]

Similarly, concentrations of these compounds in biota and fish should not be excessively high because of their low octanol/water partition coefficients, K_{ow}s, and low bioconcentration factors, BCFs. Mackay[38] has fitted the equation, $\log BCF = \log K_{ow} - 1.32$, to a set of literature data. From the K_{ow} data in Table 1 ($\log K_{ow}$, 0.6 to 3.4), the maximum bioconcentration factor in fish for these compounds should be about 100. Values in good agreement with this equation for bluegill sunfish[39] and for rainbow trout[40] have been measured in the laboratory. Oliver and Niimi[41] have reported somewhat higher BCFs, 270 to 420, for dichlorobenzenes in rainbow trout exposed to environmental concentrations of these chemicals. Since typical environmental water concentrations for these chemicals are in the low ppt range, the maximum chemical concentrations in fish should be in the low ppb range. Field studies have shown low ppb levels of dichlorobenzenes in lake trout from the Great Lakes[20] and in Dover sole from southern California.[21] Similar low concentrations of $CHCl_3$, CCl_4, C_2HCl_3, and C_2Cl_4 have been found in various species of fish and other biota from Liverpool Bay,[17] from the U.S.,[42] and from Norway.[43] Biomagnification of these types of

chemicals does not occur because of the rapid establishment of equilibrium between fish and water concentrations of the chemicals.[17,41] Thus tissue residue levels are governed mainly by the chemical concentration in the water and are not significantly influenced by the fish's food.[41]

2. Drinking Water

The contamination of drinking water with purgeable organics is a problem in many countries. Table 3 shows the concentrations of trihalomethanes in several of these countries.[2,3,44-47] Some limited data are available for other countries,[4] but only fairly extensive studies are included in the table. In general, all water that is disinfected with chlorine contains THMs because of the reaction of chlorine with natural organic matter. Concentrations up to several hundred ppb have been observed in several locations (Table 3). Chlorinated groundwaters contain somewhat lower THM concentrations than chlorinated surface waters from the same region. Groundwaters usually have a much lower total organic carbon (TOC) concentration than surface waters, so usually contain less THM precursor material.[48] Also, groundwaters are usually not as contaminated with bacteria as surface waters so they are not as heavily chlorinated.

The concentration of THMs in water supplies has been related to TOC, chlorine dose, pH, temperature, and bromide concentration — the higher the value for any of these parameters the higher the yield.[8,49-52] The presence of bromide in the water not only leads to the formation of the brominated THMs but also has been shown to increase the total THM yield.[51,53] The bromide reacts with hypochlorous acid to yield hypobromous acid ($Br^- + HOCl \rightarrow HOBr + Cl^-$) which is a more efficient and faster reacting halogenating agent. Several water supplies have reported quite high concentrations of brominated THMs.[2,54] Chlorination of seawater yields almost exclusively $CHBr_3$[55] because of the presence of high bromide concentrations.

High concentrations of purgeable organics, which are *not* chlorination byproducts, have been found in some drinking waters which use groundwater as the source. For example, in Dubendorf, Switzerland, average tetrachloroethylene concentrations in the water supply in one part of the city were 69 ppb.[12] One well from which the city drew its water had average C_2Cl_4 concentrations of 76 ppb.[12] Similarly, C_2Cl_4 was found at concentrations up to 300 ppb in groundwater wells used by the city of Kalamazoo, Michigan for drinking water.[56] Contamination from dry cleaning establishments were the cause of the above two problems. In Nicaragua, CCl_4 concentrations of 1.1 ppb were found in a city's water supply and tests conducted on source wells close to an industrial park showed concentrations up to 2500 ppb CCl_4.[4] More and more contaminated groundwater aquifers in the vicinity of industrial dumps are being discovered, especially in the southern U.S. where surface water supplies are in short supply.[57,58,59]

Groundwater contamination is usually the result of improper disposal of industrial chemicals. Most C_1 and C_2 chlorinated hydrocarbons have little affinity for soils[34] so, when they are dumped on the soil surface, their movement through the soil with water is only minimally retarded.[60,61,62] This mobility in the soil can result in the contamination of groundwater aquifers.[4,12,56] Most of these chemicals are highly resistant to biological degradation so they pass through the soil unaltered.[62]

C. Health Effects

1. Toxicity

The toxicity of these chemical is low to moderate so direct toxic effects are not expected at environmental concentrations.[63] Occupational exposure to high concentrations or improper use of these chemicals in confined spaces can lead to toxic responses.[64]

Table 3
TRIHALOMETHANE CONCENTRATIONS (μg/l) IN WORLD DRINKING WATERS

Location	Number of cities	$CHCl_3$		$CHBrCl_2$		$CHBr_2Cl$		$CHBr_3$		Ref.
		Range	Median	Range	Median	Range	Median	Range	Median	
U.S.	80	<0.1—311	21	<0.2—116	6	<0.4—100	1.2	<1.0-92	<1.0	2
Texas, U.S. (Ground waters)	11	1.1—14	2.5	ND[a]—53	0.3	ND—173	ND	ND-242	ND	44
Texas, U.S. (Surface water)	14	20—882	190	31—89	49	ND-125	11	ND-53	ND	44
Canada	70	ND-3	9.0	ND-15	1.0	ND-6.5	ND	ND-2.1	ND	3
Ontario, Canada	22	2—121	22	ND-9	4.0	ND-5	ND	NOT MEASURED		45
West Germany	39	0.1—52	2.5	ND-3.4	ND	ND	ND	ND	ND	46
Belgium (Ground waters)	9	ND-26	2.5	0.2—5.3	0.8	0.2—5.5	1.5	ND-2.7	0.7	47
Belgium (Surface waters)	7	4.4—106	49	2.4—38	20	0.4—13	5.8	ND-0.7	ND	47

[a] Not detected.

2. Carcinogenic and Mutagenic Responses

Reviews of the carcinogenic and mutagenic properties of these chemicals have been compiled by Fishbein.[65,68] Vinyl chloride has been clearly implicated in causing angiosarcoma of the liver in occupationally exposed humans.[65] Increased incidences of cancer of the pancreas, lung, and brain also occur in occupationally exposed workers.[65] In addition to vinyl chloride, 1,1-dichloroethylene, trichloroethylene, tetrachloroethylene, chloroform, carbon tetrachloride, 1,1,2-trichloroethane, and 1,1,2,2-tetrachloroethane have been shown to cause cancer (mainly of the liver) in experimental animals.[60,61] These compounds have also been demonstrated to be mutagenic in several bacterial assays.[65,66,69] Very little data on the carcinogenic or mutagenic properties of the fluorocarbons and the chlorobenzenes is currently available.[68]

3. Epidemiologic Studies and Risk Factor Calculations

Since the discovery of the ubiquitous presence of THMs in drinking water, several studies have been conducted to see whether exposure to chlorinated drinking water (and the chlorination byproducts) poses an additional cancer risk.[70-81] Because of the difficulties in the design of epidemiological studies such as the presence of confounding factors, inaccurate records of exposure levels, etc., these studies have not provided conclusive proof of the association between chlorinated compounds in drinking water and increased cancer risk.[82] But the evidence from these studies suggests the possibility of a causal relationship for rectal cancer and, to a lesser extent, for bladder and colon cancer.[92]

Crouch et al.[83] have attempted to calculate cancer risk factors for several U.S. drinking waters using analytical data for specific organics plus carcinogenic potency data for these organics from animal studies. The total cancer risk was assumed to be the sum of the risks for the individual chemicals. A large portion of the total risk factor was found to be due to the purgeable chlorinated organics because of their presence at reasonably high (μg/l) concentrations. The major deficiency of the study was the uncertainties caused by lack of good dose-cancer response data for the brominated trihalomethanes. The investigators concluded that the consumption of certain U.S. drinking waters might pose moderately high risk.[83]

4. Exposure Routes and Doses

A person's total daily intake of a chemical will be the sum of his water, air, and food exposure. Volatile halogenated compounds have concentrations in the range μg/l for water (~2 l consumed/d), μg/m^3 for air, (~22 m^3 consumed/d), and μg/kg for food (~2 kg consumed/d).[84] For a typical North American the daily intake of $CHCl_3$ is about 60 μg — 67% from water, 23% from air, and 10% from food.[84] For CCl_4 the typical daily dose is 7.7 μg — 23% from water, 62% from air, and 15% from food.[84] For people who consume chlorinated drinking water, their main source of THM exposure will be from their drinking water.[84] If a groundwater is contaminated with, for example, tetrachloroethylene, the major source of this compound will also be the drinking water.[85]

The exposure of rats to $CHCl_3$, CCl_4, and C_2HCl_3 resulted in elevated serum and adipose concentration of these chemicals.[86] The rats quickly reached a steady state concentration after which continued exposure did not lead to increases in tissue or serum concentrations. Within three to six days after exposure was terminated, most of these halogenated compounds had disappeared from the serum and adipose tissue.[86] The analysis of blood from humans exposed to chlorinated drinking water (chloroform concentration ≈100 μg/l) showed that they had higher serum $CHCl_3$ levels than a control group which used unchlorinated ($CHCl_3$ free) water.[87] Serum $CHCl_3$ levels were about 12 μg/l in the exposed group.[87]

From this information it is apparent that exposure to volatile halogenated compounds at doses in the 100 μg/d range leads to chemical concentrations in the body in the μg/kg range. A concentration of chemical at the 1 μg/kg level in the body corresponds roughly to 1000

molecules of chemical per cell.[88] Whether or not long-term exposure to chemicals in this concentration range can cause problems is presently a matter of controversy, but it would seem prudent to reduce our exposure to these chemicals where possible. For example, several methods have been proposed for reducing drinking water THMs: aeration after chlorination; carbon adsorption; flocculation prior to chlorination for precursor removal; ozone, chlorine dioxide, and chloramines as disinfection alternatives, etc.[89-91] The World Health Organization has established a drinking water guideline value of 30 μg/l for chloroform.[92] The Environmental Protection Agency[93] have set 100 μg/l total THMs as the maximum permissible concentration in U.S. drinking waters. A less stringent standard of 350 μg/l has been proposed by the Department of Health and Welfare for Canada.[94]

II. GENERAL ANALYSIS PROCEDURES

A. Sampling and Sample Preservation

The collection of an appropriate representative sample is a vital part of performing an environmental assessment of a chemical. For water, grab samples are most commonly used, but the preferred method for sampling is to collect a composite sample which integrates the effluent, stream, or river over a much longer time frame, e.g., days. Commercially available composite samplers have been tested for volatiles and they collect the sample with minimal losses.[95] But the sample vessels in these devices are open so sample storage over hours or days will lead to volatilization losses. Westrick and Cummins[96] have designed a composite sampler for effluents. The collection vessel in this devise is a modified 2-l graduated cylinder into which a Teflon® float is snugly fitted. A series of samples is introduced through an inlet at the base of the cylinder using a switching valve, and the float moves upward as the sample volume increases. The float seals the liquid surface inhibiting volatilization losses. More recently Tigwell et al.[97] have combined a multichannel positive displacement Teflon® and glass sampler with the cylinder-Teflon® float collection vessel above, to collect composite samples for volatile organics analyses. Unfortunately these two composite samplers are not currently commercially available.

Recently Blanchard and Hardy[98] have proposed a new method to obtain time-weighted-average concentration values for volatiles in water. The method is based on the permeation of volatile organics through a silicon polycarbonate membrane and should prove very useful with further development.

Bottles used for sample collection and storage should be filled to overflowing and sealed with Teflon®-faced silicon rubber septa. Samples stored at room temperature in this way were shown to be stable for at least 8 to 10 days.[99] Partially filled bottles can be stored at 4°C for at least 2 days without significant losses.[95] It is recommended that water samples be stored with as little headspace as possible at ≈4°C and be analyzed within 1 week.

Because these compounds have a low tendency for adsorption or bioconcentration the most important compartment in the aquatic ecosystem will be the water phase.[100] However, if it is necessary to analyze sediments, fish, or other biota for purgeable organics, the samples should be sealed in glass jars with aluminum- or Teflon®-lined caps and frozen on collection. Amin and Narang[101] have shown that sediment samples could be stored up to 90 days if methanol was added at the time of collection. Untreated samples should be analyzed within 7 days of collection to minimize volatilization losses.

B. Extraction, Concentration, and Cleanup

1. Sediments and Fish

Very few methods have been tested for determination of volatile organics in sediments and fish. As mentioned earlier, this is primarily because only a limited amount of partitioning into these phases in the aquatic environment is expected. The methods that have been used fall into two categories — headspace analysis and solvent extraction.

Speis[102] has tested the purge-and-trap technique for sediments (purge-and-trap methodology will be discussed later). A sediment slurry consisting of 15 g of sediment in 100 ml of water is heated to 80°C and purged with helium (60 ml/min) for 4 min. Recoveries from the Tenax trap for sediments spiked with chlorform, 1,1,1-trichloroethane, toluene, tetrachloroethylene, and chlorobenzene in the concentration range 7 to 200 μg/kg were fairly low, 24 to 52%, but were consistent over the concentration range examined. Minimum detectable levels were about 0.1 μg/kg. Michael et al.[103] have described a similar purge-and-trap procedure for volatiles in soils, sediments, and sludges, and reported recoveries mainly in the 60 to 100% range. Michael et al.[104] have used a similar procedure, for recovery of volatiles from human biological samples. Their recoveries from spiked urine and blood were higher and more consistent than Speis' but their recoveries from spiked adipose tissues (which should behave similarly to fish) varied from 13% for chlorobenzene to 80% for methylene chloride.

Recently, Amin and Narange[101] have described a closed-loop-stripping technique for volatiles in sediments. The method uses a Porapak N cartridge for adsorption of the organics and methanol for elution of the chemicals from the cartridge. Recoveries over 80% were obtained for many volatile priority pollutants.

The best procedure developed to date for fish appears to be the solvent extraction procedure of Ofstad et al.[43] This procedure could also be used for sediments although they did not test it for this purpose. The method consists of extracting 5 g of homogenized fish with a mixture of 5 ml pentane and 20 ml isopropanol in a 100-ml glass-stoppered centrifuge flask. After 2 hr of shaking, enough water is added to the mixture to separate the isopropanol and to bring the pentane layer into the narrow part of the flask. After the addition of a small amount of Na_2SO_4 the flask is centrifuged to separated the phases completely. The pentane layer is transferred to a glass-stoppered 10-ml centrifuge tube. The extract is cooled in ice, treated with 3 ml of concentrated H_2SO_4 to remove the lipids, and centrifuged to separate the layers. The pentane layer is then transferred to another centrifuge tube where it is washed with 3 ml of water and then centrifuged prior to gas chromatographic analysis.

Pearson and McConnell[17] used direct pentane extraction for volatiles in sediments and fish, but did not report recoveries. Ofsted's procedure[43] would appear to be preferable since wet sediments and fish must be used for analysis, so the isopropanol in the solvent mixture would tend to dissolve the water in the sample providing better contact between the solvent and the sample.

Hiatt[105] has reported a vacuum distillation procedure using capillary gas chromatography/mass spectrometry for qualitative analysis of fish tissue for volatiles. The procedure is complex and would appear to require further development and simplification to be useful for quantitative analysis.

2. Resin Adsorption

XAD resins have been used for isolating and concentrating volatile organics from water samples.[106-115] The most commonly used resins are XAD-2 and XAD-4. Various sizes of columns have been used from 1.2 mm × 25 mm[107] up to 2.3 cm × 10 cm[108] and flow rates through the columns are kept at ≈5 to 10 times the column bed volume using nitrogen or helium pressurized water reservoirs. Sized resins with finer mesh sizes (e.g., 100/120 Chromosorb 102 or 104) have been shown to give better recoveries (63 to 100%).[109] In general, a 100-fold concentration factor can be achieved using this technique for the THMs.[109] Higher concentration factors are possible for chlorobenzenes using large water volumes,[114] but breakthrough of more volatile compounds such as chloroform occurs under these conditions.[108,109] Detection limits are generally in the low ppb range. Most investigators purify the resin using sequential soxhlet extraction with methanol, acetonitrile, and diethylether,[106] and store the resin under methanol until use. James et al.[115] reported that the use of the

solvent series methanol-diethyl ether-water sample, instead of the commonly used series methanol-water sample, reduced impurities arising from the XAD-2 resins. Although resin adsorption is widely used in the analysis of medium and low volatility compounds, it has never been widely adopted for volatiles because of breakthrough problems and because it is less convenient than several other procedures.

3. Direct Aqueous Injection

Nicholson et al.[116] were first to report the determination of THMs in water using the direct aqueous injection (DAI) technique. The water sample (9 μl) is injected into a gas chromatograph equipped with a packed column and a scandium tritide electron capture detector. A comparison of the THM results from the DAI method with the purge-and-trap technique showed it produced much higher results (up to a factor of two).[116] This discrepancy was thought to be due to the conversion of nonvolatile THM intermediates to THMs in the high temperature gas chromatographic injector. The DAI method was studied further by Pfaender et al.[117] They used a ^{63}Ni electron capture detector and found that injection of more than 1 μl of water led to loss in detector sensitivity. Therefore, they implemented a bypass valve to vent the water so that larger injection volumes (up to 10 μl) could be used. In agreement with the earlier study, Pfaender et al.[117] showed that the DAI technique produced higher results than the purge-and-trap method. But, they showed that a value close to the true THM could be obtained if the sample was reinjected after purging it for 30 min with purified nitrogen, and subtracting this value from the THM value determined before purging.

The DAI method is simple, since it does not require any sample treatment, and it can easily be automated with a GC autoinjector. Automation would be more difficult if it was nonvolatile THM intermediates. The method detection limit is about 1 μg/l and reproducibility is in the 2 to 5% range. Provided that suitable GC separation can be achieved, the method should work well for THMs and for chlorinated ethanes and ethylenes, but it may be insufficiently sensitive for mono- and dichlorobenzenes. To date, its main use has been for monitoring THM concentrations in drinking water.[8,45,118]

4. Liquid-Liquid Extraction.

Extraction of volatile organics into a water immiscible organic solvent is one of the simplest procedures for sample concentration. The organic contaminants tend to partition preferentially into the organic solvent from the water. The equilibrium between the two phases can be expressed mathematically by the Nernst distribution law:

$$K_D = C_s/C_w \tag{1}$$

where K_D is the distribution coefficient and C_s and C_w are the concentration of the chemicals in the solvent and water, respectively. The extraction efficiency of the solvent can be represented by the following equation:

$$E = \frac{100\ K_D}{K_D + V_w/V_s} \tag{2}$$

where E is the percent extraction efficiency and V_s and V_w are the volumes of the solvent and water. If the distribution coefficient of the chemical is known, it is possible to predict the volume of solvent and the number of extractions required to achieve the desired recovery efficiency using plots such as those developed by Robbins.[119]

The most common solvent used for liquid-liquid extraction (LLE) of volatile organics is pentane,[110,120-127] although hexane,[128] hexane-diisopropylether 1:1,[129] methylcyclohexane,[130,131] and xylene,[132] have also been used. The use of pentane (boiling point 36°C) is