STUDY OF WATER TREATMENT EFFECTS ON ORGANIC VOLATILES IN DRINKING WATER

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SUMMARY

Volatile organics were determined during all stages of the water treatment process in a municipal water works. Analytical parameters for a quantitative procedure were investigated. The method used allows simultaneous determination of both halogenated and non-halogenated purgeable organics. Approximately 70 substances were identified by gas chromatography–mass spectrometry with capillary columns. Well water contained considerable quantities of aliphatic and aromatic substances. Halocarbons were formed during both steps of a double chlorination procedure, but the largest quantity was generated during the first step. Only tetrachloroethylene was present in untreated surface water in significant quantities. Most hydrocarbons were carried through the treatment process from the raw water to the finished water with little change in concentration.

INTRODUCTION

Since organohalogens have been detected in virtually all chlorinated drinking waters[1,2], much attention has been devoted to establish the nature and distribution of such halogenated compounds due to their demonstrated toxic and mutagenic properties[3]. Only a few studies have been undertaken to evaluate the potential of organic substances present in raw water for transformation into organohalogens. This is of interest, since raw water of different origin may contain a wide variety of such precursors. Natural bacterial decay of organic matter, humic acids and synthetic chemicals from industrial point sources are such sources. Only approximately 20% of the total U.S. population is served by domestic wells[4], where chlorination is seldom practiced. It is therefore necessary to look at different sources of raw water.

In a nationwide study[5], concentration levels were established for six halogenated substances in the drinking water supplies of 79 U.S. cities. Considerable controversy has arisen from the practice of current treatment methods for water disinfection which results in the generation of organohalogens. The U.S. Environmental Protection Agency recently proposed regulations to limit certain organic chemicals

in potable water. A combined upper limit of 100 ppb has been suggested for the group of the so-called trihalomethanes[6]. At this time no simple method leading to a reduction of these substances has been found.

Some research has been undertaken to establish the critical steps in the formation of such substances[7], but only a few experimental results have been made available which link these mechanistic effects to analytical data from real water samples. Chlorine dioxide, ozone, bromine and bromine chloride[8,9] have been considered as alternatives to chlorination. It appears, however, that chlorine is by far the most effective means to control bacterial growth.

Chlorine has been introduced as a water disinfectant since the turn of the century. It is the most widely used chemical for such purposes. In water, chlorine rapidly hydrolyzes according to:

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \qquad (1)$$

Hypochlorous acid in turn may dissociate by the mechanism

$$HOCl \rightleftharpoons H^+ + OCl^- \qquad (2)$$

The equilibrium for reaction 1 is shifted by far to the right side of the equation. The equilibrium of eqn. 2 obviously depends on pH. It should be noted that it is the HOCl species which is most bacteriacidal[8].

The production of organohalogens is thought to proceed through a series of steps where HOCl acts as an electrophile[10,11]. Most experimental work, however, has been performed under higher concentrations of model precursors than usually found in drinking water[12-14]. An exceedingly large number of organohalogens can be produced under such conditions[15]. Experimental evidence has recently been presented indicating differences between the total quantity of halogenated organics (as may be determined by microcoulometry) and the fraction which can be removed by purging[16,17]. The concept of an "intermediate bonding state", has been proposed where the halocarbon has not been formed yet but an association has taken place between an organic molecule which acts as precursor and halogen. More research is needed to establish the significance of such species. Ozone and chlorine dioxide which do not produce organohalogens[18,19], are considerably more expensive and less effective than chlorine.

The major sample enrichment methods of organics from water are based on liquid–liquid partitioning, liquid–gas partitioning, liquid–solid adsorption, membrane separation, freeze drying and distillation. Only the first three principles have significance in drinking water analysis. If only organohalogens are of analytical interest, enrichment factors can be rather moderate, since sensitive and selective detectors can make up for the lack of sample size. Even headspace analysis[20], partitioning with a large amount of solvent[21], or direct injection[22] are feasible under such conditions.

General requirements for concentration and analysis of trace organics in drinking water have been discussed by Grob and co-workers[23-26] who developed miniaturized versions of gas-phase stripping and solvent extraction. The key to these methods is avoidance of solvent concentration steps after extraction, and the use of highly efficient gas chromatographic (GC) columns. Another important general meth-

od based on liquid–solid adsorption has been introduced by Fritz and co-workers[27],[28]. Trace organics were passed over a large surface area polymer which was then solvent extracted. The extract was then further concentrated.

Several authors have reported on the use of polymers in conjunction with gas-phase extraction and thermal elution. The purged compounds are trapped at ambient temperature on a suitable polymer and then flushed into a GC column[29]. Substances with high vapor pressure and low polarity are most readily removed from water, especially when the temperature is raised[23],[30],[31]. Fractional purging was suggested[16] and a number of semiautomated devices have been described[32],[33].

In spite of the widespread use of chlorination practices and availability of suitable instrumentation for analysis of low levels of halogenated substances, it is rather surprising that the widespread presence of organohalogens was detected only within the last few years.

The appearance of organohalogens in potable water has been studied from many angles. However, some discrepancies still exist. The purpose of this paper is to report results on the background of organics in surface and subsurface water which may act as precursors. These substances are identified and followed through each step of a typical water treatment procedure. Organohalogens produced during the chlorination process are also identified and quantitated.

EXPERIMENTAL

A gas-phase stripping apparatus was used which has been based on an earlier design[30]. Several sizes of containers were employed, ranging from 20 to 250 ml. The smallest vessel, which was made in one piece was used for the quantitation of halomethanes. Only the larger of the containers which were equipped with joints were submerged in a water bath to prevent interference from organics in air. Frit porosities ranged from medium to very fine. Nitrogen which was used as purge gas was scrupulously purified in a packed trap at dry ice temperature. Stripping was performed at room temperature and volatiles were retained by adsorption onto Tenax GC (80–100 mesh; Applied Science Labs., State College, Pa., U.S.A.). Glass tubes containing approximately 500 mg of the adsorbent were used[34]. The samples were purged at typical flow-rates of 60 ml/min but other settings, varying from 10 to 200 ml/min, were also investigated. Stripping gas volumes for the 20-ml container were around 3 l. Immediately following the stripping process, approximately 300 ml of dry nitrogen was pushed through the adsorbent to displace the bulk of physically retained water. The relationship between gas volume and stripping efficiency was examined for different volumes and sample concentrations.

Samples were collected in amber bottles of 1-gallon volume, equipped with PTFE-lined screw caps. The bottles were filled to overflow. Processing usually proceeded within a few hours. The water samples originated from the Tuscaloosa, Alabama Water Works which uses a double chlorination process and derives its water from a nearby artificial lake. Water originating from a deep well which was subjected to a single chlorination procedure was also investigated.

Analysis was performed by capillary column GC and GC–mass spectrometry (MS). Both glass and nickel capillaries were employed as described previously[35]. The nickel columns were coated with Witconol LA23 (Witco, Houston, Texas, U.S.A.)

a surfactant type stationary phase of intermediate polarity. Glass capillaries were coated with OV-101. For GC a Hewlett-Packard gas chromatograph 5830A, equipped with single flame-ionization detector (FID) and integration capability was used. A Perkin-Elmer Model 900 gas chromatograph with dual detectors was also employed. The column effluent in this instrument was split into an FID and an electron-capture detector (ECD) (Nickel 63) at a ratio of approximately 5:1. A fixed restrictor in each manifold transfer line resulted in stable and reproducible splitting conditions. The manifold lines of this instrument were replaced with glass-lined stainless-steel tubing (SGE, Austin, Texas, U.S.A.). A detector make-up gas line was installed. Helium served as carrier gas and nitrogen as make-up gas. Peak areas were integrated with an Infotronics integrator.

Identifications were performed on a LKB 9000 GC–MS combination, equipped with a single-stage jet separator[34]. Chromatographic conditions were similar to the settings used in GC analysis. Assignment of structures was done by comparison with published MS data, such as the eight peak index[36], the data compiled by Junk[37] and by comparison with spectra from previous work, kept in a small library. Organohalogens for calibration purposes and MS verification were obtained from the EPA Southeastern Research Labs. (Athens, Ga., U.S.A.) from Theta (Media, Pa., U.S.A.) and from RFR (Hope, R.I., U.S.A.). 1-Chloroalkanes were used occasionally as internal standards.

RESULTS AND DISCUSSION

It is well documented that surface waters contain a variety of organic materials. The pattern of the more volatile compounds in surface water which has been exposed to urban air is always strongly dominated by the compounds found in gasoline and other fuels[38]. It is likely that an effective mechanism exists which transports these substances through the air–water interface. The compositions of organics in urban air show a strong correlation to the pattern of gasoline with the addition of some antropogenic substances. Evidence has been presented suggesting that rain is an effective scrubber for organics in air. Volatiles in water therefore represent a rather complex mixture. It is of importance to determine if any particular group of chemicals which are present in water preferentially reacts with chlorine and is thus reduced in concentration. There is also a possibility that the concentration of some substances increases as a result of the water treatment process or that entirely new compounds appear. Such observations have been made when water was subjected to ozonization[39,40].

At present, GC has the best potential of any separation method to deal with complex samples, especially in conjunction with MS. Its major drawback is that it cannot be used for non-volatile substances which unfortunately make up a large proportion of all organics in water.

It has been postulated that the potential of halocarbon production strongly depends on the concentration and composition of organics dissolved in water[5]. The significance of polar precursors in surface water has been established but volatile compounds have also been shown to be reactive. It seems to be necessary to include the entire range of organics to evaluate the potential of a particular source of raw water for haloform formation. It is difficult, if not impossible, to obtain reliable data

on the composition of humic substances and other intermediates which arise from bacterial degradation processes. Such data can only be described in terms of "gross parameters", including elemental composition and molecular weight distribution, although molecular structures have been suggested. The purpose of our study was to evaluate the possible contribution of the volatile components in a source of relatively non-polluted surface water to the formation of halocarbons.

In spite of some shortcomings, gas-phase stripping is currently the most widespread method for the determination of volatiles in water, in particular of halomethanes. The method produces nearly quantitative recoveries for non-polar substances at sub-ppb levels[2,31]. Tenax has been shown to be an effective adsorbent for trace volatiles in the presence of large amounts of water[34]. The surface area of this adsorbent is, however, rather limited. To verify its feasibility for water analysis, breakthrough volumes were determined for most of the halocarbons found during this investigation using regression analysis under statistical control. The data are summarized in Table I. Taking a safety factor of three into consideration it can be seen that a sufficient stripping volume can be applied to nearly quantitatively extract the common halomethanes from a 20-ml sample. Difficulties arise only for dichloromethane. Table I also shows that adsorbent capacity is a strong function of adsorbent temperature.

TABLE I

BREAKTHROUGH VOLUMES FOR SOME REPRESENTATIVE HALOCARBONS ON TENAX GC AT DIFFERENT TEMPERATURES (IN l/g OF ADSORBENT)

Compound	25°	50°	75°
CH_2Cl_2	3.1	0.8	0.2
CH_2BrCl	10.3	2.4	0.6
$CHCl_3$	13.9	2.9	0.7
$CHBrCl_2$	22.9	5.2	1.3
CCl_4	26.8	5.3	1.2
1,1,1-Trichloroethane	28.8	5.5	1.2
Trichloroethylene	43.3	7.9	1.7
1,1,2-Trichloroethane	149.4	24.0	4.7
Tetrachloroethylene	167.3	26.5	5.1
$CHBr_3$	647.8	94.4	16.7

The effects of container shape, frit size, purge gas flow-rate and salt content were briefly investigated with a few model compounds. The results can be summarized as follows. The finest frits produced the most rapid stripping (mass transfer seems to be a contributing factor) but were difficult to maintain and could not be effectively regenerated. We recommend the porosity designated "fine". Container shape and purge gas flow-rate were not found to exert a strong effect. Addition of salts such as sodium sulfate caused problems with frits and produced interferences.

Our previous experience has shown that substances of intermediate molecular weight, like methylnaphthalene, can easily be gas phase extracted at sub-ppb levels from sample volumes as high as 1.5 l if the temperature is raised to above 70° (ref. 36). Even polar substances which do not have favorable distribution coefficients can readily be sampled under such conditions[41]. Several investigators demonstrated, how-

ever, that additional amounts of halomethanes are generated upon prolonged storage and when the sample is heated. This phenomenon was observed even after reducing agents had been added[26]. We confirm these observations. Some arguments have been brought forward for[42] and against[43] heating of the sample to increase the yield. We decided to operate at room temperature, taking a reduction in the quantity of the less volatile and polar substances into account. Our primary aim was to investigate if significant changes between halogenated and non-halogenated compounds occur at different steps of the treatment process. Halocarbons were quantitated from 20-ml samples by ECD. For analysis of non-chlorinated species, the sample volume was increased. The extraction efficiency is not quantitative for some substances under such conditions. However, with constant sampling parameters, relative amounts remain constant and therefore permit direct comparison between different samples.

The treatment of raw water to produce drinking water usually consists of several steps. Fig. 1 shows a diagram of the process used at a modern water treatment plant (Tuscaloosa, Alabama Municipal Water Works). This type of treatment is fairly typical for most facilities in the U.S. Samples were taken over a period of about one year. More than 100 samples were analyzed by GC and three complete sets of data from all treatment steps were subjected to GC–MS.

Water filtration plant
purification scheme

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┌─────────────────────────┐
│ Raw water               │
└─────────────────────────┘
             │
┌─────────────────────────┐
│ Addition of lime, KMnO₄ │
│ Alum. chlorine (≈0.5 ppm)│
└─────────────────────────┘
             │
┌─────────────────────────┐
│ Second chlorine addition│
│     (≈0.8 ppm)          │
└─────────────────────────┘
             │
┌─────────────────────────┐
│ Second lime addition    │
└─────────────────────────┘
             │
┌─────────────────────────┐
│ Filtration              │
└─────────────────────────┘
             │
┌─────────────────────────┐
│ Finished water          │
│ Residual chlorine (1 ppm)│
│ Fluorine (1 ppm)        │
└─────────────────────────┘
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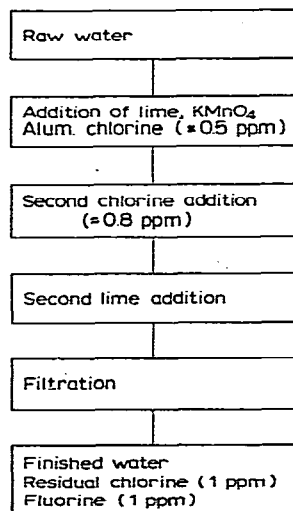
Fig. 1. Diagram of water treatment steps in a typical municipal water treatment plant (see text).

The combination of an FID and an ECD in parallel is an ideal arrangement for an investigation where both halogenated and non-halogenated substances are to be observed. Quantitation of organohalogens was therefore done by ECD, using individual calibration curves. Fig. 2 shows a chromatogram of finished water on a glass capillary column. A large number of components are observed on the ECD, most of which remain under the detection limit of the FID. For reasons of operator
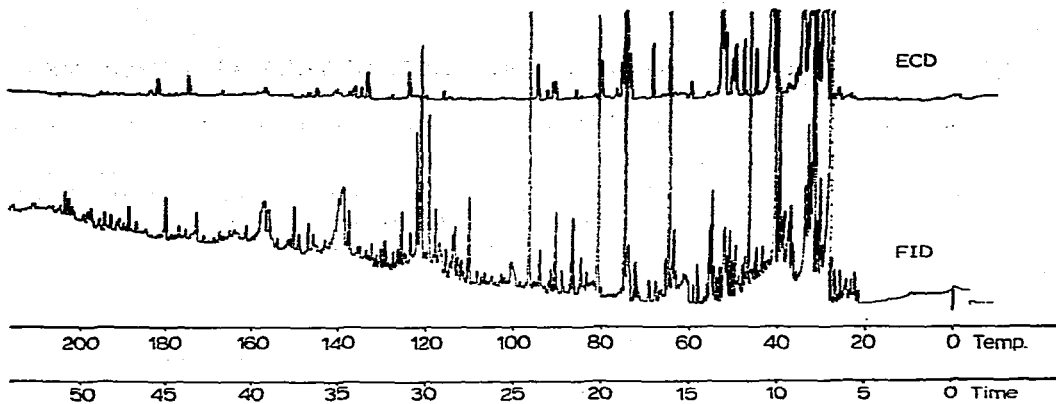
Fig. 2. Volatiles in drinking water by FID and ECD in parallel. Sampling: sample size 250 ml, purge at 50 ml/min for 1 h, room temperature. Analysis: glass capillary column, 45 m × 0.4 mm I.D. coated with OV-101.

convenience and speed, large-bore metal capillary columns were substituted for most of the study. Fig. 3 compares the chromatograms obtained from samples taken during various steps of the water treatment proces. (The large peak at the beginning of the chromatogram is caused by water which produces a signal in the ion source of the
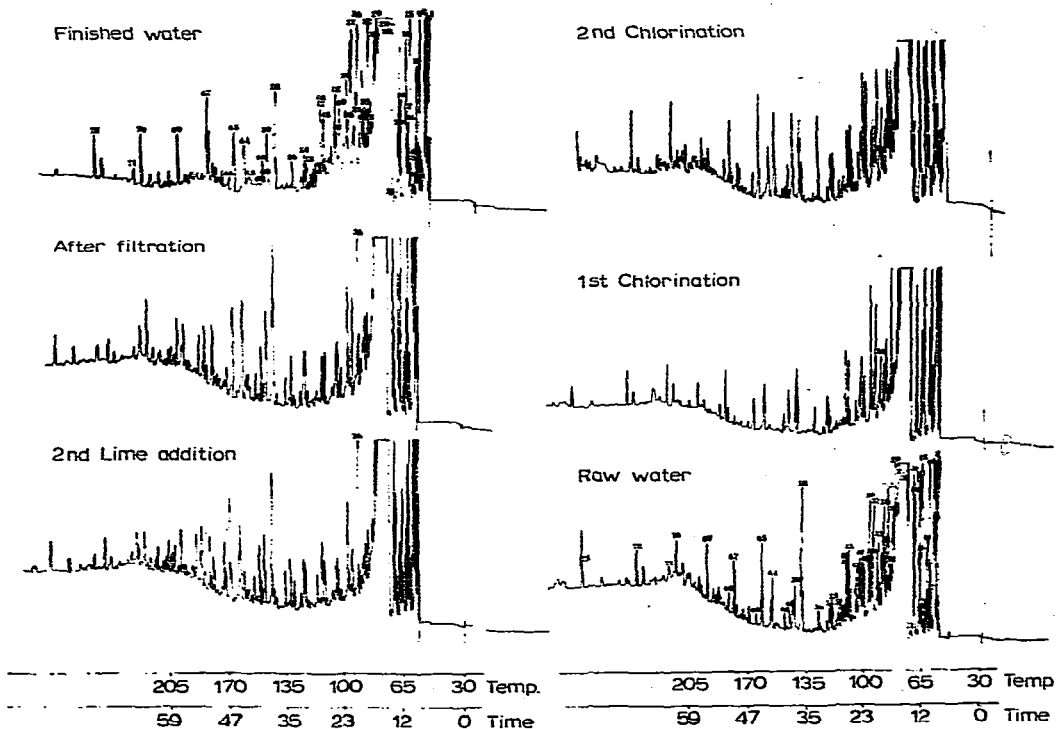

Fig. 3. Total ion current chromatograms of volatiles in surface water after each treatment (steps according to Fig. 1). Sampling: sample size 250 ml, purge at 50 ml/min for 1 h, room temperature. Analysis: nickel capillary column, 80 m × 0.5 mm coated with Witconol LA 23.

TABLE II

VOLATILES IDENTIFIED DURING DIFFERENT STAGES OF THE WATER TREATMENT PROCESS

+ = Compound detected; × = type of identification; nd = not detected; tr = trace amount detected.

Peak No.	Compound	M.W.	Raw water	1st Chlori- nation	2nd Chlori- nation	2nd Lime addition	After filtra- tion	Finished water	MS	GC
1	n-Pentane	72	+	+	+	+	+	+	×	×
2	FCCl$_3$	136	+	+	+	+	+	+	×	
3	Isoprene	68	+	+		+	+		×	×
4	1-Hexene	84	nd	nd	+	nd	nd	nd	×	
5	1,2-Dichloroethylene	96	nd	nd	+	nd	+	nd	×	
6	Hexane	86	+	+	+	+	+	+	×	×
7	Methylcyclopentane	84	+	+	+	+	+	+	×	
8	C$_7$-Alkane	100	+	+	+	+	+	+	×	
9	C$_7$-Alkane and acetone	100, 58	+	+	+	+	+	+	×	×
10	Methylhexene and n-heptene	98, 100	+	+	+	+	+	+	×	
11	C$_7$-Alkene	98	+	+	+	+	+	+	×	
12	C$_8$-Alkene	112	+	+	+	+	+	+	×	
13	Methylfuran and 2-butenal	82, 70	+	+	+	+	+	+	×	
14	C$_7$-Alkene	98	+	+	+	+	+	+	×	
15	Ethyl acetate	88	+	+	+	+	+	+	×	×
16	Butanone and C$_8$-alkane	72, 114	+	+	+	+	+	+	×	
17	1,1,1-Trichloroethane	132	+	+	+	+	+	+	×	×
18	Dichloromethane	84	+	+	+	+	+	+	×	×
19	n-Octane and C$_8$-alkene	114, 112	+	+	+	+	+	+	×	
20	Benzene	78	+	+	+	+	+	+	×	×
21	2-Methylpropanenitrile	69	+	+	+	+	+	+	×	
22	Trimethylcyclohexane	126	+	+	+	nd	+	+	×	
23	Methylethylhexane	128	+	+	+	+	+	+	×	
24	Trichloroethylene	130	+	+	+	+	+	+	×	×
25	Chloroform	118	+	+	+	+	+	+	×	×
26	C$_3$-Cyclohexane	126	+	+	+	+	+	+	×	
27	C$_3$-Hexane	128	+	+	+	+	+	+	×	
28	n-Nonane	128	+	+	+	+	+	+	×	
29	Toluene	92	+	+	+	+	+	+	×	×
30	Tetrachloroethylene	164	+	+	+	+	+	+	×	×
31	Methylethyl cyclohexane	126	+	+	+	nd	+	+	×	
32	Methyldecane	156	+	+	+	+	+	+	×	
33	C$_4$-Cyclohexane	140	+	+	+	+	+	+	×	
34	C$_{11}$-Alkane	156	+	+	+	+	+	+	×	
35	C$_{11}$-Alkane	156	+	+	+	+	+	+	×	
36	Bromodichloromethane	162	nd	+	+	+	+	+	×	×
37	Ethylbenzene and C$_{12}$- alkane (trace)	106, 168	+	+	+	+	+	+	×	×
38	m-Xylene	106	+	+	+	+	+	+	×	×
39	p-Xylene and C$_{11}$-branched alkane	106, 156	+	+	+	+	+	+	×	×
40	C$_{11}$-Alkane	156	+	+	+	+	+	+	×	
41	o-Xylene and methyldecene	106, 154	+	+	+	+	+	+	×	×
42	n-Propylbenzene	120	+	+	+	+	+	+	×	
43	C$_{11}$-Alkene	154	+	+	+	+	+	+	×	
44	C$_3$-Benzene	120	+	+	+	+	+	+	×	
45	Styrene*	104	+	+	+	+	+	+	×	

TABLE II *(continued)*

Peak No.	Compound	M.W.	Raw water	1st Chlori-nation	2nd Chlori-nation	2nd Lime addition	After filtra-tion	Finished water	MS	GC
46	Dibromochloromethane	206	nd	nd	tr	nd	nd	nd	×	×
47	*n*-Undecane	156	+	+	+	+	+	+	×	×
48	C₃-Benzene	120	+	+	+	+	+.	+	×	
49	1-Undecane	154	+	+	+	+	+	+	×	
50	C₃-Benzene	120	+	+	+	+	+	+	×	
51	C₃-Benzene	120	+	+	?	?	?	?	×	
52	Chlorotoluene	126	tr	?	?	?	+	+	×	
53	C₃-Benzene	120	+	+	+	+	+	+	×	
54	1-Chlorooctane	148	+	+	+	+	+	+	×	
55	C₄-Benzene	134	nd	+	+	nd	nd	nd	×	
56	*n*-Dodecane	170	+	+	+	+	+	+	×	
57	C₄-Benzene	134	+	+	?	nd	?	?	×	
58	Dichlorobenzene	146	+	+	+	+	+	+	×	
59	Benzaldehyde*	106	+	+	+	+	+	+	×	×
60	C₅-Benzene	120	tr	nd	nd	nd	nd	nd	×	
61	Tridecane	184	+	+	+	+	+	+	×	×
62	Tridecane	182	+	+	+	+	+	+	×	
63	Benzonitrile	103	tr	+	+	+	+	+	×	
64	Tetradecane isomer	196	+	+	+	+	+	+	×	
65	Acetophenone and tetradecane	120, 198	+	+	+	+	+	+	×	
66	C₁₄H₂₈ isomer	196	+	+	+	+	+	+	×	
67	Pentadecane	212	+	+	+	+	+	+	×	×
68	Pentadecene	210	+	+	+	+	+	+	×	
69	Hexadecane	226	+	+	+	+	+	+	×	×
70	Heptadecane	240	+	+	+	+	+	+	×	×
71	Diphenyl	154	+	+	+	+	+	+	×	
72	Octadecane	254	+	+	+	+	+	+	×	×
73	Nonadecane	268	+	+	+	+	+	+	×	×

* Sometimes found in the background of Tenax in small quantities.

mass spectrometer.) The components are identified in Table II. No quantitation was attempted except for the halogenated substances. Fig. 3 shows that most compounds, in particular the alkanes, are carried through all steps of the treatment process virtually unchanged. As expected, several halogen-substituted compounds are generated during the chlorination process, primarily during the first addition of chlorine.

　　Raw water, derived from a lake, was relatively free from chlorinated substances, although a number of peaks were detected on the ECD. Two halogenated substances, 1,1,2-trichloroethane and tetrachloroethylene, however, appeared consistently in all chromatograms throughout the study. Some minor constituents such as trichloroethylene also were constantly present. It is likely that these organohalogens are derived from industrial point sources. Well water, on the other hand, did not contain these two chemicals. The level of organics was also lower by a factor of approximately five. Both sources contained chemicals of the same identity.

　　Upon chlorination, a far higher concentration and wider variety of halogenated hydrocarbons was generated from the raw water which originated in the lake. Table III provides some data. It is surprising that a considerable quantity of chlorodibromo-

methane was produced from the well water. This substance was found only in trace quantities in the finished water which originated from the lake. We do not have an explanation for this unexpected behavior and are currently studying a larger number of samples. The observations made during this investigation are consistent with the view that chlorinated water containing a large amount of organic materials produces increasing quantities of halogen substituted compounds. It is difficult to assess if any particular compound or class of chemicals present in natural surface waters has an increased tendency to react as precursor. More studies are needed, in particular with humic substances. The use of model compounds (stable isotopes or with radioactive labels) would be very helpful to gain insight with fundamental mechanisms and reaction kinetics.

TABLE III

CONCENTRATIONS (μg/l) OF SOME ORGANOHALOGENS IN DRINKING WATER

Compound	High	Low	Average*
Chloroform	5.5	4.4	4.6
Bromodichloromethane	4.4	2.1	2.5
Dibromochloromethane	0.012	0.007	0.01
Bromoform	1.1	0.85	0.94
Bromochloromethane	0.012	0.001	0.005
Bromotrichloromethane	0.02	0.002	0.006
Trichloroethylene	Trace	Trace	Trace
Tetrachloroethylene	0.62	0.38	0.58
1,1,2-Trichloroethane	1.1	0.76	0.99

* Average of 10 determinations; samples taken during the month of Febr. 1978.

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