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MONITORING AND INVESTIGATION OF THE CONCENTRATION LEVELS OF THE REGULATED FIVE HALOACETIC ACIDS AND DALAPON IN THE DRINKING WATER AND DURING THE TREATMENT STAGES

S. A. SOLIMAN, H. A. HAMMAD AND TAMER E. EMAM*

Chemistry Department, Faculty of Science - Al Azhar University, Cairo, Egypt.
** Central Lab. of Greater Cairo Water Company.*

Abstract

Disinfection of some types of surface water by Chlorine produces many groups of halogenated disinfection by-products (DBPs). Haloacetic Acids and Dalapon (2,2`-Dichloropropionic acid) belong to these groups. Since chlorinated by-products were discovered in drinking water in 1974, several toxicological studies have shown some disinfection by-products (DBPs) including certain Trihalomethanes (THMs) and Haloacetic acids (HAAs), to be carcinogenic in the laboratory animals. Several of these studies showed an increased risk for specific outcomes (e.g. early-term miscarriage) from long term average exposure to the disinfection by-products. Due to the probable health effects of Haloacetic Acids and Dalapon, the US Environmental Protection Agency regulates the sum of five Haloacetic Acids at a maximum contaminant level of 60 µg/L and Dalapon of 200µg/L in the finished drinking water in the Stage 1 Disinfection / DBP rule. This work was proposed to throw light on the concentration levels of Five Haloacetic Acids (HAAs) & (Dalapon) in the drinking water and during the treatment stages in the General Organization for Greater Cairo Water Supply (GOGCWS) water plants. Samples were collected from four plants monthly for one year started in Aug. 2001 and finished in Jul. 2002. The four selected plants were Gezirat Al Dahab, El Giza, Rod El Farag, and Embaba Water Plants. The sampling process included one sample from the intake, one from the clarifier inlet, one from the clarifier outlet, one from the filter outlet, and one from the finished water of each plant per month. Solid phase extraction method was used to extract the collected samples and a GC. System with capillary column and Electron Capture Detector was used in the analyses of the samples. The results of this work showed that the mean average values of the Total Five Haloacetic Acids (THAAs) in the finished drinking water were varied from (30.24 µg /L) to (41.81 µg /L) and the mean average values of (Dalapon) were varied from (8.08 µg /L) to (10.39 µg /L) in the collected water samples. This work showed the levels of the ($THAA_s$) and (Dalapon) in the finished drinking water of the selected plants did not exceed the regulations of the USEPA Stage I Disinfection / DBP rule.

Introduction

Surface fresh water "e.g. rivers, streams, and lakes" is considered as a major source of the drinking water. Due to the nature of the surface water supplies which are in contact with the atmosphere they are exposed to be contaminated by either the

human activities or by the nature itself. Pervious studies showed that water could be a mode of communication of dread diseases after a careful epidemiological study of the 1854 London cholera epidemic[1]. In order to kill the diseases precursors, an appropriate disinfectant must be used in the drinking water treatment process. In 1881 the lethal effect of chlorine on the bacteria was discovered, in 1905, continuous chlorination of a public water supply was used for the first time in London after the outbreak of typhoid fever, after that in 1908 the regular use of disinfection in the United Stats was initiated. Although chlorine is one of the most versatile and effective chemical oxidants where its uses include the oxidation of manganese, color removal, control of off-tastes and odors, and a flocculent aid but unfortunately chlorine reacts with the natural organic matter (NOM) that remains in waters and forms halogenated by-products. [2]. A variety of precursor compounds are probably involved; humic acid and fulvic acids (themselves a complex mixture of compounds), chlorophyll, and other components or metabolites of algae and bacteria grow in municipal water supplies [3]. Since chlorinated by-products were discovered in drinking water in 1974, several toxicological studies have shown some disinfection by-products (DBPs) including certain (THMs) and (HAAs), to be carcinogenic in the laboratory animals. Several of these studies showed an increased risk for specific outcomes (e.g. early-term miscarriage) from long term average exposure to the disinfection by-products. The principal chlorination by-products of health concern are low-molecular-weight chlorinated compounds and brominated compounds, including trihalomethane THMs, whose general formula is CHX_3 where X is chlorine or bromine (Chloroform, Dichlorobromomethane, Dibromochloromethane and Bromoform). Another group of by-products are haloacetic acids HAAs which are (Monochloroacetic acid, Dichloroacetic acid, Trichloroacetic acid, Monobromacetic acid and Dibromoacetc acid). Also chloropicrin and halogenated acetonitriles are formed [4]. Other studies that were carried out on the laboratory animals showed that the exposure to certain HAAs compounds e.g. dichloro (DCAA), dibromo (DBAA) and bromochloro (BCAA) acetic acids are developmentally toxic [5]. A very large number of other compounds are also formed in small quantities, including halogenated ketones and various halogenated aliphatic compounds like dalapon (2, 2'-dichloropropionic acid) [6]. Due to the probable health effects of Haloacetic Acids and Dalapon, the US Environmental Protection Agency regulates the sum of five Haloacetic Acids at a maximum contaminant level of (60 µg/L) and Dalapon of (200µg/L) in the finished drinking water in the Stage 1 Disinfection / DBP rule[7]. In Egypt there is a very little knowledge about the distribution of the regulated five HAA5 and their concentration

levels in drinking water and through the purification steps. This study is concerning with the regulated five HAAs and Dalapon. To achieve this aim, four drinking water treatment plants were selected.

Experimental

Methods and Materials:

- *Samples Collection and Handling:*

Samples were collected from four water treatment plants (Gezirat Al Dahab produces 470000 m3/day, El Giza produces 150000 m3/day, Rod El Farag produces 900000 m3/day and Embaba produces 700000 m3/day) monthly during the period from August 2001 to July 2002. The samples were collected from five locations in each plant (raw, clarifier inlet, clarifier outlet, filter outlet, and finished drinking water) according to the instruction of samples collection and handling illustrated in the EPA method N^{o}. 552.1[8].

- *Working Calibration Standards:*

Five levels of the target analytes were prepared in order to calibrate the gas chromatography system. These five levels are as shown in the following table:

Compound	1st Level µg / L	2nd Level µg / L	3rd Level µg / L	4th Level µg / L	5th Level µg / L
Monochloroacetic Acid	120	96	72	48	24
Monobromoacetic Acid	80	64	48	32	16
Dalapon	80	64	48	32	16
Dichloroacetic Acid	120	96	72	48	24
2-Bromopropionic Acid *	40	32	24	16	8
Trichloroacetic Acid	40	32	24	16	8
Dibromoacetic Acid	40	32	24	16	8

** (surrogate)*

- *Gas Chromatography System:*

Hewlett-Packard (HP) Gas chromatograph Model 5890 Series II equipped with Electron Capture Detector, split / splitless injector capillary column (DB-1701, 30 m × 0.32 mm I.D., 0.25 µm film thickness), HP 7673 autosampler (tray 100 vials), and data system for measuring and calculating the peaks areas and convert them into concentrations. The GC conditions were programmed as follows: Injector

Temperature was 200ºC, Detector Temperature was 260ºC, Helium (carrier gas) linear velocity was 27 cm / sec. (1.3 ml / min.), make up Nitrogen gas (20 ml / min.), and Splitless injection with 30 seconds delay. Thermal Program oven temperature hold at 50ºC for 10 minutes, rate to 200 ºC at 10 ºC / min. and hold for 5 minutes, and then to 230 ºC at 10 ºC / min. and hold for 5 minutes. The sample injected volume is 2 µl of the standards and extracts which must be in MTBE.

- *Extraction and Analysis:*

Extraction of the five regulated Haloacetic acids and Dalapon were carried out according to the EPA method No. 552.1 which is utilizes a liquid-solid extraction technology which requires the use of very small quantities of organic solvents. This feature eliminates the hazards involved with the use of large volumes of potentially harmful organic solvents needed for conventional liquid-liquid extractions. This method also, uses acidic methanol as the derivatizing agent in place of the highly toxic diazomethane and the Methyl Tertiary Butyl Ether (MTBE) as extracting solvent. Also in this method 1,2,3-trichloropropane of concentration (10 µg / ml) is used as an internal standard.

Results and discussion:

The method of purification used in the selected water plants depends upon the pre-chlorination, coagulation, filtration, and post-chlorination. The results showed that the most predominant haloacetic acids were the dichloroacetic and trichloroacetic acids in all the investigated samples that were collected from the cascading steps of the purification process. Also, the data illustrated in Table (1) showed that all the samples that were taken from the Nile were free from any of the regulated five haloacetic acids. These results were logically expected because in the pumping of the Nile water into the intake of the plant there was no chlorine addition. The reaction between the chlorine gas and the by-products precursors starts instantaneously after the addition of the chlorine, so the haloacetic acids were observed firstly in the clarifier inlet samples of the selected plants and their concentrations depend on many factors e.g. the added chlorine dose concentrations, the natural organic matter (NOM) concentration (i.e. DBPs- precursors) in the raw water, the contact time of the chlorine with the precursors (the time from the addition of chlorine dose until the sample was taken), the pH value of the medium, and the atmospheric temperature (i.e. the season in which the sample was collected). Each of these factors contributed by a ratio in the formation of the chlorination by-products. Also, Table (1) clarified that the total concentration of the five haloacetic

acids (THAAs) was varied unsystematically during the purification stages and these variations may be due to an operational conditions like the accumulation of these compounds in the sludge in the clarifiers, the free chlorine from the previous stage, the quality of the filtration sand in the filters, or the post-chlorination dose which added in the plant final storage tank.

The lowest value in the drinking water samples (10.30 µg / L) was observed at Rod El Farag water plant in the period from Aug.2001 to Oct. 2001 due to the low TOC concentrations in the filter outlet samples which were ranged from (2.1 to 2.7 mg / L). The highest value in the drinking water samples (60.70 µg / L) was observed at El Giza water plant in the period from Nov.2001 to Jan. 2002 due to the high TOC concentrations in the filter outlet samples which were ranged from (3.06 to 5.00 mg / L) and free chlorine concentrations were (1.5 to 3.0 mg / L). The presentation of the mean average values of THAAs recorded in Nile water, during the purification stages, and the finished drinking water sample in each period in Figs. (1-4) shows that the concentrations of THAAs did not exceed the permissible limitation that regulated by the USEPA for the finished drinking water (60 µg/L), but the mean average values of the regulated five Haloacetic acids and Dalapon recorded in the Nile water samples in each season not detected.

Data illustrated in Table (2) showed that the concentrations of the 2,2'-Dichloropropionic acid (Dalapon) in the Nile water, during the purification stages, and the finished drinking water of the selected water plants during the period of the study from Aug.2001 to Jul.2002. An over view on these data will clear that about 43% of the collected samples gave a undetectable result particularly in the first period (Aug.2001-Oct.2001) and the second period (Nov.2001-Jan.2002) whereas the third period (Feb.2002-Apr.2002) and the fourth period (May2002-Jul.2002) showed various concentrations of dalapon. This observation may be explained on the bases of the precursors' nature itself. As mentioned before the precursors of the DBPs are the humic materials which are divided into humic acids (consist of polymers of polyhydroxybenzenes, polyhydroxybenzoic acids, benzene polycarboxylic acids, sugars and nitrogen bases and other components or metabolites of algae and bacteria grow in municipal water supplies) and fulvic acids[9].

The degradation products of these complicated compounds are the reacting species with the chlorine in the formation of the DBPs and where this degradation is not controlled depending on the concentration of these compounds, the added

chlorine doses, the matrix of the raw water, the atmospheric temperature, and other factors it may expected that on spring and the next months to find a DBPs of relatively long chains like dalapon. The highest concentration of dalapon which recorded in a filter outlet sample in G.El Dahab water plant was (52.083 µg / L) on December 2002 and this may be due to the accumulation of algae in the filtration sand. The highest concentration in a finished drinking water sample in G.El Dahab water plant was (43.01 µg / L). The mean average concentrations of the 2,2'-Dichloropropionic acid (Dalapon) ranged from a undetected concentration in Gezirat El Dahab water plant to (20.15 µg / L) in the same plant. Table (2), showed that no samples exceeded up to the permissible limitation that regulated by the WHO or the USEPA (200 µg / L) during the period of the study.

Conclusions

- In general, the results showed that the regulated five haloacetic acids are present in concentrations matched with the regulations of World Health Organization (WHO) and the US Environmental Protection Agency (USEPA).
- These concentrations were affected by the precursors concentrations, the chlorine dose added, the temperature, and the pH of the medium.
- Also they were affected by the efficiency of the plant equipments and the operational circumstances.
- Dalapon is not a principle by-product in the investigated water due to nature of its matrix.
- Dalapon concentrations not exceeded the permissible limits that regulated by the previously mentioned organizations.

Recommendations

This study recommended that:

- Continuous monitoring to the concentrations of the total organic carbon TOC as a good indicator to the DBPs precursors.
- Adjustment of the added chlorine doses depending on the concentration of the TOC and the season with a careful regarding to the microbiological quality of the treated water.
- Periodical maintenance of the clarifiers, filters, and the plants tanks must be done to avoid the accumulation of the precursors and the formed by-products.

Table (1) :The mean average of the totals of the regulated five Haloacetic acids (HAAs) of four drinking water treatment plants in each season during the Period of Aug. 2001 to Jan. 2002, in µg/L

Month	Location	Aug. 2001- Jan. 2002				
		Nile Water	Clarifier Inlet	Clarifier Outlet	Filter Outlet	Finished Water
Aug.2001-Oct.2001	G. EL DAHAB	ND	10.21	25.46	14.50	30.24
	ELGIZA	ND	14.41	16.15	16.54	21.72
	R. EL FARAG	ND	7.59	7.57	8.20	10.30
	EMBABA	ND	19.24	38.60	32.03	29.15
Nov.2001-Jan.2002	G. EL DAHAB	ND	38.70	17.57	22.74	56.42
	ELGIZA	ND	15.25	60.56	32.50	60.70
	R. EL FARAG	ND	47.97	21.44	13.99	30.99
	EMBABA	ND	43.86	30.09	57.49	21.49
Feb.2002-Apr.2002	G. EL DAHAB	ND	42.85	36.23	28.51	29.00
	ELGIZA	ND	25.66	46.38	38.90	35.89
	R. EL FARAG	ND	29.32	10.87	29.07	22.08
	EMBABA	ND	26.05	39.91	58.64	33.78
May.2002-Jul.2002	G. EL DAHAB	ND	24.07	29.02	17.16	15.93
	ELGIZA	ND	29.91	49.64	62.66	58.73
	R. EL FARAG	ND	34.37	40.29	40.41	54.31
	EMBABA	ND	22.79	32.01	46.25	51.88

ND: NOT DETECTED

Table (2) : Levels of the 2,2′- dichloropropionic acid (Dalapon) in Nile water, purification stages, and finished water during the period from Aug. 2001 to Jul.2002 in µg/L

Month	Location	Aug. 2001- Jan. 2002				
		Nile Water	Clarifier Inlet	Clarifier Outlet	Filter Outlet	Finished Water
Aug.2001-Oct.2001	G. EL DAHAB	ND	ND	ND	ND	ND
	ELGIZA	ND	ND	ND	3.82	4.04
	R. EL FARAG	ND	ND	3.17	1.92	2.68
	EMBABA	ND	ND	3.17	1.92	2.68
Nov.2001-Jan.2002	G. EL DAHAB	ND	23.85	2.07	24.45	4.56
	ELGIZA	ND	ND	13.09	0.99	11.84
	R. EL FARAG	ND	3.42	5.69	6.63	2.74
	EMBABA	ND	8.68	6.25	9.48	4.94
Feb.2002-Apr.2002	G. EL DAHAB	ND	7.94	21.77	22.14	20.15
	ELGIZA	ND	5.81	28.34	4.65	9.71
	R. EL FARAG	ND	17.42	4.39	13.38	14.53
	EMBABA	ND	14.04	14.58	24.84	17.39
May.2002-Jul.2002	G. EL DAHAB	ND	1.33	5.43	1.20	16.83
	ELGIZA	ND	15.34	14.17	19.79	14.84
	R. EL FARAG	ND	11.19	10.86	15.01	15.06
	EMBABA	ND	2.74	9.20	16.35	16.35

ND: NOT DETECTED

Figures

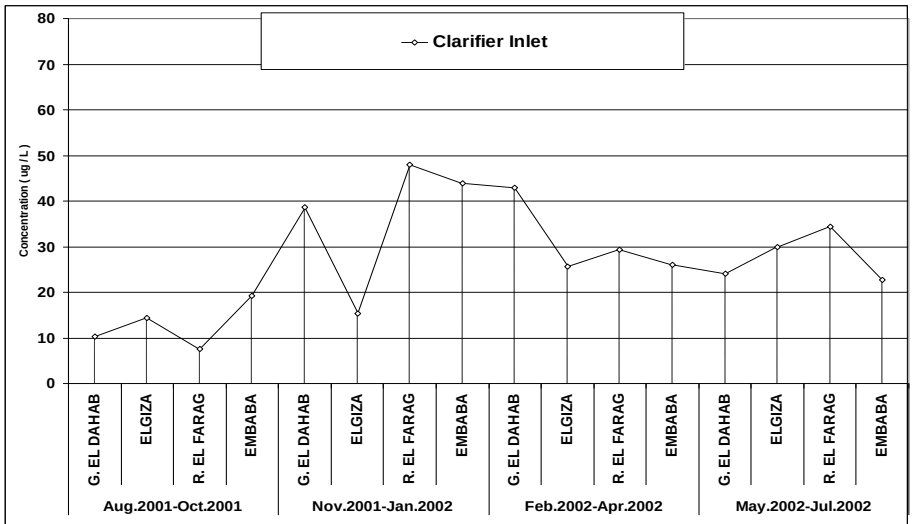

Fig.(1): The Mean Average Values of the Regulated Five Haloacetic Acids Recorded in the Clarifier Inlet Samples in each Season

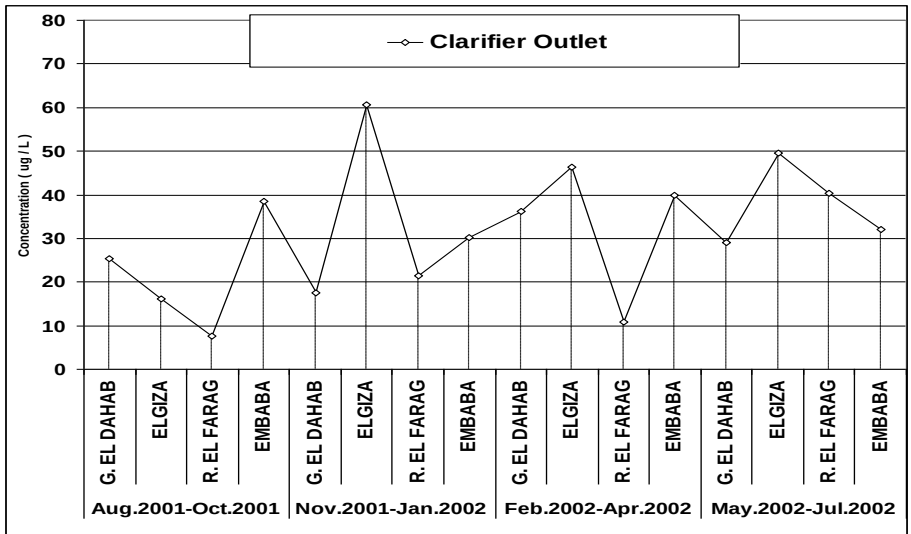

Fig.(2): The Mean Aaverage Values of the Regulated Five Haloacetic Acids Recorded in the Clarifier Outlet Samples in each Season

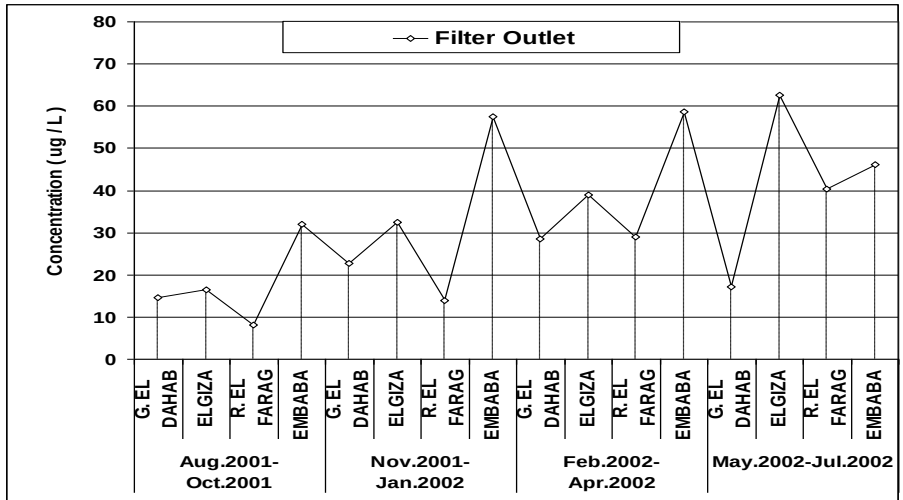

Fig.(3): The Mean Average Values of the Regulated Five Haloacetic Acids Recorded in the Filter Outlet Samples in each Season

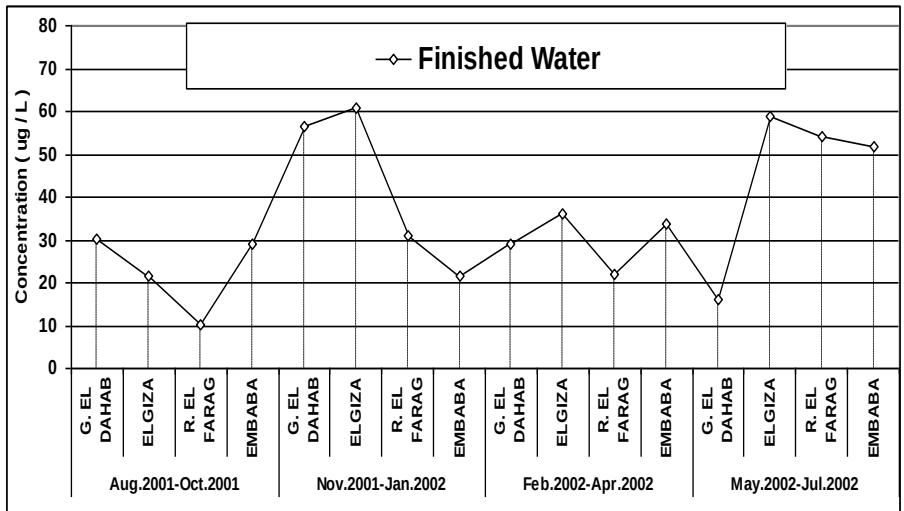

Fig.(4): The Mean Average Values of the Regulated Five Haloacetic Acids in the Finished Drinking Water Samples in each Season

References

1. ROSENAU, M. J., Preventive Medicine and Hygiene, 6th ed. Appleton-Century-Crofts, New York (1940).
2. MI HYUNG KIM AND MYONG JIN YU,"Characterization of NOM in Han River and evaluation of treatability using UF-NF membrane", Environmental Research, Vol. **97**, No. 1 , Jan., P. 116-123, (2005).
3. R. L. JOLLEY, R. J. BULL, W. P. DAVIS, S. KATZ, M. H. ROBERTS, JR., AND V. A. JACOBS, Water Chlorination: Chemistry, Environmental Impact and Health Effects, vol. **5**, Lewis Publishers, Chelsea, Mich., (1985)..
4. A. A. STEVENS, L. A. MOORE, C. J. SLOCUM, B. L. SMITH, D. R. SEEGER, AND J. C. IRELAND, " By-Products of Chlorination at Ten Operating Utilities," Water Chlorination: Chemistry, Environmental Impact and Health Effects, vol. **6**, R. L. Jolley et al., editors) Lewis Publishers, Inc., Chelsea, Mich., (1989.)
5. J.E. ANDREWS, H.P. NICHOLS, J.E. SCHMID, L.M. MOLE, E.S. HUNTER, AND G.R. KLINEFELTER. "Developmental toxicity of mixtures: the water disinfection by-products dichloro-, dibromo- and bromochloro acetic acid in rate embryo culture", Reproductive Toxicology, vol. **19**, No. 1, p. 111-116, Nov.(2004).
6. ROOK, J.J.,."Haloforms in Drinking Water". J.AWWA, **68**: 3:168. (1976).
7. USEPA, 1998." National Primary Drinking Water Regulations; Disinfection By-Products, Final Rule. Fed. Reg., vlo.**63** № 241; 69390 Dec. 16, (1998).
8. Methods for the Determination of Organic Compounds in Drinking Water, Supplement II, EPA Publication # EPA/600/R-92/129, , Method 552.1, (Aug.,1992).
9. JOHANNES J. Rook, Chlorination Reaction of Fulvic acids in Natural Waters, Environmental Science and Technology, , pages 478-482 (May 1977).