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OF AQUATIC HUMIC MATERIAL: THE EFFECT OF
MOLECULAR WEIGHT, ENVIRONMENT AND SEASON

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EXECUTIVE SUMMARY

Extractable organic matter from various aqueous environments and from laboratory microbial cultures was segregated into humic and fulvic acid fractions and then each fraction was separated into eight molecular weight ranges by ultrafiltration. The fractionated material was then chlorinated in aqueous solution and the amount of chloroform produced was measured. Chloroform concentration per unit weight humic material passed through a maximum at molecular weight about 20,000-30,000 for the fulvic acids, whereas the CHCl_3 concentration decreased with increasing molecular weight above 20,000-30,000 for the humic acids. Only minor fluctuations in chloroform concentrations were apparent for samples from various aqueous environments (lake, river, stream, swamp, microbial) and for samples from a single environment obtained during different seasons of the year. Based on the total amount of material isolated from the original samples and the chloroform production per unit weight, the major chloroform precursors in aquatic humic material were the low molecular weight (<30,000) fulvic acid fractions. Unfortunately, because of their low molecular weight and high surface activity, these fractions will probably prove to be the most difficult to remove by standard water treatment processes.

ABSTRACT

Humic material from various aqueous environments and from laboratory microbial cultures was segregated into humic and fulvic acid fractions and then each fraction was separated into eight molecular weight ranges by ultrafiltration. The fractionated material was then chlorinated in aqueous solution and the amount of chloroform produced was measured. Chloroform concentration per unit weight humic material passed through a maximum at molecular weight about 20,000-30,000 for the fulvic acids, whereas the CHCl_3 concentration decreased with increasing molecular weight above 20,000-30,000 for the humic acids. Only minor fluctuations in chloroform concentrations were apparent for samples from various aqueous environments (lake, river, stream, swamp, microbial) and for samples from a single environment obtained during different seasons of the year. Based on the total amount of material isolated from the original samples and the chloroform production per unit weight, the major chloroform precursors in aquatic humic material were the low molecular weight (<30,000) fulvic acid fractions. Unfortunately, because of their low molecular weight and high surface activity, these fractions will probably prove to be the most difficult to remove by standard water treatment processes.

INTRODUCTION

The ubiquitous occurrence of chloroform and other trihalomethanes (THMs) in chlorinated water supplies is well documented (Rook, 1974; Symons et al., 1975; Foley and Missingham, 1976). These compounds are produced by the reaction of chlorine with organic precursor molecules, since they are not present in significant concentrations in non-chlorinated water (Symons et al., 1975). Although algae (Hoehn, 1978), tannic acid (Youssefi et al., 1978) and nitrogen-containing compounds (Morris and Baum, 1978) have been shown to produce THMs on chlorination, in most instances, the major THM precursors appear to be aquatic humic materials (Rook, 1976; Stevens et al., 1976; Oliver and Lawrence, 1979). It has been postulated that m-dihydroxy aromatic linkages of the resorcinol type are the major THM producing groups in humic material, since they react efficiently with chlorine to produce chloroform (Rook, 1977) and oxidative degradation studies have shown that such linkages are present in aquatic humic material (Christman et al., 1978).

Humic materials can be separated chemically into base soluble humic acid (HA) and acid and base soluble fulvic acid (FA) fractions (Schnitzer, 1970). Also, a separation based on molecular weight can be accomplished using either sephadex gels (Ghassemi and Christman, 1968) or ultrafiltration (MacFarlane, 1978). Since the chemical nature and molecular size of aquatic humic material can affect the humic removal efficiency by water treatment processes such as alum coagulation (Kavanaugh, 1978) and this removal efficiency can, in turn, affect the ultimate THM concentration in the drinking water, it is important to find out whether or not there are

any differences in the THM production of fractionated aquatic humic material. This paper reports the chloroform production from the chlorination of aquatic humic and fulvic acids that have been fractionated into eight molecular weight segments by ultrafiltration.

EXPERIMENTAL

(a) Origin of Material

Humic material of natural origin was obtained from 150 \pm water samples collected during September 1974 from a watershed comprising of a lake (Lake Picauba), a river (River Chicoutimi), a forest stream and a swamp, situated in the Laurentide Park in the Precambrian Shield region of the province of Quebec. The river had previously been sampled at various intervals during the course of 1973-1974.

Humic material of microbial origin was also obtained from a glucose-yeast extract medium inoculated with an actinomycete obtained from a Quebec forest soil, and incubated under constant conditions of aeration, temperature (25°C) and pH (7.0). Samples were collected for recovery of fulvic and humic matter after 14, 60 and 180 days of incubation.

For samples of both natural and microbial origins, fractionation procedures were started within one day of collection.

Fractionation Method

After the adjustment of the pH of the samples to 8.4, they were centrifuged at 28000 g in a Sorval ultra-centrifuge fitted with a continuous-flow head in order to remove any particulate organic and inorganic matter. The supernatant was next filtered consecutively over Amicon filters no. DP06, DP045 and DP02 with respective pore sizes of 0.6 μm , 0.45 μm and 0.2 μm .

Very large volumes, such as was the case of samples collected from natural environments (150 l) were then reduced by concentrating the organic matter by means of Diafiber membrane cartridge filters no. HIDP10* until the eluate became coloured.

The humic acid fraction was precipitated by adjusting the pH to 1.5 after which the above-mentioned centrifugation and filtration procedures were repeated. The final solution (containing the fulvic fraction) was then reduced in volume by ultrafiltration using a Diaflo UM05 ultra-filter membrane (see Table I).

The humic acids were purified by repeating a cycle of precipitation at pH 1.5 followed by dissolution at pH 8.0 until the supernatant at pH 1.5 remained virtually colourless.

In the case of the fulvic acids, the concentrate, after adjustment to pH 1.5, was passed over Amberlite resin XAD-2 (B.D.H.), previously purified and activated by refluxing it in a Soxhlet apparatus with methanol for a period of two days (Junk et al., 1974). The absorbed fulvic matter was partially eluted (up to 90%) using a TRIS buffer (pH 8.4, I = 1.5) after which the eluate was concentrated over a Diaflo UM 05 ultrafiltration membrane.

* Amicon Corporation, Lexington, Mass, U.S.A.

Some residual brown-coloured material obtained from the XAD-2 resin column by washing it subsequently with methanol appeared to contain a high percentage of lyophilic material. This fraction, which amounted to approx. 10% of the total fulvic acid content of the original sample, was not further investigated in this study.

Both fulvic and humic acids were next fractionated into a series of eight m.w. fractions, whilst suspended in a TRIS buffer (pH 8.4, $I = 1.5$), by using the Diaflo membranes as listed in Table I, fitted into continuously-stirred Amico ultra-filtration cells.

After fractionation the concentrates were thoroughly washed with TRIS buffer until the ultra-filtrate remained completely colourless. The buffer was finally removed by washing the humic fractions (present in the form of their K salts) with distilled water until the filtrate had a pH of 7.0 and was completely chloride free.

(c) Chlorination Procedure

Chlorination conditions designed to optimize chloroform production were: [Humic Material] = 1 mg/l T.O.C.

[Cl_2] = 15 mg/l (NaOCl)

pH = 11 (buffered)

Temperature = 20°C

Reaction Time = 72 hrs.

Earlier studies (Oliver, 1978; Oliver and Lawrence, 1979) showed that at least 90% of the total organic chlorine incorporation by humic materials resulted in CHCl_3 production at high pH and long reaction times, and that a leveling off of CHCl_3 production occurred at [Cl_2]/humic material T.O.C. ratios of greater than 10.

Chloroform concentrations were determined by a simple pentane liquid-liquid extraction technique (Richard and Junk, 1977) on a Tracor 550 gas chromatograph equipped with an electron capture detector and a 1.8 m glass column with 10% OV-1 Gas Chrom Q, 80/100 mesh. All samples were run in duplicate with a blank. The duplicate chloroform analyses were within $\pm 5\%$ for all samples.

RESULTS AND DISCUSSION

Figures 1 and 2 show the chloroform production from the chlorination of humic material from natural waters ($\mu\text{g}/\text{g}$ CHCl_3/mg T.O.C. humic material) as a function of molecular weight. It is quite evident from the plots that there are large variations in CHCl_3 production with molecular weight. The CHCl_3 concentration from the FA samples (Fig. 1) seems to pass through a maximum at approximately 20,000-30,000 with marked decreases in CHCl_3 production at higher and lower molecular weights, whereas, chloroform production from the HA samples (Fig. 2) seems to decrease with molecular weight. The 20,000-30,000 fraction produces consistently high chloroform concentrations per unit weight for both the FA's and HA's.

Therefore, the 20,000-30,000 fraction was chosen to see whether or not environment (lake, river or swamp) or seasonal changes made any significant difference in the CHCl_3 production. Table II shows the CHCl_3 production from HA and FA from three different locations for this molecular weight fraction. While there are fluctuations in CHCl_3 production they are not very large. It is also apparent that there

is only small differences in CHCl_3 production between the HA and the FA fractions. This supports earlier work by Oliver and Lawrence (1979) who found almost no difference between CHCl_3 production from Aldrich HA and a soil FA, but is contrary to work by Babcock and Singer (1979) who found HA produced more than twice as much CHCl_3 as FA (both extracted from Michigan peat).

Table III shows the effect of season on the CHCl_3 production of the 20,000-30,000 fraction of HA and FA from a river. Over a period of more than a year, it is evident that there are only minor fluctuations in the CHCl_3 production from either the HA or the FA fractions. Again it is apparent that there are only small differences between the CHCl_3 production from the HA and FA fractions. In this case the FA's produced slightly more CHCl_3 than the HA's.

Humic-like material produced microbiologically and fractionated into molecular weight ranges was also studied to see whether it produced similar amounts of CHCl_3 to the natural material. The data (Fig. 3) for short-term and long-term incubation showed marked differences. The CHCl_3 production for the short-term incubation experiments produced low and almost constant amounts of CHCl_3 in all the molecular weight fractions. The long-term incubation samples (6 months) produced more CHCl_3 and also showed variations with molecular weight more typical of samples of natural origin. These results suggest that the age of the humic material in the natural waters studied is probably at least several months. They also suggest that after long incubation periods of several months, microbially produced HA's and FA's contain roughly the same number of THM-producing groups as naturally-occurring materials. This would be expected given that oxidative processes were operating on recalcitrant aromatic structures.

Although it is important to know how CHCl_3 production per unit weight of material varies with molecular weight (Fig. 1 and 2) for practical purposes it is probably even more important to know the total CHCl_3 production from each molecular weight fraction in the original water sample. Data in this form is presented for a river and lake sample in Fig. 4. It is apparent from the histogram that when the amount of sample isolated in the various fractions is taken into consideration, the most important fraction for the FA's for both river and lake environments is in the 1000-10,000 fraction. For the HA's, the most important fraction is the 10,000-20,000 for the lake and the 20,000-30,000 fraction for the river. It is also evident that the FA fraction is much more important than the HA fraction. For the lake sample, about 72% of the CHCl_3 came from the FA fraction, whereas, for the river sample 80% of the CHCl_3 production came from the FA fraction.

Conclusions

The major THM precursor fraction in aquatic humic material is the low molecular weight fulvic acid fraction. This fraction has a high charge density and a high surface activity (Visser, 1979). The low molecular weight and high surface activity of material will make it difficult to remove from water by normal coagulation/flocculation and/or adsorption water treatment processes.

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TABLE 1. Diaflo membrane ultrafilters used for the fractionation of the humic material*.

Type	Average pore size (nm)	Nominal mw cut-off measured on proteins
UM05	1.1	500
UM2	1.2	1,000
UM10	1.5	10,000
UM20 ^E	2.0	~20,000
PM30	2.4	30,000
XM50	3.2	50,000
XM100 ^A	5.2	100,000
XM300	18.0	300,000

* information supplied by Amicon Corporation, Lexington, Mass, U.S.A.

TABLE II. Chloroform production during chlorination of the 20,000-30,000 mw fraction of fulvic and humic acids from different environments (data in $\mu\text{g CHCl}_3/\text{mgTOC}$ of humic material).

Sample	FA	HA
lake	135	171
river	151	108
swamp	93	121

TABLE III. Seasonal variations in chloroform production during chlorination of fulvic and humic acids from the river environment with the same mw range (20,000-30,000) (data in $\mu\text{g CHCl}_3/\text{mg TOC}$ of humic material)

	June 1973	Feb. 1974	April 1974	May 1974	July 1974	Sept. 1974
FA	151	122	151	*	144	151
HA	117	*	108	108	111	126

* no data available.

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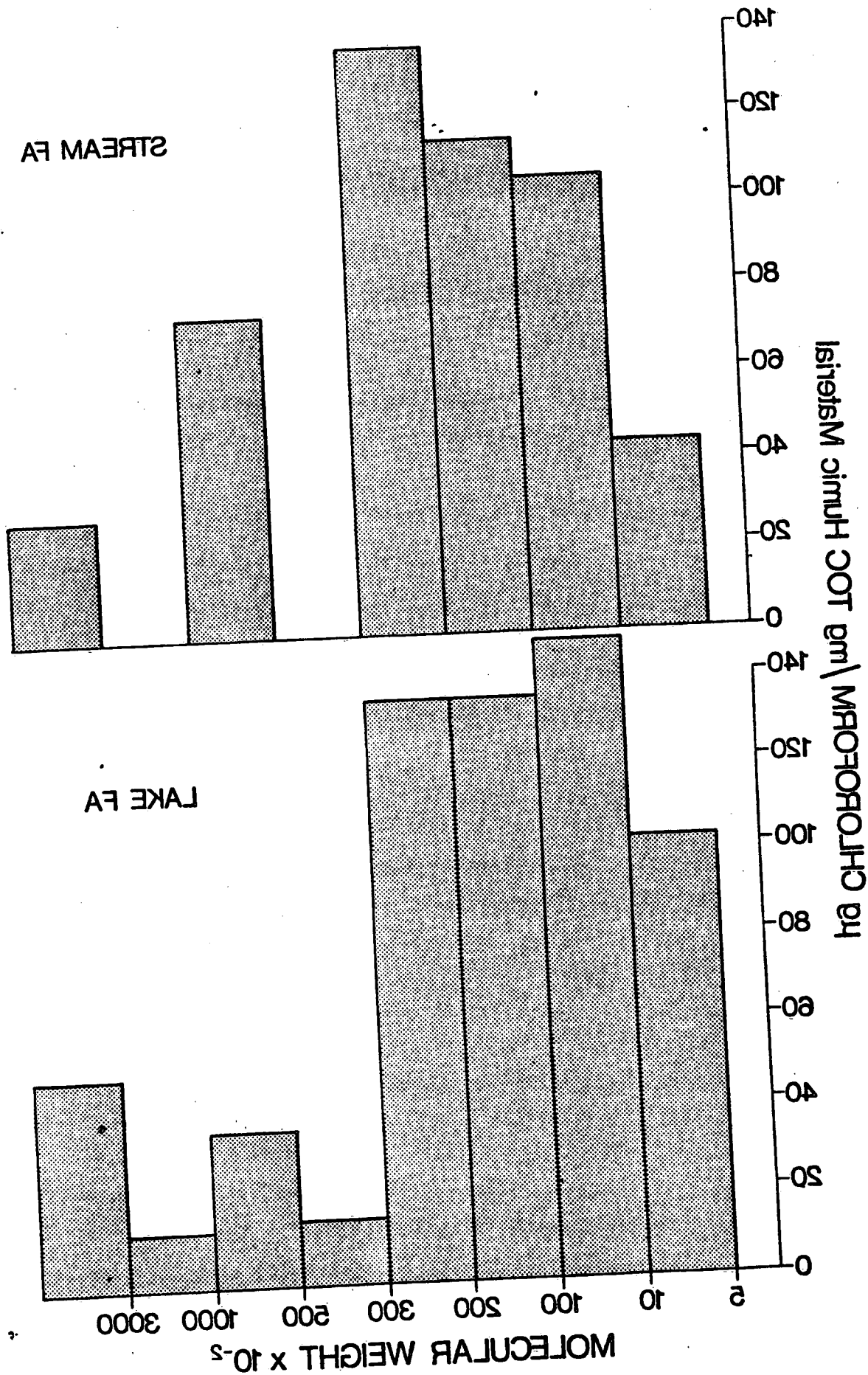
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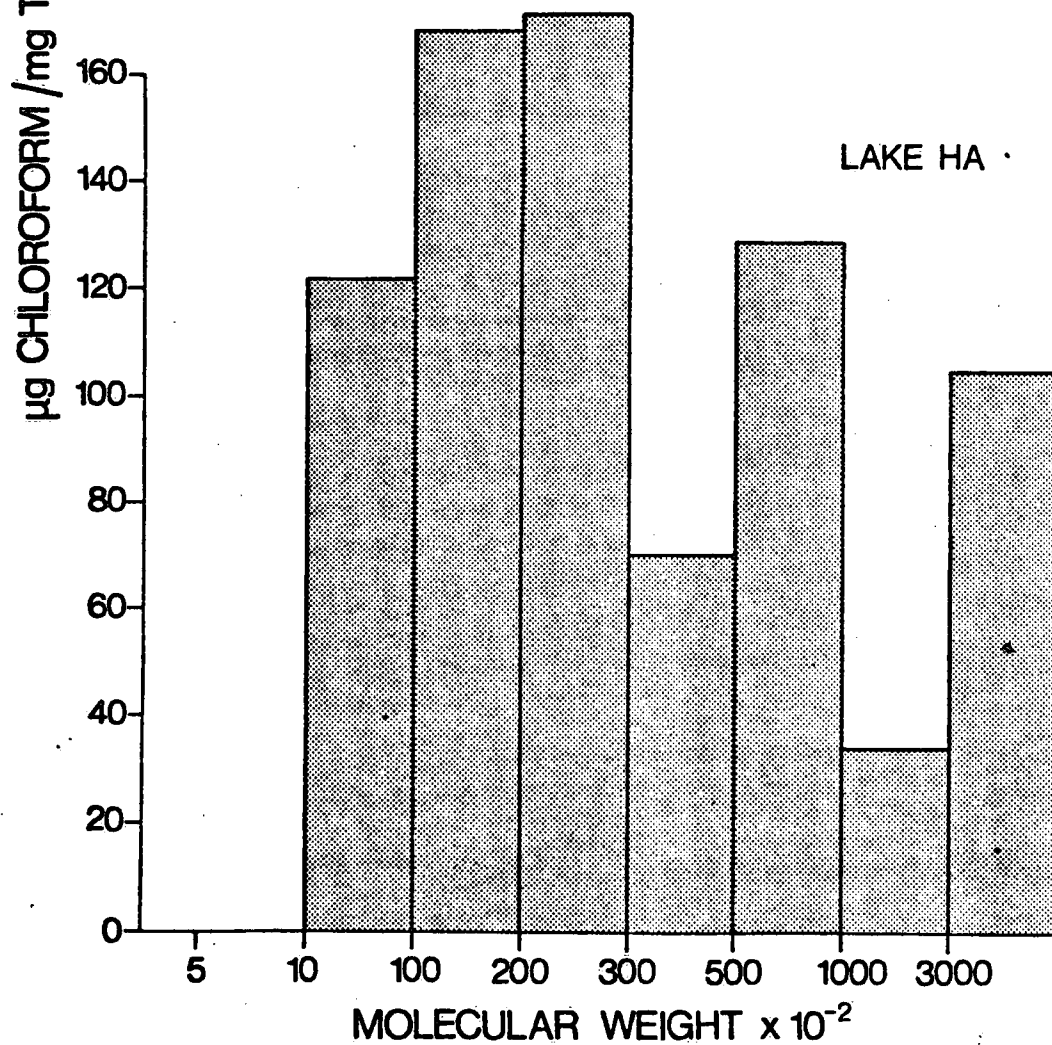
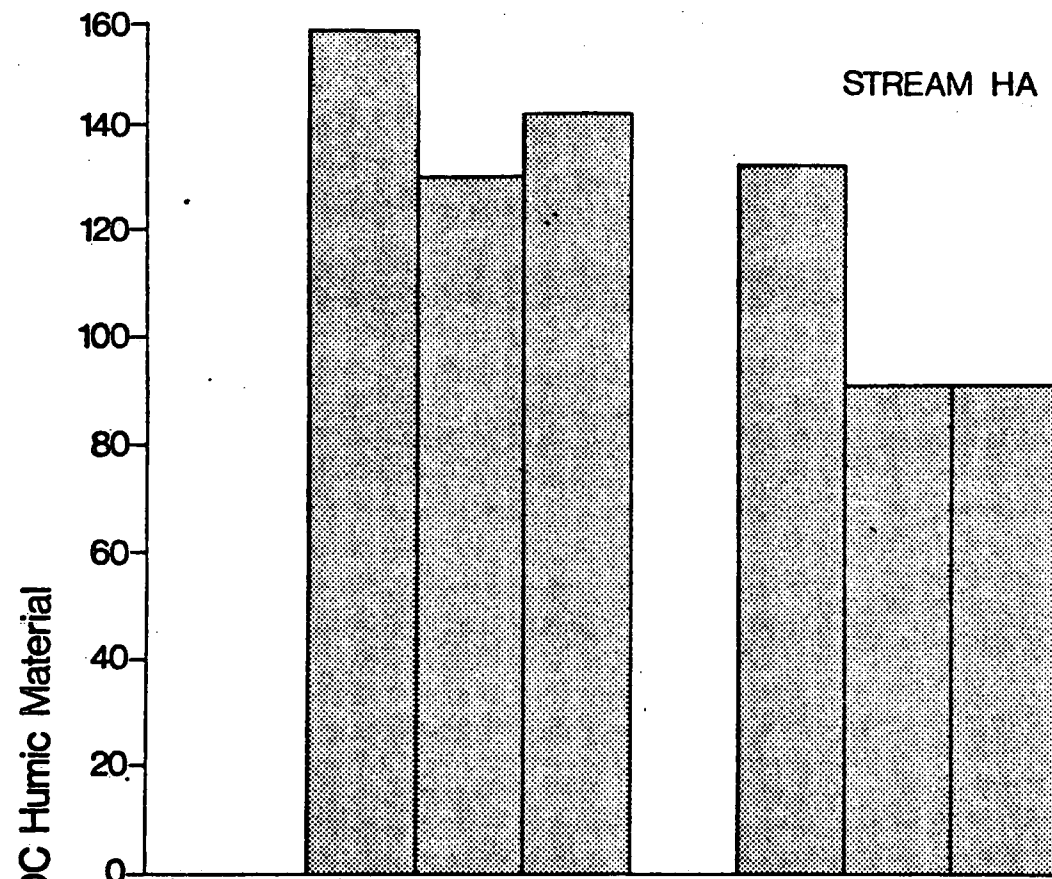
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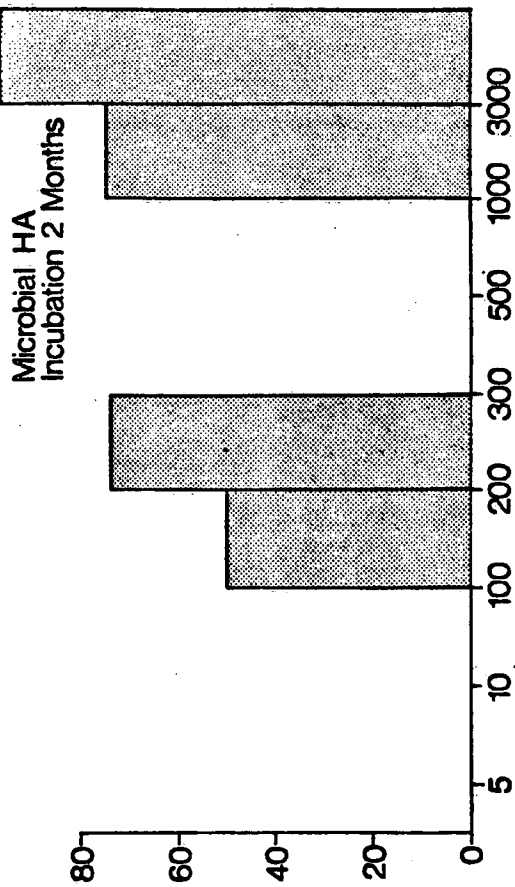
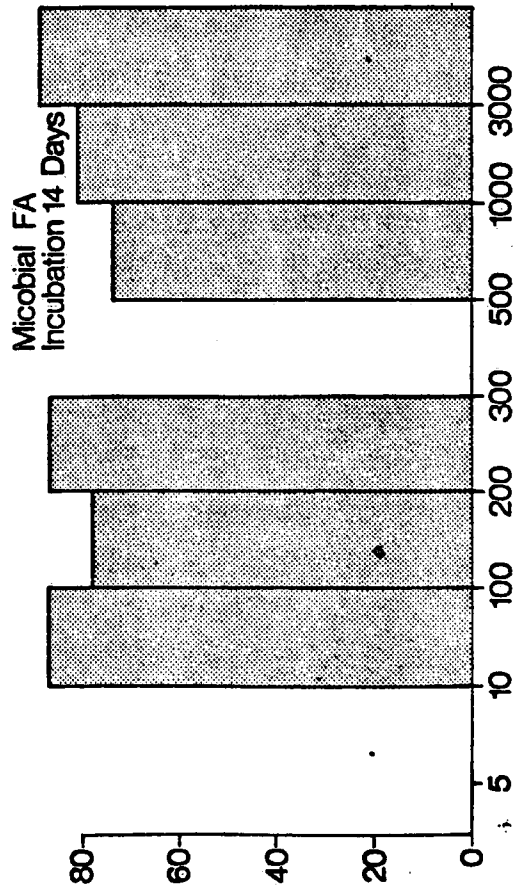
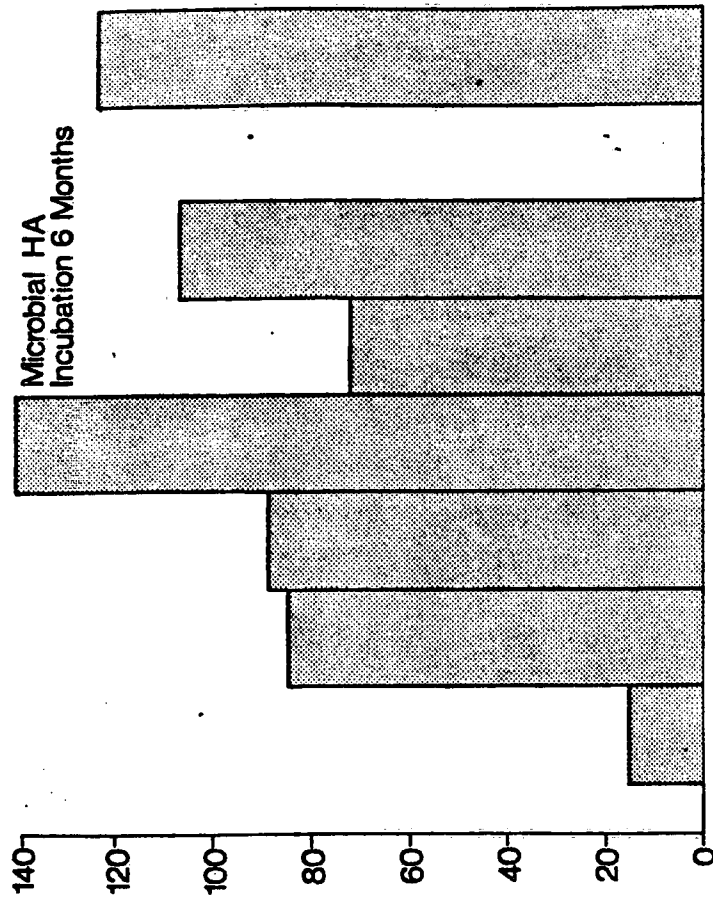
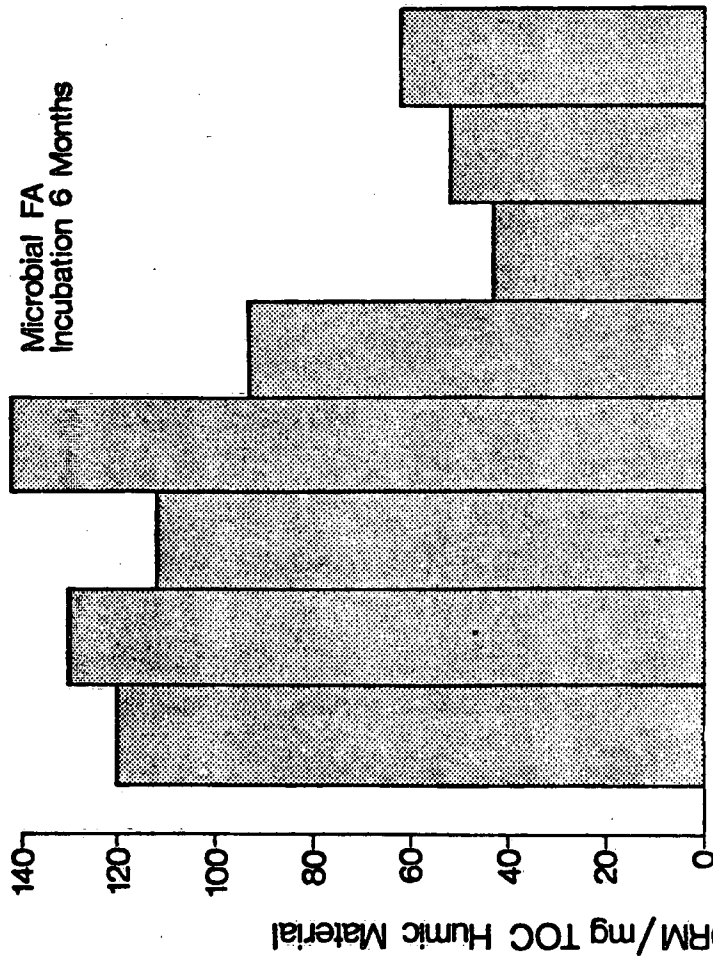
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FIGURE CAPTIONS

- Fig. 1. The effect of molecular weight on the chloroform production from chlorination of lake and stream fulvic acid.
- Fig. 2. The effect of molecular weight on the chloroform production from chlorination of lake and stream humic acid.
- Fig. 3. The effect of molecular weight on the chloroform production from chlorination of microbially-produced humic and fulvic acids.
- Fig. 4. The effect of molecular weight on the chloroform production per liter of original sample from chlorination of lake and stream fulvic and humic acids.







MOLECULAR WEIGHT $\times 10^{-2}$

