

Studies on the evaluation of physical chemical processes for the removal of organohalogen precursors during water purification: Part I. Preliminary investigations of polymaleic acid as a model organohalogen precursor.

DI Welch*, RA van Steenderen and PG van Rossum

National Institute for Water Research, Council for Scientific and Industrial Research, P.O. Box 395, Pretoria 0001, South Africa

Abstract

The use of polymaleic acid (PMA) as a model organohalogen precursor is an innovation in water chemistry. The distribution of pentane-soluble organohalogens formed by the chlorination of PMA, in the absence and presence of bromide ions is presented. Chloroform accounted for 96% of the identified volatile organohalogens, but in the presence of bromide ions, bromoform was the major product.

Preliminary investigations revealed similarities between the molecular size distribution of PMA and a municipal sludge effluent when illustrated as dissolved organic carbon (DOC) and ultraviolet absorption (UVA). In terms of total organohalogen formation potential (TOHp) however, the active fractions of PMA and the natural material did not coincide under the experimental conditions described.

Mutagenic activity, as measured by the Ames *Salmonella* mutagenicity assay was not detected for either PMA or chlorinated PMA.

Introduction

Soil organic matter is continuously subjected to chemical and biological processes until the chemical constituent components are no longer recognisable. Humification is the name given to such processes, and the relatively stable brown or black amorphous polymers formed are collectively known as the humic substances. Humic substances are the most extensively distributed natural product in the biosphere. They are found not only in soils but also in freshwater, marine environments and sediments. Humic substances are most commonly separated chemically into base soluble humic acid (HA) and acid and base soluble fulvic acid (FA) (Odén, 1919).

Most surface water sources contain a certain amount of aquatic humus which imparts a characteristic yellowish-brown colour (Gjessing, 1976). Until comparatively recently, aquatic humus was never considered to be a major pollution problem (Gjessing, 1976). However, Rook (1974) and Bellar *et al.* (1974) were the first of many researchers world-wide to have shown that when drinking-water is disinfected using chlorine, the chlorine reacts with the organic matter naturally present to form organohalogenated compounds, and especially the volatile trihalomethanes (THMs). The possible deleterious health effects of the long-term exposure to small quantities of organohalogens in drinking-water, have led health authorities in many countries to set maximum contaminant levels to limit the formation of these compounds in potable supplies (USEPA, 1978).

Although tannic acid (Youssefi *et al.*, 1978), nitrogen-containing compounds (Morris and Baum, 1978) and both algal biomass and extracellular products (Hoehn *et al.*, 1980) can react with chlorine to produce organohalogens, many workers (Stevens *et al.*, 1976; Babcock and Singer, 1979; and Fielding, 1980) have shown in laboratory experiments that the major organohalogen precursors are the aquatic fulvic acids.

Conventional treatment methods, whether physical/chemical or biological are capable of removing a proportion of the organohalogen precursors when optimized specifically to do so (Semmens and Field, 1980; Zabel, 1980). Humification however,

is a dynamic process which is affected by environmental conditions and seasonal variations. Thus the production and compositional complexity of aquatic humus do not remain constant. The variable nature of humus production makes the detailed laboratory-scale evaluation and optimization of treatment processes to remove aquatic humic substances extremely difficult, and has led to uncertainty amongst water treatment engineers as to which of the many treatment alternatives is most suitable to control organohalogen formation. A completely synthetic model compound which very closely resembles the structural backbone of aquatic humus, but does not contain the complex array of variable non-humic moieties which are associated with the natural substances, would be an extremely valuable tool in gaining an in-depth understanding of the processes and reactions which occur during drinking-water treatment and chlorine disinfection.

The major component of fulvic acid (FA) is a polycarboxylic acid (PCA) together with smaller amounts of metals, polysaccharides, peptides, phenols and possibly natural growth regulators and synthetic herbicides and pesticides (Linehan, 1977).

The product arising from the hydrolysis of pyridine-catalysed homopolymerised maleic anhydride (Braun and Pomakis, 1974), namely polymaleic acid (PMA), has been suggested by Anderson and Russel (1976) and later verified by Welch (1981), to be chemically and structurally closely related to the PCA fraction of soil fulvic acid. Linehan (1978), Malcolm and Vaughan (1979) and Linehan and Shephard (1979) have also shown that PMA acts as a physiological model for soil fulvic acid.

This paper, the first in a series, describes some preliminary investigations concerning the suitability of PMA as a model for aquatic humus, and as an organohalogen precursor. Some comparisons are made between PMA and the natural aquatic humus of the raw water intake to the Windhoek Water Reclamation Plant in South West Africa (SWA) to gain a better understanding of the reactions which take place between aquatic humus and chlorine in order to modify water purification configurations to control organohalogen formation.

The raw water intake to the WRP was selected for comparison for the following reasons:

- The raw water intake (WR1) is derived from an activated sludge plant. This type of plant is commonly found in South Africa.

*To whom all correspondence should be addressed.

Received 25 February 1985.

- The Windhoek Water Reclamation Plant has been intensively studied by the National Institute for Water Research over the past 18 years.
- Windhoek drinking-water supply is supplemented with reclaimed water, and as such its quality is continuously monitored.
- The plant treats activated sludge effluent which is principally derived from domestic sources, and is not subjected to industrial effluent contamination prior to reclamation.
- Large fluctuations in the quality of WR1 are largely prevented by passage through a series of stabilization ponds.

Materials and experimental

The pyridinium salt of polymaleic acid was prepared by the pyridine-catalysed homopolymerisation of maleic anhydride (Braun and Pomakis, 1974), and acidified to the acid form with Amberlite IR-120 (H⁺) cation-exchange resin.

The water used in this study (WR1) was taken from the raw feed water to the Windhoek Water Reclamation Plant, which was derived from the activated sludge plant effluent (Gamman's Sewage Purification Plant) in Windhoek. This effluent passed through a system of nine maturation ponds with a retention time of 14 days, before gravitating to the Windhoek Water Reclamation Plant (Van Steenderen, 1982).

Polymaleic acid (PMA) and the Windhoek water (WR1) were fractionated separately by membrane ultrafiltration, using an Amicon Model 202 cell with 62 mm diameter Diaflo ultrafilters maintained at their maximum operating pressures (241 x 10³ Pa to 345 x 10³ Pa). Fractions of the polymeric organic matter which were retained by filters having molecular weight exclusions of 100 000, 10 000, 1 000 and 500 atomic mass units (AMU) (calibrated with respect to globular proteins) were collected. The exact characterization of the PMA molecular size fractions has been described elsewhere (Welch, 1981). Prior to fractionation by membrane ultrafiltration, both PMA and WR1 were passed through a 46 mm diameter, 0,45 µm pore size filter (Gelman Sciences Inc., Michigan) at water pump vacuum on a Büchner funnel.

The fractionated and unfractionated materials were analysed for total organohalogen formation potential (TOH_p) by the microcoulometric titration method (Van Steenderen, 1980), for dissolved organic carbon (DOC) using the potassium persulfate/UV irradiation technique (Van Steenderen and Lin, 1981), and for UV absorbance at 275 nm in a 10 mm quartz cell using a Perkin Elmer LC 55 spectrophotometer.

The rapid liquid-liquid extraction process using pentane (Van Rensburg *et al.*, 1978) was used to extract the volatile organohalogens produced by an aliquot (50 ml) of a 5 mg/l stock solution of unfractionated PMA, subjected to 1 ml of a hypochlorous acid solution containing 13 mg/ml Cl₂, and incubated in the dark for 48 h. The volatile pentane-soluble products were separated and identified using a HP 5700 gas chromatograph with a flexible quartz column (30m x 0,32mm ID) wall-coated with D3-5 (J & W Scientific Inc. Rancho Cordova, Ca, USA). The carrier gas (helium) flow rate was 1 ml/min and electron capture detection (300°C) was used. A temperature programme of 4 min at 40°C, followed by heating at 3,5°C/min to 70°C, then further heating at 20°C/min to 270°C, resulted in good separation of the volatile products. Identification of the major pentane-soluble products was based upon co-elution with authentic compounds. Chlorobromopropane was used as the internal standard. The experimental procedure was repeated using a 50 ml aliquot of the same stock solution of PMA (5 mg/l) which had been chlorinated to 13 mg Cl₂ in the presence of bromide ions. During the chlorination, the pH of the PMA solutions was left unadjusted at pH 5,31.

Mutagenicity testing of filter sterilized (0,22 µm) unfractionated PMA solution (50 ml containing 50 mg PMA) which had been subjected to chlorination (0,5 ml of a solution 13 mg/ml Cl₂) for 168 h, in the dark, was carried out according to the plate incorporation assay (Ames *et al.*, 1975), using *Salmonella typhimurium* strain TA98 (Ames *et al.*, 1975) as the test organism without rat liver enzyme. Strain TA98 had been found in previous studies (Van Rossum *et al.*, 1982) to be the most responsive to XAD resin and methylene chloride extracts of Pretoria tap water. An unchlorinated control sample was also tested. All tests were conducted in triplicate (Grabow, *et al.*, 1980).

The elemental analysis of the total PMA polymer was

TABLE I
VOLATILE HALOGENATED HYDROCARBON ANALYSIS OF CHLORINATED PMA (A) AND CHLORINATED PMA IN THE PRESENCE OF BROMIDE IONS (B)

| Compound | Peak number | Retention time (min) | Concentration (µg/l) | |
|--|-------------|----------------------|----------------------|--------------------|
| | | | A | B |
| Chloroform | 1 | 3,46 | 373,1 ¹ | 280,3 ¹ |
| Dichlorobromomethane | 4 | 6,01 | 3,7 | 4,9 |
| Dibromochloromethane | | 9,48 | ND | 2,4 |
| Bromoform | 8 | 13,46 | ND | >650 ² |
| Chlorobromopropane (Internal standard) | 5 | 6,46 | | |
| Tetrachloromethane | | 4,30 | 0,3 | 0,3 |
| 1,1,1-trichloroethane | 2 | 4,06 | 2,4 | 2,3 |
| 1,1,2-trichloroethane | 3 | 4,36 | 9,1 | 11,5 |
| 1,2-dibromoethane | 6 | 10,30 | ND | 2,1 |
| 1,1,2,2-tetrachloroethylene | 7 | 10,42 | 0,2 | 0,2 |
| 1,1,2,2-tetrachloroethane | 9 | 15,54 | ND | 293,5 ¹ |
| 1,1,2,2-tetrabromoethane | | 19,30 | ND | 5,2 |
| Unknowns | | | 65,9 | 1321 |
| Total trihalomethanes | | | 377 | 288 ⁺ |
| Total halogenated solvents | | | 13 | 315 |

ND = Below detection limit (detection limits for CHCl₃ are 2-150 µg/l)

1 = Concentration exceeds detection limit but is extrapolated by the data system

2 = Excessive concentration, exceeds detection limit and extrapolative capacity of data system

conducted on a Hewlett Packard 185 CHN analyser. Oxygen content was estimated by difference.

Results and discussion

PMA reacted with chlorine at room temperature (22°C), in the dark, to produce an array of chlorinated organic products. Figure 1A is a gas chromatogram of the major pentane-soluble volatile chlorinated products. From Table 1, it can be seen that the predominant product was chloroform which accounted for 82% of the total detectable products and 96% of the identified vola-

tile organohalogenes. Small quantities of 1,1,1-trichloroethane, 1,1,2-trichloroethylene were also detected. The formation of dichlorobromomethane, and 1,2-dibromomethane was indicative of the presence of a trace amount of bromide contamination in the reaction mixture. Unknown volatile organohalogenes accounted for approximately 15% of the total volatile products detected.

It can be estimated from the elemental analysis of PMA (C = 48,76; H = 3,30; N = 0,82; O = 47,12%) that a 5 mg/l solution contained 2 438 µg of carbon, of which 37,5 µg reacted to form chloroform. Thus 1,5% of the organic carbon reacted in 48 h to produce chloroform. Clearly the overall reaction of PMA with chlorine was relatively minor in terms of the polymer converted, but the percentage organic carbon of natural aquatic humus which reacted to form chloroform has also been estimated to be small, in the order of 0,2 to 1,6%, as reported by Fielding (1980). Therefore, when compared with the natural materials, PMA is a vigorous organohalogen precursor.

Bromide ions strongly affect organohalogen formation because they compete with the organic precursor sites on the humic polymers for the oxidising potential of chlorine. As a result of bromide oxidation by chlorine, bromine is formed which reacts more intensely than chlorine itself with aquatic humus, and thus favours the formation of halogenated products (Rook, 1978). Figure 1B is the gas chromatogram obtained of the pentane-soluble volatile organohalogenes formed when PMA solution was chlorinated in the presence of bromide ions. The chromatogram shows that PMA like aquatic humus is more reactive to hypobromous acid than to hypochlorous acid. The major product formed in the presence of bromide was bromoform, followed by a series of unknown products which were all present in excessive concentrations, above the detection limits of the gas chromatograph and extrapolative facility of the chromatographic data system. It can therefore be stated that PMA is a model organohalogen precursor which is as reactive with chlorine and as receptive to bromide interference as aquatic humus.

The molecular size distribution of PMA and some of the properties of the fractionated material are presented in Figure 2, together with data on the fractionation of Windhoek raw water (WR1) as a comparison with a natural material.

The number average molecular weights (M_{na}) of both PMA and WR1 occur between 10 000 and 100 000 AMU. Although the molecular size distribution of aquatic humus varies between water sources, different physical/chemical treatment processes, and changes in environmental conditions (Grady *et al.*, 1984; Veenstra *et al.*, 1983; Oliver and Visser, 1980), the M_{na} of the activated sludge effluents obtained from the Windhoek and Pretoria areas commonly falls within the range 10 000 to 100 000 AMU (NIWR/CSIR, 1974). Thus PMA is a good model, in terms of molecular size distribution, expressed as DOC, for those particular effluents. However, if the reaction temperature during the polymerization of maleic anhydride is kept below 40°C the M_{nd} of the resulting PMA has been estimated to be 1 800 AMU (Welch, 1981). The PMA used in this study was polymerized at a temperature of 45°C which resulted in increased decarboxylation and a shift in the molecular size distribution towards larger molecules.

Differences exist between the distributions of both UV absorbance at 275 nm and total organohalogen formation potential (TOH_p) in the PMA and WR1 fractions. The UV absorbance showed a peak in the PMA fraction which passed through a 0,45 µm filter but was retained by a 100 000 AMU filter, whereas the maximum UV absorbance was detected in the WR1 fraction >10 000 but <100 000 AMU. The fraction of PMA which was the

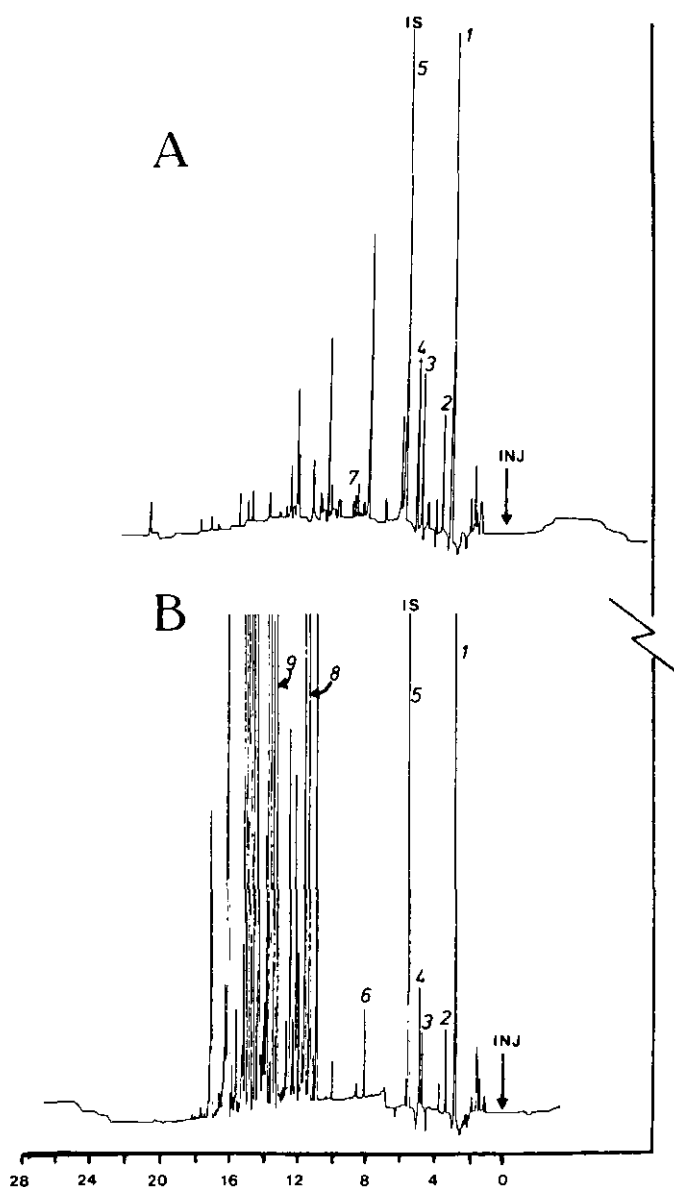


Figure 1

A - Gas chromatogram of pentane-soluble products from the chlorination of a 5 mg/l solution of polymaleic acid (PMA) for 48 h in the dark at pH 5,31.

B - The chlorination of the same stock solution of PMA under the same experimental conditions in the presence of bromide ions. Products identified by co-elution with authentic compounds; (1) chloroform; (2) 1,1,1-trichloroethane; (3) 1,1,2-trichloroethylene; (4) dichlorobromoethane; (5) internal standard, chlorobromopropane; (6) 1,2-dibromoethane; (7) 1,1,2,2-tetrachloroethylene; (8) bromoform; (9) 1,1,2,2-tetrachloroethane. GC conditions: flexible quartz column (30 m x 0,32 mm ID) wall-coated with DB-5; carrier gas 1 ml min⁻¹ (helium); temperature programme 40°C isothermal for 4 min, 3,5°C min⁻¹ to 70°C followed by 20°C min⁻¹ to 270°C.

most active organohalogen precursor was that which was retained by a 0,45 μm filter, compared to the fractionated WR1 material which showed a peak in the range >10 000 but <100 000 AMU. These results might suggest that the sites on humic polymers which are responsible for organohalogen formation are also UV absorbing. This assumption is reasonable if one considers that carbonyl groups, for example typically exhibit $\pi \rightarrow \pi^*$ and the forbidden $n \rightarrow \pi^*$ transitions which absorb at 190 nm and 280 nm respectively. Acetyl groups contain carbonyl functions and readily undergo the classical haloform reaction (Morris and Baum, 1978). Unfractionated PMA contains 1,8 meq g^{-1} carbonyl, whereas the PMA fraction of >10 000 relative molecular mass contains 3,6 meq g^{-1} carbonyl (Welch, 1981). The differences which are ex-

hibited (Figure 2) between PMA and WR1 in terms of TOHp are probably the result of the presence in WR1 of an array of non-humic substances which would compete with aquatic humus content of WR1 for the oxidising potential of chlorine. PMA has previously been shown to closely resemble fulvic acids (Anderson and Russell, 1976 and Welch, 1981) which are the most active organohalogen precursors found in water (Stevens *et al.*, 1976 and Babcock and Snger, 1979). In future studies PMA models will be prepared which contain 'guest' molecules, such as phenolic acids, peptides and carbohydrates which are undoubtedly present in activated sludge effluent. Present studies by the authors (Welch and Van Steenderen) indicate that the molecular size profile of WR1, in terms of TOHp (Figure 2) is altered by the addition of

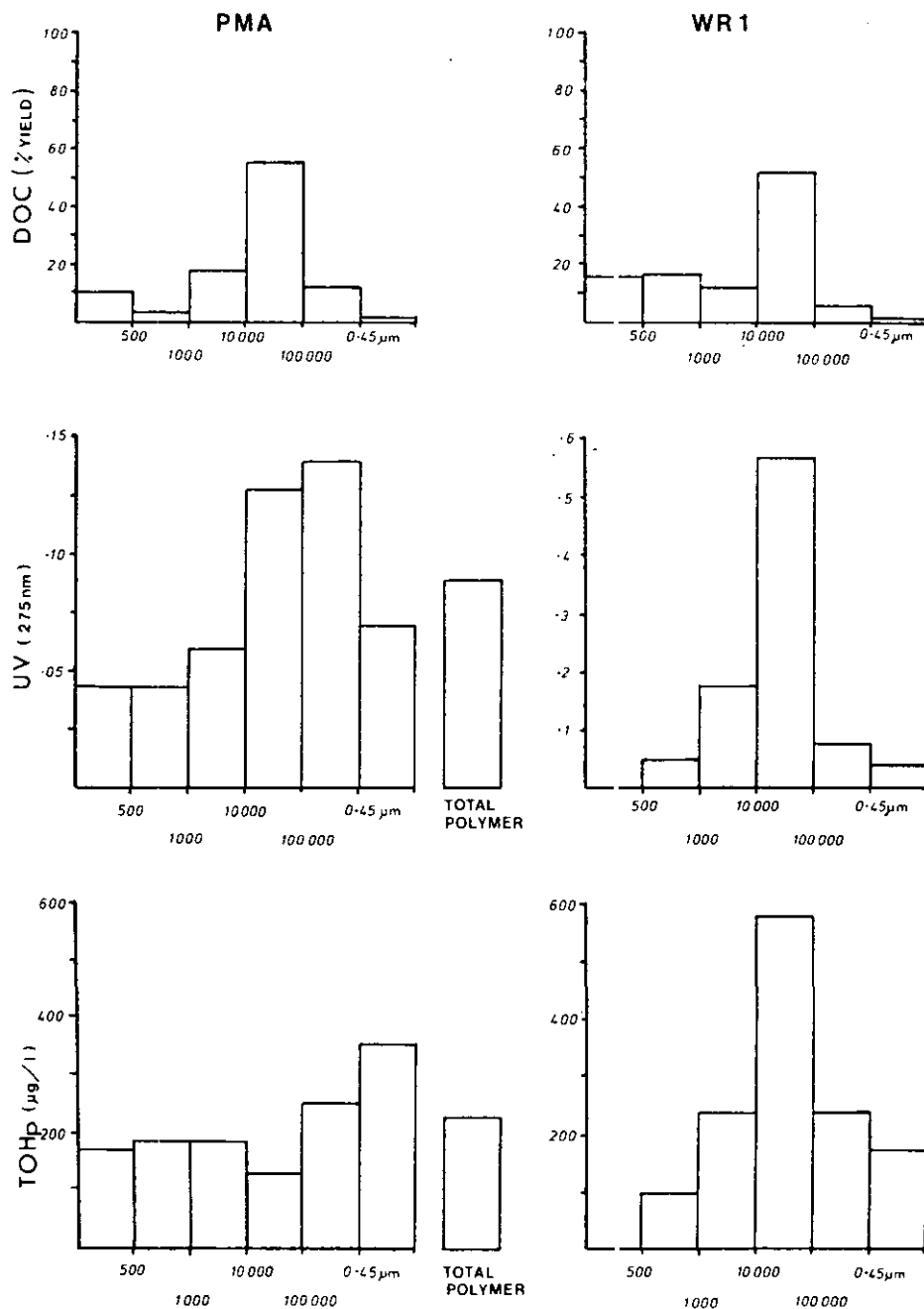


Figure 2
Molecular size distribution (AMU) by membrane ultrafiltration of polymaleic acid (PMA) and Windhoek raw water (WR1), expressed in terms of the percentage yield of dissolved organic carbon (DOC) fractionated, ultraviolet absorption at 275 nm, and total organohalogen formation potential (TOHp) as $\mu\text{g}/\text{l}$ chloroform.

different coagulants and activated carbon to show a closer resemblance to the profile of PMA.

Today it is known that organohalogens are produced in any surface water which contains dissolved organic matter and is subjected to chlorination. In South African drinking-waters, Grabow *et al.* (1980) have detected mutagenic activity, as indicated by the Ames *Salmonella* mutagenicity assay (Ames *et al.*, 1975), specifically associated with the presence of chlorinated organohalogens. Mutagenic activity however, was not detected by means of the Ames test using tester strain TA98 in the absence of S9 liver preparation using the Ames test (Ames *et al.*, 1975) on either PMA or chlorinated PMA. Thus the organohalogens produced by aquatic humus which are associated with producing mutagenic activity as measured by the Ames test (Ames *et al.*, 1975) are probably not produced by PMA. This result may indicate that it is not the organohalogen products arising from the reaction of chlorine with the humic polymer which are responsible for producing mutagenic activity, but the products arising from the reaction of chlorine with "non-humic" species, such as lignin degradation products, which are associated with the humic polymer. PMA closely associates with carbohydrates, amino acids, peptides and phenolic acids, and these molecules can also be introduced at the polymerization stage as "guest molecules" in the polymer structure. Thus studies on the mutagenic activity of PMA polymers with "guest molecules" which have been subjected to chlorination would show if this assumption is correct. The ability of PMA to incorporate 'guest molecules', is a further reason why conceptually PMA is an attractive model compound for aquatic humus.

Although the complete structure of PMA has yet to be elucidated, it is known to have an aliphatic or alicyclic 'backbone' substituted by vicinal carboxyl groups (Anderson and Russell, 1976; Welch, 1981). The suggestion that PMA is a model for the PCA fraction of FA (Anderson and Russell, 1976) is an innovation in humic substance chemistry, since the more widely accepted structures for humic substances have been based on the aromatic residues derived from the microbial degradation of lignin or tannin (Ogner and Schnitzer, 1971; Khan and Schnitzer, 1971; Flaig *et al.*, 1975). These aromatic structures for humic substances have been adduced largely on the basis of chemical degradation studies. To interpret polymer structure from the distribution of degradation products which in themselves may only account for a small proportion of the total polymer degraded is extremely difficult. An example of the inherent difficulties in interpreting degradation data into polymer structure was seen during a controversy over the aromatic (Hayatsu *et al.*, 1975; Hayatsu, 1976) or non-aromatic (Chakrabartty and Berkowitz, 1976) structure of coal. Each group draws very different conclusions from similar studies.

The close chemical, structural and physiological similarities between PMA and the PCA fraction of soil fulvic acid shown in a previous study (Welch, 1981) and the fact that it reacts with chlorine, as shown in the present study, make PMA an attractive model for aquatic humus, and an innovation in the field of water chemistry. Because PMA is the product of a defined polymerisation process it is possible to introduce structural modifications during polymerisation, perhaps allowing for a precise definition of the relationship between the structure of humic substances, organohalogen formation and the reactions which occur during their removal by physical/chemical processes. It can be synthesized with ¹⁴C labelling of carbon other than carboxyl with high levels of radioactivity, thus simplifying the investigation of its reactions in water, and providing further opportunities for understanding the properties of aquatic humus.

Further research

The results reported in this paper represent the first phase of investigations which will involve the use of PMA as a model organohalogen precursor for the following purposes:

- To gain a better understanding of the reactions and reaction kinetics which take place between aquatic humus and chlorine.
- Modification of water purification systems to control organohalogen formation. This could include, for example, evaluation and optimization of coagulants, activated carbons, resins, oxidants and high lime treatment for removing organohalogen precursors; application of disinfectants that minimise organohalogen formation, and their efficacy as disinfectants when in contact with aquatic humus; evaluation of the importance of biological activity versus adsorption when removing organohalogen precursors by granular activated carbons; investigation of membrane fouling by aquatic humus during reverse osmosis; and the use of UV radiation and oxidants to remove organohalogen precursors.
- To trace the formation of mutagenic activity as measured by the Ames test (Ames *et al.*, 1975) in chlorinated drinking-water.

Acknowledgements

The efficient analytical services of Mr A.J. Hassett and Mrs A. van Rossum are acknowledged. This paper is published by permission of the National Institute for Water Research.

References

- AMES, B.N., McCANN, J. and YAMASAKI, E. (1975) Methods for detecting carcinogens and mutagens with the *Salmonella*/mammalian-microsome mutagenicity test. *Mutation Research* 31 347-364.
- ANDERSON, H.A. and RUSSEL, J.D. (1976) Possible relationship between soil fulvic acid and polymaleic acid. *Nature, Lond.* 260 p. 597.
- BABCOCK, D.B. and SINGER, P.C. (1979) Chlorination and coagulation of humic and fulvic acids. *J. Am. Wat. Wks. Ass.* 71 149-152.
- BELLAR, T.A., LICHTENBURG, J.J. and KRONER R.C. (1974) The occurrence of organohalides in finished drinking-waters. *J. Am. Wat. Wks. Ass.* 66 703-706.
- BRAUN, D. and POMAKIS, J. (1974) Über die Polymerisation von Maleicäureanhydrid mit organischen Basen. *Makromolek. Chem.* 175 1411-1425.
- CHAKRABARTTY S.K. and BERKOWITZ, N. (1976) Aromatic structures in coal. *Nature, Lond.* 261 76-77.
- FIELDING, M. (1980) Formation of trihalomethanes in water. Paper No. 1 of a Seminar: Trihalomethanes in Water, held at Water Research Centre, Medmenham Laboratory, Medmenham, P.O. Box 16, Marlow, Bucks SL7 2HD, England. 3-26.
- FLAIG, W., BEUTELSPACHER, H. and REITZ, E. (1975) Chemical composition and physical properties of humic substances. In *Soil Components* (J.E. Gieseking, ed) Vol. 1, 1-212. Springer, New York.
- GJESSING, E.T. (1976) *Physical and Chemical Characteristics of Aquatic Humus*. Ann Arbor Science, Michigan, 48106.
- GRABOW, W.O.K., DENKHAUS, R. and VAN ROSSUM, P.G. (1980) Detection of mutagens in waste-water, a polluted river and drinking-water by means of the Ames *Salmonella*/microsome assay. *S. Afr. J. Sci.* 76 118-123.
- GRADY, Jr. C.P.L., KIRSCH, E.J., KOCZWARA, M.K., TRGOVEICH, B. and WATT, R.D. (1984) Molecular weight distributions in activated sludge effluents. *Water Research* 18 239-246.
- HAYATSU, R., SCOTT, R.G. MOORE, L.P. and STUDIER M.H. (1975) Aromatic units in coal. *Nature, Lond.* 257 378-380.

- HAYATSU, R. (1976) Aromatic structures in coal. *Nature, Lond.* 261 p. 77.
- HOEHN, R.C., BARNES, D.B., THOMPSON, B.C., RANDALL, C.W., GRIZZARD, T.J. and SHAFFER, P.T.B. (1980) Algae as sources of trihalomethane precursors. *J. Amer. Wat. Wks. Ass.* 72 344-350.
- KHAN, S.U. and SCHNITZER, M. (1971) Further investigations on the chemistry of fulvic acid, a soil humic fraction. *Can. J. Chem.* 49 2302-2309.
- LINEHAN, D.J. (1977) Growth promoting properties of soil fulvic acid and a synthetic polycarboxylic acid. *Soil Biol. Biochem.* 9 427-428.
- LINEHAN, D.J. (1978) Humic acid on iron uptake by plants. *Plant and Soil* 50 663-670.
- LINEHAN, D.J. and SHEPHERD H. (1979) A comparative study of the effects of natural and synthetic ligands on iron uptake by plants. *Plant and Soil* 52 281-289.
- MALCOLM, R.E. and VAUGHAN, C. (1979) Comparative effects of soil organic matter fractions on phosphatase activities in wheat roots. *Plant and Soil* 51 117-126.
- MORRIS, J.C. and BAUM, B. (1978) Precursors and mechanisms of haloform formation in the chlorination of water supplies. In, *Water Chlorination: Environmental Impact and Health Effects*, (Edited by Jolley, R.L., Gordev, H. and Hamilton, D.H.). Ann Arbor Science, New York, 29-48.
- NIWR/CSIR (1974) Health aspects of drinking-water supplies, 2nd Annual Project Report, Part 1, pp. 17-18.
- ODÉN, S. (1919) Die Huminsäuren. *Kolloidchem. Beibefte* 11 75-98.
- OGNER, G and SCHNITZER, M. (1971) Chemistry of fulvic acid, a soil humic fraction, and its relation to lignin. *Can. J. Chem.* 49 1053-1063.
- OLIVER, B.G. and VISSER, S.A. (1980) Chloroform production from the chlorination of aquatic humic material: The effect of molecular weight environment and season. *Water Research* 14 1137-1141.
- ROOK, J.J. (1974) Formation of haloforms during chlorination of natural waters. *J. Wat. Treat. Exam.* 23 234-243.
- ROOK, J.J. (1978) Bromide oxidation and organic substitution in water. *J. Envir. Sci. Health* A13 91-116.
- SEMMENS, M.J. and FIELD, E.K. (1980) Coagulation: Experiences in organics removal. *J. Am. Wat. Wks. Ass.* 72 476-488.
- STEVENS, A.A., SEEGER, D.R. and ROBECK, G.G. (1976) Chlorination of organics in drinking-water. *J. Am. Wat. Wks. Ass.* 68 615-620.
- USEPA (UNITED STATES ENVIRONMENTAL PROTECTION AGENCY) (1978) *Control of organic chemical contaminants in drinking-water* Federal Register 4 5756.
- VAN RENSBURG, J.F.J., VAN HUYSTEEEN, J.J. and HASSETT, A.J. (1978) A semi-automated technique for the routine analysis of volatile organohalogenes in water purification processes. *Water Research* 12 127-131.
- VAN ROSSUM, P.G., WILLEMSE J.M., HILNER, C. and ALEXANDER, I. (1982) Examination of a drinking-water supply for mutagenicity. *Wat. Sci. Tech.* 14 163-173.
- VAN STEENDEREN, R.A. (1980) The construction of a total organohalogen analyser system. *Laboratory Practice* 29(4) 380-385.
- VAN STEENDEREN, R.A. and LIN, J.S. (1981) Determination of dissolved organic carbon in water. *Analytical Chemistry* 53 2157-2158.
- VAN STEENDEREN, R.A. (1982) An evaluation of the Windhoek water reclamation plant concerning the occurrence and fate of dissolved organic carbon and halogenated organic compounds during the period 16-21 September 1982. *CSIR/Department of Water Affairs joint research report* NIWR, P.O. Box 395, Pretoria 0001.
- VEENSTRA, J.M., BARBER, J.B. and KHAN, P.A. (1983) Ozonation: Its effect on the apparent molecular weight of naturally occurring organics and trihalomethane production. *Ozone, Science and Engineering* 5 225-244.
- WELCH, D.I. (1981) Studies on the structure and behaviour of (poly)-maleic acid as a model soil organic polymer. Ph.D. thesis, University of Aberdeen, Scotland.
- YOUSSEFI, M., ZENCHELKY, S.R. and FAUST, S.D. (1978) Chlorination of naturally-occurring organic compounds in water. *J. Environ. Sci. Health* A13 629-637.
- ZABEL, T. (1980) Treatment practice and trihalomethane control. Paper No. 8 of a seminar: Trihalomethanes in Water, held at Water Research Centre, Medmenham Laboratory, Medmenham, P.O. Box 16, Marlow, Bucks SL7 2HD, England 175-210.

GUIDE TO AUTHORS

AIMS AND SCOPE

This journal publishes refereed, original work in all branches of water science, technology and engineering. This includes water resources development; the hydrological cycle; surface hydrology; geohydrology and hydrometeorology; limnology; mineralisation; treatment and management of municipal and industrial water and wastewater; treatment and disposal of sewage sludge; environmental pollution control; water quality and treatment; aquaculture; agricultural water science; etc.

Contributions may take the form of a paper, a critical review or a short communication. A paper is a comprehensive contribution to the subject, including introduction, experimental information and discussion of results. A review may be prepared by invitation or authors may submit it for consideration to the Editor. A review is an authoritative, critical account of recent and current research in a specific field to which the author has made notable contributions. A short communication is a concise account of new and significant findings.

GENERAL

Submission of manuscripts

The submission of a paper will be taken to indicate that it has not, and will not, without the consent of the Editor, be submitted for publication elsewhere. Manuscripts should be submitted to: The Editor, WATER SA, P O Box 824, Pretoria, 0001, South Africa

Reprints

One hundred free reprints of each paper will be provided. Any additional copies or reprints must be ordered from the printer (address available on request).

Language

Papers will be accepted in English or Afrikaans. Papers written in Afrikaans should carry an extended English summary to facilitate information retrieval by international abstracting agencies.

Abstracts

Papers should be accompanied by an abstract. Abstracts have become increasingly important with the growth of electronic data storage. In preparing abstracts, authors should give brief, factual information about the objectives, methods, results and conclusions of the work. Unsubstantiated viewpoints should not be included.

Refereeing

Manuscripts will be submitted to and assessed by referees. Authors bear sole responsibility for the factual accuracy of their publications.

Correspondence

State the name and address of the author to whom correspondence should be addressed on the title page.

SCRIPT REQUIREMENTS

Lay-out of manuscripts

An original typed script in double spacing together with three copies should be submitted. Words normally italicized should be typed in italics or underlined. The title should be concise and followed by authors' names and complete addresses. A paper may be organized under main headings such as Introduction, Experimental, Results, Discussion (or Results and Discussion), Conclusions, Acknowledgements and References.

Contents of manuscripts

The International System of Units (SI) applies. Technical and familiar abbreviations may be used, but must be defined if any doubt exists.

Tables

Tables are numbered in arabic numerals (Table 1) and should bear a short but adequate descriptive caption. Their appropriate position in the text should be indicated.

Illustrations and line drawings

One set of original figures and two sets of copies should accompany each submission. Photographs should be on glossy paper (half-tone illustrations should be kept to a minimum) and enlarged sufficiently to permit clear reproduction in half-tone. All illustrations, line-drawings and photographs must be fully identified on the back, numbered consecutively and be provided with descriptive captions typed on a separate sheet. Authors are requested to use proper drawing equipment for uniform lines and lettering of a size which will be clearly legible after reduction. Freehand or typewritten lettering and lines are not acceptable. The originals should be packed carefully, with cardboard backing, to avoid damage in transit.

References

Authors are responsible for the accuracy of references. References to published literature should be quoted in the text as follows: Smith (1982) or (Smith, 1982). Where more than three authors are involved, the first author's name followed by *et al.* and the date should be used.

All references are listed alphabetically at the end of each paper and not given as footnotes. The names of all authors should be given in the list of references. Titles of journals or periodicals are abbreviated according to Chemical Abstracts Service Source Index (Cassi).

Two examples of the presentation of references are the following:

Grabow, W.O.K., Coubrough, P., Nupen, E.M. and Bateman, B.W. (1984) Evaluation of coliphages as indicators of the virological quality of sewage-polluted water. *Water SA* 10(1) 7-14.

Wetzel, R.G. (1975) *Limnology*. W.B. Saunders Company, Philadelphia, p 324..