

REMOVAL OF DISSOLVED HYDROPHOBIC AND HYDROPHILIC ORGANIC SUBSTANCES DURING COAGULATION/FLOCCULATION OF SURFACE WATERS

J. P. Croué*, E. Lefebvre**, B. Martin* and B. Legube*

* *Laboratoire de Chimie de l'Eau et des Nuisances, URA 1468, Université de Poitiers, 86022 Poitiers Cedex, France*

** *SAUR, Laboratoire Central de Maurepas, BP 126, 78312 Maurepas Cedex, France*

ABSTRACT

Dissolved organic carbon (DOC) from raw and coagulated surface waters was fractionated at acidic pH using two superposed XAD 8 and XAD 4 resin columns, into three fractions : hydrophobic substances (i.e. humic substances) adsorbed on XAD 8, hydrophilic acids adsorbed on XAD 4 and "non-acid" hydrophilics which represent the organics contained in the final effluent. DOC of untreated waters was evenly split between the hydrophobic and hydrophilic fractions. The "non-acid" hydrophilics were generally as or slightly more abundant than the corresponding hydrophilic acids. For three of the six waters studied, DOC distribution was not modified after coagulation/clarification treatment. These waters also exhibited a low reduction in THMFP and TOXFP per unit of DOC after treatment. One water showed moderate change and two a significant change in DOC distribution. With the latter, a large decrease of their THMFP/DOC and/or TOXFP/DOC ratios was observed. As expected, the apparent molecular weight distributions (1000 daltons nominal membrane cutoff) have been shifted toward the low molecular weight fraction. Aluminum coagulation experiments were carried out on isolated humic, fulvic and hydrophilic acids. Humic acids were identified as the most reactive fraction, with a dramatical reduction of their THMFP/DOC and TOXFP/DOC ratios after coagulation. Fulvic and hydrophilic acids were found to react to the same extent with the coagulant, and showed comparable THMFP and TOXFP per unit of DOC before and/or after coagulation.

KEYWORDS

Surface waters, coagulation, chlorination, ultrafiltration, Amberlite XAD 8 and 4, Hydrophobic/hydrophilic fractionation, Humic substances, Hydrophilic acids

INTRODUCTION

Among the various clarification processes employed in water treatment, coagulation is widely used for the reduction of turbidity or color in surface waters. A considerable amount of effort has been focused toward optimizing this process for dissolved organic matter (DOM) removal. The principal motivation has been removal of trihalomethane (THM) precursors.

Parameters used to evaluate DOM reduction efficiency of this treatment process have included, dissolved organic carbon (DOC) content, UV absorbance and color, trihalomethane formation potential and apparent molecular weight distribution. Studies have shown that coagulant selection and dose are governed by raw water quality including DOC, temperature and turbidity (O'Melia *et al.*, 1987). Many investigators have noted the importance of DOC in controlling coagulant dose (Semmens and Field, 1980; Dempsey *et al.*, 1985). For a given water, one of the most significant variable affecting coagulants is pH. Using optimal pH conditions, Semmens and Field (1980) have shown that 50 % of the DOC of the Mississippi river can be removed with alum. A 75 % reduction yield was obtained by Vik *et al.* (1985) on Norwegian lake waters using similar conditions and coagulant. The optimum pH condition was also found different for color or turbidity removal (Hall and Packham, 1965 ; Semmens and Field, 1980). As a general rule, higher molecular weight organics were found to be better eliminated during coagulation (Vik *et al.*, 1985 ; Semmens and Staples, 1986). Data obtained by Collins *et al.* (1985) indicated that THM yield increased with increasing

molecular weight. This led the same authors to conclude in a later work (Collins *et al.*, 1986) that the most reactive THM precursors are preferentially removed in water treatment.

To investigate source related effects on DOC and THM precursor removals, Semmens and Staples (1986), Collins *et al.* (1986) developed a DOC characterization technique based on the hydrophobic/hydrophilic fractionation by adsorption chromatography using XAD-8 resin. The hydrophobic fraction, defined as the organic compounds adsorbed on XAD-8 resin at acidic pH (Malcolm *et al.*, 1977; Thurman and Malcolm, 1981; Leenheer and Huffman, 1976) represents the most commonly used operational definition of aquatic humic substances. The results obtained in both studies have shown that hydrophobic compounds were slightly better removed than hydrophilic compounds during alum coagulation of river waters. Trihalomethane precursors were found evenly split between hydrophobic and hydrophilic fraction of untreated Mississippi river (Semmens and Staples, 1986), while hydrophobic organic compounds were more reactive in producing THMs in the untreated Grasse river (Collins *et al.*, 1986). In each case, hydrophobic THM precursors were preferentially removed during this clarification process.

Considerable attention has been directed on the coagulation of humic substances because of their role as precursors to the formation of organic halide compounds such as THM (Rook, 1977; ; Oliver and Lawrence, 1979 Babcock and Singer, 1984). Differences in the experimental conditions (speed rate, pH, buffers, settling time, effect of filtration step), in the origin and nature of the humic substances and in the isolation procedures used make comparison of the data difficult. Some general conclusions which can be draw are: 1) the stoichiometry of coagulation has shown a linear relationship between initial concentration of humic substances and coagulant dose (Glazer and Edzwald, 1979; Narkis and Rebhun, 1977), 2) the stoichiometric value is mainly related to pH, coagulant type, humic substances nature (Edzwald *et al.*, 1977; Dempsey *et al.*, 1984, Angbo, 1989; Kim *et al.*, 1989; Lefebvre et Legube, 1990). An optimum of pH 4 to 5 has been reported for iron, and pH 5-6 for aluminum (Hall and Packham, 1965; Van Breemen *et al.*, 1979; Jekel, 1985; Lefebvre et Legube, 1990). Aquatic fulvic acids were observed to be less amenable to removal than the corresponding aquatic humic acids (Babcock and Singer, 1979; Jekel, 1985; Lefebvre et Legube, 1990). While attention has focused on aquatic humic substances, relatively little is known about the hydrophilic acids which account for a significant percentage of the DOC in natural waters (Thurman, 1985).

Recently, Croué *et al.* (1992) developed a fractionation and isolation procedure of aquatic humic, fulvic and hydrophilic acids based on adsorption chromatography using XAD-8 and XAD-4 resins. The results obtained with both moderate (2 litre columns) and small (50 ml columns) size filtration units were found very reproducible. The fractionation analytical procedure that was developed with a small adsorption unit made of two superposed XAD-8 and XAD-4 resin columns was proposed as a characterization parameter for DOM.

In the studies described below, this analytical procedure was first applied to determine the change in the DOM distribution of six surface waters after coagulation/clarification. The DOM characterization was completed by the determination of trihalomethanes and total organic halide formation potentials (THMFP and TOXFP) and apparent molecular weight fractionation. In the second phase chlorination and coagulation/clarification experiments were conducted on isolated humic, fulvic and hydrophilic acids obtained from one of the studied waters.

MATERIALS AND METHODS

Surface Water Location and Coagulation/Clarification Process

The origin and nature of the studied surface waters, nature and dose of the coagulant, specific pH conditions are summarized in table 1. All are used for drinking water production. The treatment processes for each include a coagulation/flocculation step with or without preoxidation. Raw water samples were collected, from September 1991 to March 1992, in 2 litre glass vessels which had been washed with detergent, rinsed with Milli-Q water and dried at 100°C. Raw waters were filtrated on 0.45 µm porosity membrane, previously rinsed with 1 litre of Mill-Q water, prior to further experiments.

Because preoxidation used in water treatment plants may lead to a partial modification of the chemical properties of the natural organic matter, coagulation/clarification studies were made in the laboratory with a Jar Test device, except for the Mayenne river water which is not subject to preoxidation in the plant. For each studied water, the coagulation conditions, type and dose of coagulant and pH, used for laboratory scale experiments were the same as practised in the water treatment plants. Other experimental conditions were typical of laboratory scale studies. Coagulation (250 rpm, 10 min) and flocculation (30 rpm, 30 min) were performed in triplicate on 1 litre samples using Vittadini test jars with rectangular paddles. Coagulant from fresh stock solution prepared with technical quality product was added over the course of the first minutes of the rapid mixing. According to the water treatment conditions, the pH was monitored continuously and adjustments were made by the dropwise addition of NaOH or HCl. The temperature was maintained at 20°C

± 0.5 . Settled waters were filtered on $0.45 \mu\text{m}$ porosity membrane prior to analysis and characterization procedures. Coagulation/clarification studies of isolated hydrophilic and hydrophobic substances were carried out with similar experimental conditions.

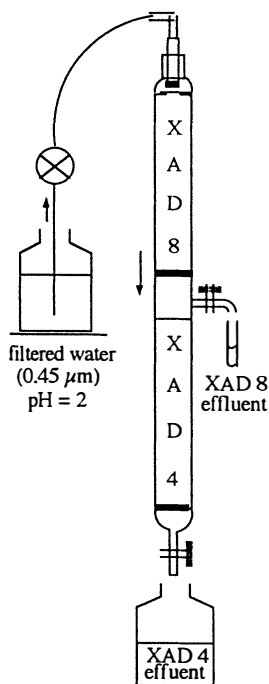
XAD-8/XAD-4 Resins Analytical Fractionation and Isolation Procedures

The distinction between the analytical fractionation procedure and the isolation procedure used was the size of the XAD-8/XAD-4 resin filtration unit. Both procedures were described in a recent publication (Croué *et al.*, 1992). These procedures consist in first isolating hydrophobic substances, essentially represented by humic substances, on XAD-8 resin according to the method proposed by Thurman and Malcolm (1981), then isolating the hydrophilic acids from the XAD-8 effluent on XAD-4 resin by the use of the same method.

TABLE 1: Nature and Location of the Studied Surface Waters - Water Treatment Coagulation Conditions

Water Source	Location (France)	date	Water Treatment Plant Coagulant	Coagulation Process dose (Al_2O_3)	pH
Apremont Reservoir	Apremont / Vendée	5/12/91	Aluminum Sulfate	11 g m^{-3}	7.0*
Chamboux Reservoir	St Martin de la Mer / Côte d'or	27/12/91	WAC	6 g m^{-3}	6.8
Mayenne River	Lelion d'Angers / Maine et Loire	30/01/92	Aluminum Sulfate	4 g m^{-3}	7.0
Mervent Reservoir	Mervent / Vendéc	24/02/92	Aluminum Sulfate	6 g m^{-3}	7.0*
Charente River	Coulonges / Charentes Maritime	29/02/92	Aqualenc	3 g m^{-3}	8.2
Loire River	La Possonnière / Maine et Loire	23/03/92	Aluminum Sulfate	4.5 g m^{-3}	7.4

*regulated pH



The analytical fractionation procedure was applied to both untreated and treated samples. This procedure was performed on two superposed 50 mL XAD-8 and XAD-4 resin columns (figure 1). Before using, resins were Soxhlet extracted with various solvents and rinsed with acidic Milli-Q water until the DOC of the resin effluents were less than 0.5 mg.l^{-1} . After the filtration of 1.2 litre of water at a flow rate of 200 ml.h^{-1} , XAD-8 and XAD-4 effluent samples were collected for DOC and UV absorbance (254 nm) analysis. Resins were changed after filtration of each untreated or treated water sample. The fractionation procedure separated the DOM into three different polarity groups of organic compounds: hydrophobic substances, hydrophilic acids and "non-acid" hydrophilics.

Hydrophobic substances in mg.l^{-1} DOC = $\text{DOC}_{\text{raw water}} - \text{DOC}_{\text{XAD-8 effluent}}$

Hydrophilic acids in mg.l^{-1} DOC = $\text{DOC}_{\text{XAD-8 effluent}} - \text{DOC}_{\text{XAD-4 effluent}}$

"Non-acid" hydrophilics in mg.l^{-1} DOC = $\text{DOC}_{\text{XAD-4 effluent}}$

This analytical fractionation procedure was reproduced five times on the Mayenne river. The relative standard deviations of the DOC concentrations obtained for each fraction varied from 8 to 12%.

DOC concentrations were analysed using a Dohman DC 80 analyser after acidification and stripping of CO_2 . UV absorbance was measured with a one centimetre cell using a Varian DMS 90 spectrophotometer.

Fig 1: XAD-8/XAD-4 resins characterization unit

JST 27:11-K

The DOM fractionation and isolation procedure was performed on the Apremont Reservoir water. A 200 liter sample was collected on November 1990. The XAD-8/XAD-4 isolation pilot was made with two separate glass columns containing 1.8 litre of resin each. All the connection lines and valves were Teflon. Humic and fulvic acids adsorbed at acidic pH on the XAD-8 resin were backeluted with 0.1 NaOH and purified. Hydrophilic acids contained in the XAD-8 effluent and adsorbed on the XAD-4 resin were isolated with the same method.

Apparent Molecular Weight Fractionation

Apparent molecular weight (AMW) fractionation of dissolved organic matter was accomplished by ultrafiltration. The AMW distributions of treated and untreated waters were determined by using a tangential flow device (Minitan Ultrafiltration System-Millipore) with a 1000 daltons nominal molecular weight cutoff membrane. DOC and UV absorbance analysis were performed on all permeates and retentates.

Total THM and TOX Formation Potential Determinations

Chlorination of treated and untreated waters were carried out according to the following set of conditions:

- $\text{Cl}_2/\text{DOC} = 4 \text{ mg/mg}$, incubation at 20°C in darkness
- pH 7.5 adjust with HCl or NaOH as necessary
- 72 hour-contact time, fixed by adding sodium metaarsenite as a residual chlorine quenching agent with a dose higher than the requisite stoichiometric dose.

Chlorination of the isolated fraction solutions was performed using the same experimental conditions. Dilute solutions were prepared by adding 10 mg.l^{-1} of isolated organics in Milli-Q water buffered at pH 7.5 with phosphate (10^{-2} M).

These chlorination conditions were chosen to allow comparison with our previous work on humic substances (Legube *et al.*, 1990).

THMs were analyzed in duplicate using a Dani HSS 3950 head-space sampler (100 μl loop) coupled with a Varian 3300 gas chromatograph equipped with a ^{63}Ni electron capture detector and a split mode injector. The carrier gas used throughout the experiments was high purity nitrogen used at a flow rate of 10 ml/min. A JW DB-624 widebore column (0.53 i.d.x 30 m, 3.0 μm film thickness) was installed. A programmable column temperature from 80°C to 120°C at $3^\circ\text{C}/\text{min}$, a detector temperature of 250°C and a injector temperature of 200°C were used. Chromatograms were recorded and peak areas measured on a MERCK D 2500 chromatogram integrator. Ten ml of sample was added in the Dani autosampler tube (24 ml), teflon capped and heated at 40°C .

Total organic halides (TOX) were determined in duplicate by the adsorption-pyrolysis-microcoulometric procedure, using a Dohrmann DX-20A Total Organic Halide Analyser equipped with four dual carbon adsorption modules. Neutralized samples (25 to 100 ml) were filtrated on activated carbon after acidification with concentrated nitric acid (pH 1.5).

RESULTS AND DISCUSSIONS

Characterization Study of Raw and Treated Waters

Table 2 presents the general characteristics, as DOC concentration and UV-absorbance, of the untreated and treated waters. Raw waters collected from reservoirs had higher DOC concentrations than waters sampled from rivers. DOC removals observed after coagulation/clarification treatments were similar with values ranging 38 to 46%, except for Charente and Loire river waters which were determined to be less amenable to the process used. Prior to treatment, the latter waters were characterized by the lowest relative-UV absorbance values (UV/DOC). For each water source, results have shown that the UV-absorbing organic fraction were preferentially removed. Similar results were reported by Van Breemen *et al.* (1979), Semmens and Ayers (1985), Sinsabaugh *et al.* (1986).

TABLE 2 : DOC and UV absorbance (254 nm) of the Untreated and Corresponding Treated Waters

Water Source	Untreated Water		Treated Water		Removal (%)	
	DOC mg l ⁻¹	UV abs *	DOC mg l ⁻¹	UV abs *	DOC	UV abs
Apremont Reservoir	7.1	0.25	4.3	0.1	39	60
Chamboux Reservoir	7.8	0.29	4.1	0.064	47	78
Mayenne River	4.2	0.14	2.2	0.048	47	64
Mervent Reservoir	6.8	0.22	4.2	0.08	38	63
Charente River	2.8	0.057	2.1	0.04	25	30
Loire River	3.9	0.084	3.0	0.047	23	44

*254 nm wavelength

Hydrophobic/Hydrophilic fractions distribution. The hydrophobic/hydrophilic fractions distribution obtained for each treated and untreated water are summarized in table 3.

TABLE 3 : Hydrophobic/hydrophilic Fractions Distribution of the Untreated and Corresponding Treated Waters

Water	Hydrophobic Substances				Hydrophilic Acids				Non-acid Hydrophilics			
	DOC mg l ⁻¹	DOC/DOC ₀ %	UV abs ^b	UV/UV ₀ %	DOC mg l ⁻¹	DOC/DOC ₀ %	UV abs ^b	UV/UV ₀ %	DOC mg l ⁻¹	DOC/DOC ₀ %	UV abs ^b	UV/UV ₀ %
Apremont Reservoir / untreated	3.94	56	0.178	70	1.67	23	0.045	17	1.5	21	0.035	13
Apremont Reservoir / treated	2.50	58	0.057	62	1.00	23	0.022	24	0.8	19	0.013	14
Chamboux Reservoir/untreated	3.97	51	0.217	76	1.88	24	0.040	14	2.01	25	0.027	10
Chamboux Reservoir / treated	1.31	32	0.041	66	0.79	20	0.012	21	1.98	48	0.008	13
Mayenne River / untreated	2.01	48	0.094	68	0.82	20	0.026	19	1.32	32	0.019	12
Mayenne River / treated	1.15	51	0.028	59	0.42	19	0.011	24	0.68	30	0.008	17
Mervent Reservoir / untreated	3.76	55	0.145	64	1.49	22	0.043	19	1.6	23	0.039	17
Mervent Reservoir / treated	2.05	49	0.056	72	0.85	20	0.017	23	1.28	31	0.004	5
Charente River / untreated	1.42	50	0.031	58	0.43	16	0.012	23	0.96	34	0.01	19
Charente River / treated	0.73	35	0.025	60	0.49	23	0.008	20	0.89	42	0.008	20
Loire River / untreated	1.59	41	0.05	60	0.99	25	0.025	30	1.33	34	0.008	10
Loire River / treated	1.28	42	0.027	58	0.62	20	0.011	24	1.16	38	0.008	18

DOC₀ and UV₀ : DOC and UV of untreated or treated waters

DOC of untreated waters was almost evenly split between the hydrophobic and hydrophilic fractions, with the exception of the Loire river water that showed a significant difference with 41 % hydrophobics and 59 % of hydrophilics. Results are similar to literature values (Thurman, 1985). One can note that water from large rivers like the Mississippi River (Semmens and Staples, 1986), the Colorado river (Collins *et al.*, 1986), the Seine river (Legube *et al.*, 1990) was found to contain less hydrophobics than hydrophilics such as the case of the Loire River. "Non-acid" hydrophilics were found to be as abundant as the hydrophilic acids for the studied reservoir waters, and significantly more concentrated in the river waters with values around 34 % of the DOC. Using a different fractionation procedure, Leenheer and Huffman (1979) have shown that hydrophilic acids accounted for approximately 25 % of the DOC of U.S. river waters. For all the waters studied, hydrophobic substances contributed the major part of the UV absorbance, while the "non-acid" hydrophilics were identified as the least aromatic fraction.

The hydrophobic/hydrophilic fraction distributions of Apremont Reservoir, Mayenne river and Loire river waters were found to be unchanged after coagulation/clarification. A similar result was observed by Collins *et al.* (1986) on the Grasse river water (New York, USA). These results indicate that for a studied water, the relative reduction in DOC of one fraction (removed DOC of one fraction divided by the DOC of the same untreated water fraction) was in the same order of magnitude of the others.

The DOC distributions of Chamboux reservoir and Charente river waters were significantly modified by the applied treatment. In both cases, the hydrophobic substances showed the higher relative DOC reduction, while the "non-acid" hydrophilics were not found to be affected. This last fraction became predominant in the treated waters. Hydrophilic acids fraction of the Chamboux river water was reduced by approximately 50 %, and the Charente river one was as important after as before treatment. The Mervent reservoir water has shown similar results with less significant variation in the DOC distribution.

Overall, hydrophobic substances were found to be better removed than the hydrophilic organics with four of the studied waters, Apremont, Chamboux, Mervent reservoirs, and Charente river. "Non-acid" hydrophilic organics, a high polarity fraction according to the adsorption procedure, were found to be poorly removed by coagulation/clarification in most cases. Except for the Charente river water, 40 to 48 % of the hydrophilic acids were removed by this treatment. Decreases in the relative UV absorbance (UV absorbance/DOC) were observed with the different fractions with all studied waters. This indicates that coagulation preferentially removed the UV-absorbing organics whatever their nature. No relationship between DOC distribution variations and the origin and nature of surface waters could be deduced from our results. Nevertheless, one can note that Chamboux reservoir and Charente river waters that showed significant reduction of the hydrophobic fraction (i.e. humic substances) were coagulated with polyaluminum chloride chemicals (WAC and Aqualenc). All others were treated with aluminum sulfate. This result is somewhat surprising, since polyaluminium chloride (PACl) has been shown less efficient for the removal of humic substances than aluminium (Van Benschoten, 1988).

TTHMFP, TOXFP and AMW fractionation of untreated and corresponding treated waters. The analytical hydrophobic/hydrophilic fraction procedures have shown interesting variation in the DOC distribution between some untreated and corresponding treated waters. The objective of this part of our work, was to correlate these results with commonly used characterization parameters, Total THM and TOX formation potentials (TTHMFP, TOXFP) and AMW fractionation. Table 4 presents the data obtained on the untreated and corresponding treated waters.

"Relative TTHMFP and TOXFP" ($\mu\text{g of Cl}^-$ per mg of C) of untreated waters increased with increasing UV-absorbance. This correlation does not include the Apremont reservoir untreated water that is characterized proportionally, with the most important hydrophobic fraction. The Loire river untreated water, the only source water that contained more hydrophilics than hydrophobic compounds, has shown the highest TTHMFP/TOXFP ratio.

Waters that did not show any significant modification (Apremont reservoir, Mayenne and Loire rivers) in the DOC distribution after coagulation/clarification have shown low (sometimes nil) "Relative TTHMFP and TOXFP" removals. Chamboux river water was characterized by an important reduction of its "Relative TTHMFP and TOXFP". The TTHMFP/DOC ratio of Mervent reservoir treated water was reduced by approximately 60 % after treatment. These results can be correlated with the decrease of the hydrophobic fraction observed in both cases. The Charente river water which also showed a hydrophobic content reduction had an increased TTHMFP/TOXFP ratio.

One can see that TTHMFP and TOXFP ($\mu\text{g Cl}^-$ per litre) were reduced after the applied treatments. TTHMFP reductions varied from 25 to 74 % and TOXFP from 40 to 76 %. No correlation can be proposed between the organic halide formation potential removals and the hydrophobic/hydrophilic fraction distributions.

All of the raw waters gave a similar AMW distribution with 23 percent of DOC below 1000 daltons as average value, except for the Loire river water which showed a higher proportion of organics below 1000 daltons. This result is consistent with the particular hydrophobic/hydrophilic distribution of Loire river. Malcolm *et al.* (1977) demonstrated that the aqueous solubility (molecular weight and polarity dependent property) of an organic solute is the major control on the hydrophobic/hydrophilic separation. Given this, AMW of hydrophilic fractions are probably lower than the AMW of hydrophobics. Organics above 1000 daltons represented the most UV absorbing fraction.

TABLE 4: TTHMFP, TOXFP and Apparent Molecular Weight Fractionation of Untreated and Corresponding Treated Waters

Water	Potential Reactivity with Chlorine					Apparent Molecular Weight Distribution (%)				Recovery	
	TTHMFP ^a	TOXFP ^a	$\frac{\text{TTHMFP}^b}{\text{DOC}}$	$\frac{\text{TOXFP}^b}{\text{DOC}}$	$\frac{\text{TTHMFP}}{\text{TOXFP}}$ (%)	<1000 d DOC	UV abs ^c	>1000 d DOC	UV abs ^c	DOC	UV abs ^c
Apremont Reservoir / untreated	291	1079	41	152	27	26	20	85	68	111	88
Apremont Reservoir / treated	129	512	30	119	25	40	33	73	70	113	83
Chamboux Reservoir/untreated	405	1670	52	214	24	27	15	92	73	119	86
Chamboux Reservoir / treated	90	402	22	98	21	45	49	60	52	105	101
Mayenne River / untreated	155	701	37	167	22	23	17	98	73	121	90
Mayenne River / treated	81	275	37	125	29	30	28	71	71	101	99
Mervent Reservoir / untreated	340	1197	50	176	28	17	10	82	81	99	92
Mervent Reservoir / treated	88	554	21	132	16	24	26	75	87	99	113
Charente River / untreated	109	372	39	133	29	25	25	81	85	106	110
Charente River / treated	82	220	39	105	37	38	43	69	85	107	128
Loire River / untreated	211	628	54	161	34	50	34	78	67	128	101
Loire River / treated	126	333	42	111	38	65	53	63	63	126	116

^aµg Cl/l. ^bµg Cl/mg C. ^c254-nm wavelength.

The AMW distribution of all the studied waters was influenced in the same degree by coagulation, with a shift in DOC and UV absorbance to the <1000 daltons fraction. Chamboux river gave the most important variation. Organic compounds with AMW above 1000 daltons were essentially removed during the treatment, since DOC concentrations were found almost unchanged in the <1000 daltons fraction (data not shown). This is consistent with observations which indicated that coagulation preferentially removes high molecular weight and UV absorbing organic fractions.

In general, the significant removal of high molecular weight compounds is followed by a small reduction in the "Relative TTHMFP and TOXFP" as discussed above. The hydrophobic/hydrophilic fraction distributions have been shown unchanged after coagulation with most of the studied waters. Since Joyce *et al.* (1984) and Collins *et al.* (1985) indicated that THM yield increases with increasing precursor molecular weight, it was interesting to study in a second part of our work, the reactivity with coagulant and chlorine of isolated hydrophobic and hydrophilic fractions.

Chlorination and Coagulation of Isolated Hydrophobic and Hydrophilic Substances

Experiments were conducted on humic, fulvic and hydrophilic acids previously isolated from the Apremont reservoir water sampled in November 1990 and April 1991. For the two water samples, fulvic acids were 45 to 50 % of the DOC, hydrophilic acids 22 to 25 % of the DOC and humic acids 3 to 5 % of the DOC (Croué *et al.*, 1992).

Coagulations of Apremont fulvic and hydrophilic acids with aluminum sulfate have been studied with similar experimental conditions. Percent removal of DOC and UV absorbance versus coagulant dose are presented figure 2. Because hydrophilic acids contained less carbon than the corresponding fulvic acids, 42 % and 50 % respectively, relative aluminum doses (mg Al/mg C) were, in fact, slightly different. Despite this, the data obtained for the two isolated samples gave similar DOC removals, except for the 1 mg.l⁻¹ Al dose which looked more efficient in removing hydrophilic acids. The carboxylic acidity, that may represent an important parameter in coagulation mechanisms (Collins *et al.*, 1986), was found to be similar for the Apremont fulvic and hydrophilic acids (data not shown). A maximum of 45 % DOC reduction was observed for both fractions. In contrast, for Al doses above 1 mg.l⁻¹, the UV absorbing fraction eliminated was greater for the fulvic acids than the hydrophilic acids, 75 % and 62 %. Fulvic acids were found more aromatic in nature than the corresponding hydrophilic based on the relative UV absorbance measurement at 254 nm (Croué *et al.*, 1992). The optimum dosage of coagulant can be estimated around 4 mg.l⁻¹, which is close to the 1 mg Al/mg C optimal dose obtained by Van Benschoten (1988) on aquatic fulvic acid at pH 7.

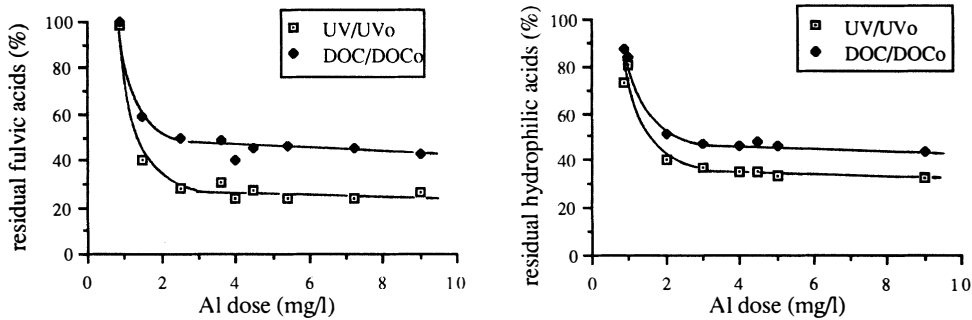


Fig 2: Effect of increasing coagulant dosage on Apremont fulvic and hydrophilic acids removal (water sampled in November 1990, 10 mg/l ; pH adjusted to 6.50)

Table 5 summarizes the Relative THMFP and TOXFP of the Apremont humic, fulvic and hydrophilic acids before and after coagulation with aluminum sulfate.

TABLE 5: Effect of Aluminum Sulfate Coagulation on Apremont Humic, Fulvic and Hydrophilic Acids THMFP and TOXFP (fractions isolated from water sampled on November 1990)

Organic Substances	Uncoagulated Substances				Coagulated ^d Substances				Removal (%)			
	DOC ^a	UV abs ^b	THMFP ^c DOC	TOXFP ^d DOC	DOC ^a	UV abs ^b	THMFP ^c DOC	TOXFP ^d DOC	DOC	UV abs	THMFP	TOXFP
Fulvic Acids	4.9	0.167	27	144	2.2	0.046	27	103	55	72	55	68
Humic Acids	5.0	0.24	46	307	0.63	0.008	4.5	63	87	93	99	97
Hydrophilic Acids	4.3	0.097	27	117	2.08	0.034	26	95	52	65	53	61

^amg l⁻¹. ^b254-nm wavelength. ^cμg CHCl₃/mg C. ^dμg Cl⁻/mg C. ^e10 mg l⁻¹ Substances, [Al³⁺] = 4.5 mg l⁻¹, regulated pH = 6.5.

Prior to coagulation, humic acids were characterized by the highest relative THMFP and TOXFP. Fulvic and hydrophilic acids have shown comparable organic halide formation potentials. As observed by Legube *et al.* (1990) on various aquatic humic and fulvic acids, THMFP and TOXFP increased with increasing UV absorbance. We observed a similar trend with hydrophilic acids.

DOC and UV removals indicated that humic acids were more amenable to removal than the corresponding fulvic and hydrophilic acids. THMFP and TOXFP removals calculated for the isolated humic acids indicate that THM and TOX precursors were preferentially eliminated during the treatment. Relative THMFP and TOXFP of the uncoagulated fraction of humic acids were then found to be much lower than the original organic substances (63 compared to 307 μg CHCl₃ per mg of C). THMFP/DOC and TOXFP/DOC ratios of the coagulated hydrophilic acid solutions were almost unchanged, while fulvic acids have shown a small reduction of the TOXFP/DOC ratio as compared to humic acids.

Similar results were obtained with humic, fulvic and hydrophilic acid fractions isolated from the Apremont reservoir water sampled on April 1991.

Humic acids represent generally a relatively small fraction of the DOC of surface waters, less than 5%. Whatever its behaviour during coagulation/clarification, this fraction can be considered as insignificant before and after treatment. For most of the studied waters, no significant or small variations in the DOC distributions were observed after treatment. This is an expected result since fulvic and hydrophilic acids react to the same extent with aluminum coagulant.

Considering their THMFP and TOXFP, the contribution of humic acids to the organic halide production in surface waters is not significant when compared to the fulvic and hydrophilic acids. Given this, a related observation is that the THMFP and TOXFP per unit of DOC was essentially the same for untreated and corresponding treated waters. This supports the conclusion that the bulk of the dissolved organic carbon, regardless its type and reactivity, has similar relative THMFP and TOXFP before and after coagulation treatment.

Contrasting behaviour was observed with the Chamboux reservoir and Charente river waters. A possible explanation is the use of polyaluminum chloride coagulant or a very high proportion of humic acids.

CONCLUSIONS

DOC removals observed after coagulation with aluminum and clarification, of three river and three reservoir waters ranged from 23 to 47 %. For each water source the UV-absorbing fractions were preferentially removed. Dissolved organic matter (DOM) represents a mixture of various types of complex organic structures and simple compounds. DOC and UV absorbance measurements of raw and treated waters give only global quantitative information of the DOM. In this study, an analytical XAD-8/XAD-4 resins fractionation procedure, based on the polarity of the organics, was developed. It was applied to the six waters before and after coagulation to provide more specific information regarding the reactivity of different fractions of the DOC.

DOC distribution determined on the six raw waters showed that the DOC was evenly split between the hydrophobic and hydrophilic fractions. However, the "non-acid" hydrophilic fraction which may represent low molecular weight neutral and basic organics was found to be proportionally more important in river waters than in reservoir waters

Three of the six waters showed a significant variation in their DOC distribution after coagulation/clarification due to the preferential elimination of the hydrophobic substances (humic substances) and to the low reactivity of the "non-acid" hydrophilics. The change in the hydrophobic/hydrophilic distribution after treatment was associated with an important reduction in TTHMFP/DOC and/or TOXFP/DOC or TTHMFP/TOXFP ratios. Waters that showed little variation in their DOC distribution after treatment with coagulant were characterized by a slight decrease in their relative TTHMFP and TOXFP. Surprisingly, results indicated that hydrophilic acids were removed in similar proportion to the hydrophobic substances.

For all the studied waters, TTHMFP and TOXFP per unit of DOC remained high after coagulation/clarification treatment. This is an expected result since experiments carried out on isolated fulvic and hydrophilic acids, which represent approximately 45 % and 25 % of the DOC respectively, confirmed that these two major fractions react to the same extent with aluminum coagulant. The data also indicated that they are characterized by similar THMFP and TOXFP before and/or after coagulation.

As anticipated, AMW distributions determined on raw and treated waters showed that higher molecular weight matter was preferentially removed during coagulation. We also found that the residual DOC, which had a higher proportion of low molecular weight compounds, was almost as reactive with chlorine as the original bulk of DOC.

The two main conclusions are as follows.

- 1- The relative distribution of hydrophobic and hydrophilic compounds in the DOC of surface waters does not vary widely with the origin of the water. Furthermore, the hydrophilic acids and fulvic acids, the two main fractions, react similarly with coagulant and chlorine.
- 2- Coagulation treatment may reduce THMFP and TOXFP, nevertheless residual DOC has significant THMFP and TOXFP per unit organic carbon. Further reduction in organic halide precursors requires application of alternative treatment techniques.

REFERENCES

- Angbo (1989). Etude de l'adsorption des acides humiques sur floes préformés d'hydroxyde d'aluminium. Thèse de Doctorat, Limoges, 41.
- Babcock D.B. and Singer P.C. (1979). Chlorination and coagulation of humic and fulvic acids. *J. Am. Wat. Wks Ass.*, 71,3, 149-152.

- Collins M.R., Amy G.L., Steelink C. (1986). Molecular weight distribution, carboxylic acidity, and humic substances content of aquatic organic matter : Implications for removal during water treatment. Environ. Sci. Technol., 20, 1028-1032.
- Croué J.P., Martin B., Simon P. and Legube B. (1992). Les matières hydrophobes et hydrophiles des eaux de retenue: Extraction, caractérisation et quantification. To be presented at the AIDE conference, Amsterdam, 1-2 September.
- Dempsey B.A., Sheu H. and Tanzeer Ahmed T.M. (1985). Polyaluminium chloride and alum coagulation of clay-fulvic acid suspension. J. Am. Wat. Wks Ass., 77, 3, 74-80.
- Dempsey B.A., Ganho R.M. and O'Melia C.R. (1984). The coagulation of humic substances by means of aluminium salts. J. Am. Wat. Wks Ass., 76, 4, 141-150.
- Edzwald J.K., Haft J.D. and Boak J.W. (1977). Polymer coagulation of humic acid waters. Jour. Environ. Engineering, Div-ASCE, 103, 989-1000.
- Glazer H.T. and Edzwald J.K. (1979). Coagulation and direct filtration of humic substances with polyethelenimine. Environ. Sci. Technol., 13, 3, 299-305.
- Hall E.S. and Packham R.F. (1965). Coagulation of organic color with hydrolyzing coagulants. J. Am. Wat. Wks Ass., 57, 9, 1149-1166.
- Jekel M. (1985). Removal of humic substances in groundwater treatment. Water Supply, 3, 1, 61-66.
- Joyce W., DiGiano F.A. and Uden P.C. (1984). THM precursors in the environment. J. Am. Wat. Wks Ass., 76, 102-106.
- Kim J.S., Chian E.S.K., Saunders F.M., Perdue E.M. and Giabbai M.F. (1989). Characteristics of humic substances and their removal behaviour in water treatment - In "Aquatic humic substances : Influence on fate and treatment of pollutants", Ed. by SUFFET I.H. and Mac CARTHY P., Advances in Chemistry Series 219, American Chemical Society, Washington, chap. 29, 472-497.
- Leenheer J.A. and Huffman E.W.D. (1976). Classification of organic solutes in water by using macrorreticular resins. J. Res. U.S. Geol. Surv., 4, 737-751.
- Leenheer J.A. and Huffman E.W.D. (1979). Analytical method for dissolved organic carbon fractionation. U.S. Geological Survey Water-Resources Investigations, 79, 4, 1-16.
- Lefebvre E. et Legube B. (1990). Coagulation par Fe(III) de substances humiques extraites d'eaux de surface : Effet du pH et de la concentration en substances humiques. Wat. Res., 24, 5, 591-606.
- Legube B., Xiong F., Croué J.P. et Doré M. (1990). Etude sur les acides fulviques extraits d'eaux superficielles françaises. Extraction, caractérisation et réactivité avec le chlore. Revue des Sciences de l'Eau, 3, 399-424.
- Malcolm R.L., Thurman E.M. and Aiken G.R. (1977). The concentration and fractionation of trace organic solutes from natural and polluted waters using XAD8, a methylmetacrylate resin. Proceedings of the 11th Annual Conference on Trace Substances in Environmental Health. 307-314.
- Narkis N. and Rebhun M. (1975). The mechanism of flocculation processes in the presence of humic substances. J. Am. Wat. Wks Ass., 67, 2, 101-108.
- Oliver B.G. and Lawrence J. (1979). Haloforms in drinking water - Study of precursors and precursor removal. J. Am. Wat. Wks Ass., 71, 3, 161-163.
- O'Melia C.R., Yao C., Gray K. and Tobiason J.E. (1987). Raw water quality, coagulant, selection, and solid liquid separation. Presented at the AWWA annual conference, Kansas City, Missouri.
- Rook J.J. (1977). Chlorination reactions of fulvic acids in natural waters. Environ. Sci. Technol., 11, 478-482.
- Semmens M.J. and Ayers K. (1985). Removal by coagulation of trace organics from Mississippi river water. J. Am. Wat. Wks Ass., 77, 5, 79-84.
- Semmens M.J. and Field T.K. (1980). Coagulation : Experiences in organics removal. J. Am. Wat. Wks Ass., 72, 8, 476-483.
- Semmens M.J. and Staples A.B. (1986). The nature of organics removed during treatment of Mississippi river water. J. Am. Wat. Wks Ass., 78, 2, 76-81.
- Sinsabaugh R.L., Hoehn R.C., Knocke W.R. and Linkins A.E. (1986). Removal of dissolved organic carbon by coagulation with iron sulfate. J. Am. Wat. Wks Ass., 78, 5, 74-82.
- Thurman E.M. (1985). Developments in Biochemistry : Organic Geochemistry of Natural Waters. M. NIJHFF, Dr W. JUNK Publishers, Dordrecht.
- Thurman E.M. and Malcolm R.L. (1981). Preparative isolation of aquatic humic substances. Environ. Sci. Technol., 15, 463-466.
- Van Benschoten J.E. (1988). PhD thesis, Speciation and fate of aluminum in water treatment. Department of Civil Engineering, University of Massachusetts at Amherst (MA, USA).
- Van Breemen A.N., Nieuwstad T.J., Van Der Meent-Olieman G. C. (1979). The fate of fulvic acids during water treatment. Wat. Res., 13, 8, 771-780.
- Vik E.A., Carlson D.A., Eikum A.S. and Gjessing E.T. (1985). Removing aquatic humus from Norwegian lakes. J. Am. Wat. Wks Ass., 77, 3, 58-66.