

**EFFECTS OF OZONATION vs. CHLORINATION  
WATER TREATMENT OPERATIONS ON NATURAL ORGANIC MATTER  
FRACTIONS**

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Abstract

Isolation and fractionation of natural organic matter (NOM) by resin adsorption was conducted at two surface drinking water treatment plants that treat the same source water. The first treatment plant uses conventional treatment (coagulation, sedimentation, and filtration) with chlorination while the second plant uses conventional treatment with pre and intermediate ozonation, and multi-media granular activated carbon filtration. Several different sampling locations within each plant were selected for NOM isolation and fractionation into six fractions (hydrophobic acid, neutral and base, and hydrophilic acid, neutral, and base). Chemical fluorescence of the NOM was used to monitor the removal/reactivity of each fraction. The effectiveness of each treatment plant on the oxidation and removal of each organic fraction are discussed.

Introduction

The study of natural organic matter (NOM) has become critically important as it significantly influences many aspects of water treatment, including the behavior of unit processes, the application of disinfectants, and biological disinfection. NOM represents

the raw organic material that plays a role in many of the regulatory challenges facing utilities. NOM is considered to contain many of the precursors to disinfection by-products (DBPs). Both, the proposed Disinfectant/Disinfection By-Product (D/DBP) Rule (USEPA, 1994a) and the Enhanced Surface Water Treatment Rule (ESWTR) (USEPA, 1994b) have provisions to limit the formation of DBPs by controlling reactivity and/or removal of NOM (Marhaba et. al., 1998).

NOM is very heterogeneous, in that it contains many classes of high molecular weight organic compounds. Humic substances constitute a major portion of the dissolved organic carbon (DOC) from surface waters. They are complex mixtures of organic compounds with relatively unknown structures and chemical composition. Even the definition of Humic substances is rather ambiguous and is frequently operationally defined according to the physical/chemical isolation procedure. In this study, NOM was isolated from locations within two surface treatment plants, which use the same source water. Resin adsorption methods were used to isolate and enrich six fractions; hydrophobic acid, hydrophobic neutral, hydrophobic base, hydrophilic acid, hydrophilic neutral, and hydrophilic base. The effectiveness of unit processes within each treatment plant for the removal of each fraction is presented.

### Experimental and Analytical Methods

#### WATER TREATMENT PROCESSES

The Raritan/Millstone (R/M) and the Canal Road (CR) surface water treatment plants of Elizabethtown Water Company (Westfield, NJ) are located in central New Jersey and have an average combined process flow of about 570,000 m<sup>3</sup>/day. Sources of water for both plants are the Raritan and Millstone rivers, augmented by Spruce Run and Round Valley reservoirs, and the Delaware and Raritan Canal.

The CR plant utilizes pre-ozonation, coagulation, sedimentation, intermediate ozonation, and granular activated carbon (GAC) multimedia filtration, whereas the R/M plant utilizes conventional treatment with chlorination as the disinfection process as shown in Figures 1 and 2, respectively. Table 1 contains unit process descriptions and chemical

feed data. Sampling locations for this study were collocated with the Information Collection Rule points in the treatment train and are illustrated in figures 1 and 2.

TABLE 1. DESCRIPTION OF WATER TREATMENT PLANTS

Unit Process	CR Water Treatment Plant	R/M Water Treatment Plant
Plant Flow	90,000 m <sup>3</sup> /day	380,000 m <sup>3</sup> /day
Pre-Ozone Number of contactors Contact time Dosage	2 (1 in service) 9.25 min 0.25 mg/l	N/A
Rapid Mixing Number of trains Number of stages Type of mixer	2 2 Turbine	2 2 Turbine & pump impeller
Pre-Treatment Chemicals & Dosages	Liquid alum (23 mg/l)	Liquid alum (27 mg/l) Sulfuric acid (20 mg/l)
Flocculation Number of trains Number of stages Flocculator type	2 4 Paddle wheel	2 2 Paddle wheel
Sedimentation Number of trains Surface loading Detention time Type	2 667 gpd/sq.ft 4.31 hrs. conventional	2  Tube settler
Intermediate Ozone Number of contactors Contact time Dosage	3 30 min. 0.50 mg/l	N/A
Filters Number of filters Filtration rate Filter media	8 1.56 gpm/sq.ft 7 with multi- media(GAC w/ EBCT ??? min, sand, ilmenite) 1 with dual-media (GAC w/ EBCT ?? min, sand)	36 ? anthracite, sand, garnet
Post-Treatment Chemicals	Sodium hypochlorite (1.7 mg/l) Aqua ammonia (0.37 mg/l) Sodium hydroxide (8.7 mg/l) Zinc orthophosphate (0.50 mg/l)	Sodium hypochlorite (2.1 mg/l) Aqua ammonia (0.36 mg/l) Lime (12 mg/l) Zinc orthophosphate (0.44 mg/l)
Filtered Water Reservoir Number of tanks Volume, each Contact time	2 2.5 million gallons 361 min.	3

## MATERIALS AND METHODS

All samples were directly collected, secured and transported by member of the research team to ensure consistent quality control. Samples were refrigerated at 4<sup>0</sup>C. Milli-Q water was used for all dilutions, solution preparation and final glassware washing. All chromatography columns were of borosilicate glass (Kontes, Vineland, NJ) with 20-micron polyethylene bed support disc. Fractions (70-250ml) were kept refrigerated at 4<sup>0</sup>C in quality-assured amber glass bottles.

## NOM ISOLATION & FRACTIONATION

Natural organic matter (NOM) fractionation was carried out using a modified resin isolation fractionation procedure to the one described elsewhere (Leenheer, 1981). The following is a summary of the fractionation procedure that was implemented in this research.

Original samples of 9-liter volume each were collected on the same day from the plant locations shown in figures 1 and 2. All samples were filtered through a 0.45 um cellulose filter. Amberlite resin DAX-8, a macroporous methylmethacrylate copolymer (Supelco, Bellefonte, PA), AG-MP-50, a strong acid, sulfonated, polystyrene macroporous resin (BioRad, Hercules, CA) and Duolite A7, a weak base, phenol-formaldehyde condensation macroporous resin (Supelco, Bellefonte, PA) were all purified by soxhlet extraction prior to being used in the process. Filtered samples were pumped through the DAX-8 column. The adsorbent, hydrophobic base was then eluted by a sequential flow of 0.1N and 0.01N HCl. The DAX-8 column effluent was then acidified with 6N HCl (dropwise) to pH 2 to be recycled through the DAX-8 column. The adsorbent, hydrophobic acid was then eluted with 0.1N NaOH. The DAX-8 resin was then dried prior to being soxhlet-extracted with anhydrous methanol. The methanol solution at the end of the process contained the hydrophobic neutral fraction. The effluent was pumped through the AG-MP-50 resin column from which the adsorbent, hydrophilic base was eluted with 1N NaOH. This was a deviation from Leenheer's (1981) procedure using 1N

NH<sub>4</sub>OH to address the concern of possible formation of chloramine in subsequent trihalomethane formation potential study (Korshin et al., 1997). The effluent was then pumped through a third column containing Duolite A7 resin. The effluent was collected as the hydrophilic neutral fraction and the adsorbent was eluted by 2N NaOH as hydrophilic acid fraction and inorganic salts. The 2N NaOH was used in place of 3N NH<sub>4</sub>OH used by Leenheer (1981) for the same justification described above.

All elutions in this procedure were done in a forward direction or gravity flow (not backflush). This was done to facilitate the recovery procedure. Forward elution was conducted by Day (1991) and is the preferred flow configuration for the column.

As a result of the above fractionation technique, 6 fractions of the DOM were isolated based on chemical characteristics. They are termed operationally as hydrophobic base, hydrophobic acid, hydrophobic neutral, hydrophilic base, hydrophilic acid and hydrophilic neutral. All fractions were preserved in the applicable eluting hydrochloric acid or sodium hydroxide and refrigerated at 4<sup>0</sup>C.

## ORGANIC CARBON ANALYSIS

DOC was analyzed by an O.I. Analytical 700 system (O.I. Corp., College Station, TX) total organic carbon analyzer using the method of sodium persulfate oxidation (*Standard Methods* 5310-D, 1995). Original source samples were filtered through a 0.45 µm cellulose filter prior to analysis and fractionation to remove suspended particles. Five percent (5%) phosphoric acid was used to first acidify the sample which was then purged of total inorganic carbon (TIC) by nitrogen. Sodium persulfate was subsequently introduced as an oxidant in the process for the oxidation of the organic compounds at 100<sup>0</sup>C. As CO<sub>2</sub> is purged and trapped at the end of the oxidation process, an infrared photometric beam was used for the analysis of carbon mass. The analyzer was regularly

calibrated with 1000-ppm potassium hydrogen phthalate (KHP) standard in either the TIC or total organic carbon (TOC) calibration mode, as recommended by the manufacturer. Each sample was prepared and diluted differently depending on whether the solvent was 0.1N HCl, 1N NaOH or 2N NaOH. The analyzer was programmed accordingly with the proper amount of acid, oxidant and reaction time as recommended by the manufacturer. At least 3 blanks were analyzed prior to the analysis of each sample to establish and verify the appropriate background for quality assurance and control. Duplicates were run randomly.

### Results and Discussion

Mass of fractions are tabulated in table 2 for mass balance purposes. NOM components of the Canal Road and Raritan-Millstone plants, and their variation, are also presented along the treatment train for comparison and discussion.

#### MASS BALANCE

Mass balance confirms the effectiveness of the fractionation procedure giving a 10-15% tolerance of DOM recovery. Similar tolerance was reported by Day (1991), although it was on the deficit side of the recovery, which was due to loss of the hydrophilic acid fraction from the strong anionic nature of the AG-MP-1 resin. Variations from 8-12% were also reported by Croue et al. (1993). Surplus recovery in this study was probably due to the attribution of inorganics that were introduced in the process such as HCl and NaOH for acidity adjustment as well as elution. Rotary vacuum evaporation of the fractions were not conducted because concentrated forms of the isolated fractions were not of interest to the study and certainly not at the expense of “considerable” losses of the volatile organic compounds (Schnoor et. al., 1979). Although the process is time-consuming, it provided the opportunity to isolate the components of the DOM and

ascertain their respective reactivity with oxidants to for DBPs. The fractionation procedure was repeated several times for different ICR sampling points in the treatment plants prior to actually implementing the experimental strategy to statistically confirm the precision of the results.

TABLE 2. MASS BALANCE OF DOM FRACTIONS ALONG THE TREATMENT TRAINS

Plant Location		MASS (mg)						
		DOC	Hydrophobic Base	Hydrophobic Acid	Hydrophobic Neutral	Hydrophilic Base	Hydrophilic Acid	Hydrophilic Neutral
CR	Intake	34.02	2.03	4.13	6.21	1.32	16.44	7.07
	Pre-ozonation	31.64	0.13	3.02	5.75	2.08	16.23	6.62
	Sedimentation Basin	23.58	0.09	1.86	2.99	1.08	12.15	5.49
	Filter	17.69	0.07	1.12	2.68	0.98	10.08	4.73
	Finished	14.92	0.06	0.94	2.49	0.73	8.08	4.21
R/M	Intake	34.02	2.03	4.13	6.21	1.32	16.44	7.07
	Sedimentation Basin	26.64	1.60	3.08	5.83	1.92	15.00	2.70
	Filter	21.01	1.12	1.84	4.50	1.29	12.60	1.35
	Finished	19.80	1.06	1.68	4.38	1.38	10.00	1.80

Figures 3 and 4 show the DOM mass fractions at the R/M and CR plants, respectively.

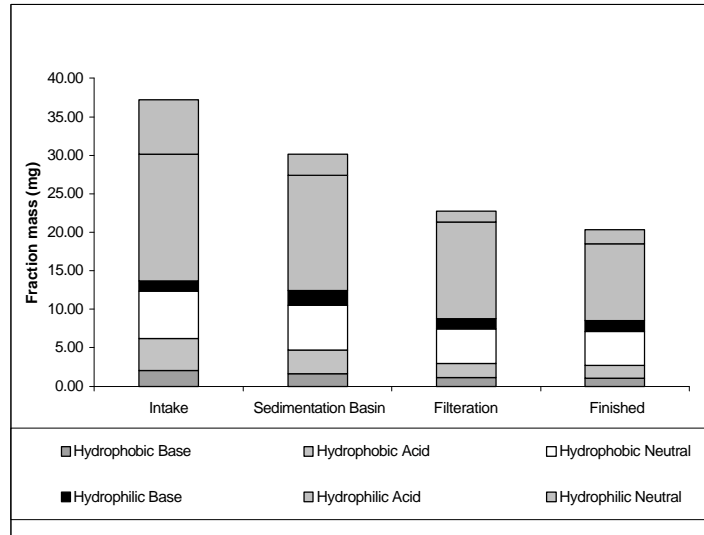


Figure 3. DOM Fraction Mass – R/M



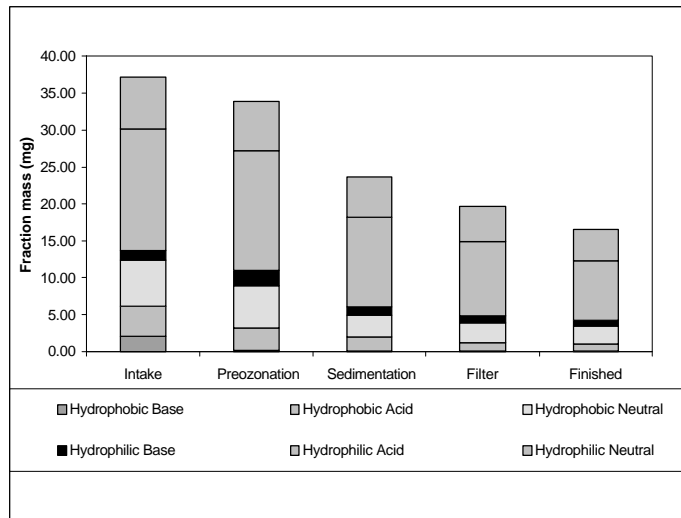


Figure 4. DOM Fraction Mass – CR

#### VARIATIONS IN DOM FRACTIONS

At the influent, which is common to both treatment plants, the hydrophobic component is about 30% of the DOC in the water. Others have reported the fraction to be in the range of 34% to 76% (Day et. al, 1991; Croue et al, 1993 and Leenheer, 1981) in natural waters. The makeup of the fraction components was found to be very dependent on the condition of the water samples and the watersheds investigated. To establish a background for the discussion of each fraction, the organic compounds that relate to the fractions are defined as follows:

- hydrophobic base— a Humic substance containing amino acids, proteic materials, sugars and polysaccharides (Bruchet et al., 1990)
- hydrophobic acid— a soil fulvic (Schnitzer, 1978)
- hydrophobic neutral— a mix of hydrocarbon and carbonyl compounds such as sugars and Humic substances (Leenheer, 1981)
- Hydrophilic base— a amphoteric proteinaceous materials containing amino acids, amino sugars, peptides and proteins (Leenheer, 1981)

- Hydrophilic acid— an organic compound of the hydroxyl acid group (Leenheer, 1981). And finally,
- Hydrophilic neutral— an organic compound made up of polysaccharides (Tipson, 1968)

### Hydrophobic Base

Hydrophobic base represented a mass fraction in the range of 0-6% of DOC (6% in the raw water). A range of 0-22% was reported in raw waters elsewhere (Aiken et al., 1993; Day, 1991; Korshin et. al., 1997). The effect of ozonation on the hydrophobic base fraction was significant as shown in figure 5.

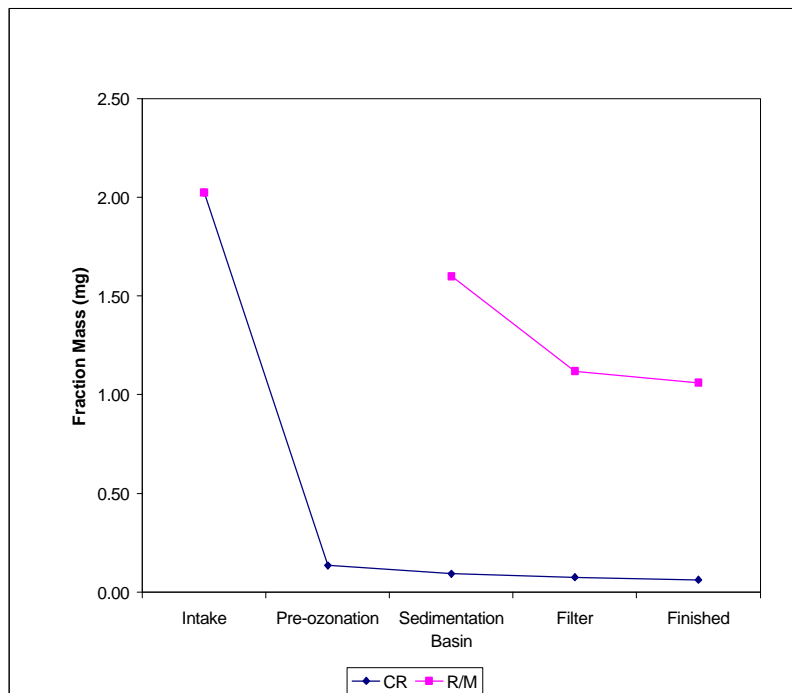


Figure 5. Hydrophobic Base Fraction Variation

When examining the overall removal at the outlet of the sedimentation basin, this fraction was noticeably reduced (95%) in the case of the CR water treatment plant, which has a pre-ozonation process. The R/M plant, with  $\text{KMnO}_4$  pre-oxidation, coagulation and chlorination in sedimentation, had a reduction of 21%. Ozonation is known to effectuate physical changes by breaking larger molecular structures into smaller ones. Chemical changes will also result in more oxalic acid type compounds, which contains more oxygenated moieties than are found in nature making the materials more amenable to biodegradation (Rice, 1980; Amy, 1993; Becker et al., 1996). Hydrophobic base fraction, being a Humic substance (as it is widely referred to in the literature), fits well in the criteria for being suitable to oxidation by ozonation. Sharp reduction of this fraction, therefore, represented a mass transformation to hydrophilic fractions as will be discussed later.

Being a Humic substance consisting of amino acids, proteic materials, sugars and polysaccharides (Bruchet et al., 1990), the hydrophobic base fraction will react with ozone to produce aldehydes as DBPs (Amy, 1993). This same fraction, when exposed to chlorination, will also produce aldehydes in addition to trihalomethanes (Amy, 1993). Hence, more aldehydes may form at the CR plant than the R/M plant.

The fraction is otherwise gradually reduced as it flows through other treatment units (i.e. GAC multimedia filtration or sand filtration), as expected.

### Hydrophobic Acid

Hydrophobic acid represented about 8-12% of the DOC by weight at all locations (12% in the raw water). Others have reported a range of 19-68% in raw waters (Aiken et al., 1993; Day, 1991; Korshin et. al., 1997). Figure 6 shows the reduction of this fraction along the treatment train. The reduction again is more pronounced (30% more) in the CR plant indicating the influence of pre-ozonation in the removal process. Hydrophobic acid fraction had a comparatively lesser slope in the mass-reduction curve than that of the hydrophobic base (Figure 5) through the pre-ozonation process. One of the reasons may be that hydrophobic acid, being a fraction that has the characteristic of soil fulvic, has

relatively low comparative concentration to other DOC fractions. In addition, its smaller molecular weight does not have the surface area to provide the large reaction coordinate sites for targeting by the ozone oxidant.

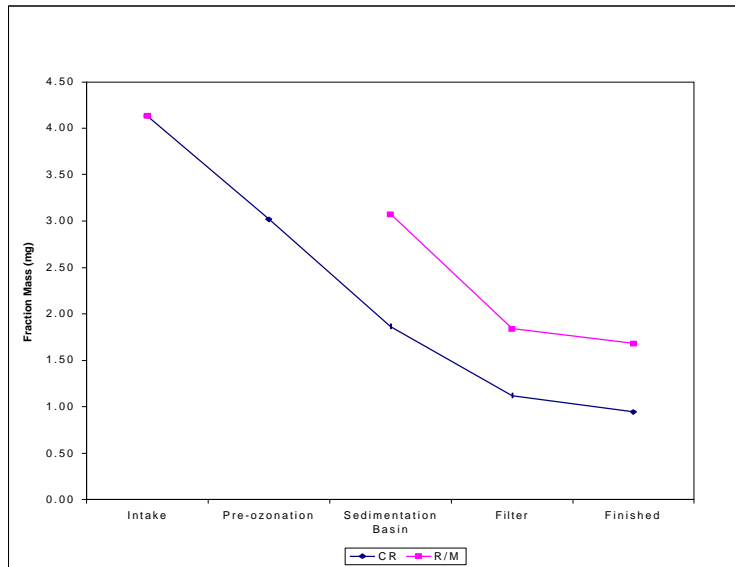


Figure 6. Hydrophobic Acid Fraction Variation

### Hydrophobic Neutral

Hydrophobic neutral was the most abundant fraction of the hydrophobic substances ranging from 13-22% in all locations (18% in the raw water). This range fell within the raw water range of 0-25% reported by others for raw waters (Aiken et al., 1993; Day, 1991; Korshin et. al., 1997). Hydrophobic neutral is a Humic substance in nature, which contains a mixture of hydrocarbon and carbonyl compounds (Leenher, 1981). Because of these characteristics, a steady but noticeable reduction of this fraction is shown in Figure 7. The CR plant with pre-ozonation, however, was more effective in removing this fraction (60% vs. 30%).

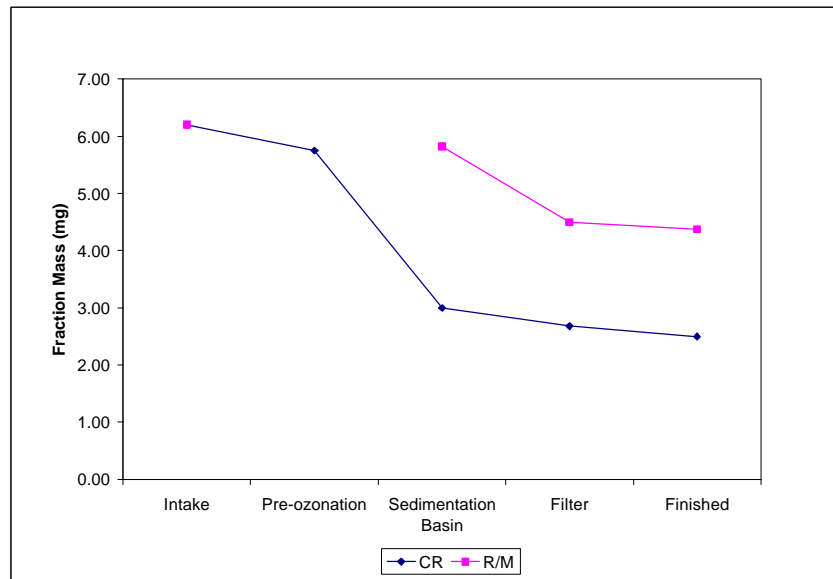


Figure 7. Hydrophobic Neutral Fraction Variation

It was noted that the findings were in agreement with those reported by others (Amy, 1993; Bose, 1994) in that ozonation does not change the DOC concentrations substantially. The results showed, however, that ozonation changed the content of the DOC substantially in terms of the operationally defined fractions investigated. This is more evidenced in the following discussions.

### Hydrophilic Base

Hydrophilic Base fraction at all locations ranged from 4-6% of the DOM (4% in the raw water). This range falls within the range of 1.5-10% reported by others for raw waters (Aiken et al., 1993; Day, 1991; Korshin et. al., 1997). Pre-ozonation increased the hydrophilic base fraction as shown in figure 8. The increase of 58% is believed to be the transformation of mass from the hydrophobic base fraction (figure 5). The breakup of mass into smaller molecular sizes and the transformation of materials from non-biodegradable to biodegradable (by the oxidation process) have been well established by others (Rice, 1980; Amy, 1993; Becker et. al., 1996). Figure 8 shows that, for the CR

plant, the increase of the hydrophilic base fraction mass following pre-ozonation was immediately followed by a comparable decrease following coagulation/sedimentation.

Overall, despite the local increase, the CR plant showed a higher reduction of this fraction compared to the R/M plant. Besides the micro-flocculation phenomena, the physical condition and design of the flocculation-sedimentation units may also have played an important role in performance.

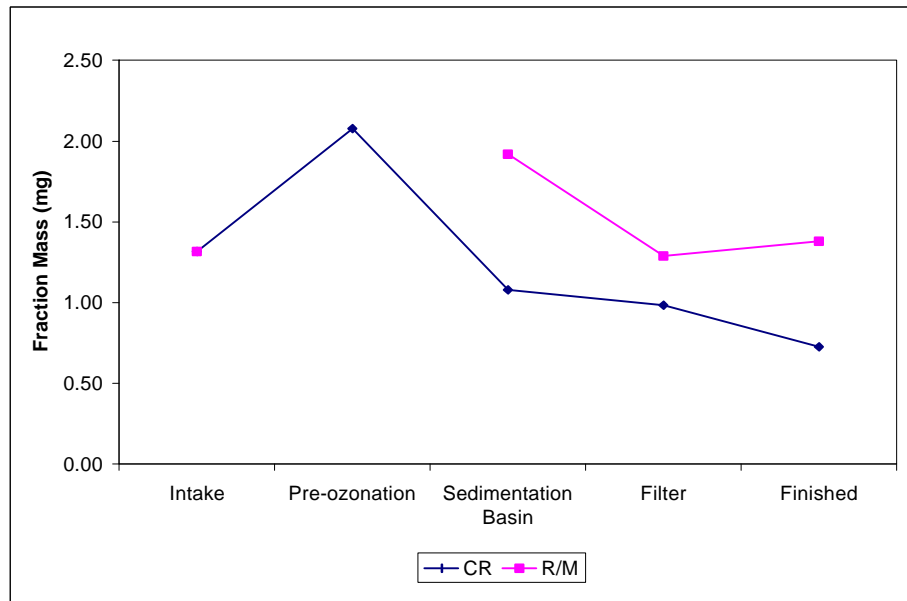


Figure 8. Hydrophilic Base Fraction Variation

### Hydrophilic Acid

This fraction was the most abundant and was found to be in the range of 44 to 55% of the DOC at all locations (48% in the raw water). It has been reported by others to be in the range of 8 to 50% in raw waters (Aiken et al., 1993; Day, 1991; Korshin et. al., 1997). The comparison, as shown in Figure 9, does not indicate any significant difference between the two plants on the removal of this fraction. This was a confirmation of earlier study (Bose, 1994) which found that hydrophilic acid was the least among the NOM fractions that form carboxyl group in the presence of the oxidant, ozone.

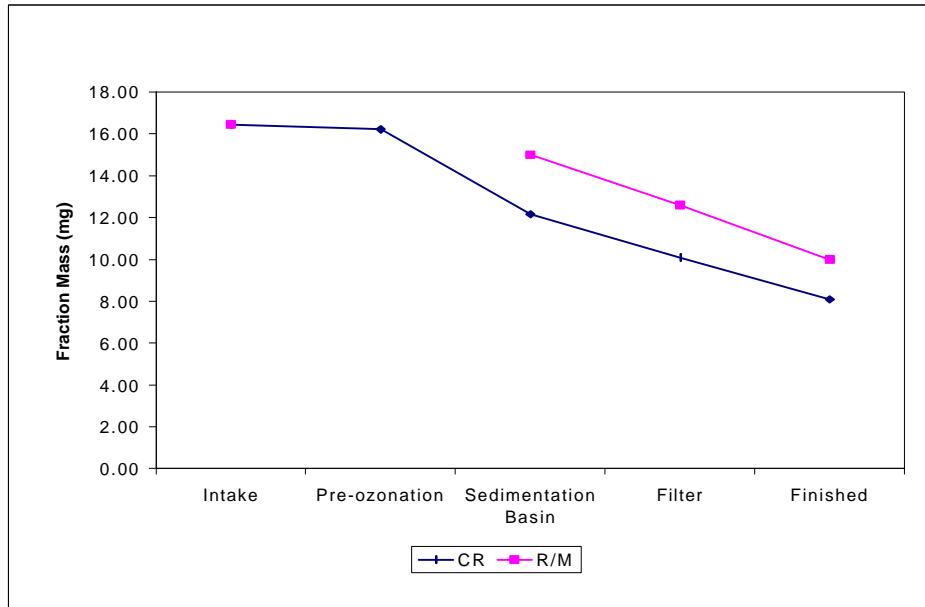


Figure 9. Hydrophilic Acid Fraction Variation

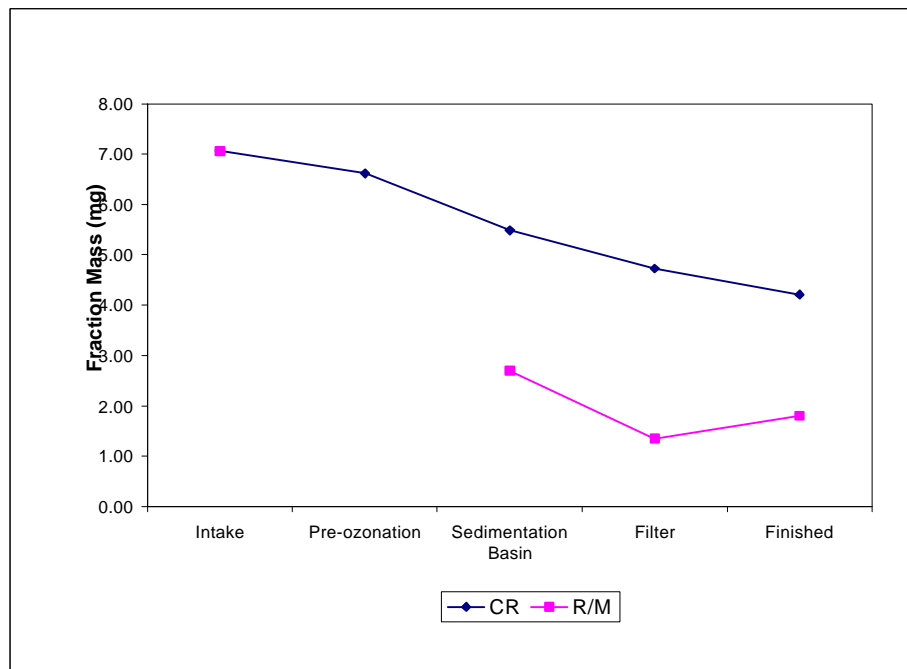


Figure 10. Hydrophilic Neutral Fraction Variation

