

NATURAL ORGANIC MATTER CHARACTERIZATION BY HPSEC AND ITS CONTRIBUTION TO CBPS FORMATION IN ATHENS WATER SUPPLY NETWORK. IMPLICATIONS FOR ALTERNATIVE DISINFECTANTS USE

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ABSTRACT

Natural organic matter (NOM) as the main component of natural colloidal matter in raw water is a major concern in drinking water treatment due to well-documented disadvantages. Chlorination by-products (CBPs) are formed after chlorine reaction with NOM and some of them such as trihalomethanes (THMs) are regulated by European Union, US EPA, WHO and other global organisations, because of their potential carcinogenic effects. As a result, it is crucial to understand NOM properties in order to determine the dissolved organic matter treatability. Since NOM is a mixture of fulvic and humic acids of a very complex structure, carbohydrates, low molecular weight organic acids as well as proteins, a lot of techniques have been applied to define structural or functional information about it. On the past, researchers made attempts to determine fulvic and humic acids molecular structures and interrelate with their CBPs. Fourier-transform infrared (FT-IR), nuclear magnetic resonance (NMR) or even elemental analysis have been used to characterize NOM fractions worldwide and predict CBPs formation potential. High-performance size exclusion chromatography (HPSEC) is a relatively simple technique to determine different NOM fractions concentration according to Molecular Weight. Athens Water Supply and Sewerage Company (AWSC) is a provider of potable water to four million people processing raw water from Mornos, Yliki as well as Marathon lakes in four water treatment plants (WTPs). Continuous monitoring of THMs in WTPs and in a fairly large number of Athens supply network sites started from 1993 does not complete the framework to potable water quality improvement. Minimisation of CBPs formation is one of the goals that can be accomplished through activated carbon use and/or alternative disinfection techniques. The main purpose of this study was to reveal the structural composition of NOM and identify the individual differences between the two main watersheds NOM so as to minimize CBPs formation.

Keywords: hydrophilic neutrals, hydrophilic acids, hydrophilic bases, high-performance size exclusion chromatography (HPSEC), natural organic matter (NOM)

1. Introduction

Natural organic matter (NOM) is a mixture of humic and fulvic acids, proteins, carbohydrates, low molecular weight organic acids. Since it contains a lot of diverse chemical compounds, there is no analytical method for defining structural or functional information about it. Fourier-transform infrared (FTIR) and UV/Vis spectroscopy, elemental analysis (EA), nuclear magnetic resonance (NMR), size-exclusion chromatography (HPSEC) are some of the most interesting analytical methods applied for the characterization of NOM fractions (Swietlik and Sikorska, 2004). During raw water disinfection, oxidation of NOM occurs and a variety of DBPs is formed, some of them are suspect for carcinogenicity. Among them, trihalomethanes (THMs) as well as haloacetic acids (HAAs) are regulated by health organisations and Maximum contaminant Levels (MCL) vary from country to country. Hence, European Union (EU) initiated the maximum contaminant level (MCL) of total (THMs) TTHMs to 100 µg/L but the trend is to minimize their levels. In order to minimize chlorination by-products (CBPs) levels, various water treatment techniques have been applied globally such as oxidation with potassium

permanganate, use of granular activated carbon (GAC), disinfection with other disinfectants than chlorine such as ozone or chlorine dioxide. The main objective of this work was to continue the investigation of NOM structure that started with fulvic and humic acid isolation and FTIR application (Samios *et al*, 2007a). Size exclusion chromatography was employed for this purpose and the results are comparable with those of the previous investigations. Water supply network THMs levels are exhibited as a result of monitoring that has started since 1993. Hence, NOM fractions compositions as well as THMs levels determine the optimised disinfection technique.

2. Materials and methods

2.1. Size exclusion chromatography (SEC)

The chromatographic characterization of NOM and its molecular weight distribution was determined by HPSEC using a UV-detector at wave length of 254 nm (AD25 detector, DIONEX, USA) on a DIONEX ICS–2500 with TosoHaas TSK gel G 3000 SWXL column and TosoHaas TSK gel SW guard column (Tosoh Corporation, Japan). The eluent was a 0.01 M phosphate buffer (pH 7.0), while the samples were injected without buffer addition. All analyses were performed at a temperature of 30 °C. Calibration was accomplished using peak maximum calibrations with sodium polystyrene sulfonate standards (PSS polymer standards, Germany). The molecular weight was plotted against retention time (larger retention times to smaller molecular weights). The scale was logarithmic one.

2.2. DOC measurement and THMs gas chromatographic analysis

Dissolved organic carbon (DOC) was analysed by a LAB-TOC system (Pollution and Process Monitoring Ltd., England) total organic carbon (TOC) analyser by the sodium peroxydisulfate/orthophosphoric acid wet oxidation/UV radiation method.

The method employed for the determination of THMs is a modification of 551.1 EPA method developed by Nikolaou *et al*. (2000). Methyl-tert-butyl ether (MTBE) is the primary extraction solvent. A 35 ml sample aliquot is extracted with 2 ml of MTBE after addition of 2.5 gr sodium sulphate. One µl of the extract (splitless injection) is then injected into a GC equipped with a fused silica capillary column and electron capture detector (ECD) for separation and analysis. Procedural standard calibration is used to quantitate method analytes.

3. Results

Chromatographic studies reveal NOM of both Mornos and Yliki watersheds to be composed of molecules with relatively small molecular sizes, i.e. 1500-200 Da (retention time 9.6-13.85 min.). Table 1 presents the DOC levels detected in surface waters.

The wavelength of 220 nm was chosen to observe the molecular weight distribution (MWD) of low molecular weight NOM fractions due to their relatively higher absorptivity at 220 nm whereas fractions with the highest molecular weights and aromaticity are exhibited at the wavelength of 254 nm (Babi *et al*, 2003; Świetlik *et al*, 2004). Table 2 presents HPSEC results.

Table 1: DOC levels of surface and storage water

Sample code	Sample	DOC [mg/L]
9502	Yliki lake surface	2,405
9504	Yliki lake	2,667
9601	Mornos lake	0,958
9606	Mornos lake- elevated storage tank	1,238
9608	Red river	1,032
9609	Evinos river	2,296

According to Świetlik *et al* (2004), NOM can be fractionated using XAD and ion-exchange resins adsorption methods into six fractions: humic acids (HA), hydrophobic acids (HOA), hydrophilic acids (HIA), hydrophobic neutrals (HON), hydrophilic bases (HIB), hydrophilic neutrals (HIN).

Peaks appear retention time (t_R) from 9 to 15 min in the two chromatograms (Figs 1-2). That means that NOM of the samples is characterized as one of low molecular weight (Matilainen *et al.*, 2002) that consists mainly of fulvic acids.

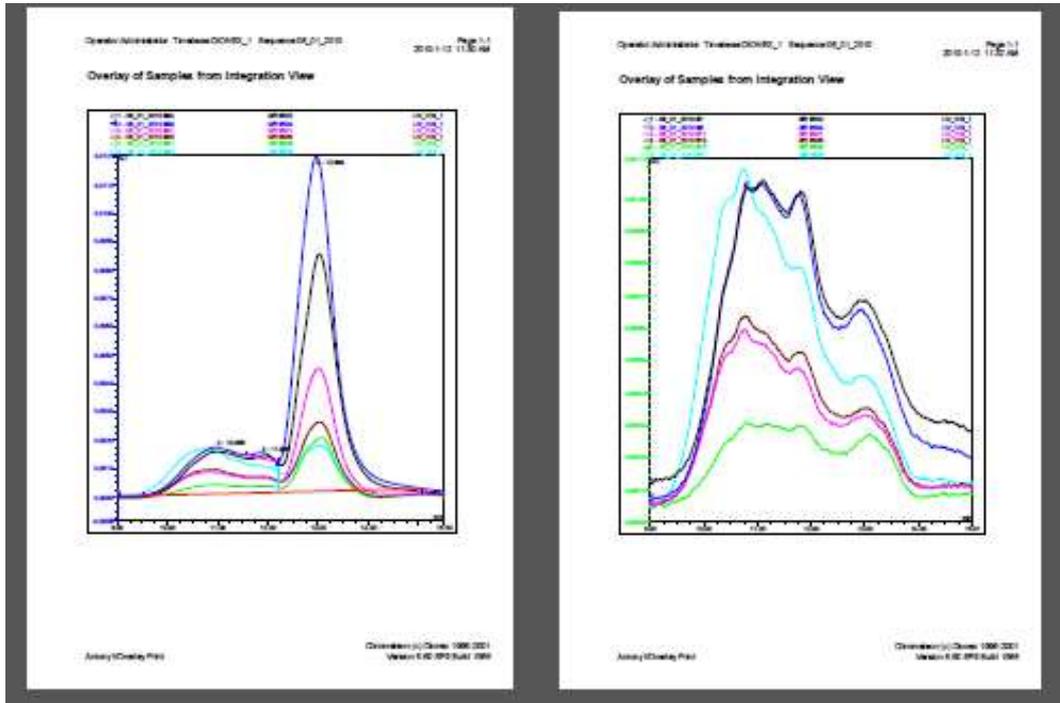


Figure 1: Chromatogram at 220 nm

Figure 2: Chromatogram at 254 nm

The strong band at 220 nm (Fig. 1) in t_R of 13 min indicates the existence of a large (HIN) fraction and the weak band in the same figure in 11 min, might prove a relatively small (HON) fraction. On the other hand at 254 nm, (Fig. 2), the band in 11 min indicates a fairly large (HIB) fraction. The other two stronger bands in 12 as well as 13 min prove that the low molecular weight NOM is a quite large part of the two different watersheds NOM. It is obvious from the parallel chromatograms of the five samples (Figs 1-2) that NOM from the two watersheds has similar composition. However, the concentration levels differ as can be seen from DOC levels (Table 1). Yliki and Mornos water NOM separation into fractions and FT-IR had been carried out and results were exhibited (Samios *et al.*, 2007a).

The NOM fractions mentioned above might be the most probable CBPs precursors. Athens Water Supply and Sewerage Company (AWSC) uses water from Mornos lake as well as from Yliki and Marathon lake. Mornos water that is processed in Aspropyrgos WTP forms THMs average 25 $\mu\text{g/L}$ even in the supply network (Fig 3). However, whenever water only from Yliki lake was chlorinated, THMs reached 40 $\mu\text{g/L}$ in the supply network extremes (Figs 4-5). The distribution network that starts from Aspropyrgos WTP and supplies drinking water to Salamina sampling location (a large water mains end) indicates an increase of TTHMs 15-20 % from the reservoir tank to the end of distribution system.

On the other hand, higher amounts of THMs are formed in Kiourka WTP (Figs 4-5) and there is a tendency for a further increase because of the residual chlorine reaction in the distribution network (Elshorgaby *et al.*, 2000; Samios *et al.*, 2007b). This is because raw water of higher DOC levels (2,5-5 mg/l) demands higher concentration of chlorine for the prechlorination (about 4 mg/l on average). Hence, during the treatment of Yliki lake raw water that supplies Kiourka WTP, the concentration of TTHMs that are formed is 30 $\mu\text{g/L}$ in WTP and 42 $\mu\text{g/L}$ TTHMs at the end of the distribution system according to Samios *et al.*, 2008 results. NBNE (another mains end at St. Marina suburb) and Artemis supply network mains from Kiourka WTP are 40 Km and 47 Km, respectively.

Table 2: Main peaks and molecular sizes at 254 nm wavelength (Fig 2 chromatogram)

Sample code	Main bands		Band major peaks at	
	Molecular size (Da)	Retention time (min)	Molecular size (Da)	Retention time (min)
9502	2820-450	9.5-11.65	950	10.75
	450-225	11.65-12.35	700	11.15
9504, 9601, 9606	2630-450	9.6-11.65	360	11.85
	450-225	11.65-12.35	950	10.75
	2290-450	9.75-11.65	700	11.15
9608	450-225	11.65-12.35	360	11.85
	3550-450	9.25-11.65	950	10.75
9609	450-225	11.65-12.35	1260	10.35
			950	10.75
			700	11.15

There might be molecular sizes below 225 Da in all samples mentioned above whose existence cannot be identified by HPSEC.

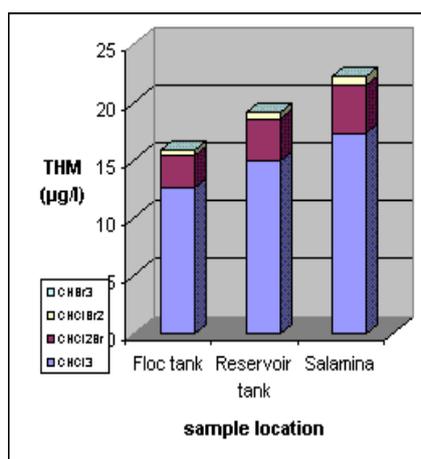


Figure 3: THM levels in Aspropyrgos WTP vs Salamina supply

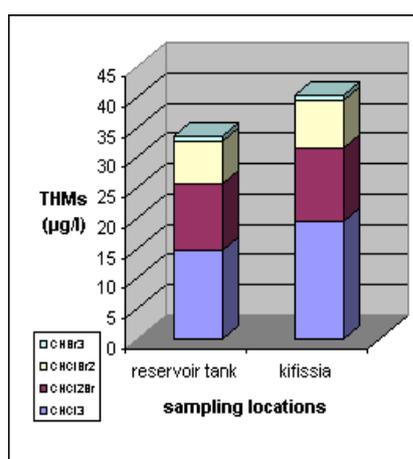


Figure 4: THM levels in old tank Kiourka WTP vs Kifissia supply

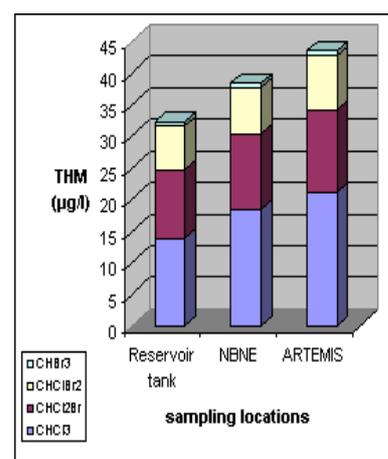


Figure 5: THM levels in new tank Kiourka WTP vs NBNE and Artemis supply

So, we might consider the possibility to disinfect Yliki water with a different disinfectant as chlorine dioxide. According to results of an experiment that was carried out in situ from November 2005 till June 2006, Yliki water disinfection with chlorine dioxide yielded levels of chloroform below 2 µg/L and dichlorobromomethane below 0,5 µg/L (Samios *et al.*, 2007c). However chlorine dioxide disinfection by-products may include chlorites and chlorates, carboxylic acids, aldehydes (Dabrowska *et al.*, 2003) so it is necessary to compare these two disinfectants as it concerns the formation of by-products as well as their efficiency against microbial population. It was shown (Swietlik *et al.*, 2004) that the oxidation of NOM with both ozone and chlorine dioxide caused the decomposition of the compounds with higher molecular weights into smaller molecular weight fractions. However, HPSEC chromatograms (figures 1-2) indicated that the largest NOM fraction is that of LMW that consists mainly of fulvic acids, amines, amides, carbohydrates and polysaccharides and a low degree of condensed aromatic moieties.

According to Swietlik *et al.* (2002) experiments, size exclusion chromatography proved that the reaction of chlorine dioxide with humic fraction of NOM proceeds mainly on an aromatic part of the molecules. Hence, HMW fractions are attacked by chlorine dioxide and a part of them is converted to LMW (Swietlik *et al.*, 2002). Also, LMW fractions are the least probable parts of NOM that can be removed from water after conventional treatments including coagulation-flocculation (Matilainen *et al.*, 2002) or after GAC filtration (Swietlik *et al.*, 2002).

Raw water DOC determines chlorine dioxide demand (Swietlik *et al.*, 2002). As usually Yliki water DOC is well below 5.0 mg/L, chlorine dioxide demand might scarcely exceed 1.0 mg/L. This is in accordance with past experiments *in situ* (Samios *et al.*, 2007c) where Yliki water disinfection with chlorine dioxide never needed dosage above 1.0 mg/L. According to Dabrowska *et al.* (2003) results, there is an increase to about 50 µg/L for the chlorine dioxide highest dose of 1.2 mg chlorine dioxide /mg TOC whereas a dosage of 1.0 mg chlorine dioxide/2.5 mg TOC = 0.4 mg chlorine dioxide /mg TOC might yield an average level of total aldehydes below 17 µg/L after chlorine dioxide application to Yliki water. However, measurements of aldehydes as well as carboxylic acids must be carried out during experimental chlorine dioxide application to Yliki water since both are readily biodegradable, so, their presence in potable water should be avoided.

4. Conclusions

As can be seen from the above, THMs levels of Athenian supply network are well below EU regulations. Higher TTHM levels resulted after the treatment of raw water from Yliki lake with higher DOC levels in Kiourka WTP. HPSEC experiments revealed that fulvic and humic acids of Mornos and Yliki lake appear with similar composition (mainly hydrophilic neutrals, hydrophilic bases of Low Molecular Weight) but different concentrations. The experimental data of Yliki water disinfection as well as from water processed in a water treatment plant indicated that the use of the alternative oxidant chlorine dioxide eliminates THMs.

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