Separation and Purification Technology 120 (2013) 162–171

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

# Variation in character and treatability of organics in river water: An assessment by HPAC and alum coagulation

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ARTICLE INFO

*Article history:*
Received 9 January 2013
Received in revised form 2 August 2013
Accepted 29 September 2013
Available online 8 October 2013

*Keywords:*
NOM
Coagulation
HPSEC
Fluorescence
Humics
Proteins

ABSTRACT

The treatability of NOM present in surface waters in South Australia (River Murray) impacted by a La Niña climate cycle was investigated. Over extended dry and wet climate conditions, the water quality had changed markedly from low to high DOC (and turbidity), requiring reassessment and adjustment of treatment conditions of these waters for potable supply. Investigation was conducted on the character and treatability of NOM through fractionation using DAX-8 resin before and after coagulation with alum and HPAC (a novel composite polyaluminum chloride coagulant), by high performance size exclusion chromatography with fluorescence detection (HPSEC-Fl) and by Excitation Emission Matrix (EEM) spectroscopy. In contrast to corresponding earlier dry periods where the DOC ranged from 2.7 to 4.8 mg/L, the DOC in the study period (summer–autumn) ranged from 10.1 to 15.8 mg/L. HPSEC-fluorescence indicated consistency in the presence of humic-like compounds over a molecular weight range of about 400 and 3000 Da for samples collected, while the presence of protein like compounds varied between months. High molecular weight (>50 kDa) protein like compounds were able to be removed but another protein-like component (4–9 kDa) was found to be recalcitrant to removal by coagulation. Alum was found to have high efficiency for removal of very hydrophobic, sorbed DAX-8 fraction (SDF) compounds in these waters while HPAC demonstrated better removals of organics over a wider range of molecular weights, i.e. smaller MW compounds. However, the overall removals of DOC were found to be similar for the two coagulants.

## 1. Introduction

Surface water quality can be affected by a wide range of pollutants including synthetic organic compounds (SOC) such as biocides used in agriculture, natural organic matter (NOM), both allochthonous and autochthonous and suspended materials. The nature of the pollutants present in water is impacted directly by catchment characteristics (land management practices, soils and vegetation types and loadings), seasonality and climate conditions [1]. NOM can be a significant pollutant in source waters used for drinking water supply as, depending on its character, can only be partially removed by conventional treatment processes, i.e. coagulation, and where the residual acts as an energy source for microorganism activity in water distribution systems and reacts with chlorine leading to the formation of disinfection by products that pose risks to human health. It comprises a complex heterogeneous mixture of organic compounds, including humic and fulvic acids, low molecular weight (MW) organic acids, carbohydrates, proteins and their derivatives. Terrestrially derived DOC has relatively low nitrogen content and large amounts of aromatic carbon which is believed to be a major reactive element to produce disinfectant by products in treated water [2].

In determination of the treatability of NOM by coagulation, understanding of its character such as its MW/size distribution is an important factor [3–8]. Another parameter that provides insight into the nature and treatability of NOM is specific UV absorbance (SUVA). SUVA is correlated with the average molecular weight of NOM, and this increases with increasing MW [9]. Resin fractionation of aquatic NOM such as by DAX-8, can be used to classify organic solutes into broadly defined hydrophobic and hydrophilic fractions [1,10]. The most frequently applied procedures for isolation/fractionation of NOM are based on non-ionic macro porous copolymers (such as DAX resin) which in conjunction with ion exchange resins and fractionation conditions applied, allow

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http://dx.doi.org/10.1016/j.seppur.2013.09.033

classification of organic solutes into different hydrophobic, ctransphillic and neutral fractions [11–14].

HPSEC analysis is commonly implemented to determine the AMW profile of NOM sourced from aquatic and terrestrial environments [15,16]. The advantages of HPSEC over other analytical techniques include the need for only a small sample volume, minimal pre-treatment, ease and speed of analysis and capability for using different detectors, such as ultraviolet (UV) and DOC in-line analyzers [17]. The combined use of multiple detectors has been shown to overcome the low sensitivity of the UV absorbance detector to DOM dominated by non-chromophoric structures [18,19]. Fluorescence studies of NOM and identification of particular fluorophores remains difficult due to its complex chemical structure and to the spectral overlapping and peak shifting and broadening [20,21]. The use of EEM analyses and exclusion chromatography by fluorescence detection has been receiving increased attention because dissolved humics and protein-like compounds have different fluorescence responses at specific wavelength ranges [18,22,23].

Very hydrophobic organics (SDF) can be efficiently removed by coagulation [24–26]. The hydrophobic content influences the coagulant demand as this fraction contains the majority of charged (carboxylic acids) organics. In contrast, the non sorbed DAX-8 fraction (NSDF) is considered to be less amenable to removal by coagulation, attributed to a lower charge density. These fractions which are not adsorbed by DAX 8 resin are of lower molecular weight and include hydrophilic and non acidic components [11,27,28].

Although climate and environmental conditions from the effects of El Niño and La Niña events are well documented in literatures [29–31]. There is a lack of information on the impacts from La Niña events on drinking water quality and particularly on the character and treatability (by conventional drinking water treatment processes) of dissolved organic matter. In this study we report the investigations and findings of the variability of coagulation treatability of natural organics present in River Murray water during a climate cycle (La Niña) of high rainfall conditions throughout eastern Australia. This cycle had followed an extended drought period that had significantly affected both water quality and its flow in rivers of Australia's major catchment system, the Murray–Darling Basin (MDB). In this study, the character of NOM in River Murray water was investigated by combination of resin fractionation, HPSEC with fluorescence detection and EEM analyses for detection of humics, fulvic and protein-like substances. Treatability was assessed by the conventional coagulant, alum and an aluminum-based polymer coagulant, HPAC.

## 2. Materials and methods

### 2.1. Water source

The River Murray is a major fresh water resource for the states of New South Wales, Victoria and South Australia of Australia. The River Murray together with the Darling River and their tributaries are of the Murray–Darling Basin. The basin covers over 1 million square kilometers or 14% of Australia [32]. MDB water is used for agriculture, industry and domestic water supply. South Australia is highly dependent on the River Murray for domestic and potable water supply. For investigations conducted, water samples were collected from the River Murray, at Morgan South Australia, from summer to autumn (January–May 2011) and were stored at 4 °C following collection and transport to the laboratory.

### 2.2. Reagents

All chemicals used were of analytical grade unless otherwise stated. An aluminum sulphate stock solution 20,000 mg $l^{-1}$ as $Al_2(SO_4)_3 \cdot 18H_2O$ was prepared using Milli-Q water. HPAC used in this study was sourced from the Beijing Wanshui Water Cleaning Company, China. The efficiency of HPAC for DOC removal in high alkalinity and turbidity waters has been previously reported [33,34]. Sodium hydroxide (NaOH) and sulphuric acid ($H_2SO_4$) were used for pH adjustment and reagents used for size exclusion chromatography were of HPLC grade.

### 2.3. Jar testing

A variable speed, six paddle gang stirrer and Gator jars were used for jar testing, conducted at room temperature. Water samples (2L) were placed on the gang stirrer with six samples tested at a time and the coagulant doses were added while stirring at 220 rpm. The coagulation pH for these experiments was targeted at 6 [7]. The amount of acid or alkali required to achieve the target pH was determined by pH titration and then added prior to the addition of coagulant for coagulation pH control. After 1 min of flash mixing at 220 rpm, the speed was reduced to 25 rpm for 14 min. The samples were then allowed to settle for 15 min. The settled water samples were then filtered through Whatman No. 1 to measure the filtered turbidity and subsequently through 0.45 μm (pre-rinsed membrane with Milli Q water) before measurement of color, UV, DOC and through 0.22 μm for HPSEC.

### 2.4. DOC and UV absorbance

DOC concentrations were determined using a total organic carbon analyzer (Model 820, Sievers Instruments USA). The UV absorbance at 254 nm ($UV_{254}$) was measured using a UV/VIS spectrophotometer (Model 918, GBC Scientific Equipment, Australia) with a 1 cm quartz cell. For DOC and $UV_{254}$ measurements, samples were filtered through 0.45 mm pre-rinsed membranes. SUVA was used to determine the character of organics and was calculated as:

$$\text{SUVA} = 100 * \text{UV}_{254}\ \text{cm}^{-1}/\text{DOC mg L}^{-1}$$

For assessment of the variance of quantitative analytical techniques used to quantify and characterize DOM in raw waters, the co-efficient of variation (CV) and standard errors (SE) were determined. Water samples were collected from River Murray and representative water quality parameters such as DOC, UV, color and turbidity were determined in triplicate. The standard errors determined for these water quality parameter were as follows: DOC (0.015), UV (0.005), color (0.636) and turbidity (0.882). CV and SE values are presented in Supplementary information (Table S1).

### 2.5. Determination of apparent molecular weight (AMW)

AMW was determined by HPSEC attached with fluorescence detector using xenon light as excitation source. The carrier solvent was 0.02 M phosphate buffer solution (pH 6.8, ionic strength adjusted to 0.1 M with sodium chloride). The flow rate of sample was 1 mL $min^{-1}$ and calibration was performed using polystyrene sulfonate (PSS) standards [7]. Fluorescence was measured in terms of fluorescence units (FU) or fluorescence intensity. HPSEC fluorescence detection of humics and proteins-like substances was carried out on samples filtered through 0.22 μm membranes pre-rinsed with Milli Q water. Excitation wavelengths for humics ($E_x$ 320 nm) and proteins ($E_x$ 280 nm) were based on a study by Chen et al. [21].

### 2.6. Peak fitting of HPSEC chromatographs

A commercially available software, Peak Fit (Version 4, Systat Software Inc.), was used to resolve overlapping peaks of HPSEC