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Treatability of organic matter derived from surface and subsurface waters of drinking water catchments

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HIGHLIGHTS

- DOM not complexed with clay is less amenable to removal by alum.
- Lowest alum dose rates were for waters from native vegetation on sandy soil.
- Soil-water from prominent O horizon sites show similarity in DOM treatability.

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ABSTRACT

The treatability of NOM present in runoff and subsurface waters from discrete zero-order catchments (ZOCs) with three land management practices (Australian native vegetation, pine plantation, grasslands) on varying soil textures of a closed drinking water reservoir-catchment was investigated. Subsurface water samples were collected by lysimeters and shallow piezometers and surface waters by installation of barriers that diverted waters to collection devices. For small sample volumes collected, a 'micro' jar testing procedure was developed to assess the treatability of organics by enhanced coagulation using alum, under standardised conditions. DOM present in water samples was quantified by measurement of DOC and UV absorbance (at 254 nm) and characterized using these and F-EEM. The mean alum dose rate (mg alum per mg DOC removed or Al/DOC) was found to be lower for DOM from sandy soil ZOCs (21.1 ± 11.0 Al/DOC) than from clayey soil ZOCs (38.6 ± 27.7 Al/DOC). ZOCs with *Pinus radiata* had prominent litter layers (6.3 ± 2.6 cm), and despite differences in soil textures showed similarity in DOM character in subsurface waters, and in alum dose rates (22.2 ± 5.5 Al/DOC). For sandy soil ZOCs, the lowest alum dose rates (16.5 ± 10.6 Al/DOC) were for waters from native vegetation catchment while, for clayey soil ZOCs, waters from pine vegetation had the lowest alum dose rates (23.0 ± 5.0 Al/DOC). Where ZOCs have a prominent O horizon, soil minerals had no apparent influence on the treatability of DOM.

1. Introduction

Natural organic matter (NOM) present in raw waters of reservoirs used for drinking water supply can pose significant aesthetic problems and health risks that need to be addressed through treatment processing prior to supply. Dissolved organic matter (DOM), often the major component of NOM can be derived from two distinct sources: (1) allochthonous inputs derived from catchment sources and (2) autochthonous organic matter production from within the water body (e.g., reservoir), for example, by microbial activity (Sachse et al., 2005) and by photosynthesis. Water quality in catchment fed reservoirs is largely influenced by land management practices within the catchment (Bryan et al., 2009), and catchment properties such as vegetation type and loading (Naidu et al., 1993; Chantigny, 2003; Yang et al., 2013), topography

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Abbreviation: $\%DOC_{Rem}@ED$, percentage removal of DOC at enhanced alum dose; $\%DOC_{Rem}@HD$, percentage removal of DOC at high alum dose; Al/DOC, alum dose rate at enhanced dose; C, DOC removal rate co-efficient; DOC, dissolved organic carbon; DOC_C , coagulable DOC; DOC_{NC} , non-coagulable DOC; DOC_R , DOC residual after treatment by alum; DOM, dissolved organic matter; ED, enhanced alum dose; FA, fulvic-like components; G, grass; HA, humic-like components; HD, high alum dose; HMW, high-molecular weight; MQW, High purity Milli-Q water; NV, native vegetation; P, pine; PI, protein1-like components; PII, protein2-like components; S, sandy soil; SC, sandy clay soil; SCL, sandy clay loam soil; SL, sandy loam soil; SMP, soluble microbial protein-like components; SpCol, Specific colour; SUVA, specific UV absorbance; UV_{254} , UV absorbance at wavelength 254 nm; ZOCs, zero-order catchments.

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(Ågren et al., 2007), climate (Chow et al., 2011; Yang et al., 2013) and soils (Nelson et al., 1992).

Dissolved organic matter (DOM) can have significant impacts on drinking water quality with potential concerns to public health. Such concerns include: (1) disinfection by-product formation when organics react with chemical disinfectants (Richardson and Postigo, 2012), (2) increase microbial regrowth in the drinking water distribution system (Drikas et al., 2003), and (3) increases colour, taste and odor levels in drinking water that can make it unacceptable by the community. The removal of organics that are the precursors of DBPs of health concern, is therefore of high importance. Coagulation and flocculation are the most widely used processes for removal of DOM from drinking water (Matilainen et al., 2010) even though it can only be partially removed. The treatability (or removal capacity) of organics present in drinking water by coagulation/flocculation is affected by the raw water alkalinity and the character of DOM (Chow et al., 2009). DOM is a complex assemblage of chemical structures (McElmurry et al., 2014) that varies in molecular weight and functionality (Matilainen et al., 2010). These include humic substances that are collections of diverse, relatively low molecular mass components forming associations stabilized by hydrophobic interactions and hydrogen bonds (Sutton and Sposito, 2005). The coagulation process has been reported to be more effective in the removal of high-molecular weight hydrophobic compounds than low-molecular weight hydrophilic compounds (Matilainen et al., 2010; Sillanpää and Matilainen, 2015).

Catchment surface runoff and stream waters generally have higher concentrations of organics that are more aromatic and humic in nature (Inamdar et al., 2012) than shallow and deep groundwater. This is attributed to either absorption of high molecular weight (Banaitis et al., 2006), hydrophobic and aromatic compounds (Ussiri and Johnson, 2004) to mineral soils or by microbial modification (Sun et al., 2013), as the DOM in waters move through the soil profile. Nelson et al. (1992) found that differences in concentrations of dissolved organic carbon (DOC) between streams are dependent on the adsorption capacities of the catchment soils. DOM present in catchment waters is influenced by vegetation loading and, in a comparative study, highest DOM concentrations were found from catchments under forest cover followed by grassland and then arable soils (Chantigny, 2003). Naidu et al. (1993) reported that DOC concentrations in water flow along the soil A horizon/B horizon boundary under pine plantation, was at least twice that under native woodland or pasture. The highest concentration of DOC released into subsurface waters can occur during the first seasonal rainfall event, demonstrating the importance of fresh litter material in generating high amounts of soluble organic matter (Chow et al., 2011).

Although several studies have reported an association between land management practices and NOM present in waters, as exemplified above, to date there have been few studies reported on the relationships between the qualities of waters within discrete land-use catchments and the treatment needs of waters for potable supply. Previously we reported the findings of a study (Awad et al., 2015) on the characters and concentrations of DOMs (measured as DOC) present in surface runoff and in the upper horizons of the soil profile in ZOCs, with distinct vegetation and soil texture. The results of that study showed that DOC concentrations of surface flow waters were similar or higher than of sub-surfaces waters. It was also found that waters from grass catchments had the least loading of DOM for a particular soil texture, as compared with native vegetation and *Pinus radiata*. The aim of the study reported here was to determine the treatability of DOMs present in surface and subsurface waters sourced from contrasting ZOCs of a drinking water reservoir catchment. In this study, DOC, UV absorbance at 254 nm and F-EEM data were acquired to characterize DOM before and after a 'micro' jar testing procedure, developed to assess the treatability of organics present in small volumes (~100 mL) of subsurface water samples collected.

2. Material and methods

2.1. Site descriptions and instruments

This study was conducted in the Myponga reservoir-catchment (35°22′ to 35°25′S and 138°24′ to 138°28′E) which is part of the Mount Lofty Ranges watershed, 50 km south of Adelaide, South Australia, Australia. The catchment area (123 km^2) (Bryan et al., 2009) of the Myponga Reservoir (26,800 ML holding capacity) has high levels of organic loading (~15.0 mg L^{-1} DOC) in Reservoir water. Six zero-order catchments (ZOCs), with distinct soil texture (sandy and/or clayey) covered by native vegetation, pine or grass, were selected for this study. ZOCs are largely non-channelized drainages common on hill-slopes and referred to as hollows or swales (Dietrich et al., 1987).

Land-uses, predominant vegetation, average slopes and detailed soil descriptions of ZOCs studied have been previously reported (Awad et al., 2015). The key features of the study sites are as follows: Site 1: native vegetation on sandy soil (NV-S); Site 2: pine on sandy soil (P-S); Site 3: grass on sand over sandy clay (G-S/SC); Site 4: native vegetation on sandy clay loam over sandy clay (NV-SCL/SC); Site 5: pine on sandy clay loam over sandy loam (P-SCL/SL); Site 6: grass on sandy clay loam over sandy clay (G-SCL/SC).

ZOCs were instrumented with surface runoff collection devices as detailed by Awad et al. (2015). Ceramic cup lysimeters were installed at depths of approximately 30 and 60 cm to capture soil water samples through application of a vacuum at ~60 psi. Subsurface through-flow water samples were collected by installation of 90 mm diameter PVC piezometers. The tops of piezometers were loosely capped.

The rainfall pattern of Myponga, South Australia, is strongly seasonal with hot dry summers and cool wet winters (in 2013, 643 mm rainfall occurred between June and November compared with 178 mm between December and May). Water samples were collected in winter and spring seasons (between June and November 2013). In summer-autumn seasons, neither surface water runoff nor subsurface water flow were recorded in any ZOCs.

2.2. Water analyses

2.2.1. DOC concentrations and UV–Vis absorbance measurements

The DOC and UV absorbance measurements were made of water samples, pre-filtered through 0.45 μm pre-rinsed sterile cellulose membrane filters. DOC concentration was determined using a TOC analyser (Model 900, Sievers Instruments). UV–Visible light absorbances were measured using a spectro-photometer (UV-120, MIOSTECH Instruments) for wavelengths from 200 nm to 700 nm, using a quartz cuvette of 1 cm path length. Colour in Hazen Units (HU) was determined by absorbance at 456 nm using a 5 cm path length, glass cuvette and a platinum/cobalt standard (50 HU). Specific UV absorbance or SUVA (the ratio of absorbance at 254 nm m^{-1} to the concentration of DOC), (Edzwald and Tobiason, 1999) and Specific colour (SpCol, the ratio of colour in HU to DOC concentration) were determined.

2.2.2. Fluorescence excitation-emission matrix

Fluorescence excitation-emission matrix (F-EEM) spectra were acquired (Model LS 55, PerkinElmer) to characterize NOM based on the relative abundances of humic (HA), fulvic (FA), protein1