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Treatability and characterization of Natural Organic Matter (NOM) in South African waters using newly developed methods

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ABSTRACT

Managing the removal of Natural Organic Matter (NOM) or problematic components from water has become increasingly important. NOM is a heterogeneous mixture of organic compounds of human origin and derived from plant and microbial residues. The inadequate removal of NOM has a bearing on the capacity of the other treatment processes to remove organic micro-pollutants or inorganic species that may be present in the water. In addition the action of certain disinfection processes has been shown to lead to the formation of harmful disinfection by-products (DBPs). Owing to the complexity, in composition and structure, of NOM, the techniques currently employed for its characterization have a number of limitations, both in terms of quantification and removal of the NOM within short periods of time. The dissolved organic carbon (DOC), biodegradable dissolved organic carbon (BDOC) and Fluorescence Emission Excitation Matrices (FEEM) were used to characterize NOM from various water samples collected around South Africa. Characterization results gave an indication of the character of NOM present in all the water samples. FEEM and UV–Vis results indicated that most of the water samples were aromatic in nature, since they had high hydrophobic and humic acid-like materials content. Generally, the characterization data indicated a varying composition of NOM amongst the various sampling points. The polarity rapid assessment method (PRAM) was then employed as a rapid NOM characterization tool. The characterization under PRAM is based on preferential adsorption of dissolved organic matter (DOM) fractions onto solid phase extraction (SPE) sorbents. The PRAM also allows the separation of DOM into fractions by polarity, hence reducing the molecular heterogeneity of NOM and thus aiding the removal of specific NOM fractions from water. The PRAM provided a quick characterization of the NOM character. However, DOC quantification by the PRAM analysis was hindered by excessive carbon leaching from the SPE cartridges. The BDOC method of analysis is based on the bacteria fixed on the biologically active sand and gives a ratio of the biodegradable NOM versus the non-biodegradable NOM. For the BDOC analysis, the percentage DOC removal for the samples ranged from 12% to 61%.

1. Introduction

The Integrated Water Resources Management (IWRM) principle recognizes that water is required for many different purposes, functions and services; management therefore, has to be holistic (integrated) and involve consideration of the demands placed on the resource and the threats to it (Mostert, 2009). The integrated approach to management of water resources necessitates co-ordination of the range of human activities which create the demands for water, determine land uses and generate waterborne waste products. An emerging issue in drinking water treatment is Natural Organic Matter (NOM), which is a highly variable mixture of chemicals formed by the decomposition of plant and animal material into water systems and soils (Rosario-Ortiz et al., 2007). Due to the different sources of NOM, it is widely acknowledged that the composition of NOM in different water bodies is also not uniform (Nkambule et al., 2009).

Characterization of the structure and reactivity of NOM is important as it affects water treatment processes such as transport of contaminants (Pederson et al., 2002), formation of disinfection by-products (DBPs) (Marhaba and Daonh, 2000) and fouling of membranes during water treatment (Taniguchi et al., 2003). NOM also affects water quality in many other ways: it could be responsible for colour, undesirable taste and odour of natural waters, is a source of nutrients for heterotrophic bacteria and also inhibits precipitative processes that form the backbone of drinking water treatment. These problems can in turn affect human health and the environment. There is therefore little doubt that NOM management, as a precursor to or direct cause of the problems highlighted above, should be one of the critical design and operational parameters for drinking water treatment. Unless we gain a

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deeper understanding of NOM in South African raw water, together with their treatability and fate by different technologies, water treatment, plant design and operation will not be able to deal with the ever increasing NOM levels in a predictable and satisfactory way.

A review of NOM characterization at water treatment plants in South Africa has revealed attempts to try and characterize the NOM occurring at individual plants, but they are unable to conclusively determine the nature of NOM occurring in the country (Haarhoff et al., 2010). The primary objective of this study is thus to characterize the NOM occurring in South Africa through an extensive sampling of different water types, both as raw water and following certain treatment steps. Much of the raw water can be classified into five categories:

- Oligotrophic water; such as that from the Vaal dam, supplemented by the Lesotho highlands project. This serves Rand Water, by far the largest water supplier in South Africa.
- Montaigne water flowing eastwards from the Drakensburg and Amatola escarpments; utilized, for example, by Amatola and Umgeni Water. This water is fairly high in organics, but low in colour.
- Highly coloured water; e.g. water found on the south-western coast that is very high in colour, usually from humic and fulvic substances.
- Eutrophic water; found in many of the dams on the Highveld, with the eutrophication being determined by large return flows and agricultural run-off.
- Treated water sewage effluent; which dominates the NOM character in many streams and rivers in South Africa, especially during periods of low flow.

It is important to note that not all components of NOM are equally problematic. For example, the biodegradable dissolved organic carbon (BDOC) content in drinking water is an indicator of bacterial re-growth potential in the distribution network (Hammes and Egli, 2005). It is, however, also a good indicator of the performance of those treatment processes that rely on biological mechanisms to reduce the amount of NOM. Owing to the complexity and structure of NOM, the techniques employed for its characterization have a limitation in terms of an all inclusive characterization protocol of NOM to molecular level (Tinnnachev and Honeyman, 2007). The presence of some components of NOM in drinking water sources has a bearing on the treatability of the water, particularly with respect to NOM removal. The following are the most commonly used methods to remove NOM: enhanced coagulation, advanced oxidation processes, ozonation, and bio-filtration, adsorption and membrane separation. The high variability in the levels and composition of NOM in South African water sources in different regions means that no single treatment process can be prescribed for the entire country. Further, the treatability of NOM varies along the water treatment train and there are varying effects of NOM on the efficiency of these processes.

The polarity of NOM greatly influences its reactivity and is used as a measure of chemical alterations during environmental and treatment processes. However, there are no analytical techniques available to simultaneously characterize different polarity properties of NOM under environmentally relevant conditions (Rosario-Ortiz et al., 2007). A modified polarity rapid assessment method (PRAM) will be used to characterize the changes in NOM polarity through the water treatment process. These methods characterize the polarity of aqueous NOM by quantifying the amount of material adsorbed onto different solid phase extraction (SPE) sorbents.

Herein, we thus report on the development of a rapid method of NOM characterization and results obtained for eight water-treatment plants in South Africa, distributed among the five major source-water types (*vide supra*). Understanding the character of NOM within a short period of time would help inform water treatment engineers on necessary adjustments to be carried out within the water treatment plant as the composition of NOM changes during the process, or as a result of external factors like weather or season. By extension we also propose a rapid NOM removal strategy to remove NOM from source, during pre-treatment and at certain points along the water treatment train.

2. Experimental design

2.1. Sample collection and preservation

The sampling points were chosen such that they should be a representative of the main surface water type's encountered in South Africa and the main treatment processes that are likely to remove significant amounts of NOM. Eight water treatment plants were selected: the Loerie (L) water treatment plant of the Nelson Mandela Metropolitan Municipality, the Olifantsvlei (O) wastewater treatment plant north of Johannesburg (Johannesburg Water), the Plettenberg Bay (P) water treatment plant in the Southern Cape, the Rietvlei (R) water treatment plant of the Tshwane Metropolitan Municipality, the Stilfontein (M) water treatment plant of Midvaal Water, the Umzoniana (U) water treatment plant of the Buffalo Metropolitan Municipality, the Vereeniging (V) water treatment plant of Rand Water and the Wiggins (W) water treatment plant of Umgeni Water.

There were between two and four sampling points at each water treatment plant depending on the treatment processes used at that particular plant. These were raw water samples; i.e. before treatment, intermediate samples [usually before sand filtration, after granular activated carbon (GAC) dosage, or after dissolved air-flotation (DAF)] and a final sample after sand filtration. Sampling was repeated twice at intervals of three months. All samples underwent two sets of analyses; one at the time of collection, namely: pH, turbidity, conductivity and temperature (using a HANNA 98129 multi-meter), and another set up in the laboratory. All water samples were filtered through a 0.45 μm cellulose filter paper and stored in the refrigerator at 4 °C for not longer than 72 h prior to laboratory analysis.

2.2. Laboratory analysis

2.2.1. Organic carbon analysis

Dissolved organic carbon (DOC) was used as an indicator of the organic content in the water samples. DOC is the organic constituent that can pass through a 0.45 μm filter paper (Nkambule et al., 2009). Standards of 1, 5, 10, 20 and 25 mg/L carbon were prepared with potassium hydrogen phthalate (KHP) and de-ionized water. The DOC of each NOM sample was measured using a total organic carbon (TOC) analyzer (Teledyne Tekmar, TOC Fusion).

2.2.2. Ultra violet-visible (UV–Vis) spectrophotometric analysis

The water samples were subjected to UV–Vis spectrophotometric analysis in two formats: firstly, the ultraviolet domain provides a quick and accurate measure of the organic material in water, based on the fact that most NOM components have a UV chromophore, and secondly as a full-scan. A Shimadzu UV-2450 spectrophotometer was used to analyze the samples in the UV range at the following four wavelengths; 214 nm (indicative of nitrites and nitrates), 254 nm (indicative of humic substances and aromatics), 272 nm (reported in the literature to be the best predictor for Trihalomethane (THM) formation, Liu et al., 2006) and 300 nm (used by Rand Water and other treatment plants as a measure of