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# The use of MSSV pyrolysis to assist the molecular characterisation of aquatic natural organic matter

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## ABSTRACT

Microscale sealed vessel pyrolysis (MSSVpy) with online gas chromatography mass spectrometry (GC–MS) was used with several other established and complementary analytical methods to robustly characterize the structure of aquatic natural organic matter (NOM) and to practically assess the analytical value of MSSVpy. The NOM used in the study was from North Pine (NP) reservoir, which is one of the major source waters supplying Brisbane, the capital city of the Australian state of Queensland. The reservoir has moderate dissolved organic carbon (DOC; $5\ \mathrm{mg\ L^{-1}}$) levels and is impacted by algae which periodically occur in bloom proportions. The hydrophobic (HPO; 65% initial DOC) and transphilic (TPI; 12%) fractions showed H/C values $>1$, low $\mathrm{UV_{abs}}$ and low aryl-C measured by NMR which are all indicative of low aromaticity. MSSVpy produced distinctly higher product concentrations than traditional flash pyrolysis and the molecular profile of the HPO and TPI fractions revealed by MSSVpy was correlated with the other analytical data to help establish their structural relevance. Prolific distributions of alkyl substituted aromatic (e.g., benzenes, naphthalenes) and hydroaromatic (e.g., tetralins) products detected in the HPO fraction were attributed to the aromatisation of terpanes and other aliphatic compounds from algal, and possibly also plant sources. Alkyl phenols also detected in HPO in high abundance, are probably from algal biopolymers, but may also reflect a contribution from non-methoxylated lignin units of catchment grasses. There was no analytical evidence of the dihydroxy or methoxy aromatic structures typical of wood lignin or tannin. N-organic pyrolysates (e.g., alkyl pyrroles, pyridines, indoles) of diagenetically altered proteins were concentrated in the TPI fraction. The quantitative importance of the N-organic moiety of the TPI fraction was corroborated by a low C/N ratio and distinctive amide and amine signals detected by $^{13}$C NMR and FTIR. This

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integrated study demonstrates that the qualitative speciation provided by MSSVpy can make a significant contribution to the structural characterisation and source recognition of aquatic NOM.

## 1. Introduction

Aquatic natural organic matter (NOM) comprises a complex mixture of organic compounds and is subject to high spatial heterogeneity due to the wide diversity of soluble biochemical precursors and other environmental factors. Its chemical characterisation typically requires an integrated analytical approach. Analytical pyrolysis is one of the more commonly applied methods of NOM characterisation, yet is limited to the GC–MS detection of thermally labile, apolar products which usually represent only a small proportion of the gross sample (Saiz-Jimenez, 1994). Controlled thermal treatment strategies such as microscale sealed vessel pyrolysis (MSSVpy), however, have recently been shown to promote the reduction of polar NOM moieties and significantly increase the yields of GC amenable products (Greenwood et al., 2006; Berwick et al., 2007).

MSSVpy is conducted in a closed tube at temperatures typically in the range 250–350 °C for several days. This modest thermal regime contrasts the open system and ballistic heating to >500 °C typical of flash pyrolysis methods. Excessive degradation, secondary structural alteration or inadequate chromatographic resolution of pyrolysates of high structural polarity limit the flash pyrolysis characterisation of NOM. MSSVpy has been used widely to characterize organic sediments and to study the kinetics of petroleum generation (e.g., Horsfield et al., 1989; Schenk and Horsfield, 1993; Diekmann et al., 2000). Recent MSSVpy studies of NOM and related humics have also shown it can assist the thermal defunctionalisation of a wide variety of organic biochemicals and provide new speciation data useful for establishing structures and source inputs (Greenwood et al., 2006; Berwick et al., 2007; Berwick, 2009).

Here, the characterisation potential of MSSVpy is more rigorously evaluated in an analytical case study of the NOM of the North Pine (NP) reservoir. NP is a major potable resource of south east Queensland, including the state capital Brisbane. It was one of four waters representative of common Australian potable sources studied in a recent research project (2.3.1.3) supported by the Co-operative Research Centre for Water Quality Treatment (CRC-WQT; http://www.crca.asn.au/crc/crc-water-quality-and-treatment), recently succeeded by Water Quality Research Australia Limited (http://www.wqra.com.au/). Analytical performance is more stringently tested by this relatively low DOC (<5 mg L$^{-1}$) water than higher DOC waters such as the waters of Adelaide and Perth which have been more extensively researched (e.g., Davidson, 1995; Fabris et al., 2008; Chow et al., 2009) and were also part of CRC-WQT project 2.3.1.3. The MSSVpy data was directly compared to corresponding flash pyrolysis and thermochemolysis data. The qualitative pyrolysis speciation was complemented by size exclusion chromatography (SEC), UV absorbance, $^{13}$C nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopy providing quantitative assessments of molecular size, carbon structural environment and functional group distribution.

## 2. Materials and methods

### 2.1. Sample, site and collection

The North Pine (NP) Dam impounds the North Pine River to form Lake Samsonvale in Pine Rivers Shire, approximately 30 km north of Brisbane (Queensland, Australia). This reservoir has a surface area of 21.6 km$^2$, a storage capacity of 215,000 mL and a mean annual rainfall of 1175 mm – subject to extreme annual and seasonal variation. The drainage basin covers an area of 348 km$^2$, and includes 70 km$^2$ of mixed forest; 100 km$^2$ of grassland and pasture; and 6 km$^2$ of cropping land (Littlejohn, 2004; Schneider et al., 2006).

NP is a high quality source water. It typically has low colour, relatively low dissolved organic carbon (DOC) concentrations ($\leq$5 mg L$^{-1}$) and relatively low alkalinity (<65 mg L$^{-1}$ $CaCO_3$). Periodic cyanobacterial blooms in the reservoir represent the major potable risk (Littlejohn, 2004; Burford et al., 2007).

In July 2005 93 L of water was collected from the NP reservoir, vacuum-filtered using pre-washed 0.5 μm glass fibre filters (43 mm, Whatman) and stored in a stainless steel vessel at 4 °C.

### 2.2. Isolation and fractionation procedure

The filtered source water (93 L; 4.8 mg L$^{-1}$ DOC) was concentrated approximately 5-fold using a combination of reverse osmosis (at 414 kPa) and rotary evaporation (97% recovery DOC) to a volume (17.3 L, 25.1 mg L$^{-1}$) which could be accommodated in a single pass of a 300 mL superimposed XAD-8/XAD-4 (Amberlite) resin system. XAD resin preparation and separation was carried out using established procedures (Croué et al., 2000; Leenheer et al., 2000) to isolate HPO and TPI fractions, the basic chemical composition and elemental details of which are shown in Table 1. Some of the HPO material was so strongly adsorbed to the XAD-8 resin that it could not be recovered by elution with MQ/acetonitrile (75% recovered). Total recovery of source water DOC was 60%.

### 2.3. General analysis

#### 2.3.1. Ultraviolet absorbance

Ultraviolet/visible (UV/vis) absorbance at 254 nm and 400 nm was measured using a Shimadzu Pharmaspec UV-1700 UV–visible spectrophotometer. The absorbance at 400 nm was converted to colour units (CU) by calibration with colour standards. Standards of 10, 15, 25, 35, 50, 60, 70, 150, 250, 300 and 350 CU at 400 nm were obtained by dissolving aliquots of