

Comparison and development of advanced techniques for organic matter characterisation in water and wastewater processing

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ABSTRACT

Organic matter (OM) is one of the most complex natural mixtures on Earth. It is ubiquitous in all natural environments and plays an important role in a number of natural processes. However, despite the rich literature on its role and function in many environments, key aspects of OM composition remain unclear. What is now appreciated, is that OM exists as a complex mixture rather than as a single, defined material, whose structure depends on the source of the OM, the environment in which it was produced or transported to, and its stage of degradation.

There are different analytical techniques currently available that are used to study the composition and structure of OM. The more sophisticated techniques, including spectroscopic and chromatographic techniques, can provide valuable chemical or structural information on a sample, and have been widely applied to the study of OM. Characterisation of OM now commonly involves the combined use of techniques for an informative analysis. However, when they are used together, it is unclear how much information provided by the different techniques is the same, and how much is unique.

The focus of this study was to develop a protocol to quantitatively compare the information provided by different techniques when used in combination to characterise OM. This approach to assess the extent of technique complementarity relies on multivariate statistics. It involves the use of ordination plots to assess the information qualitatively, and the Spearman Rank Correlation method to assess the information quantitatively. The sophisticated analytical techniques chosen for the multi-technique approach are at the forefront of OM characterisation and include (i) solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy, (ii) flash pyrolysis-gas chromatography mass spectrometry (py-GCMS), and (iii) high performance size exclusion chromatography (HPSEC).

The protocol was initially developed for the combination and comparison of solid-state ^{13}C NMR spectroscopy and flash py-GCMS data. The approach was demonstrated on a set of well understood plant residues, where NMR and py-GCMS results could be compared to the literature. This methodology was further demonstrated on a different set of sediment organics. The approach was expanded to include HPSEC data in the analysis of pulp and paper mill water and wastewater (WW) organics. The three-technique approach was

then applied to the final set of samples in this thesis, consisting of partially and fully treated sewage effluent OM.

In each case, the ordination plots were able to help determine and compare how the different techniques differentiated between the organics in the sample sets. What is novel about the protocol developed is the quantitative comparison of this information. The Spearman Rank Correlation method was able to determine that two techniques in each study provided some complementary information to the analysis, and when the third technique was used, one technique provided unique information only. From this, it was determined that the most beneficial combination of techniques was when some complementary information and some unique information were provided. There was little benefit to the analysis when a large degree of complementary information was provided by two techniques. With the ability to determine how much complementary information is provided, analytical techniques can be more appropriately applied to OM characterisation therefore improving the allocation of resources including time and money.

Importantly, the degree of technique complementarity varied with each study. This was a promising result, as the complexity and variability of OM was therefore reflected in the analysis. The limits to the protocol were thought to have been reached in the final study of sewage effluents, as the ordination plots were thought to reflect primarily random variation due to the high degree of similarity between the spectral results. However, these results were put into context by the addition of reference organics to the ordination plots.

DECLARATION

I certify that this work contains no material which has been accepted for the award of any other degree or diploma in my name, in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. In addition, I certify that no part of this work will, in the future, be used in a submission in my name, for any other degree or diploma in any university or other tertiary institution without the prior approval of the University of Adelaide and where applicable, any partner institution responsible for the joint-award of this degree.

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PUBLICATIONS ARISING FROM THIS THESIS

Plant EL, Smernik RJ, van Leeuwen J. 2011. Comparison and development of advanced techniques for organic matter characterisation in water and wastewater processing. Platform presentation at: Water Quality Research Australia Limited's Members Meeting, Gold Coast, Australia.

Plant EL, Smernik RJ, van Leeuwen J, Macdonald LM, Dewy R, Nothrop S, Everson A. 2012. Lake Bonney: how have mill wastewater treatment practices influenced organics? Poster presentation at: Australian Water Association's OzWater '12 Conference, Sydney, Australia.

Plant EL, Smernik R, Greenwood P, van Leeuwen J, Macdonald LM, Everson A. 2013. Stirring-up sediment in Lake Bonney: multivariate comparison of organic profiling. Poster presentation at: Australian Water Association's OzWater '13 Conference, Perth, Australia.

Plant EL, Smernik R, Greenwood P, Macdonald LM, van Leeuwen J (2013) The organic chemistry of plant residues: comparison of NMR and pyrolysis data using multivariate statistical approaches. *Current Organic Chemistry*. 17:3006-3012.

Plant EL, Smernik RJ, van Leeuwen J, Greenwood P, Macdonald LM (submitted) Can organic residues from a pulp and paper mill be identified in the sediments of the receiving environment using NMR and pyrolysis techniques? *Environmental Science and Pollution Research*.

Plant EL, Smernik RJ, van Leeuwen J, Greenwood P, Macdonald LM (2013) Changes in the nature of dissolved organics during pulp and paper mill wastewater treatment: a multivariate statistical study combining data from three analytical techniques. *Environmental Science and Pollution Research*. DOI 10.1007/s11356-013-2351-0.

Plant EL, Smernik RJ, van Leeuwen J, Greenwood P, Macdonald LM, Leverett D. 2013. Pushing the limits of organic matter characterisation in wastewater: a quantitative approach to technique complementarity. Poster presentation at: SETAC North America 34th Annual Meeting, Nashville, Tennessee.

STRUCTURE OF THIS THESIS

This thesis is presented as a combination of papers that have been accepted for publishing, submitted for publication or have been prepared for submission.

Chapter One provides an overview of the literature on the nature, behaviour and importance of OM in different environments and the analytical techniques used to study it. It is in this chapter that the analytical challenges facing characterisation of OM are discussed. This chapter includes the proposed objective of this research. Introductory material relevant to the accepted, submitted and prepared papers is not presented in detail in the literature review because it appears in the introduction of each chapter.

Chapter Two comprises a paper published in *Current Organic Chemistry*. It describes the development and demonstration of a multivariate statistical method to combine and compare data from solid-state ^{13}C NMR spectroscopy and flash py-GCMS.

Chapter Three comprises a paper that has been submitted to *Environmental Science and Pollution Research*. It describes a demonstration of the method in Chapter Two to the characterisation of a set of sediment organic samples.

Chapter Four comprises a paper published in *Environmental Science and Pollution Research*. It describes the expansion of the method to include HPSEC for the characterisation of a set of pulp and paper mill WW organics.

Chapter Five comprises a paper that has been prepared for submission to *Environmental Monitoring and Assessment*. It describes a demonstration of the expanded method to the characterisation of a set of partially and fully treated sewage effluent organics.

Chapter Six provides a synthesis of the findings contained in this thesis and includes recommendation for future research.