

Characterisation of Dissolved Organic Carbon by Thermal Desorption - Proton Transfer Reaction - Mass Spectrometry

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Dissolved organic carbon (DOC) is an integral component of the global carbon cycle. DOC represents an important terrestrial carbon loss as it is broken down both biologically and photochemically, resulting in the release of carbon dioxide (CO₂) to the atmosphere. The magnitude of this carbon loss can be affected by land management (e.g. drainage). Furthermore, DOC affects autotrophic and heterotrophic processes in aquatic ecosystems, and, when chlorinated during water treatment, can lead to the release of harmful trihalomethanes. Numerous methods have been used to characterise DOC. The most accessible of these use absorbance and fluorescence properties to make inferences about chemical composition, whilst high-performance size exclusion chromatography can be used to determine apparent molecular weight. XAD fractionation has been extensively used to separate out hydrophilic and hydrophobic components. Thermochemolysis or pyrolysis Gas Chromatography – Mass Spectrometry (GC-MS) give information on molecular properties of DOC, and ¹³C NMR spectroscopy can provide an insight into the degree of aromaticity.

Proton Transfer Reaction – Mass Spectrometry (PTR-MS) is a sensitive, soft ionisation method suitable for qualitative and quantitative analysis of volatile and semi-volatile organic vapours. So far, PTR-MS has been used in various environmental applications such as real-time monitoring of volatile organic compounds (VOCs) emitted from natural and anthropogenic sources, chemical composition measurements of aerosols etc. However, as the method is not compatible with water, it has not been used for analysis of organic traces present in natural water samples.

The aim of this work was to develop a method based on thermal desorption PTR-MS to analyse water samples in order to characterise chemical composition of dissolved organic carbon. We developed a clean low-pressure evaporation/sublimation system to remove water from samples and thermal desorption system to introduce the samples to the PTR-MS. With thermal desorption lasting just 5 min (at 200°C) we successfully detected more than 200 organic ions in the water samples yielding up to 800 ng/mL in total (which corresponds to 1.5% of total DOC present in the sample). Samples were from tropical peatlands in Borneo and Malaysia. Principle component analysis showed a clear separation of the samples when comparing intact and degraded peat swamp forest, and between an oil palm plantation and natural forest. This suggests that the degradation and conversion of tropical peatlands result in distinct changes to DOC composition, with possible implications for associated CO₂ emissions.

As the method is sensitive and reproducible it has wide potential application in the characterisation of water and of soils. It could provide important information on how land management, microbial activity, vegetation and water treatment control the chemical composition of DOC.