



How can advances in dissolved organic matter characterisation lead to more effective water treatment?

One of four FREEDOM-BCCR project briefing notes considering options to increase resilience in the water industry to climate change impacts on dissolved organic matter

Dissolved Organic Matter (DOM) in upland drinking water sources poses an increasing challenge to the water industry as concentrations have risen substantially in recent decades. Nutrient enrichment of lowland rivers and reservoirs can also lead to DOM-related difficulties for water treatment. Work undertaken during the FREEDOM-BCCR project has highlighted the potential of future climate change to exacerbate concentrations further, with important implications for water treatment. There is an urgent need to consider the most efficient and effective adaptation and mitigation options open to the industry to manage any resulting deterioration of raw water quality.

The concentration and chemical composition of the molecules that comprise DOM varies between water supply catchments as a consequence of differences in soils, land use, hydrology and climate. Work conducted under the FREEDOM-BCCR project has shown that variations in temperature,

precipitation and soil moisture also contribute to well-recognised seasonal oscillations in DOM in reservoirs, and, together with changes in rainfall chemistry, can drive long-term change in DOM in drinking water sources.

The molecular composition of DOM (which includes the structural arrangement of molecules) is often referred to in terms of DOM “quality”. It determines the efficacy of methods to remove DOM in water treatment works (or “treatability”) and the potential for the formation of potentially toxic disinfection by-products (DBPs) during chemical disinfection. Precise quantification of the molecular composition of DOM is complex, but highly detailed information on quality is not always necessary from a treatment perspective. Hence, characterisation of DOM to inform approaches to treatment tends to focus on broad functional similarities such as their hydrophobic or hydrophilic properties (Box 1, p2).

Hydrophilic DOM is more difficult to remove from raw water than hydrophobic DOM using conventional techniques such as coagulation. While some types of hydrophilic DOM are derived from soils, particularly in lowland agricultural landscapes, the least treatable components of hydrophilic DOM are predominately produced by algae and bacteria within water supplies.

Consequently the concentration of the least treatable DOM fractions tend to correlate with nutrient concentrations. Hydrophilic compounds, particularly those produced by algae, can be rich in nitrogen. Chemical treatment of water containing such compounds can result in the production of specific DBPs that are relatively toxic, such as nitrosamines. In coastal regions, disinfection

Natural DOM comprises hydrophobic ('water-repelling') and hydrophilic ('water-attracting') compounds - terms that relate to their relative solubility in water (a polar solvent).

Hydrophobic DOM is largely derived from the degradation of terrestrial plant matter in soils. Often described as "humic substances", this DOM type includes humic acids (insoluble at low pH / high acidity) and fulvic acids (soluble at high and low pH / acidic and alkaline). Hydrophobic DOM molecules tend to be larger than hydrophilic DOM, and have structures that result in high specific absorbance of UV (i.e. high SUVA) and visible light. Electrostatically charged functional groups included in hydrophobic DOM influence its solubility and bonding with metals, e.g. aluminium and iron that are used to coagulate and thus remove them from solution.

Hydrophilic DOM is produced during the growth and decay of terrestrial and aquatic plants and via aquatic bacteria and algae activity. It includes carbohydrates, sugars, and amino acids. Hydrophilic DOM molecules typically contain more nitrogen and have lower molecular size/weights in comparison with hydrophobic DOM, and have few if any UV-Visible light absorbing characteristics (low SUVA). The absence of functional groups restricts the susceptibility of hydrophilic DOM to coagulants.

Conventional DOM fractionation

Fractionation at specific pH is used by the water industry to partition DOM into broad hydrophobic and hydrophilic categories using a range of resin adsorbents. Three resin adsorbents are typically used to give four overall DOM fractions: 'Very hydrophobic acids'; 'Slightly hydrophobic acids'; 'Charged hydrophilics' and 'Neutral hydrophilics'. Chemical modification of DOM through the fractionation process can be problematic and recovery rates for the hydrophobic fraction are variable.

BOX 1

Terminology and conventional DOM fractionation

reactions with elevated levels of bromide can produce brominated, halogenated DBPs with high toxicity. DOM molecules that react in such ways during chemical treatment are therefore known as DPB precursors.

Evidence suggests that climate change will alter both the concentration and quality of DOM in soils and reservoirs, thus impacting the nature and relative abundance of DBP precursors in raw water. A pressing concern for the water industry, therefore, is how to target the removal of the most problematic precursors and thus minimise

generation of the more toxic DBPs, while limiting treatment costs.

The FREEDOM-BCCR project has identified two immediate challenges associated with the potential for climate change to alter DOM concentration and quality. First, there is a need to improve the identification and quantification of DBP precursors in raw water in order to understand sources, temporal variability and how concentrations might change in future.

Second, there is a need to develop on-line systems for DOM characterisation to provide

Analysis type	Cost / impracticality	Adaptable for in-situ measurement	Level of characterisation (No. of DOM components)
DOC concentration	low-moderate	no	1
Optical-absorbance	low	yes	2-3
Optical-fluorescence	low-moderate	yes	c.5-15 (2-3)
DOM fractionation by resin absorbents	moderate	no	c. 2-6
Molecular size HPLC-SEC	high	no	2-8
Pyrolysis GC/MS	moderate	no	5-8
Mass spectrometry FT-ICR-MS / Orbitrap	moderate-high	no	Molecular composition / derived stoichiometry (c. 4-10k formulae)
DOM stoichiometry	moderate-high	no	~ DOM C:N; DOM-N content re: DBPs

TABLE 1
Comparison of DOM characterisation methods

early warnings of DBP risk, monitor treatment performance and increase the potential for tailoring treatment procedures in near real time.

The efficacy of specific treatment procedures can be assessed using both established and emerging methods for DOM characterisation (Table 1, p3). A range of techniques are available for the quantification of hydrophobic and charged DOM fractions, which can be removed with relatively high efficiency. Optimisation of coagulant dosing typically involves the use of simple colour/ absorbance metrics. In contrast, characterisation of hydrophilic fractions to inform treatability and DBP risk is less common, and there are currently limited options available for efficient, cost-effective removal of this fraction using present technologies.

DOM removal rates via water treatment

Incomplete removal of DOM, coupled with the selective removal of certain DBP precursors by different treatment procedures, can leave residual DBP problems (Figure 1, p5), and in some cases lead to the development of microbiological biofilms within the water distribution network. Residual dissolved organic carbon (DOC) concentrations tend to correlate with the total concentration of many classes of DBPs generated, so that the former typically remains the most reliable predictor of the latter. The concentration of the hydrophilic neutral fraction is indicative of the minimum achievable residual DOC concentration.

For the reasons given above, conventional, routinely applied metrics, typically based on colour or UV absorbance, provide only limited qualitative information on DOM characteristics, and associated risks of DBP generation. This shortfall can be overcome by targeted application of resin fractionation approaches to assess overall treatment performance, as well as the potential requirement and suitability of additional

treatment processes. However, such approaches are seldom used for regular surveillance due to the complexity and cost.

In recent years, advances have been made in methods that characterise DOM composition into anything between a handful and thousands of functional groupings. Ultimately the goal is to generate the type of functionally important information, currently only obtainable via expensive and complex DOM fractionations (e.g. resin fractionation), using rapid, less expensive methods that are amenable to on-line measurement. UV absorbance remains a relatively cheap and effective characterisation tool. It is typically only measured at an individual UV wavelength, although absorbance at more than one wavelength across the UV to visible parts of the spectrum can permit more detailed characterisations. 'UV-Vis fluorescence' (the wavelengths DOM emits light at across a wavelength spectrum of absorbed UV light) is also proving to convey useful information on molecular properties (Figure 2, p6). The combination of data generated by these two techniques is therefore likely to prove particularly effective in rapid and robust characterisation of specific DBP precursor compounds and their sources and drivers in water supply catchments.

In some situations, the current capacity of treatment works to limit DBP production to acceptable levels could be exceeded if concentrations of DOM continue to rise, and/or if there is a shift towards more hydrophilic, i.e. harder-to-treat, DOM. This problem is further compounded by anticipated increases in water temperature over the next century due to warming, as DBP formation rates increase significantly with temperature. At this point the emphasis of DOM management might have to shift to mitigation options within reservoirs and their catchments to maximise the quality of raw water prior to treatment. However, in moving to

a holistic view of the treatment chain from source to treatment end-point, there is an urgent need to better understand how interventions within catchments and reservoirs are likely to affect DOM

forms and concentrations with respect to treatability, the efficacy and cost-effectiveness of treatment measures, and timescales of response.

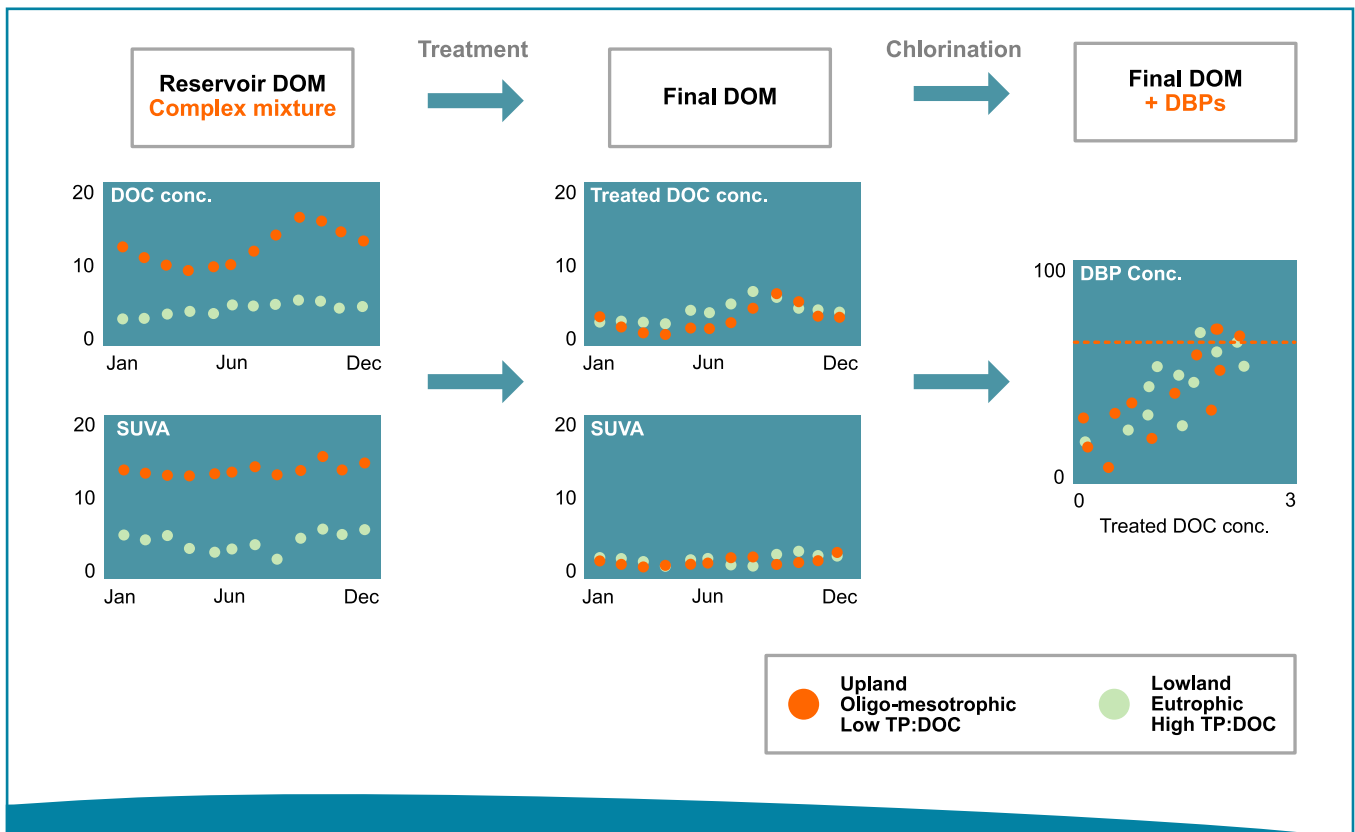


FIGURE 1

Hypothetical DOM concentration and composition (SUVA) seasonally for raw abstraction, and final treated water for two reservoir types: i) An upland low nutrient, high colour reservoir within a peatland catchment; and, ii) a lowland high nutrient, low colour reservoir within a mineral soil, agricultural catchment. Despite large differences in source water DOM quantity and quality, final treated water concentrations and their relation to DBP concentrations can present similar levels of DBP risk. (TP - Total Phosphorus; DOC - Dissolved Organic Carbon. Dashed line on right-most plot represents a hypothetical regulatory DBP threshold concentration, which varies by DBP and applies at the customer tap rather than the WTW).

- Low removal efficiency – low colour DOM (low SUVA, hydrophilic)
- High removal efficiency – highly coloured DOM (high SUVA, hydrophobic)
- Seasonality can alter source concentration and composition (catchment & in-reservoir drivers)
- Final treated water DOM concentrations tend to correlate positively with DBP concentrations
- Elevated treated water concentrations are indicative of incomplete removal of hydrophilic DOM, and/or under-optimised removal of hydrophobic DOM.

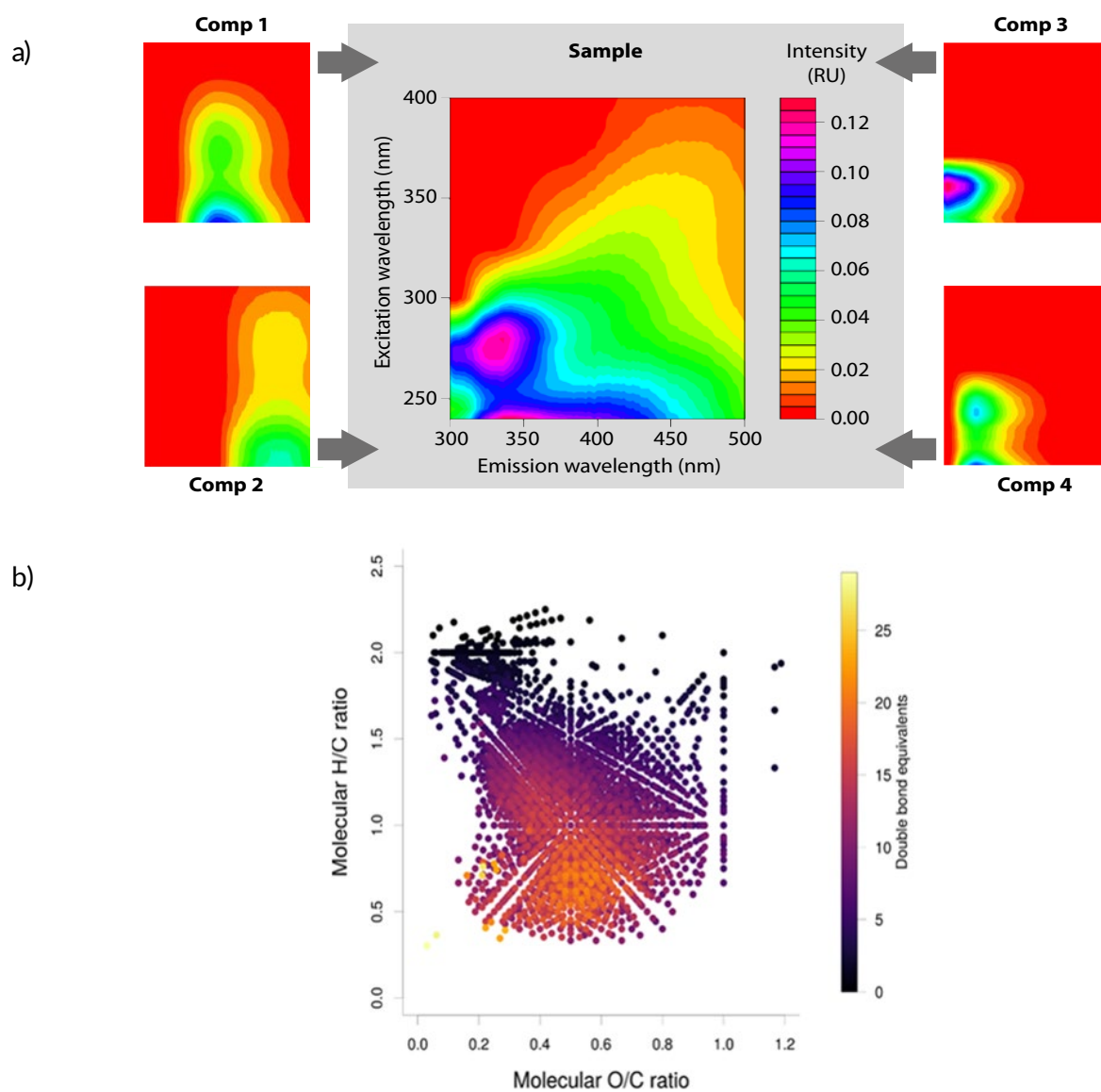


FIGURE 2

Example plots of data pertaining to DOM quality: a) Fluorescence spectra, where the central sample plot represents the combined fluorescence of a number of constituent, overlapping fluorophores (molecular structures within DOM that fluoresce). Modelling approaches, such as parallel factor analysis (PARAFAC), can be used to distinguish between the signals from these fluorophores, which are associated with different DOM sources. In this example, components 1 and 2 are 'humic-like' with terrestrial origins, are sensitive to degradation by sunlight, but not readily degraded by microbes, while components 3 and 4 are 'protein-like' and reflect lower molecular weight, more nitrogen rich DOM and tend to be associated with microbial activity.

b) van Krevelen plot derived from the molecular formulae of different types of DOM determined using fourier-transform ion cyclotron resonance mass spectrometry (image courtesy of Dr Nicholle Bell, School of Chemistry, University of Edinburgh). In this plot the constituent DOM molecules contained within a single water sample are arranged according to their hydrogen/carbon (H/C) and oxygen/carbon (O/C) ratios, with the colour scale indicating the sum of unsaturations and rings in each DOM molecule. Molecular level analyses provide data not only relating to the chemical diversity of the DOM molecules but also provide an indication of the likely DOM source and its potential reactivity with respect to DBP precursor material.

Take home message: Climate change threatens to increase the vulnerability of drinking water supplies by influencing the concentration and treatability of DOM. This has potential implications for the capacity of water treatment works and treatment costs, particularly where the concentration of less-treatable hydrophilic fractions may rise. Better characterisation of DOM would allow more targeted and, therefore, more efficient treatment, and will help to improve understanding of the sources and drivers of the different constituents of DOM. Emerging, complementary DOM characterisation approaches are providing new opportunities in this respect, and raise the prospects of new near real-time reactive treatment options.



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About the FREEDOM-BCCR project

FREEDOM-BCCR (Forecasting Risks of Environmental Exacerbation of Dissolved Organic Matter in the upland drinking water supply – Building Climate Change Resilience) is led by the UK Centre for Ecology & Hydrology and funded by the Climate Resilience Programme (www.ukclimateresilience.org) - jointly led by UK Research & Innovation (UKRI) and the Met Office under the Strategic Priorities Fund (SPF).

Through the development of a community of scientists and water industry representatives, FREEDOM-BCCR aims to improve understanding of the risks posed by climate change to the quality of water in upland drinking water sources and develop a conceptual framework of mitigation and adaptation options to maximise the future resilience of the supply. The vision of the Climate Resilience Programme is “To enhance the UK’s resilience to climate variability and change through frontier interdisciplinary research and innovation on climate risk, adaptation and services, working with stakeholders and end-users to ensure the research is useful and usable.”

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Partners



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