

EFFECT ON DISSOLVED NATURAL ORGANIC MATTER PROXIES BY INCREASED COMPLEXATION WITH IRON

Effekter av økte jernkonsentrasjoner på parametere som beskriver egenskapene til løst naturlig organisk materiale

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Abstract

Absorbency of UV and visible light by dissolved natural organic matter (DNOM) is used in proxies (sUVa, SAR) to assess its physiochemical characteristics and thereby removability of the DNOM by waterworks. The ongoing browning of surface waters is partly due to increased concentration and change in characteristics of DNOM. However, it is also likely that the browning is partly due to the increased iron complexation by DNOM. The significance of absorbency by the Fe-DNOM complex needs to be assessed in order to distinguish between the drivers of brownification.

Key words – DNOM; Iron complex, adsorbency, sUVa, SAR

Sammanfatning

Løst naturlig organisk materiale (DNOM) absorberer lys i UV og i den synlige delen av spekteret. Relativ absorpsjon i forhold til mengde DOC (sUVa) og mellom absorpsjon i UV og synlig lys (SAR) brukes som mål for å vurdere fysiokjemiske egenskaper og dermed fjernbarhet av DNOM ved vannverket. Den pågående økningen i farge (bruning) av overflatevann skyldes blant annet økt konsentrasjon og endring i egenskapene til DNOM. Imidlertid er det også sannsynlig at bruningen er delvis på grunn av økte konsentrasjoner av jern bundet til DNOM. Betydningen av absorpsjonen til Fe-DNOM kompleksene må derfor undersøkes for å skille mellom de forskjellige driverne til farge-økningen.

Introduction

Increased concentration of Dissolved Natural Organic Matter (DNOM) in the Nordic countries, and northern UK represents a challenge for waterworks (WW) using surface waters as raw water sources. The increase in DNOM is also causing changes to the water chemistry and physical conditions in the lakes: Along with the increase in DNOM there are significant increased concentrations of pollutants, nutrients and iron associated with the DNOM. Increased colour is also reducing euphotic

zone depths and primary production in lakes, and will also alter their temperature gradients and energy budgets (Read and Rose, 2013). Moreover, the colour of DNOM is increasing more than the DOC (Hongve et al., 2004). It has thus been implied that the organic compounds are becoming more aromatic, larger and thus more hydrophobic.

Two confounding factors are that while increased precipitation amount and intensity affect the colour of DNOM (Hongve et al., 2004), this change in climate is also causing more iron to be leached into surface waters.

Increased reducing conditions in the more water logged soils allow additional of the relatively more mobile ferrous iron (Fe^{2+}) to form. Reduced sulphur deposition is also likely augmenting the leaching of iron as less ferrous iron is fixated as pyrite (FeS). Increased water flux causes shorter retention time and thereby less loss of iron along the water continuum (Weyhenmeyer et al., 2014). In addition, the decreased leaching of aluminium due to declined acid rain, renders more functional sites on the DNOM available for iron complexation.

This increased amount of ferric iron (Fe^{3+}) complexed to DNOM (Fe-DNOM) will likely increase the colour of DNOM (Kritzberg and Ekström, 2012).

It is thus likely that the greater increase in colour than in DNOM is partly due to the increased density of complexed iron on the DNOM. This has strong bearing on the conceived ability of the WWs to remove the DNOM, as well as our assessment of processes and flow-paths governing the mobility and transport of DNOM from the terrestrial to aquatic environment. The question addressed in this article is therefore how complex binding of Fe^{3+} to DNOM affects the optical properties of DNOM.

Material and Methods

Three ongoing projects (NOMiNOR; <http://vannforsk.no/nominor/>, DOMQua; <http://www.niva.no/en/domqua>, and ECCO; <http://www.mn.uio.no/cees/english/research/projects/143792/>) are studying the DNOM characteristics in boreal raw water sources. Seasonal water samples as well as a set of isolated (freeze-dried) DNOM samples extracted by a reverse osmosis procedure (Gjessing et al., 1999; Vogt et al., 2004) are analysed using a large repertoire of techniques for characterisation of DNOM. Iron will be fractionated into labile inorganic and organic as well as dissolved, colloidal and particulate fraction. The focus will primarily be on effect of iron on the specific optical properties of the DNOM by means of UV/VIS and fluorescence emission spectroscopy.

Previous studies

In Sweden, the content of iron in freshwater was investigated as an explanatory factor for the browning of surface waters (Kritzberg and Ekström, 2012). They examined 38 years of monitoring data from 30 different lakes. Data from 27 of the rivers showed an increase in iron concentration ranging from 0.5–12.3 % per year. This assessment clearly showed that Fe^{3+} complexed to DNOM has had a major impact on the changes in absorbance of the water samples. Moreover, the increase in

colour could not be explained by DNOM alone, as colour of the organic material and colour of Fe-DNOM complex turned out to be independent of each other. The iron content explained 9–75 % of the variation in water colour. A similar study by Weyhenmeyer et al. (2014), of browning of more than 58 000 boreal freshwaters, also found that the colour relative to DOC increased by the presence of iron.

Both Kritzberg and Ekstrom (2012) and Maloney et al. (2005) studied experimentally how Fe-DNOM affected the absorbance by adding Fe^{3+} to natural water samples containing DNOM. Their results showed that the Fe-DNOM gave an approximately linear increase in both UV and visible absorbance.

Discussion

The problem with many of the most relevant assessments on the role of iron on the browning of water found in the literature is that they do not distinguish between organic and inorganic iron, and between particulate, colloidal and dissolved iron. Solubility of ferric iron at common surface water pH is very low. Adding Fe^{3+} to water samples thus cause the iron to form colloidal matter that adsorbs and scatters light. It is therefore possible that some of the increased adsorption may be due to the formation of colloidal iron rather than by a Fe-DNOM complex.

The association between iron and DNOM at different pH was studied by Tryland and Gjessing (1975) using ultra-filtration membrane. This method fractionates between organic and inorganic molecules based on that the organic molecules have a larger size so that they do not pass the membrane. They found that the amount of iron that passed through the membrane decreased with increasing pH up to pH 6, at which practically all iron was lost. The authors argue that the reason for this is that the association between iron and DNOM is stronger at higher pH. We suspect that the loss of iron by filtration at pH approaching 6 is rather due to the development of colloidal (oxy) hydroxides iron compounds. Neubauer et al. (2013) studied the Fe-DNOM complex in relation to pH. They found that iron associated with DNOM dominated at pH less than 4, while iron (oxo) hydroxides dominated at pH above 4. The size of the iron (oxo) hydroxide aggregates in water increased with increasing pH and decreasing DOC. Nevertheless, increasing DNOM concentration gave an increase in Fe-DNOM complexation on the expense of iron (oxo) hydroxide formation. The amount of DNOM-bound Fe decreased with increasing pH. This was consistent with their results from the UK, where the amount of Fe-DNOM decreased by 90 % from pH 4 to pH 7.

Conclusion

Better knowledge regarding the effects iron has on the optical properties of DNOM is required for optimal and proper custom water purification, and our understanding of governing factors for the amount and characteristics of DNOM, as well as our ability to assess the impact the changes will have on aquatic flora and fauna.

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