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## Brownification of freshwaters - the role of dissolved organic matter and iron

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BROWNIFICATION OF FRESHWATERS

—

THE ROLE OF  
DISSOLVED ORGANIC MATTER  
AND IRON



# BROWNIFICATION OF FRESHWATERS

—

## THE ROLE OF DISSOLVED ORGANIC MATTER AND IRON

SARA EKSTRÖM



**LUNDS**  
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AKADEMISK AVHANDLING  
som för avläggande av filosofie doktorsexamen vid  
naturvetenskapliga fakulteten, Lunds universitet kommer att  
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<b>Abstract</b> <p>The term brownification refers to the trend of increasing water color, i.e. the water becoming browner, which has been observed throughout the northern hemisphere over the last decades. Brownification has both ecological and societal implications. From an ecological point of view the impaired light climate may e.g. reduce aquatic primary production and affect predator-prey interactions within the water, while from a societal point of view brownification may obstruct drinking water purification and reduce the recreational value of lakes.</p> <p>Traditionally, the increasing water color has been ascribed to increasing concentrations of dissolved organic matter (DOM) from the catchment, as DOM concentrations and water color often correlate both spatially and temporally. Several mechanisms have been proposed as the driver behind the increasing DOM concentration, e.g. decreasing acidification, land-use changes and climate change with increasing precipitation and temperature. Interestingly, in many cases the water color has increased more than the DOM concentration, implying that increasing DOM concentration alone is not sufficient to explain the increase in water color. Thus, there must be other factors also affecting the water color.</p> <p>In this thesis I show, in a field experiment, that lower acid load results in a higher net charge of the organic matter in soils and thereby a higher solubility and mobility, which should facilitate a higher transport of DOM from the terrestrial to the aquatic system. Moreover, concurrent with the increase in mobility, there was a change in the quality of the DOM, where DOM from a lower acid load was relatively more colored, aromatic and of higher molecular weight. Thus, a reduction in acid load may contribute to brownification by increasing the export and the color of terrestrially derived DOM to the aquatic system. Experiments were performed to test if the altered quality of the mobile soil DOM may affect its reactivity in the aquatic system. It was found that the susceptibility to photodegradation increases, while the susceptibility to bacterial degradation decreases. The relative importance of each turnover process may hence be altered due to the decreasing acidification.</p> <p>Another factor affecting the water color of freshwaters is the concentration of iron (Fe) in the water. Still, the potential role of Fe to brownification has not previously been addressed. Data from long-term monitoring showed that water color of most Swedish rivers have increased significantly since the early 1970's. More surprisingly, most rivers also exhibit strongly increasing iron concentrations (up to 470 %). Increases in DOM concentration were significantly lower than the increase in water color and theoretically, variations in Fe concentration could explain on average 25 % and up to 75 % of increasing water color.</p> <p>Fe plays a key role in aquatic systems, affecting the biogeochemical cycling of many major elements, such as carbon, nitrogen and phosphorus. Thus the increasing Fe concentrations may have profound consequences. By analyzing within-year variations in water chemistry, air temperature, and discharge of three Swedish rivers, I explored what control Fe concentrations. It appears that variations in Fe concentrations are primarily driven by redox dynamics in the catchment. High discharge and high temperature create conditions that favor bacterial activities and reductive dissolution of the largely insoluble Fe(III) to the more soluble Fe(II). Fe(II) may then be transported from the soil to the aquatic system. Once in the oxic stream water, interactions with DOM maintain the Fe in solution. Furthermore, long-term trends of increasing air temperature and discharge in these catchments may have extended the periods of reducing conditions by increasing microbial activity and soil saturation, and thus have facilitated Fe transport to the aquatic system.</p> <p>In summary, it appears that in south Sweden, where the acidification has been high historically, the impact of decreasing acidification on organic matter mobility may be a major factor behind brownification, whereas in the north where the acidification has been much more restricted, increasing Fe concentrations may be more important. Climate change with increasing precipitation and temperature may increase the prevalence of reducing conditions in the soils, further facilitating the export of Fe to the aquatic system and causing a continuous brownification of the freshwaters.</p>		
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# SAMMANFATTNING PÅ SVENSKA

Under de senaste årtiondena har vattenfärgen i många svenska sjöar och vattendrag ökat. Detta innebär att vattnet blir brunare, och detta fenomen benämns därför brunifiering. Brunifiering är inget unikt för Sverige, utan förekommer på åtskilliga ställen på norra halvklotet. Brunifieringen påverkar det akvatiska ekosystemet och vattnets potentiella samhällsnytta. Ur en ekologisk synvinkel kan brunare vatten till exempel minska tillväxten av växtplankton och undervattensväxter i sjön, eller missgynna fiskar som är beroende av synen för att finna sitt byte. Ur ett mänskligt perspektiv kan brunare vatten innebära att det blir svårare att rena och använda det som dricksvatten, och många finner en sjö med brunt vatten mindre trevlig att bada i. Därför är det viktigt att förstå varför vattenfärgen ökar.

Brunifieringen brukar tillskrivas ökade koncentrationer av löst organiskt material (OM) – ofullständigt nedbrutna växtdelar från omgivande mark. Detta material ger vattnet en brun färg och i de flesta fall sammanfaller ökningen i vattenfärg med en ökning i OM-halt i vattnet. De ökade halterna av OM har härletts till bland annat klimatförändringar och förändringar i markanvändning. En annan teori är att det är den minskade försurningen som ligger bakom brunifieringen. Fram till åttiotalet skedde det stora utsläpp av svavel till atmosfären från bl.a. förbränning av fossila bränslen så som kol. I luften omvandlades svavlet till svavelsyra vilket sänker pH och försurar regnet. Tack vare lagstiftning har utsläppet av svavel minskat i Europa, och försurningen via regn har därmed minskat. Samtidigt som försurningen har minskat har vattenfärgen och halterna av OM i sjöar ökat, vilket gör att man tror att den minskade försurningen kan vara en av orsakerna till brunifieringen.

I ett fältexperiment där jag bevattnade skogsmark med vatten med olika svavelinnehåll visade jag att minskad försurning, dvs högre pH i regnet, gör det organiska materialet i marken mer lösligt och rörligt, vilket betyder att mer OM kan följa med regnvatten från marken till närliggande bäck eller sjö. Förutom den ökade rörligheten såg jag förändringar i det organiska materialets beskaffenhet. Lägre försurning gav OM som bl.a. hade mer färg och bestod av större molekyler. Dessa förändringar i kvaliteten hos det organiska materialet kan påverka hur det bryts ner i sjön. Två viktiga processer för nedbrytning av OM är fotooxidation, där OM bryts ner av solljus, och bakteriell nedbrytning, där bakterier använder OM som energikälla. Jag såg att OM under lägre försurning var mer tillgängligt för nedbrytning av solljus, men mindre tillgängligt för nedbrytning av bakterier. Detta kan komma att innebära att den ena processen blir viktigare än den andra för nedbrytningen av OM i det akvatiska systemet. I den utsträckning som minskad försurning är orsaken till brunifieringen kommer den att avstanna eftersom svavelhalterna i nederbörden börjar att närmar sig de nivåer som fanns innan försurningen startade.

Förutom OM så är järn i vattnet en viktig faktor bakom vattenfärgen. Dock har järn inte tidigare studerats i samband med brunifiering. Jag visar att samtidigt som vattenfärgen och OM har ökat, så har halten av järn ökat allra mest i våra ytvatten. Vattenfärgen har ökat avsevärt mer än OM, och teoretiskt sett skulle en stor del av brunifieringen kunna bero på ökade järnhalter.

Slutligen har jag studerat varför järnet i våra vattendrag ökar. Järnet kommer från omgivande mark, och variationen i järnkoncentration inom år tycks till stor del bero på förekomsten av syrefria förhållanden i marken. När det blir syrefritt i marken blir järnet lösligt och kan transporteras ut till vattendragen. Syrefria förhållanden i marken bildas när hög markfuktighet sammanfaller med höga temperaturer. De pågående klimatförändringarna med mer nederbörd och högre temperatur kan komma att öka förekomsten och utbredningen av syrefria förhållanden, och därmed öka transporten av järn från mark till vatten. Det är därför troligt att brunifieringen kommer att fortgå även i framtiden.



# LIST OF PAPERS

This thesis is based on the following papers, referred to in the text by their roman numerals:

- I. Ekström, S. M., E. S. Kritzberg, D. B. Kleja, N. Larsson, P. A. Nilsson, W. Graneli, and B. Bergkvist. 2011. Effect of Acid Deposition on Quantity and Quality of Dissolved Organic Matter in Soil-Water. *Environmental Science & Technology* 45:4733-4739.
- II. Ekström, S. M., M. Sandahl, P. A. Nilsson, D. B. Kleja, and E. S. Kritzberg. Reactivity of dissolved organic matter in response to acid deposition. *Manuscript*.
- III. Kritzberg, E. S. and S. M. Ekström. 2012. Increasing iron concentrations in surface waters – a factor behind brownification? *Biogeosciences* 9:1465-1478.
- IV. Ekström, S. M., O. Regnell, H. E. Reader, P. A. Nilsson, S. Löfgren, and E. S. Kritzberg. Increasing concentrations of Fe in surface waters as a consequence of reducing conditions in the drainage area. *Manuscript*.

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# INTRODUCTION

## Prologue

Before the start of my PhD program, I went on a field trip sampling lake water in Småland, south Sweden, as a field assistant to another PhD student. We occasionally encountered some old man or woman living by a lake in one of the typical Swedish red houses with white corners (Fig. 1). Often they had been living there their entire life and they often had a personal connection to “their” lake. All remembered the lake being clearer when they were young.

Most had noticed a gradual increase in the water color, noticing it getting browner and browner over the years.

Some had been wondering why.

A few had been wondering if the water would be even browner when their grandchildren’s grandchildren swim in the lake in the future.

With this in mind I returned to Lund and started my own PhD studies. I have since then spent a bit over four years studying the brownification phenomenon and I will now try to answer at least part of these questions.

This is my contribution to the knowledge about the *Brownification of freshwaters*.



Figure 1. A brown water lake in Småland, south Sweden, and a typical Swedish red house with white corners.

## **What is brownification?**

Brownification of freshwaters is the trend of increasing water color where the water becomes increasingly browner [1]. Already acknowledged in the 1990's [2], this phenomenon is now recognized throughout the northern hemisphere and is generally ascribed to increasing concentrations of terrestrially derived dissolved organic matter (DOM) from the drainage. When studying monitoring data running back as long as to beginning of the 1970's, increasing water color and DOM concentrations have been observed in Sweden [2-5], Norway [6-8], Finland [9, 10], the UK [11-14], central Europe [15-17], and North America [15, 18-20]. Lakes of high water color and DOM concentration generally exhibit the greatest increase in water color, although brownification has been observed in most lake types from brown water lakes to eutrophic and oligotrophic clear water lakes [10, 21]. Brown water lakes can be found throughout the world, and are especially common in areas dominated by coniferous forests, bogs, and mires. DOM concentrations may vary over time, where studies of sediment cores from Swedish lakes indicate that the DOM concentrations in the lakes may have been twice as high approximately 100 years ago, but then decreased steadily until a few decades ago [22]. Brown water is a reflection of the catchment and a natural feature, but it is the fact that the water color has been increasing so strongly during the last decades that has made it an extensively studied and widely debated research topic.

Water color and DOM concentrations often correlate both spatially and temporally and the increase in water color of freshwaters has therefore been attributed to increasing concentrations of terrestrially derived DOM. The underlying mechanism to why DOM is increasing has been widely discussed, where climate change, changes in land-use, and decreasing acidification at the present date are the prevailing theories. However, the water color has been found to increase significantly more than the DOM concentration [4, 6], implying that the change in the amount of DOM alone is not sufficient to explain the whole increase in water color. Thus, there must be something else also affecting the water color. Apart from the *concentration* of DOM, an alteration in DOM *quality* (i.e. chemical characteristics such as e.g. molecular weight and structure) may affect the color of DOM [23]. Yet another factor affecting the water color is the occurrence of iron (Fe) [24, 25], and Fe and water color often correlates spatially [26]. Recently, increasing Fe concentrations in freshwaters have been reported from e.g. Sweden [27], Finland [28], and the UK [29], in parallel with the observed brownification. Nevertheless, variations in Fe concentration have previously not been considered a factor involved in brownification of freshwaters.

Brownification has both ecological and societal implications, and the consequences of increased and altered DOM may differ from that of increased Fe. Moreover, the potential of continuous brownification depends

on the underlying mechanism. Water color in freshwaters is a fundamental and decisive variable, affecting both structure and function of the aquatic system. The most obvious consequence of brownification is the impaired light climate within the lake or stream. Browner water will efficiently reduce the amount of light penetrating the water and this will in turn reduce the visibility [30, 31]. For example, a reduced light climate may negatively affect both aquatic primary and secondary production and predators depending on vision [32-35]. Browner water color also has societal significance associated with recreational value, e.g. brown water lakes are often considered less attractive for swimming.

The increasing concentrations of terrestrially derived DOM may affect the biogeochemical role of freshwaters. In global carbon budgets, the freshwater system was previously considered a passive transport of terrestrially derived carbon to the ocean [36], but lately this view is changing. It is now estimated that approximately half of the terrestrial net production of carbon is imported into the aquatic system, where half of that is processed and transformed within the freshwater part of the aquatic system [36-38]. One estimation for example suggest that of the 2.9 Pg C<sup>yr</sup> that enters the freshwater system, 1.4 Pg C<sup>yr</sup> is mineralized through respiration and photooxidation and emitted to the atmosphere as CO<sub>2</sub>, 0.6 Pg C<sup>yr</sup> buried in the sediments and the remaining 0.9 Pg C<sup>yr</sup> transported out to the oceans [38]. With increasing transport of

DOM from the terrestrial to the aquatic system, the role lakes and streams play in the carbon cycle may become even more significant. Terrestrially derived DOM provides a source of energy and carbon for aquatic bacteria [39, 40]. Thus, high concentrations of terrestrially derived DOM promote heterotrophy both by reducing primary production and subsidizing the heterotrophic food web, and net-heterotrophic lakes, where respiration exceeds primary production [41], are common throughout the world [42]. Increased import of terrestrially derived DOM may shift a lake from a net-autotrophic towards a net-heterotrophic state so that lakes will increasingly be a source of carbon to the atmosphere [43]. From a societal point of view, increased DOM concentrations may obstruct drinking water purification processes and increase the risk of formation of carcinogens during chlorination [44, 45]. Moreover, the invasive flagellate *Gonyostomum semen*, that causes allergic skin reactions, thrives in brown water lakes with high DOM concentrations [46].

Apart from the similar effect on the light climate, the consequences of increasing Fe and DOM concentrations differ. Fe has a key role in the biogeochemical cycles of many important elements such as carbon, nitrogen, phosphorous, and trace metals. For example, Fe may increase the molecular weight of DOM [47], increase the photooxidation of DOM [48] and enhance the photo-mediated removal of DOM through increased flocculation and sedimentation [49, 50]. Moreover, Fe



affects the leaching, bioavailability, and sedimentation of phosphorous [51-53]. Fe may also control the transport of toxic substances such as arsenic and vanadium [54]. It may directly affect aquatic organisms [see e.g. 55], e.g. through its tendency to precipitate on fish gills and thereby impair the oxygen uptake [56, 57]. Fe is a co-factor for nitrogenase and nitrate reductase and act as a limiting factor for primary production in vast areas of the ocean [58, 59]. The famous quote by John Martin – “*Give me a half a tanker of iron and I’ll give you the next ice age*” – is referring to the potential importance of Fe as a fertilizer of oceanic primary production, which in theory would increase the role of the oceans as a carbon sink for CO<sub>2</sub> in the atmosphere. Higher Fe concentrations may in particular favor cyanobacterial production in e.g. the Baltic Sea [60].

In all, both increasing DOM and Fe concentrations have potentially major implications to the aquatic system. In this thesis, I explore 1) the role of decreasing acidification in brownification and DOM turnover in fresh waters, and 2) the role of Fe in brownification.

### **DOM and brownification**

Brownification has been attributed to increasing concentrations of terrestrially derived organic matter containing a mixture of incompletely degraded parts of vegetation. Terrestrially derived DOM consists to a large part of humic substances, a complex mixture of aromatic and aliphatic hydrocarbons containing multiple functional groups

such as carboxylic, hydroxyl, and phenolate groups [61, 62]. The humic substances are yellow to black in color and the color of the terrestrially derived DOM gives many lake and streams its brown color. Increasing concentrations of DOM are therefore most certainly part of why freshwaters are getting browner.

### *Why is DOM increasing?*

The DOM concentration in a lake depends both on the amount of DOM imported from the terrestrial surrounding, the internal production of autochthonous DOM, and on processes within the lake transforming and removing the DOM. The drivers of increased export of DOM from the catchment have been widely studied, and the prevailing theories focus on decreasing acidification [12, 63], altered nitrogen deposition [19, 64], reduced sea-salt deposition [65], land-use [66], climate change [2] with increasing temperature [3], precipitation [6], enhanced CO<sub>2</sub> concentrations [67], or a combination of multiple factors working at different temporal and spatial scales [4, 8, 11, 16, 68, 69]. Processes that transform DOM within the lake include photooxidation, biodegradation, and flocculation with subsequent sedimentation, and these processes are greatly affected by the water residence time. Increased runoff due to increased precipitation may reduce the residence time and thereby removal of DOM and color [70].

Climate variables affect DOM in multiple ways and several studies suggest that e.g. precipitation patterns may be an important factor affecting DOM concentrations and water color in freshwaters [4, 6]. Increased and more intense precipitation may alter the water pathways through the soil, allowing more superficial organic soil horizons to be affected by the water flow [2, 6, 71]. Moreover, elevated temperature and CO<sub>2</sub> concentration may increase terrestrial primary production that in turn may enhance the DOM export to aquatic systems [2, 72, 73]. In addition, higher temperature reduces the period with frozen ground, enabling transport of organic matter to the freshwaters during an extended period of the year. Higher temperature and longer growing seasons may not only increase the total amount of DOM exported from the terrestrial to the aquatic system, but may also cause a shift in the seasonal patterns where the importance of a spring flood may be reduced due to e.g. a less extensive snow cover [5]. Thus, climate change may affect DOM concentrations by increasing the import of terrestrially derived DOM and also by reducing the removal of DOM within the system [70]. To the extent that climate change is driving brownification, it should continue in the coming decades. However, several studies conclude that precipitation and temperature patterns mainly affect the inter-annual variation of DOM concentration, while the long-term trend of increasing DOM concentration is better explained by other factors, e.g. the decreasing sulfuric acid deposition [4, 8].

To the best of my knowledge, the first time the role of precipitation in acidification was mentioned in Sweden was in October 1967. Scientist Svante Odén then published an article in the culture section of the Swedish newspaper Dagens Nyheter called *Nederbördens försurning* (“*The acidification of precipitation*”). He there stated that the precipitation in Europe had become gradually more acidic since the 1940’s [74] and the phenomenon was later also presented in the scientific press [75]. The acidification, caused mainly by atmospheric emissions of sulfur and nitrogen, increased from the beginning of the industrial revolution until the 1970’s – 1980’s [76]. The 1979 Geneva Convention on Long-range Transboundary Air Pollution, implemented in 1983 ([http://www.unece.org/env/lrtap/lrtap\\_h1.html](http://www.unece.org/env/lrtap/lrtap_h1.html)), successfully regulated sulfate emissions and led to a reduction in the sulfuric acid deposition. The deposition is now approaching pre-industrial levels in northern Europe [76]. Concurrent with the declining sulfuric acid deposition, numerous monitoring studies have shown an increase in DOM concentrations in freshwaters since the 1980’s [7, 12, 63, 68], and the decreasing acidification has been identified as a potential driver of brownification [12, 63]. The underlying reasoning is that a reduction in acid deposition increases the net charge of organic matter in the soil, and a higher charge makes the organic matter more hydrophilic and mobile [Box 1, 77, 78]. The hypothesis of a pH and ionic strength induced mobilization

## Box 1. Acid load and organic matter solubility

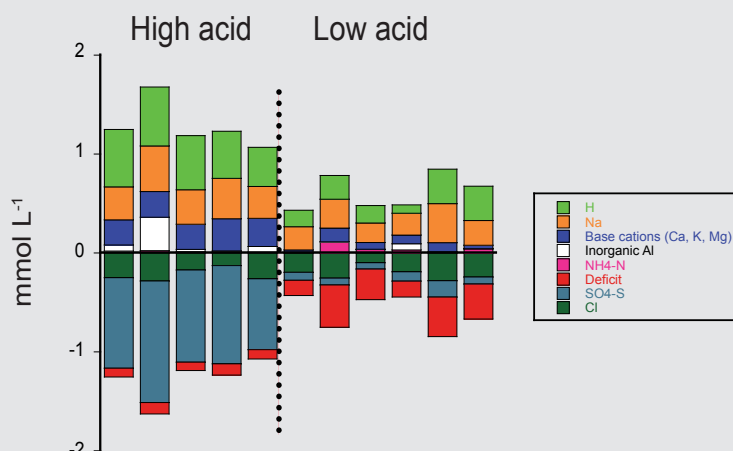
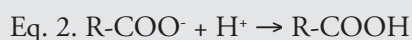
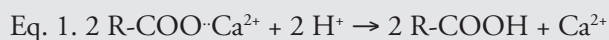


Figure B1. Ion charge balance explaining the mechanism to changed solubility of DOM depending on acid load. Each bar measured in soil water from separate lysimeters in the study in Paper I. Modified from Ekström et al. 2011, ES&T.

The functional groups, e.g. phenolic and carboxylic groups, on the surface of the organic matter regulate the solubility and mobility of organic matter. With low acid load, the concentration of sulfate (grey part of bar) and hydrogen ions in the soil is lower (light green). This causes both decreasing leakage of base cations (dark blue, Eq. 1) and decreased protonation of the functional groups (Eq. 2). Through the ion charge balance we can then see an increase in the deficit of anions (red), which increases the net charge of the DOM. This means that the organic matter pool becomes more polar and hydrophilic, which increases the solubility of the organic matter, and hence increases the concentration of DOM in solution [77, 78].



of DOM in the soil was previously mainly supported by correlations of monitoring data generally including only the period of decreasing sulfur deposition [7, 12, 63]. There have been a few experimental studies focusing on how pH and ionic strength affect DOM, but with partly

inconsistent results [e.g. 79-84]. The field experiment in **Paper I** was performed to improve the mechanistic understanding of the impact of decreasing acidification on brownification. By applying artificial rainwater with sulfuric acid concentrations corresponding to the

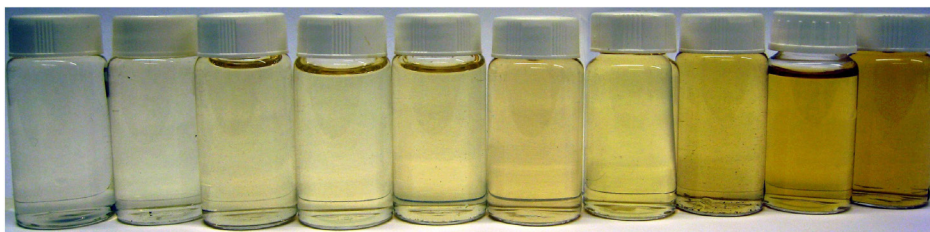


Figure 2. Soil water samples collected during the study for Paper I. Sample number 1 – 3 and 5 (from the left) originates from the high sulfuric acid addition, and sample number 4 and 6 – 10 comes from the low sulfuric acid addition.

concentration in natural rainwater in the 1980's and 2000's to boreal soil plots, the impact of acid addition on soil DOM was studied. The solubility and mobility of the organic matter was clearly affected by the acid addition, where soil water from the lower acid addition had approximately 80 % higher DOM concentration than that from the higher acid addition. The effect on the water color was even greater, where samples from the lower acid addition had approximately 140 % higher water color (Fig. 2). The dependence of DOM mobility on acid load is indicated by the strong relationship between pH and the net charge of the DOM (Fig. 3). Similar results were seen in a field experiment with artificial acidification/deacidification of peat and podzol soil plots in the UK [85], i.e. a lower acid load to the soil gave a higher DOM concentration in the soil water. Thus, the field experiments support the hypothesis that the decreasing acidification may be an important driver to the observed increase in DOM concentrations in freshwaters. These findings apply to organic soil horizons. In mineral soil layers, DOC concentration has been

found to increase with increasing acidity [79]. In line with this, DOM concentrations in soil water collected further down in the soil profile have been found to decrease over time despite the trend of decreasing acidification [86, 87]. Nevertheless, in terms of influencing the surface water chemistry, organic soil horizons should be of greater importance than mineral soil horizons [88].

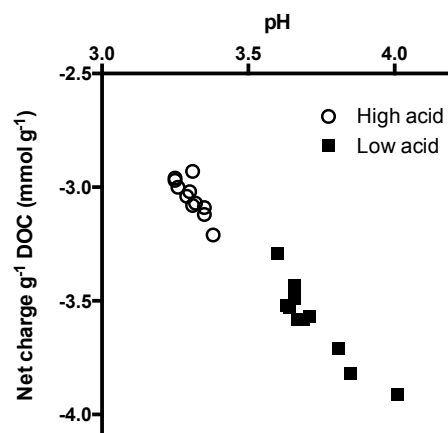


Figure 3. Relationship between pH and net charge of DOM in soil water. White circles extracted at high sulfuric acid concentration, black squares extracted at low sulfuric acid concentration. Modified from Ekström et al. 2011, ES&T.

Concurrent with the pH-induced change in the mobility of the organic matter observed in our field experiment, there was a change in the quality of the DOM. DOM released under the lower sulfuric acid addition was relatively more hydrophobic, aromatic, colored, and of greater molecular weight. Aromatic and large molecular weight fractions of organic matter require a greater net charge to become soluble, and the pH-induced increase in net charge therefore increase the relative abundance of these fractions of DOM in solution [79, 80, 84, 89]. The decreasing concentrations of divalent cations may also increase the molecular weight of the DOM [ $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ; 90]. These changes in DOM quality cause a higher color of the DOM, which could partly explain the fact that water color has increased more than DOM concentration [4]. Thus, reversed acidification may lead to increased water color through an increase in DOM concentration, but also due to changes in DOM quality.

As the DOM is transported from the terrestrial to the aquatic systems, these changes in DOM quality in the soil water should eventually be noticeable in streams and lakes. DOM quality variables are rarely included in monitoring programs. An exception is a 16-year data series that documents increased DOM concentration and hydrophobicity of the DOM (measured as a fluorescence index) concurrent with a decrease in sulfuric acid deposition [91]. The authors argue that the increased hydrophobicity reflects that a larger fraction of the DOM is

terrestrially derived. An alternative interpretation is that it reflects a change in the composition of the terrestrially derived DOM in response to reduced acid deposition.

The results from Paper I support the hypothesis of decreasing sulfuric deposition as a significant driver behind the increasing DOM concentrations and brownification of freshwaters. A parallel change in the DOM composition may darken the water even further. In a next step I wanted to study how these changes in DOM quality may affect the fate of the terrestrially derived DOM as it enters the aquatic system.

#### *What are the consequences of altered DOM quality?*

To answer this question it is necessary to understand how the three transformation and loss processes for DOM – photooxidation, bacterial degradation, and flocculation – are affected by changes in the DOM quality. **Paper II** showed that DOM extracted at the lower acid addition, which was relatively more hydrophobic, aromatic, colored, and of larger molecular weight, was more susceptible to photooxidation, but less susceptible to bacterial degradation. Aromaticity, hydrophobicity, and high molecular weight are all properties that may enhance the susceptibility to photooxidation caused by UV radiation in freshwaters [92-94], and reduce the susceptibility to bacterial degradation [95-98]. In this experiment, photooxidation caused only minor loss of the amount of DOM, while

the impact on the quality was greater. Biodegradation had only minor impact on the DOM quality, while causing a greater loss of DOM than photooxidation. The loss of DOM was low overall, but still comparable to other studies of soil-water DOM when considering the total UV dose and incubation time [93, 99, 100]. This study only concerns photooxidation and biodegradation, but higher DOM concentrations should also increase the flocculation and sedimentation rate [see e.g. 101]. In conclusion, the decreasing acidification may affect the relative importance of each turnover process, where photooxidation becomes relatively more important, and bacterial degradation becomes relatively less important. However, the responses in reactivity were quite small despite the rather extreme difference in pH

used at the extraction, and further studies with longer incubation times and combinations of photo- and biodegradation are needed to better understand the potential effects on DOM turnover.

Paper I and II support the notion of the decreasing acidification as an important driver behind the brownification (Fig. 4). If the decrease in sulfuric acid is the only driver of brownification, it is a return to a natural state. Furthermore, as the deposition approach natural levels [76] the brownification should level off and stabilize in the near future. However, there are areas with low historically low sulfate pollution that still exhibit increasing DOM concentrations and water color, for example in the north of Sweden [5] suggesting there are additional factors driving brownification.

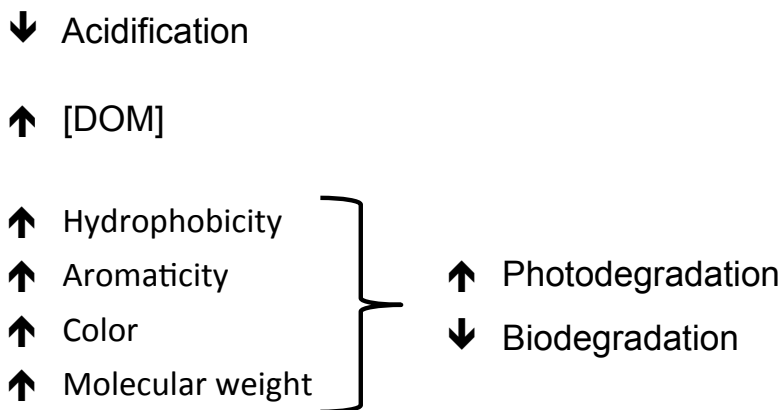


Figure 4. Schematic summary of the effects of a decreasing acidification on DOM quality and reactivity.

## **Fe and brownification**

It is well known that Fe affects the water color and it is especially the complexation between Fe and DOM that absorbs both UV and visible light [24, 25, 102]. Fe concentrations in freshwaters have increased strongly during the last decades [27-29]. Nevertheless, the variation in Fe concentrations had to my knowledge not previously been considered as a potential factor behind brownification. In **Paper III** the aim was to clarify if and to what extent brownification can be ascribed to increasing Fe concentrations in Swedish rivers. Thirty rivers with continuous monthly data from 1972 to 2010 were selected for the study. Twenty-three of these rivers exhibited significant increases in water color, with increases between 22 and 279 %. The greatest increase in water color had occurred in the south, while the increase in the north was significant but less pronounced (Fig. 5a). Water color increased more than DOM in all rivers – there were even five rivers with significantly increasing water color but without any corresponding increase in DOM concentration – implying that increase in DOM concentration alone is not sufficient to explain the entire increase in water color (Fig. 5b). Using the ratio of chemical oxygen demand and total organic carbon (COD:TOC) as an indicator of DOM quality, eight of the rivers exhibited a significant change (Fig. 5c). These rivers are located in the south of Sweden where atmospheric sulfuric deposition has been substantial, while none of the rivers in north

exhibited any change in the COD:TOC ratio. Hence, changes in DOM quality appear also insufficient in explaining the whole increase in water color.

Looking at Fe, all rivers with increasing water color show a concurrent increase in Fe concentration (Fig. 5d). Fe increases vastly, up to 468 %, and the greatest increase in Fe concentrations occurred in the south of Sweden. The next step was to estimate how much of the observed water color increase that could theoretically be explained by Fe. By adding Fe to natural water samples and measure the increase in water color, I could estimate how much water color each unit of Fe could give. Comparing that to the relationship between Fe and water color in the thirty rivers, estimations show that on average 25 % of the inter-annual variation in water color could theoretically be explained by Fe. Furthermore, there was a spatial variation and in the south about 6 % of the variation could be explained by Fe, compared to 74 % in the north (Fig. 5e). Hence, even though the increase in both water color and Fe is greater in the south, the role of Fe to brownification may be more important in the north. The results from Paper III indicate that Fe is a potentially important factor behind brownification.

### *Why is Fe increasing?*

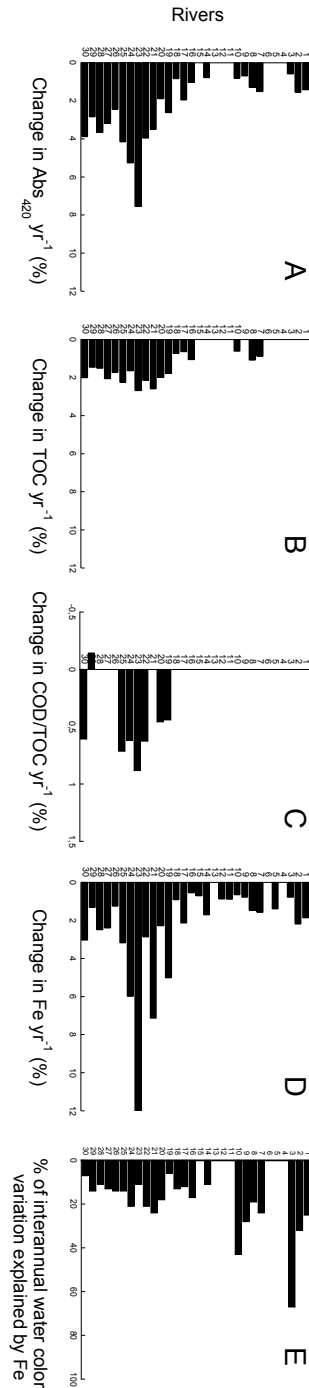
Given the decisive role of Fe to the biogeochemistry, transport and availability of many elements, and seemingly also water color, it is imperative to



understand why Fe concentrations are increasing. On average, the Fe concentrations in the Swedish river mouths doubled in four decades (Paper III). Increasing Fe concentrations have been reported also from Finland [21 - 74 % between 1995 and 2006; 28], the UK [on average 100 % between 1984 and 2006; 29], and in a single studied stream in Germany [approximately 50 % between 1987 and 2001; 103]. **Paper IV** focused on how variation in Fe concentrations may depend on the redox conditions in the drainage area. The study was based on seasonal variation in chemical and climate variables in three Swedish rivers.

Fe is highly sensitive to changes in redox potential (Box 2), and I hypothesized that redox dynamics in the catchment control the mobilization of Fe from the soil. For Paper IV, Methylmercury (MeHg) and  $\text{SO}_4^{2-}$  were used as indicators of redox conditions in the soil. The results indicate that the prevalence of reducing conditions in the drainage area facilitates Fe mobilization and that redox dynamics may be an important underlying factor to the inter-annual variations in Fe concentrations. This and previous studies show that for reducing conditions to occur, both soil moisture and high air temperature are required [104, 105]. High discharge during cold periods may also cause high export of Fe from the catchment [i.e. 106], but export may then be more directly driven by water flow through superficial soil horizons rich in Fe, than by reducing conditions in the soil.

Figure 5. The rate of change per year of water color (Abs<sub>420</sub>), DOM (TOC), COD/TOC, Fe, and the fraction of the inter-annual variation in water color that can theoretically be explained by the variation in Fe concentration for each river. The numbers denote individual rivers, where the furthestmost northern river has number 1. Modified from Krutzberg and Elström 2012, Biogeosciences.





### **Box 2. Fe and redox**

The oxidation state of Fe depends strongly on the redox potential in the environment. Under oxic and circumneutral conditions, Fe occurs predominantly as ferric iron (Fe(III)), which is highly insoluble and therefore bound in the soil through Fe-DOM or Fe-mineral interactions. If anoxia occurs, Fe(III) is reduced to ferrous iron (Fe(II)). The reduction may be caused by both Fe reducing bacteria, and sulfur reducing bacteria. Fe(II) is highly soluble and easily transported with the water flow from the soil to nearby streams. Once transported to the stream the anoxic soil water mixes with the oxic stream water and Fe is interacting with and kept in solution by DOM.

Reduction:  $\text{Fe(III)} - e^- \rightarrow \text{Fe(II)}$

Oxidation:  $\text{Fe(II)} + e^- \rightarrow \text{Fe(III)}$

The three rivers in Paper IV all exhibit significantly increasing discharge, and the air temperature in the drainage areas for two rivers in the south of Sweden has also increased. The required conditions for reducing bacterial activity in the catchment may therefore have increased. As many parts of Sweden are predicted to become warmer and wetter in the future [107, 108], redox-induced increases of Fe concentrations in freshwaters may continue, causing continuous brownification of these waters.

An alternative potential driver behind the variation in Fe concentration is the variation in DOM concentration. Fe and DOM often correlate strongly both spatially and temporally [5, Paper III, 29, 109, 110]. In oxic water under circumneutral pH Fe is dependent on interactions with DOM to stay solution,

where it otherwise would precipitate (Box 3). It has therefore been suggested that the increase in Fe concentration is a result of the increase in DOM concentration [29]. My data do not however support that DOM is the major driver behind the variations in Fe concentration. In Paper IV, Fe covaried more with redox variables rather than with DOM. For example, during a distinct discharge event in one of the rivers, DOM increased immediately together with the discharge, whereas the response in Fe was delayed and related to changes in the redox potential in the catchment. Moreover, while the thirty rivers in Paper III exhibit both a spatial and weak temporal relationship between Fe and DOM concentrations, there is a large spatial variation in the Fe:DOM ratio (from 10 to 219  $\mu\text{g Fe mg}^{-1}$  organic

### **Box 3. Fe and DOM complexation**

Due to the low solubility of Fe(III) under oxic and circumneutral conditions, it rapidly precipitates as Fe(III) (hydr)oxides (for example ferrihydrite ( $\text{Fe}_2\text{O}_3$ )) and is subsequently removed from the open water. However, Fe (III) associates with DOM which allows it to stay in solution, either through direct Fe(III)-DOM complexation or through Fe(III) (hydr)oxide-DOM absorption [25, 111, 112]. Modeling using the Stockholm Humic Model [113] suggests that over 95 % of Fe in Swedish rivers are Fe(III) (hydr)oxide [54], and hence associated with DOM to keep solubility. Consequently, Fe is highly dependent on DOM to stay in solution in freshwaters.

carbon) and Fe also increased more than DOM in most of the rivers. Moreover, the three rivers in Paper IV exhibited large inter-annual variations in the Fe:DOM ratio, implying that Fe was not driven by variations in DOM concentration. The data suggests that while Fe concentration was mainly related to the prevalence of reducing conditions in the catchment, the DOM concentration

was to a larger extent related to a direct water flow through superficial organic soil horizons. A continuous climate change with increasing temperature and precipitation may further increase the reducing conditions in the drainage area, facilitating Fe transport from the terrestrial to the aquatic system where it darkens the water (Fig. 6).

- ↑ Precipitation and temperature
- ↑ Reducing conditions in the drainage area
- ↑ Fe(III) reduction and Fe(II) mobilization
- ↑ Fe concentration in freshwater
- ↑ Water color

Figure 6. Schematic summary of the effect of climate change on Fe.

## **Brownification in the future**

From the studies in this thesis it appears that both DOM and Fe are important drivers in the ongoing brownification. In areas where the atmospheric sulfuric deposition has been historically high, as in the south of Sweden, enhanced mobility of more colored DOM appears to be of great importance to the brownification. As the decrease in atmospheric sulfuric deposition levels off in the future, brownification caused by the decreasing acidification should also level off. In areas where the atmospheric sulfuric deposition has been historically low, as in the north of Sweden, increasing Fe concentrations appear more important for the increasing water color. The effect on brownification caused by Fe should continue along with climate change. Even though Fe is dependent on DOM to be kept in solution, the DOM has the capacity to maintain more Fe in solution than it currently does, and DOM concentration should therefore not limit the continued Fe increase. My overall conclusion is therefore that the brownification most likely will continue in the future.

## **Summary of papers I – IV**

### *Objectives*

The overall objective of this thesis was to further examine the role of increasing DOM concentrations, changes in DOM composition, and increasing Fe concentrations in brownification of freshwaters. Within the thesis I have addressed the following questions:

1. What role does atmospheric sulfuric deposition play in the ongoing brownification? (**Paper I and II**)
  - a. Does the decreasing acidification act as a driver of the increasing DOM concentrations in freshwaters? What is the underlying mechanism to the change in the solubility and the mobility of organic matter the soil? Are there any changes in the DOM quality in response to differing acid deposition? (**Paper I**)
  - b. Do the acid-induced changes in the composition of soil-derived DOM affect the reactivity of the DOM in aquatic systems? (**Paper II**)
2. What role does Fe play in brownification? (**Paper III and IV**)
  - a. Are there long-term trends in Fe concentrations in Swedish rivers, and could they contribute to the observed increase in water color? (**Paper III**)
  - b. What is controlling seasonal and long-term variability in Fe concentrations in freshwaters? Can climate induced changes in redox dynamics in the catchment be an important driver? (**Paper III and IV**)

### *Study sites and methods*

To elucidate the effect of reduced sulfuric acid deposition on soil water DOM mobility and quality (**Paper I**), we conducted a 2-year field experiment at the Asa Experimental Forest and Research Station in Småland, south Sweden (57°08'N, 14°45'E; alt. 190 – 200 m.a.s.l). The area in the boreal-nemoral vegetation zone, dominated by Norway spruce, has been exposed to heavy acidification historically, and was therefore suitable for this experiment. An automatic irrigation system was used to perform irrigation with artificial rainwater (deionized water with salt additions) on soil plots, allowing the study of the effect of acid addition in a natural setting. Two different treatments were applied, high sulfuric acid addition aiming to mimic the load during the high acidification peak in the 1980's, and low sulfuric acid addition corresponding to the load at the time of the experiment. Soil-water was collected under the O-horizon using zero-tension lysimeters and analyzed for pH, absorbance, and concentration of  $\text{SO}_4\text{-S}$ , DOM (measured as dissolved organic carbon (DOC)) and major ions. The net charge of the DOM was estimated through modeling with the geochemical computer program *Visual MINTEQ* ver. 3.0. In addition, measurements of DOM quality were performed through estimation of hydrophobicity using fluorescence spectrophotometry (fluorescence index (FI) was calculated), aromaticity (measured as specific UV absorbance at a wavelength of 260 nm,  $\text{SUVA}_{260}$ ), color (measured as carbon

specific absorbance at 420 nm), and molecular weight estimation using size exclusion chromatography (SEC).

As I indeed observed changes in DOM quality in a next step I wanted to study if this affected the reactivity of terrestrially derived DOM as it enter the aquatic system (**Paper II**). I used the same artificial rainwater with the two levels of sulfuric acid additions to extract soil DOM. To explore the impact of different extraction methods on the quality and reactivity of DOM, I used two approaches for the extractions. First, resembling the approach in Paper I, I performed short-term artificial irrigation of the same soil plots and collected soil water with zero-tension lysimeters. Secondly, I collected O-horizon soil samples in close vicinity of the soil plots. The soil was extracted in the same artificial waters on a rotary table for 1 h in room temperature. Similar acid-induced changes in DOM quality as in Paper I were seen. Within each extraction method the samples were pooled together per treatment in order to create two separate batches of water with different DOM quality. The extraction method also affected the DOM quality, where DOM from the laboratory extraction was relatively more hydrophobic, aromatic, and colored, but of lower molecular weight. The reactivity of DOM of different quality was studied in three experiments: photooxidation, biodegradation, and biodegradation after UV exposure. The susceptibility to photooxidation and biodegradation were estimated as the loss of DOC and the impact on DOM

quality. DOM quality was assessed using the same methods as in Paper I. In the bacterial degradation experiment bacterial production was measured by leucine incorporation. In the photooxidation experiment the samples were absorbance normalized at 370 nm and adjusted to pH 4, before exposed to UV-A radiation during a period of three days (total UV-A dose 1800 kJ m<sup>-2</sup>). In the biodegradation experiment the samples were DOC normalized, pH adjusted to 4 and NH<sub>4</sub>NO<sub>3</sub> and KH<sub>2</sub>PO<sub>4</sub> were added to ensure that the bacterial activity in samples was carbon limited. Incubation lasted for 2 weeks at room temperature and in darkness. In the combined experiment, a subsample was removed from the photooxidation experiment after 24 h of UV exposure and thereafter incubated as in the biodegradation experiment. The difference in DOC concentration due to bacterial degradation in the UV exposed and the non-UV exposed samples was calculated. The loss in DOC concentration or alteration in quality due to photooxidation and/or biodegradation was compared between the DOM extracted at high or low acid load in order to test the hypotheses about potential changes in reactivity due to acid-induced DOM quality.

**Paper III**, that aimed to explore the potential role of Fe to brownification in Swedish rivers, was primarily based on statistical analysis of monitoring data. Monthly data between 1972 and 2010 from 30 Swedish rivers included in the Swedish national surface water monitoring program was used (run by

the Swedish University of Agricultural Sciences, SLU, freely available at <http://webstar.vatten.slu.se/db.html>). The rivers are located throughout Sweden between latitude N 54 – 69° and longitude E 10 – 24°. The fact that the rivers are located in several different climate and vegetation zones facilitates the possibility to identify spatial differences in historical trends. I analyzed trends in water color, DOM, and Fe, and co-variation between the variables. Moreover, experimental addition of Fe to four different natural waters of varying water chemistry was performed to evaluate the role of Fe in determining water color, where the response in absorbance was calculated using linear regressions. Finally, in order to estimate how much of the inter-annual variation in water color that theoretically can be explained by variation in Fe, the mean slope obtained from the linear regressions in the experiment was compared to the slopes of the absorbance and Fe relationship from the different rivers in the monitoring data.

As paper III indicated a role of Fe in brownification, I aimed to further investigate the underlying mechanism to the increasing Fe concentrations. In **Paper IV** seasonal and long-term variations in water chemistry and climate variables were studied to explore the role of reducing conditions in the catchment. I also addressed the alternative hypotheses that DOM quantity and quality, and pH, drive variations in Fe concentrations. Three Swedish rivers, River Emån, Lyckebyån, and Ume älv, which all exhibit significant

increases in Fe concentrations were selected. The rivers differ in catchment size, geography, annual flow patterns, and chemical characteristics. Again, data from the Swedish national monitoring program was used and during one year (February 2012 to January 2013) additional samples were collected for analysis of methylmercury (MeHg) that was used as an indicator of redox dynamics in the drainage.  $\text{SO}_4^{2-}$  was also used as a redox indicator. Variation in conductivity was used as an indicator of the origin of water flow. Lower conductivity was seen as indicative of water flow through superficial organic soil horizons and higher conductivity indicative of water flow from the deeper mineral soil horizons. Short-term variations in and relationships between Fe, MeHg, DOM, water flow, and air temperature were investigated using multiple regressions. Water chemistry data running between 2002 and 2011 was used for testing the generality of the within year-variation found during the main study period. Long-term trends (1972 – 2011) in water discharge and air temperature in the drainage areas were analyzed using Mann-Kendall tests.

## Results and conclusions

- A lower acid load to soils enhances the solubility and mobility of organic matter and decreasing acidification is a major driver behind the brownification. Concurrent changes in the quality of the DOM towards a relatively more colored DOM may further increase the water color. In

addition, a change towards more hydrophobic, aromatic, and higher molecular weight DOM, also affects the reactivity of DOM, and may alter the relative importance of each turnover process, where the susceptibility to photooxidation increases and to biodegradation decreases.

- Increasing Fe concentrations appear to contribute to the observed increase in water color. Increasing Fe concentrations can be seen throughout Sweden, but the increase is much more pronounced in south Sweden. On average 25 % of the increase in water color can be explained by increasing Fe concentrations, but in the north of Sweden up to 76 % of the water color increase can theoretically be explained by increasing Fe concentrations.
- Fe mobilization in soils is strongly affected by redox dynamics in the drainage area, where Fe is mobilized through the reduction of the largely insoluble Fe(III) to highly soluble Fe(II) under reducing conditions. The prevalence of reducing conditions is driven by high discharge and high temperature. As discharge and air temperature are increasing in many parts of Sweden, the occurrence of reducing conditions should increase.

- Brownification in the south of Sweden appears strongly dependent on decreasing acidification that increase export of colored DOM from the catchment. In the north of Sweden, where the sulfuric acid deposition has historically been low, increasing Fe concentrations may be a more important driver behind the brownification.
- To the extent that brownification is the result of reduction in atmospheric sulfuric acid deposition it should level off in a near future as the deposition approach background levels. On the other hand, predicted increases in temperature and precipitation should favor reducing conditions in the catchment and increasing transport of Fe to the aquatic system, resulting in a continuous brownification of freshwaters.

## **Epilogue**

So, to answer the question raised by the old man or woman living by the small lake: Yes, it is plausible that the water color will continue to increase in the future when your grandchildren's grandchildren will go for a swim in the lake.

But, that doesn't really mean that the swim will be any less pleasant, does it?

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