Three decades of change in the character and charge density of dissolved organic matter in Swedish surface waters

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Three decades of change in the character and charge density of dissolved organic matter in Swedish surface waters

Tre decennier av förändring i karaktär och laddningstäthet hos löst organiskt material i svenska ytvatten

Ted Pettersson

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Abstract

Over the recent three decades, dissolved organic matter (DOM) have increased in Swedish surface waters, contributing to brownification. Previous research has evaluated the quantity of DOM, although its character is less explored and evaluated. This study investigates the character of DOM through evaluations of long-term trends, through both quantity and quality of DOM on over 130 watercourses in Sweden using chemistry data from the MVM data portal. The character of DOM was evaluated using four different variables, or proxies: total organic carbon (TOC), coloured dissolved organic matter (CDOM), specific visible absorbance (sVISa) and organic matter charge density at pH 5.6 ($OMCD_{5.6}$). Generalized additive mixed models (GAMMs) were applied to evaluate temporal trends, while a non-parametric Kruskal-Wallis test followed with a Dunn's test was used to examine differences between three determined time periods: 1990-1997, 1998-2012, 2012-2024. Results showed that although DOM concentrations have increased, its acid-base properties have changed. In specifics, the $OMCD_{5.6}$ values have seen a reduction in negativity, indicating a reduction in dissociation of acidic functional groups. This suggests that DOM reflects weaker acidity and reduced overall charge, which affects DOM's solubility and binding affinity with metals at pH 5.6, and presumably at other pHs in proximity to 5.6. By integrating $OMCD_{5.6}$ as a proxy of DOM character, this study provides new insight on how DOM chemistry in Swedish surface waters is evolving.

Keywords: Brownification, Dissolved Organic Matter, Charge density, Water chemistry, Surface Waters, Temporal trends, sVISa, CDOM.

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Abbreviations

Abbreviation	Description
ADOM	Active Dissolved Organic Matter
CDOM	Coloured Dissolved Organic Matter
CO_2	Carbon Dioxide
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
GAMM	Generalized Additive Mixed Model
IQR	Interquartile Range
MVM	Mark-, vatten- och miljödata
$OMCD_{5.6}$	Organic Matter Charge Density at pH 5.6
pKa	Acid Dissociation Constant
sVISa	Specific Visible Absorbance
SLU	Swedish University of Agricultural Sciences
TOC	Total Organic Carbon

1. Introduction

1.1 Problem background

In recent decades, the Swedish inland waters have seen an increase in brownification, an event characterized by increased levels of dissolved organic matter (DOM) in surface waters. This change has been linked to a combination of climate change, increased land-use and recovery from acidification (Kritzberg et al. 2020). Brownification influences multiple ecosystem services, such as drinking water production, recreational experiences, aquatic biodiversity and biogeochemical processes. It also possesses the ability to synergize with other environmental stressors, for example eutrophication and warming.

Mobilization of DOM is strongly influenced by its chemical character, especially its acid-base properties. One particular aspect is the charge density of DOM, which refers to how many acidic functional groups (such as carboxylic acids) are dissociated, leading to its overall negative charge (Sjöstedt et al. 2010; Köhler n.d.). During recent decades, acid deposition from precipitation has decreased and surface water pH levels have risen. This makes DOM molecules more prone to dissociate, leading to increases in their solubility and ability to remain dissolved in water.

A change in the dissociation properties of DOM, would affect its solubility. In other words, a change in charge density of DOM at a particular pH, can affect its mobilization from soil to water, even though the total amount of carbon in the soil remains constant (Monteith et al. 2023a).

The natural acidity of DOM plays a central role in determining surface water pH. In the context of environmental management to remediate soil and surface water acidification by liming, this is particularly relevant. Liming is a strategy to reduce the acidification in surface waters. Thus decisions on which lake to lime, is partly dependent on natural acidity levels. Increased understanding of DOM and its natural acidity and acid-base properties is of importance to making successful management decisions (Laudon et al. 2000). In Sweden, these liming efforts are substantial, where annual investments of over 150 million SEK are put into restoring water chemistry (OECD 2012).

As much research has recently focused on the quantity of DOM in surface waters, less attention has been given to its chemical quality or "character", meaning its colour intensity and charge dissociation properties (Eklöf et al. 2021). The character is of importance due to its influence on how DOM interacts with metals, sediments and biological systems, which could change even if DOM concentrations remained stable. A change in the character of DOM, especially in its acid-base properties, can further influence its concentration in surface waters without requiring a change in environmental pH (Hruška et al. 2001; Sjöstedt et al. 2010).

1.2 Dissolved Organic Matter (DOM)

Dissolved organic matter (DOM) is a mix of organic molecules originating from soils, vegetation and microbial activity. In Nordic freshwaters, DOM concentrations have generally increased in recent decades. This trend is linked to multiple environmental drivers, such as climate warming, increased precipitation, enhanced biomass production, and especially the reduction of acid rain (Crapart et al. 2023; Monteith et al. 2023b; Räike et al. 2024).

As acid deposition has declined, the pH of surface and soil waters has increased. This change can enhance DOM solubility by increasing dissociation of acidic functional groups, leading to more organic matter being mobile and available to being transported from terrestrial sources into aquatic ecosystems. Thus the recovery from acidification has played a major role in mobilizing DOM, particularly in catchments which are acid sensitive (Monteith et al. 2023). These changes of DOM quantity and mobilization are not directly linked to changes in the total amount of soil carbon, but rather to changes in solubility due to pH-dependent chemical behaviour.

1.2.1 Acid-base properties and charge behaviour of DOM

A key factor that affects the solubility and mobility of DOM is its acid-base properties, particularly the behaviour of the carboxylic acid groups (-COOH) bound to organic molecules. These weak acids are prone to dissociate in water, releasing hydrogen ions (H^+) and forming negatively charged carboxylate ions ($-COO^-$). The extent of this dissociation is determined mainly by two factors, pH of the surrounding water and the acid dissociation constant (pKa) of the acid functional groups (Köhler et al. 1999).

Organic acids which are negatively charged ($R-COO^-$), are more common at higher pH levels exceeding the pKa. This leads to altered solubility and reduces the probability of aggregation or sedimentation. In comparison, at lower pH, dissociation is supressed, meaning that DOM molecules primarily remain in their neutral form, leading to increased flocculation and retention in soils (Laudon et al. 2000; Köhler n.d.).

1.2.2 Indicators used to evaluate DOM character

To increase understanding about the character of dissolved organic matter (DOM), it requires not only measuring the concentration, but also its chemical and optical properties. Previous research has applied proxies such as absorbance at 420 nm (Colored dissolved organic matter, CDOM) and specific absorbance (sVISa), which is the ratio of CDOM and total organic carbon (TOC), to evaluate DOM quality. This is useful in Nordic freshwaters where DOM composition is correlated to soil and vegetation sources (Kritzberg et al. 2020; Eklöf et al. 2021). CDOM is a measurement of the aromatic and colored fraction of DOM, which mainly is affected by humic substances coming from organic matter in soils. Meanwhile sVISa normalizes CDOM to TOC, resulting in a measure of color per unit carbon. This means that higher values of sVISa indicate more colored organic matter. These proxies allow for assessments on whether there are changes in DOM quantity, composition or a combination of both.

In this study, CDOM and sVISa will be used as proxies of DOM character. In addition, organic matter charge density (OMCD) is included. This is a less commonly used measure of character but is an informative parameter, reflecting the acid-base behavior of DOM. In more detail it represents the amount of negative charge that arises from dissociated acidic functional groups (mainly carboxylic acids), at a given pH. In this study OMCD is determined at pH 5.6 using the Visual MINTEQ model (Köhler et al. 1999; Sjöstedt et al. 2010). This pH is chosen because particularly useful information about the charge balance is available in a Swedish database of surface water chemistry where alkalinity/acidity is titrated to this pH endpoint. Therefore, OMCD will hereby be referred to $OMCD_{5.6}$. These dissociation characteristics are critical for further determination of DOM solubility and reactivity, which may change independently of DOM concentrations.

While CDOM and sVISa will primarily capture changes in DOM source and optical quality, $OMCD_{5.6}$ will further provide information on the acid-base properties of DOM. Together, this combination of indicators, or proxies, will provide a more holistic view of the character of DOM in Swedish watercourses over space and time. These properties may also be changing over time in response to environmental processes, such as acidification recovery and land-use change (Laudon et al. 2000; Köhler n.d.).

1.3 Modelling of $OMCD_{5.6}$

To assess the acid base character of DOM, this study makes use of charge density values derived from modelling performed with Visual MINTEQ. This model is a widely used chemical equilibrium model, which simulates chemical speciation in natural water by solving equilibrium equations for interactions among metals, organic matter and major ions (Sjöstedt et al. 2010).

A central parameter established in this process of modelling is ADOM/DOC ratio, where ADOM refers to the portion of dissolved organic carbon (DOC) that is assumed to carry the acidic functional groups (carboxylic acids). Adjusting this ratio for each sample, results in estimates from the model on how much of the carbon contributes to the overall negative charge of DOM. In more detail, for each sample, a range of ADOM/DOC values is tested, to determine which ratio results in the smallest charge imbalance in the solution. This results in a net organic charge, which is then normalized by the DOC concentration to get the charge density (Bishop & Lackner 2025).

The values of charge density are as previously mentioned referred to as $OMCD_{5.6}$, which represents the organic matter charge density calculated at pH 5.6. The pH of 5.6 corresponds to the endpoint of an acidity titration established on nitrogen-flushed water samples. This flushing of the samples is used to remove carbon dioxide (CO_2) in order to better quantify the charge balance (Sjöstedt et al. 2010; Köhler n.d.). Furthermore, at this titration endpoint, the acid-base equilibrium is dominated by the dissociation of DOM functional groups (carboxylic acids), along with the known addition of acid or base, while other acidic components such as dissolved CO_2 have been removed. This results in a well-defined system where the charge balance can be estimated through modelling, making it a well-defined reference point for estimating $OMCD_{5.6}$.

While this is a consistent reference point for calculating estimates of $OMCD_{5.6}$, it should however be noted that the acid-base behaviour of DOM refers to the dissociation of DOM across the entire range of natural surface water pH (ca pH 4-pH 7.5) (Bishop & Lackner 2025).

1.4 Monitoring data from MVM

The Mark-, vatten- och miljö database (MVM) contains long-term water chemistry data for multiple variables, including TOC and CDOM. This data portal contains information on samples from multiple different environmental monitoring programs. One of these is the Swedish national surface water monitoring program. The data on this portal are publicly accessible (Swedish University of Agricultural Sciences n.d.).

These monitoring programs have provided consistent observation on over 200 watercourses in Sweden covering three decades. Many of these have been sampled around 10 times per year.

Additionally, all water samples in MVM have been analysed using standardized and accredited laboratory procedures, which ensures high comparability. These include tens of thousands of measurements performed by a single laboratory over the course of more than four decades. Therefore, this database offers an opportunity to assess temporal trends in water chemistry, including properties related to DOM. The database offers a wide range of variables, including those of relevance for calculating sVISa and $OMCD_{5.6}$. Those variables accessed from the database and relevant unit conversions applied are detailed in Appendix 1, *Table A 1*.

1.5 Purpose

The purpose of this project is to evaluate the character of dissolved organic matter in Swedish surface waters over 30 years. This evaluation includes whether the specific colour (sVISa) and charge density of DOM at a specific pH (5.6) has changed over time in specific water courses.

It was hypothesized that DOM character, including its colour and acid-base behaviour, may have shifted over time due to environmental recovery and land-use changes. This study is aimed to evaluate whether such shifts could be observed and contribute to a deeper knowledge about what controls the solubility of DOM, and thus its susceptibility to move from soils to water in runoff.

2. Material & Methods

2.1 Data sources and preprocessing

Water chemistry data were obtained from the Miljödata MVM portal. The data set included over 200 watercourses each represented by a monitoring station identified with a unique MVM-ID. The whole data set compiled around 40 000 individual water chemistry measurements.

The analysis focused on four variables: TOC, CDOM, sVISa and $OMCD_{5.6}$. Data processing, unit harmonization and variable conversion on the data set were performed using RStudio following SLU-standards for units and conversion formulas, see Appendix 1, *Table A 1*.

$OMCD_{5.6}$ values were calculated using Visual MINTEQ, a chemical equilibrium model that estimates charge balance in water samples by simulating interactions among major ions, metals and organic matter. For each sample a range of ADOM/DOC values was used to identify which ratio minimized the charge imbalance, from which the charge density was calculated. Furthermore, the charge density values were determined at pH 5.6, the endpoint of the acidity titrations. For the data available to this project, pH 5.6 is the most robust reference point for modelling and quantifying $OMCD_{5.6}$. This is due to factors such as known addition of acid to titrate the sample, and control of the bicarbonate system by degassing with N_2.

The $OMCD_{5.6}$ values used in this analysis were derived by Bishop & Lackner (2025). To further ensure consistency, all observational data on TOC, CDOM and sVISa were filtered to include only stations with valid $OMCD_{5.6}$ records. After filtering, between 133 and 136 stations remained, depending on the variable.

2.2 Data grouping and period definition

To investigate differences over time, the dataset was divided into three time periods: 1990-1997, 1998-2012, and 2012-2024. These intervals were selected based on visual assessment of generalized additive mixed models (GAMMs) trend results from Eklöf et al. (2021), which showed distinct shifts or peaks in the variables TOC, CDOM and sVISa around the years 1997-1998 and 2012.
The division was not based on formal statistical change-point detection but was instead guided by patterns in increasing trends observed in the trend plots, including inflection points and consistent directional changes. Grouping data this

way enabled clearer comparisons in distributional shifts in DOM character, particularly under not normally distributed data and uneven sampling frequency.

Splitting the data into discrete periods allowed for non-parametric group comparison using Kruskal-Wallis and Dunn's tests, which are better suited for analysing differences between predefined groups than continuous trend methods like Mann-Kendall, especially given the uneven sampling frequency and gaps across stations and time.

2.3 Statistical analysis

To explore the temporal patterns GAMMs were first fitted to the four variables: TOC, CDOM, sVISa and $OMCD_{5.6}$. These models were implemented in RStudio using a source script provided by Von Brömssen et al. (2021), adapted to the current dataset.

All statistical analyses were conducted in RStudio. Data distributions for TOC, CDOM, sVISa and $OMCD_{5.6}$ were assessed visually using histograms and Q-Q to evaluate assumptions of normality. Based on these assessments, non-parametric statistical tests were selected.

To examine whether the distribution of each variable (TOC, CDOM, sVISa and $OMCD_{5.6}$) differed significantly between the three defined time-periods (1990-1997, 1998-2012 and 2012-2024), Kruskal-Wallis tests were applied individually on each variable using base R's kruskal.test() function. For stations where significant differences were detected ($p < 0.05$), Dunn's post-hoc tests were conducted to identify which specific period comparisons differed. These were performed using the FSA package with a Bonferroni correction to account for multiple comparisons.

In addition, sVISa and $OMCD_{5.6}$ summary statistics were calculated per period using the dplyr package in RStudio. These included the median, 25th percentile (P25) and 75th percentile (P75). The summaries helped describe the typical values and spread of the data across the selected time-periods.

Lastly, for sVISa and $OMCD_{5.6}$, boxplots of absolute percentage change between periods were generated. This analysis included all stations with available data across the compared periods, regardless of statistical significance, to explore the overall distribution and magnitude of change in sVISa and $OMCD_{5.6}$ values over time.

2.4 Station-level time series

To illustrate station-specific temporal variation, one station (Rokån, MVM-ID:1656) was selected. This station was chosen due to having the most even distribution of observations across all three studied time-periods (1990-1997, 1998-2012 and 2012-2024) and a high number of samples for each variable. This allowed for a consistent visual comparison of trends over time.

For each of the four variables (TOC, CDOM, sVISa and $OMCD_{5.6}$), time series plots were generated in RStudio using the ggplot2 package. The raw data points were color-coded by period and period-specific mean values were overlaid as horizontal reference lines. These plots offer a qualitative view of how each variable evolved over time at this station.

3. Results

After filtering the data around existing $OMCD_{5.6}$ values for increased comparability, 133-136 stations remained for analysis. Further information about the number of stations and samples for each variable (TOC, CDOM, sVISa and $OMCD_{5.6}$) are presented in appendix 2, see *Table A 2, A 3, A 4* and *A 5*.

3.1 TOC

The temporal trend analysis of TOC concentrations, based on generalized additive mixed models (GAMMs), shows recurring peaks in the proportion of stations with increasing trends around 1997, 2007 and 2021 (*Figure 1*). On average, approximately 20% of stations exhibit increasing TOC trends across the entire monitoring period. Up to 50% have increasing trend during two periods of several years each, centered around 1997 and 2008. The plot also highlights periods of stable or decreasing trends, although the decreases are less common. For this variable the time series are relatively complete and consistent across stations, making the use of GAMMs for TOC when assessing temporal trends viable.

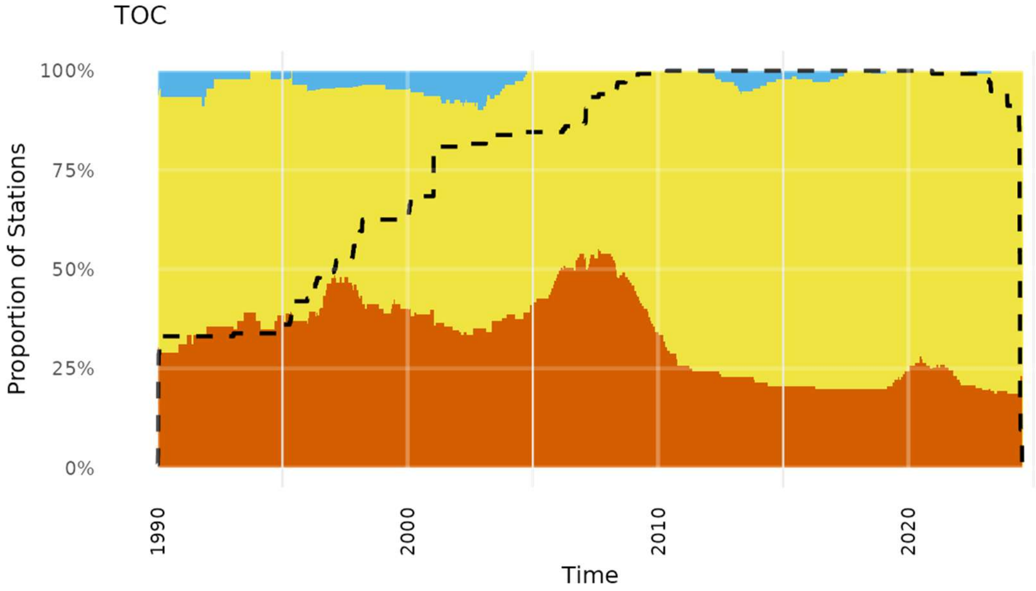


Figure 1: Proportion of stations showing a significant increasing, decreasing or no trend in TOC concentrations from 1990-2024 based on a generalized additive mixed models (GAMMs) from 136 stations. Orange indicates increasing trends, yellow no significant change and blue decreasing trends. The dashed line indicates the proportion of stations with available data at each time point. Completeness of the TOC supports viability for the use of GAMMs to identify temporal trends.

The distribution of TOC values across stations is right-skewed and unimodal, as shown in the histogram (*Figure 2*), indicating that lower TOC concentrations are more common, with a smaller number of stations exhibiting higher TOC values. The Q-Q plot (Appendix 3, *Figure A 1*) confirms deviations from normality particularly in the upper tail, where observed values are higher than expected under a normal distribution. These characteristics support the use of a non-parametric statistical methods for comparing TOC between time periods.

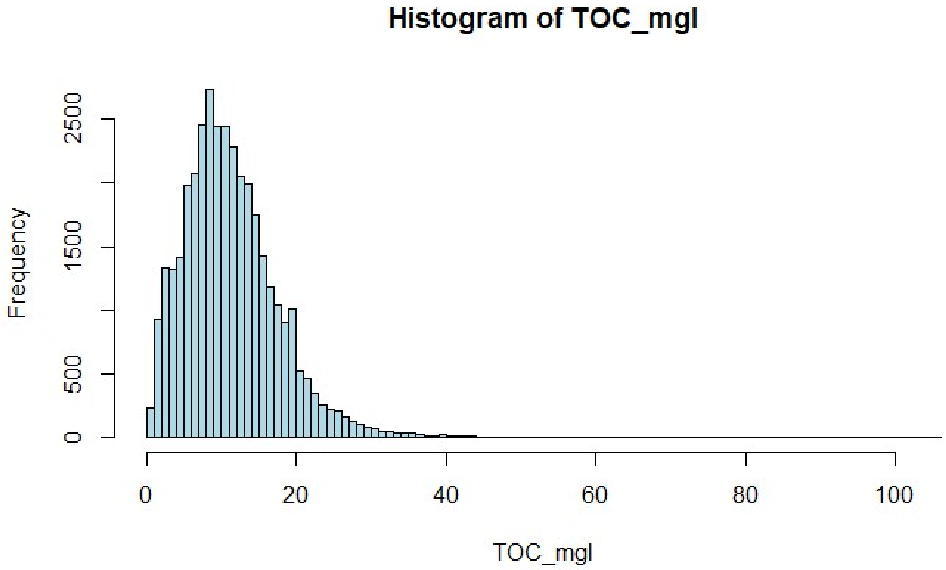


Figure 2: Histogram displaying the distribution of TOC values from 136 stations. The distribution is right-skewed and unimodal, with most values concentrated between 0-20 mg/L, and a smaller number of higher concentrations extending up to around 40 mg/L. This moderate skew supports the use of non-parametric methods for comparing values across time periods.

To assess whether TOC concentrations differed between the three time periods (1990-1997, 1998-2012 and 2012-2024), a Kruskal-Wallis test was applied at each of the 136 stations. As shown in *Figure 3*, 66 stations showed statistically significant differences in TOC across the periods.

Pairwise comparisons using Dunn’s test (*Table 1*) revealed that the greatest number of significant differences occurred between 1998-2012 and 2012-2024, with 59 stations showing statistically significant changes. Fewer stations showed significant differences between 1990-1997 and 2012-2024 (26 stations), and between 1990-1997 and 1998-2012 (21 stations).

This suggests that the most recent period (2012-2024) marks a notable shift in TOC levels compared to earlier periods. However, these patterns may also reflect greater data availability and more consistent sampling in recent years, which can improve the ability to detect significant changes.

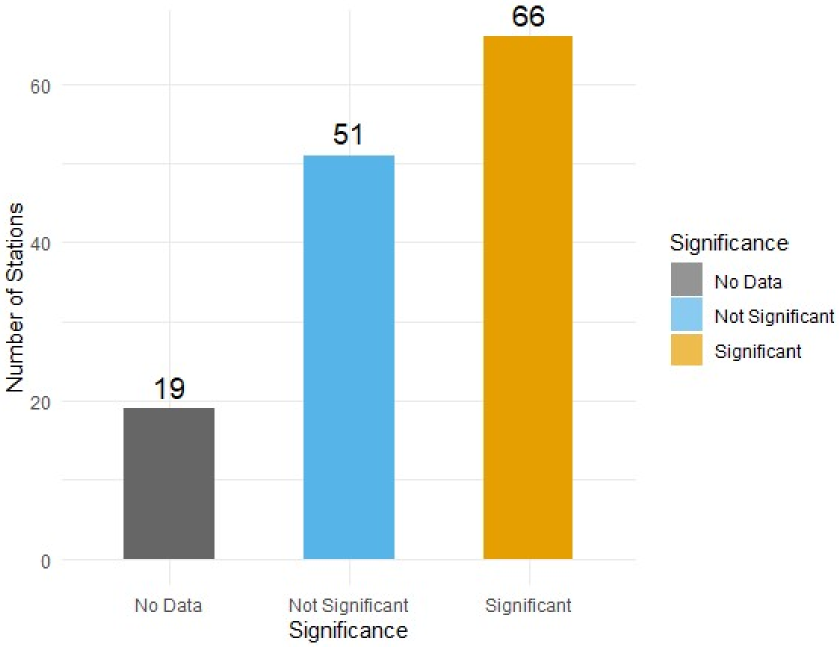


Figure 3: Number of stations with significant and non-significant differences in TOC concentrations across three time-periods (1990-1997, 1998-2012 and 2012-2024), as determined by the Kruskal-Wallis test on 136 stations. Stations with p-values below 0.05 were classified as significantly different.

Table 1: Pairwise comparisons of TOC concentrations between time-periods using Dunn's test following a significant Kruskal-Wallis result. The number of stations showing statistically significant ($p < 0.05$) and non-significant differences is shown for each period pair.

Comparison	Not Significant	Significant
1990–1997 – 1998–2012	16	21
1990–1997 – 2012–2024	11	26
1998–2012 – 2012–2024	7	59

3.2 CDOM

The temporal trend in CDOM, modelled using GAMMS, shows peaks in the proportion of stations with increasing trends around 1995, 1998 and 2020 (*Figure 4*), based on visual assessment of the plot. If these peaks are not synchronized with the changes in TOC, this would indicate shifts in the character of DOM, particularly in its light-absorbing properties across stations. Data for CDOM has a relatively good and consistent time-series across stations, which supports the use GAMMS for temporal-trends assessments.

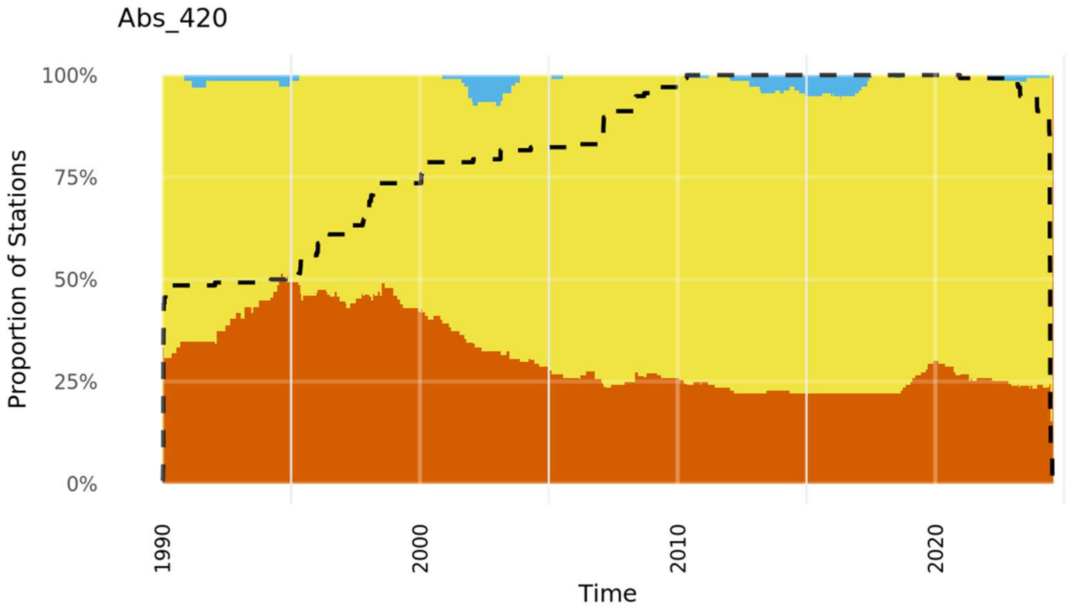


Figure 4: Proportion of stations showing a significant increasing, decreasing or no trend in CDOM from 1990-2024, based on a generalized additive mixed models (GAMMs) from 136 stations. Orange indicates increasing trends, yellow no significant change and blue decreasing trends. The dashed line indicates the proportion of stations with available data at each time point. The completeness of the CDOM dataset supports trend estimations over the entire period.

The distribution of CDOM across stations is right-skewed and unimodal, as shown in (*Figure 5*). Most values are concentrated at the lower end of the scale, with fewer stations exhibiting higher CDOM levels. The Q-Q plot (Appendix 3, *Figure A 2*) further highlights deviations from normality, particularly in the upper tail, where observed values exceed those expected under a normal distribution. These characteristics support the use of non-parametric statistical methods when comparing CDOM across time periods.

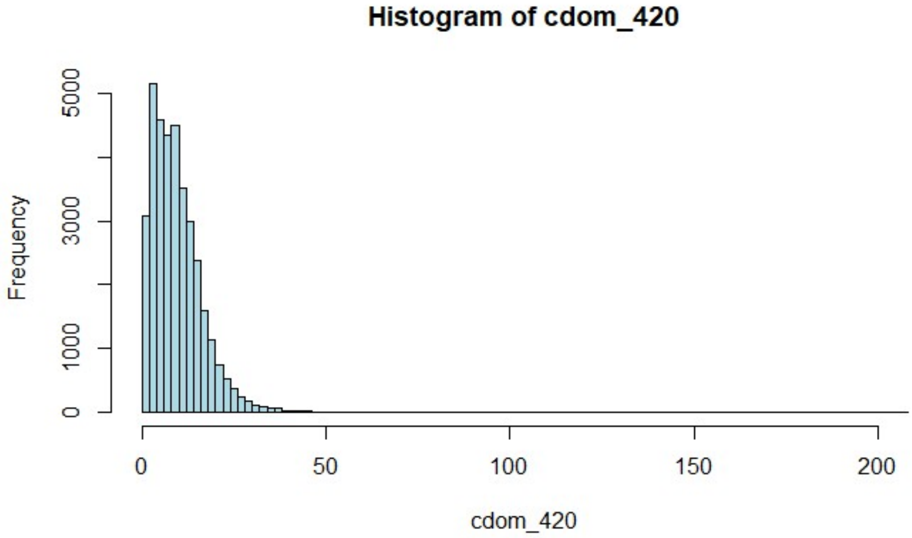


Figure 5: Histogram displaying the distribution of CDOM from 133 stations. The distribution is right-skewed and unimodal, with most values concentrated at the lower end and smaller number of stations exhibiting higher CDOM. This supports the use of non-parametric methods for comparing CDOM values across time periods.

To assess differences in CDOM between the three time periods (1990-1997, 1998-2012 and 2012-2024), a Kruskal-Wallis test was performed at each of the 133 stations. As shown in *Figure 6*, 65 stations exhibited statistically significant differences in CDOM across the periods.

Pairwise comparisons using Dunns'test (*Table 2*) revealed that the greatest number of significant differences occurred in the comparison between 1998-2012 and 2012-2024, with 44 stations showing statistically significant change. The other comparisons (1990-1997 to 2012-2024 and 1990-1997 to 1998-2012) also showed significant differences at 27 and 26 stations, respectively.

These results suggests that differences in CDOM were detected across all period comparisons, with the most pronounced separation occurring between the two most recent periods (1998-2012 and 2012-2024).

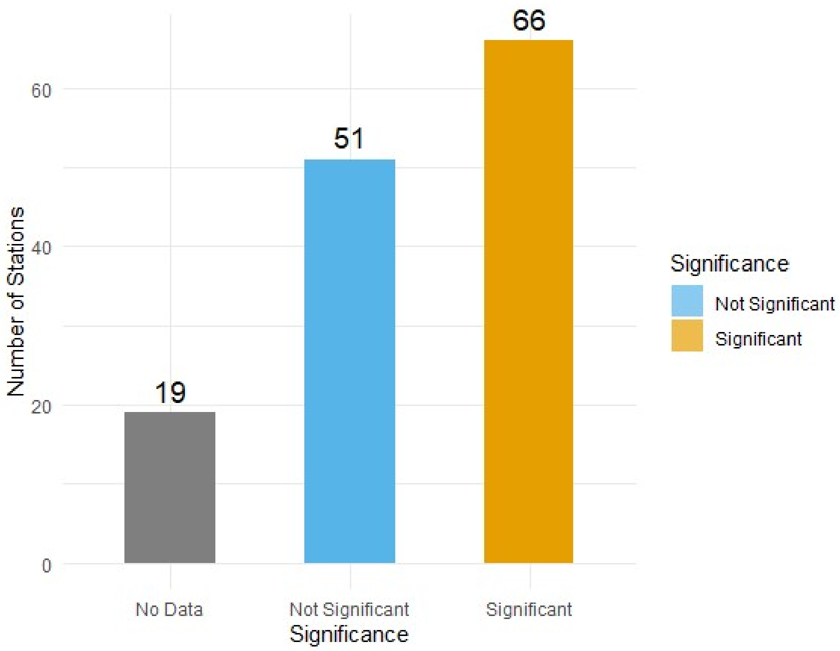


Figure 6: Number of stations with significant and non-significant differences in CDOM across three time-periods (1990-1997, 1998-2012 and 2012-2024), as determined by the Kruskal-Wallis test on 133 stations. Stations with p-values below 0.05 were classified as significantly different. Analysis was conducted using data from 133 stations.

Table 2: Pairwise comparisons of CDOM values between time-periods using Dunn's test following a significant Kruskal-Wallis result. The number of stations showing statistically significant ($p < 0.05$) and non-significant differences is reported for each period pair.

Comparison	Not Significant	Significant
1990-1997 - 1998-2012	12	26
1990-1997 - 2012-2024	11	27
1998-2012 - 2012-2024	21	44

3.3 sVISa

sVISa normalizes CDOM to TOC, providing an indication of eventual changes in DOM character. The trend analysis of sVISa over time, based GAMMs, reveals a variable pattern in both decreasing and increasing trends across stations (*Figure 7*). The proportion of stations with significant increasing trends peaks around 1998, 2012 and 2022, while a notable peak in decreasing trends appearing around 2007. Visually analysed, on average, approximately 13% of stations show increasing trends across the time span. Since sVISa is based on TOC and CDOM its time-series will therefore be relatively consistent across stations as well, supporting assessment on temporal trends.

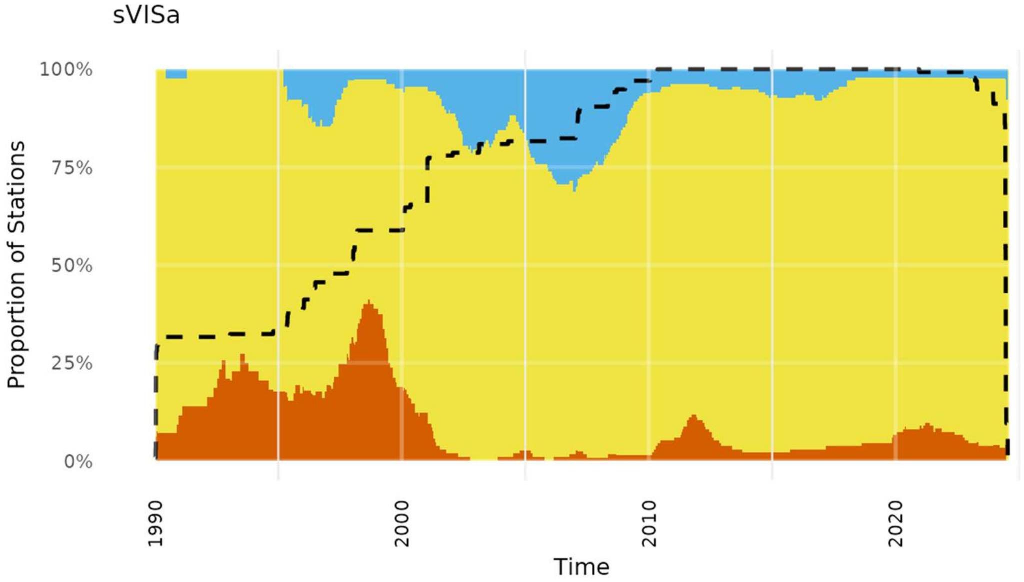


Figure 7: Proportion of stations showing a significant increasing, decreasing or no trend in sVISa from 1990-2024 based on a generalized additive mixed models (GAMMs) from 136 stations. Orange indicates increasing trends, yellow no significant change and blue decreasing trends. The dashed line indicates the proportion of stations with available data at each time point. Completeness of the sVISa dataset supports reliable assessments of temporal trends.

The distribution of sVISa values is right-skewed and unimodal, as shown in the histogram (*Figure 8*), indicating that lower values are more common across stations. The Q-Q plot (Appendix 3, *Figure A 3*) reveals further deviations from normality, particularly in the upper tail, where observed values are lower than expected under a normal distribution. These characteristics support the use of non-parametric statistical methods for comparing sVISa between time periods.

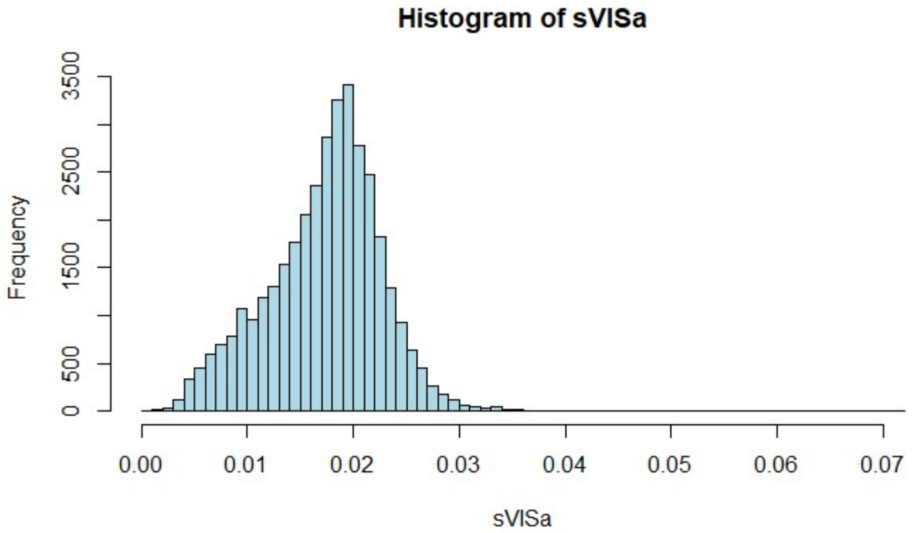


Figure 8: Histogram displaying the distribution of sVISa values from 133 stations. The distribution is right-skewed and unimodal, with most values concentrated at the lower end of the range. This supports the use of non-parametric methods for statistical comparison across periods.

To evaluate differences in sVISa between the defined time periods (1990-1997, 1998-2012 and 2012-2024), a Kruskal-Wallis test was conducted at each of the 133 stations. As shown in *Figure 9*, 80 stations showed statistically significant differences across the three periods.

To identify which periods differed most, pairwise comparisons were performed using Dunn's test (*Table 3*). The most prominent change was observed between 1998-2012 and 2012-2024, where 68 stations exhibited significant differences. This suggests that many stations showed statistically significant differences in sVISa between these two periods.

Additionally in comparison, fewer stations showed significant differences between 1990-1997 and 1998-2012 (25 stations) or 1990-1997 and 2012-2024 (15 stations), as shown in *Table 3*. This may reflect higher variability or fewer available stations in the earliest period, which can reduce the statistical power to detect differences across wider time spans.

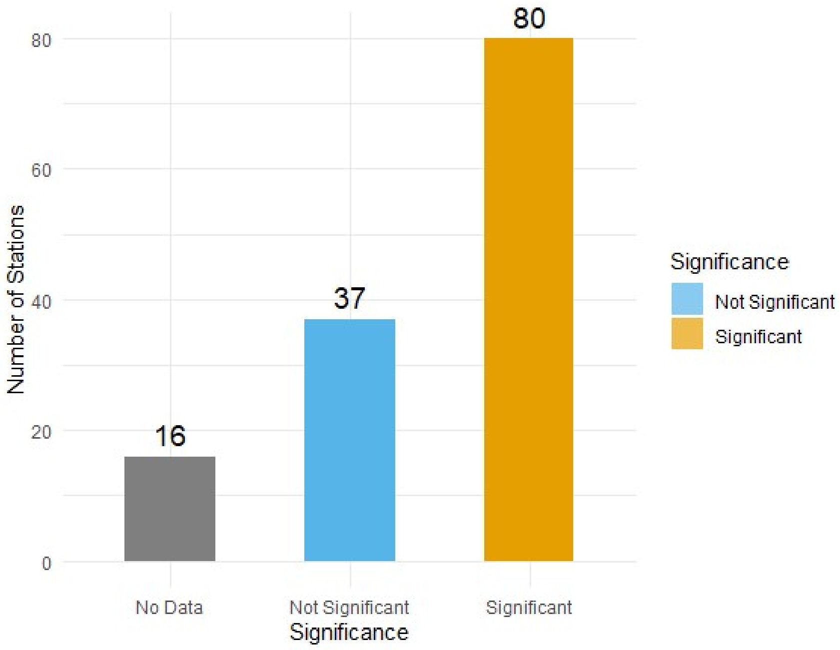


Figure 9: Number of stations with significant and non-significant differences in sVISa values across three time periods (1990-1997, 1998-2012, 2012-2024), as determined by the Kruskal-Wallis test. Stations with p-values below 0.05 were considered significantly different.

Table 3: Pairwise comparisons of sVISa values between time periods using Dunn's test following a significant Kruskal-Wallis result. The number of stations showing statistically significant (p < 0.05) and non-significant differences is reported for each pair

Comparison	Not Significant	Significant
1990-1997 - 1998-2012	13	25
1990-1997 - 2012-2024	23	15
1998-2012 - 2012-2024	12	68

The boxplot (*Figure* 10) shows the distribution of absolute percentage changes in sVISa values across three time-period comparisons (1990-1997 to 1998-2012, 1990-1997 to 2012-2024 and 1998-2012 to 2012-2024). These absolute values reflect the magnitude of change at each station, regardless of direction (i.e., whether sVISa increased or decreased).

The largest median changes are observed in comparisons involving the earliest period (1990-1997): approximately 18% for 1990-1997 to 1998-2012 and 13% for 1990-1997 to 2012-2024. Both comparisons also exhibit wide interquartile ranges (IQRs), suggesting high variability in response across these stations for sVISa values.

In contrast, the comparison between 1998-2012 and 2012-2024 shows a lower median change (~5%) and a narrower IQR, indicating a more uniform and moderate response. These results align with the pairwise statistical tests (*Table 5*), where the highest number of significant differences was observed for this period comparison. This likely reflects a consistent and widespread shift in sVISa values, with less variability within periods and greater data availability during the more recent years.

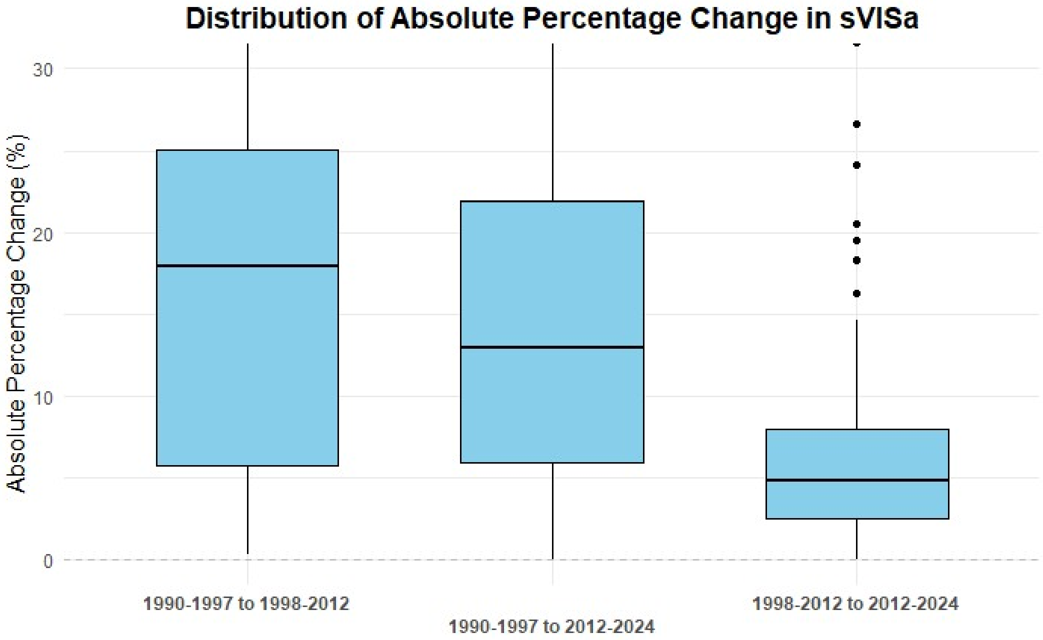


Figure 10: Boxplot showing the distribution of absolute percentage changes in sVISa values across three time-period comparison (1990–1997 to 1998–2012, 1998–2012 to 2012–2024, and 1990–1997 to 2012–2024), based on data from 133 stations. The boxes represent the interquartile range (IQR), with the horizontal line indicating the median. The largest median changes occur in comparisons involving the earliest period, while the most recent comparison shows a smaller median change and a narrower IQR, suggesting a more uniform response across stations. Outliers are included in the analysis but have been cropped from the figure for visual clarity.

3.4 $OMCD_{5.6}$

Temporal trend in $OMCD_{5.6}$ values from 1990-2024, modelled using GAMMs, shows peak in decreasing trends around 2001, followed by a peak in increasing trends around 2007 (*Figure 11*). Most of the observed increases are concentrated between 2000-2011, while the remaining time-periods are dominated by decreasing or non-significant trends.

For this analysis, only stations with at least six years of data and six samples per year were included, improving model reliability by reducing the influence of short or incomplete time series. Although $OMCD_{5.6}$ values are available from 1990 onward, data coverage before 1998 is limited, and trends from that period should be interpreted with caution.

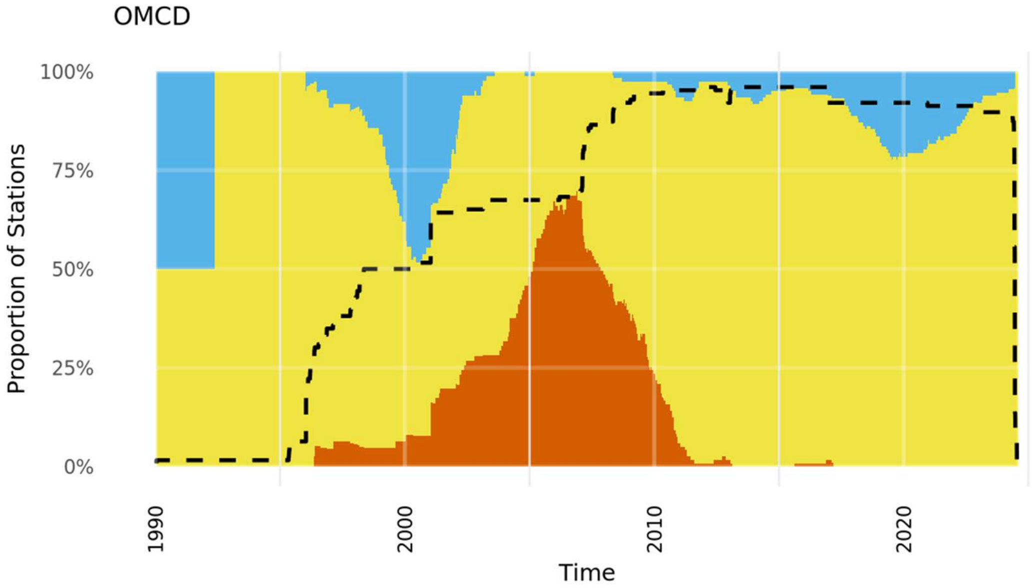


Figure 11: Proportion of stations showing a significant increasing, decreasing or no trend in $OMCD_{5.6}$ from 1990-2024 based on a generalized additive mixed models (GAMMs) from 126 stations. Orange indicates increasing trends, yellow no significant change and blue decreasing trends. The dashed line indicates the proportion of stations with available data at each time point. Only stations with at least six years of data and six samples per year were included in the analysis. While data are available from 1990, coverage is sparse before 1998, and trends in that periods should be interpreted with caution.

The distribution of $OMCD_{5.6}$ across stations is approximately symmetric and unimodal, as shown in the histogram (*Figure 12*). Unlike the other variables, $OMCD_{5.6}$ does not display strong skewness, suggesting that the values are more evenly distributed across stations. The Q-Q plot (Appendix 3, *Figure A 4*) supports this, showing only slight deviations from normality, particularly in the upper tail, where some observed values are higher than expected under a normal distribution. This approximate normality supports the interpretability of changes across time periods. However, non-parametric tests were still applied to ensure robustness and consistency across all variables, particularly given slight deviations from normality and potential differences in variance between groups.

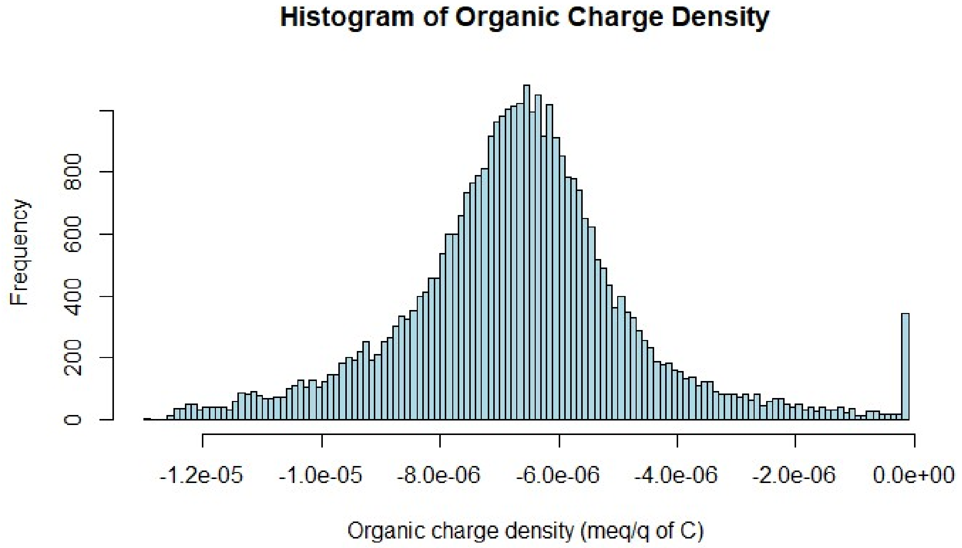


Figure 12: Histogram displaying the distribution of $OMCD_{5.6}$ from 136 stations. The distribution is approximately symmetric and unimodal, with slight deviations from normality primarily in the upper tail. These characteristics support the use of non-parametric statistical tests for comparing $OMCD_{5.6}$ values between periods.

To assess differences in $OMCD_{5.6}$ between the three time-periods (1990-1997, 1998-2012 and 2012-2024), a Kruskal-Wallis test was performed at each of the 136 stations. As shown in *Figure 13*, 77 stations exhibited statistically significant differences in $OMCD_{5.6}$ values across the periods.

Pairwise comparisons using Dunn's test (*Table 4*) showed that the largest number of significant differences occurred between 1998-2012 and 2012-2024, with 69 stations showing statistically significant changes. The earlier comparisons (1990-1997 to 2012-2012 and 1990-1997 to 1998-2012) had 21 and 17 significantly differing stations, respectively.

These results indicate that the most pronounced separation in $OMCD_{5.6}$ values occurred between the two most recent periods, suggesting that the later phase is associated with more widespread and consistent changes in $OMCD_{5.6}$.

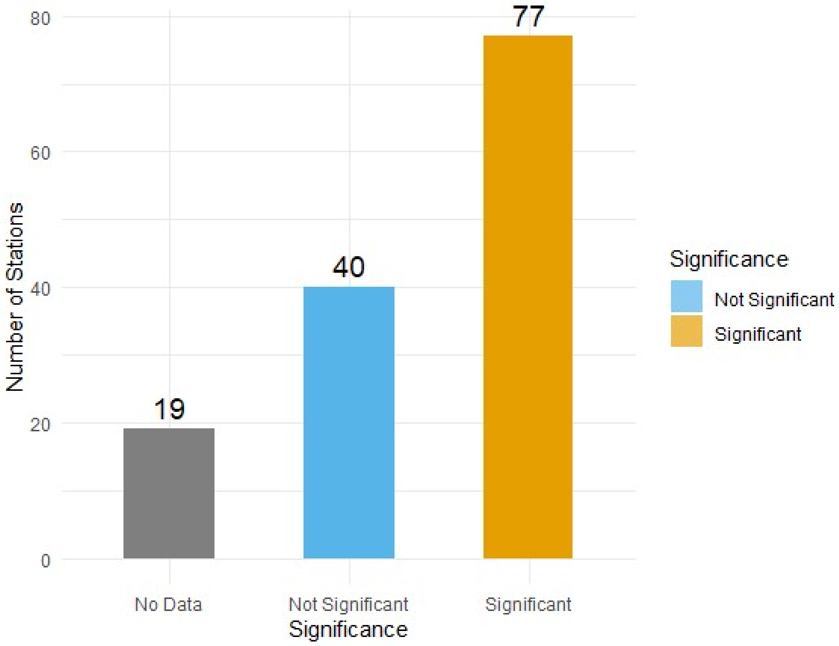


Figure 13: Number of stations with significant and non-significant differences in OMCD$_{5.6}$ values across three time-periods (1990-1997, 1998-2012 and 2012-2024), as determined by the Kruskal-Wallis test on 136 stations. Stations with p-values below 0.05 were classified as significantly different.

Table 4: Pairwise comparisons of OMCD5.6 values between time-periods using Dunn's test following a significant Kruskal-Wallis result. The number of stations showing statistically significant ($p < 0.05$) and non-significant differences is reported for each period

Comparison	Not Significant	Significant
1990-1997 - 1998-2012	21	17
1990-1997 - 2012-2024	17	21
1998-2012 - 2012-2024	8	69

The boxplot (*Figure 14*) displays the absolute percentage change in organic charge density (OMCD$_{5.6}$) between the three period comparisons. The largest median changes are observed between 1990-1997 to 2012-2024 (~18%) and 1990-1997 to 1998-2012 (~14%). Both comparisons also show a relatively wide interquartile range (IQR), indicating substantial variability in how much stations changed between these earlier and later periods.

In contrast, the comparison between 1998-2012 to 2012-2024 shows a lower median change (~7%) and a narrower IQR, suggesting that stations responded more uniformly during this more recent time interval. These results are consistent with the pairwise statistical tests (*Table 7*), where the highest number of stations with significant differences was observed between 1998-2012 to 2012-2024. This likely reflects a more consistent pattern of change in $OMCD_{5.6}$ values across stations, possible due to shared influences during the later period.

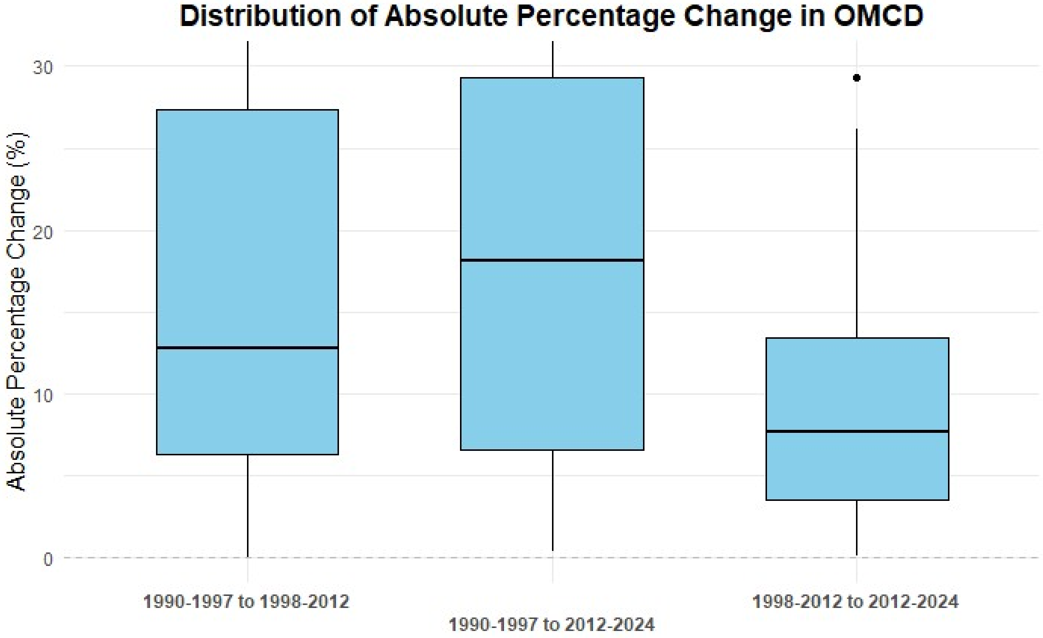


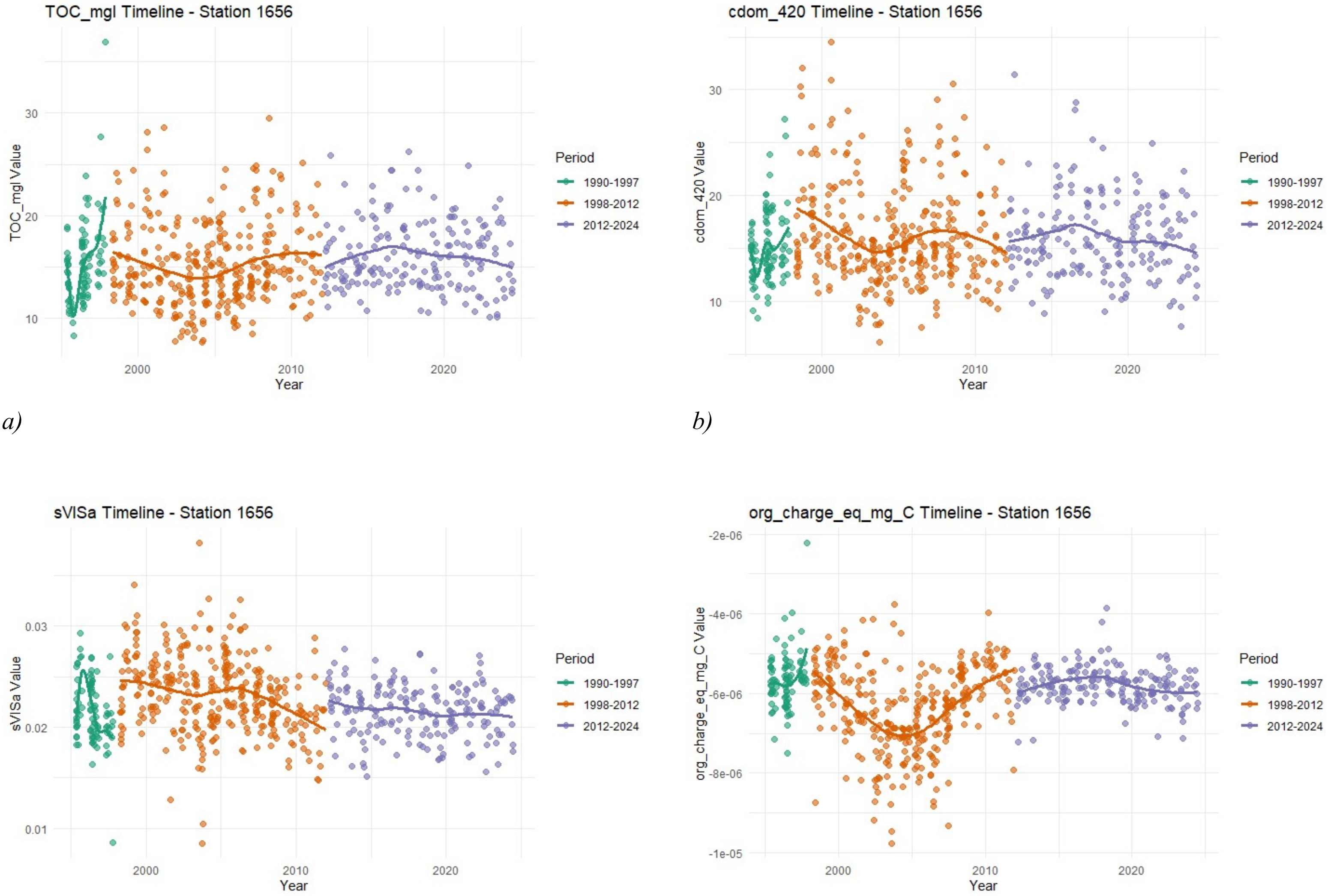
Figure 14:Boxplot illustrating the distribution of absolute percentage changes in organic charge density ($OMCD_{5.6}$) across three time-period comparisons (1990–1997 to 1998–2012, 1998–2012 to 2012–2024, and 1990–1997 to 2012–2024), based on data from 136 stations. Outliers are included in the analysis but are cropped from the figure for visual clarity.

3.5 Visual time series at a representative station

To illustrate temporal patters at the station level, *Figure 15* presents long-term time series data from stations MVM-ID: 1656. This station was selected because it has one of the most balanced distributions of the sample counts across all three time-periods (1990-1997, 1998-2012, 2012-2024), while also maintaining a relatively high number of total samples across all variables.

Each subplot shows time-series data for TOC, CDOM, sVISa and $OMCD_{5.6}$ from 1990-2024, with individual values plotted as coloured dots and period-specific means overlaid in green (1990-1997), orange (1998-2012) and blue (2012-2024).

All variables display substantial within-period variability, and none follow a fully consistent trend across the full timespan. TOC (*a*) remains variable throughout, CDOM (*b*) and sVISa (*c*) show elevated values in the middle period. Additionally, $OMCD_{5.6}$ (*d*) shows the most pronounced shifts between periods before stabilizing more recently.



a) b) c) d)

Figure 15: Time series of TOC (a), CDOM (b), sVISa (c) and OMCD$_{5.6}$ (d) for station MVM-ID: 1656, shown from 1990-2024. Coloured dots represent individual observations, and coloured lines indicate period-specific means: green = 1990-1997, orange = 1998-2012, blue = 2012-2024. This station was chosen due to its relatively even number of samples across all three periods and its inclusion of one of the most complete OMCD$_{5.6}$ records available.

4. Discussion

4.1 Changes in DOM quantity and quality

The observed difference in trends between TOC and CDOM over time (*Figure 1* and *Figure* 4), suggests that not only that concentration of DOM in Swedish streams has changed, but also its composition. This could be related to changes in the organic matter sources. The TOC quantifies carbon content, but does not fully represent DOM, which includes a range of components that influences the environmental behaviour of DOM. In the subsequent text, TOC will be referred to when talking about measurements of this property, but DOM will be used when speaking of the character organic matter has more generally.

To better assess DOM character, sVISa was obtained by normalizing CDOM to TOC (Eklöf et al. 2021).The observed shifts in sVISa indicate that a decoupling between concentration and optical properties has taken place. This represents a change in DOM quality that can reflect a change in the source of DOM coming from soils. This is likely due to broader environmental processes, such as the recovery from acidification, climate warming or changes in the vegetation. The optical quality of DOM influences light penetration in surface water.

4.2 New insights from $OMCD_{5.6}$

The primary contribution of this study is the inclusion of $OMCD_{5.6}$ as a proxy for the acid-base character of DOM. This feature of DOM quality influences both surface water pH and the speciation of metals, particularly aluminium. By modelling OMCD at pH 5.6 using Visual MINTEQ, it is possible to assess temporal changes in the dissociation behaviour of acidic functional groups, mainly carboxylic acid (-COOH). When these groups dissociate into the negatively charged form ($-COO^-$), they contribute to the solubility and reactivity of DOM.

The GAMMs for $OMCD_{5.6}$ (*Figure 11*) suggests a delayed response compared to sVISa (*Figure 7*), with the most pronounced changes occurring approximately a decade later. While sVISa showed peaks in the proportion of increasing trends around the late 1990s and early 2000s, the GAMM result for $OMCD_{5.6}$ indicated increasing trends between 2000 and 2011, in addition to the abundance of peaks of decreasing trends in early 2000. Although this significant shift in dissociation began earlier according to *Figure 11*, the medians show something else, since during the period 2012-2024 $OMCD_{5.6}$ medians became less negative (Appendix 2, *Table A 5*). $OMCD_{5.6}$ has therefore become less dissociated meaning less carboxylic acid groups exists in its charged form (-COO$^-$). A reduced dissociation results in less negative values, indicating a lower net negative charge. In other words, the summary statistics indicates that DOM has become less acidic and contains less charged functional groups at pH 5.6. Furthermore, the pairwise comparisons for $OMCD_{5.6}$ (*Table* 4) shows that the largest number of statistically significant differences occurred 1998-2012 and 2012-2024. This significant difference does not indicate a direction of change within each period; it does however indicate that the distribution of $OMCD_{5.6}$ values notable differed between the period significantly. This supports observations seen in the summary statistics, that the most distinct shift in $OMCD_{5.6}$ most likely happened in the most recent periods.

This temporal offset may indicate that $OMCD_{5.6}$ responds more slowly to environmental drivers such as acidification recovery, shifts in vegetation, or changes in soil chemistry. Unlike sVISa, which may quickly reflect alterations in DOM sources or flow paths, $OMCD_{5.6}$ likely integrates longer-term changes in the molecular structure and reactivity of DOM exported from soils. However, these modelled trends must be interpreted with caution due to data gaps, different types of data being available at different times, and limited time-series continuity, particularly in the earlier years. The $OMCD_{5.6}$ dataset was filtered to include only stations with sufficient data for reliable GAMM analysis, which may influence the representativeness of the trends.

The statistical analyses further support this temporal pattern. Many stations showed significant differences in $OMCD_{5.6}$ between 1998-2012 and 2012-2024 (*Table 4*), supporting the idea that characteristics of DOM may have shifted more clearly in the most recent decades. While some of these results may be influenced by increased data coverage in later years, the consistent differentiation across multiple variables suggests either a meaningful underlying change in DOM character, or by changes in the data over time from the MVM dataset that is available to calculate the charge balance.

To support interpretation of these shifts, summary statistics of $OMCD_{5.6}$ and sVISa values per period were calculated (Appendix 2, *Table A 4* and *Table A 5*). These indicated a general reduction in $OMCD_{5.6}$ over time. Such a decrease suggests that DOM in Swedish waters has become less dissociated at pH 5.6, meaning fewer carboxylic acid groups are present in their charged form (-COO$^-$). Lower $OMCD_{5.6}$ values reflects weaker acidity and reduced overall charge, reducing DOM's solubility and binding affinity with metals at pH 5.6 (but presumably at other pHs as well in the vicinity of 5.6).

In the context of brownification, these findings are particularly interesting. Though the overall concentration of DOM in Swedish surface water has increased, a decrease in $OMCD_{5.6}$ suggests that the acid-base properties of DOM could have shifted in a direction that reduces dissociation. This is likely to reduce the solubility of DOM and its acidity. Whether such character changes are contributing to spatial and temporal variability of brownification is a possibility that needs further investigation, particularly in the context of assigning causality to environmental drivers, such as alterations regarding climate and land-use.

To further emphasize the importance of acid-base character of DOM, which is reflected in $OMCD_{5.6}$, is its practical role in for example production of drinking water. Less dissociated DOM will have different interactions within the processes involved in the production of water production, which potentially could reduce efficiency and affect the treatment costs (Kastl et al. 2004). This highlights the importance of $OMCD_{5.6}$ not only from an ecological perspective, but also its overall importance for ecosystem services like drinking water.

4.3 Variability and limitations

Time series plots for a single monitoring station (MVM-ID:1656) illustrate the temporal evolution of all four variables (TOC, CDOM, sVISa and $OMCD_{5.6}$), within one figure (*Figure 15*). This station, previously highlighted for its even distribution of observations across all periods, also holds one of the most complete $OMCD_{5.6}$ records. Visual assessment of the plots reveals substantial variability from sample to sample within each period, likely reflecting both potential measurement uncertainty and natural fluctuations. Despite this, consistent shifts between periods are apparent, especially between 1998-2012 and 2012-2024, where median values across all four variables change noticeably.

While these shifts do appear consistently from the pairwise comparison results, it is important to note that it does not indicate whether in what direction or nature of change the distribution sees within each period. As an example, a significant difference could occur if one period has seen stable medians throughout the years, meanwhile the other period experiences trends or shifts. Therefore, using GAMMs to determine the general trends and median summary statistics, you can get a better understanding on temporal dynamics. Interpretation of the time-series from one single station, should however not be considered as a general representative of what happened across whole range of the dataset, even though its temporal shifts seem to broadly align with the trends observed on the dataset.

Despite the usefulness of GAMMs and pairwise comparisons, the possibility of systematic differences in the data available for calculating the charge balance needs considered. Reasons for this include limitations in data coverage, especially for the earliest period and possible variability in samples or $OMCD_{5.6}$ dataset exclusions of many stations due to filtering.

4.4 Conclusions and Implications

In conclusion there is much interest in the character of DOM. The acid-base properties are one aspect of character, although it is a rather difficult parameter to quantify. The reason for this is due to acid-base character being a property that covers DOM dissociation over the entire pH range in natural waters, and in the presence of different complexing agents such as aluminium. The MVM database of water chemistry made it possible to quantify one feature of this property over time, the charge balance at pH 5.6 which is the end point of the acid-base titration.

These findings do support the original hypothesis that DOM character has shifted over time. The reduced dissociation indicated by less negative $OMCD_{5.6}$ values may reflect long-term response to for example the acidification recovery or land-use changes, which affect DOM mobilization and reactivity in water catchments.

The fact that a change was found will hopefully encourage researchers to study further the implications of DOM acid-base character for aquatic life and the understanding of what is responsible for brownification. Such an investigation will also need to consider if there are systematic errors in the estimate of certain components of the charge balance (e.g. aluminium speciation).

References

Bishop, K. & Lackner, A. (2025). Variationen i surheten av löst organiskt kol över Sverige under 35 år.

Crapart, C., Finstad, A.G., Hessen, D.O., Vogt, R.D. & Andersen, T. (2023). Spatial predictors and temporal forecast of total organic carbon levels in boreal lakes. *Science of The Total Environment*, 870, 161676. https://doi.org/10.1016/j.scitotenv.2023.161676

Eklöf, K., Von Brömssen, C., Amvrosiadi, N., Fölster, J., Wallin, M.B. & Bishop, K. (2021). Brownification on hold: What traditional analyses miss in extended surface water records. *Water Research*, 203, 117544. https://doi.org/10.1016/j.watres.2021.117544

Hruška, J., Laudon, H., Johnson, C.E., Köhler, S. & Bishop, K. (2001). Acid/base character of organic acids in a boreal stream during snowmelt. *Water Resources Research*, 37 (4), 1043–1056. https://doi.org/10.1029/2000WR900290

Kastl, G., Sathasivan, A., Fisher, I. & Van Leeuwen, J. (2004). Modeling DOC Removal Enhanced Coagulation. *Journal AWWA*, 96 (2), 79–89. https://doi.org/10.1002/j.1551-8833.2004.tb10557.x

Köhler, S., Hruška, J. & Bishop, K. (1999). Influence of organic acid site density on pH modeling of Swedish lakes.

Köhler, S.J. (n.d.). pH beräkningar för ytvatten.

Kritzberg, E.S., Hasselquist, E.M., Škerlep, M., Löfgren, S., Olsson, O., Stadmark, J., Valinia, S., Hansson, L.-A. & Laudon, H. (2020). Browning of freshwaters: Consequences to ecosystem services, underlying drivers, and potential mitigation measures. *Ambio*, 49 (2), 375–390. https://doi.org/10.1007/s13280-019-01227-5

Laudon, H., Westling, O. & Bishop, K. (2000). Cause of pH decline in stream water during spring melt runoff in northern Sweden. *Canadian Journal of Fisheries and Aquatic Sciences*, 57 (9), 1888–1900. https://doi.org/10.1139/f00-131

Monteith, D.T., Henrys, P.A., Hruška, J., De Wit, H.A., Krám, P., Moldan, F., Posch, M., Räike, A., Stoddard, J.L., Shilland, E.M., Pereira, M.G. & Evans, C.D. (2023a). Long-term rise in riverine dissolved organic carbon concentration is predicted by electrolyte solubility theory. *Science Advances*, 9 (3), eade3491. https://doi.org/10.1126/sciadv.ade3491

Monteith, D.T., Henrys, P.A., Hruška, J., De Wit, H.A., Krám, P., Moldan, F., Posch, M., Räike, A., Stoddard, J.L., Shilland, E.M., Pereira, M.G. & Evans, C.D. (2023b). Long-term rise in riverine dissolved organic carbon concentration is predicted by electrolyte solubility theory. *Science Advances*, 9 (3), eade3491. https://doi.org/10.1126/sciadv.ade3491

OECD (2012). *A Framework for Financing Water Resources Management*. OECD. https://doi.org/10.1787/9789264179820-en

Räike, A., Taskinen, A., Härkönen, L.H., Kortelainen, P. & Lepistö, A. (2024). Browning from headwaters to coastal areas in the boreal region: Trends and drivers. *Science of The Total Environment*, 927, 171959. https://doi.org/10.1016/j.scitotenv.2024.171959

Sjöstedt, C.S., Gustafsson, J.P. & Köhler, S.J. (2010). Chemical Equilibrium Modeling of Organic Acids, pH, Aluminum, and Iron in Swedish Surface Waters. *Environmental Science & Technology*, 44 (22), 8587–8593. https://doi.org/10.1021/es102415r

Swedish University of Agricultural Sciences (n.d.). Miljödata MVM. https://miljodata.slu.se/MVM/ [2025-05-23]

Von Brömssen, C., Betnér, S., Fölster, J. & Eklöf, K. (2021). A toolbox for visualizing trends in large-scale environmental data. *Environmental Modelling & Software*, 136, 104949. https://doi.org/10.1016/j.envsoft.2020.104949

Popular science summary

The world changes, climate change is present, land-use is increasing worldwide, what does all this do to the water in our streams? This master thesis dives into the water of streams and investigates how the character of dissolved organic matter (DOM) in Swedish surface waters has changed the past three decades, and why that is important.

DOM is a material that exists naturally in our waters and is responsible for why waters can look brownish. It is not only responsible for colour, but it also plays an important role in stream ecosystems. DOM originates from soils, vegetation and other organic materials. DOM influences not only water clarity but also drinking water and aquatic life. DOM can vary a lot, some can vary in acidity as well as with respect to how much light it absorbs, but also in how DOM interacts with other substances. This is what makes DOM special, and why its character is interesting, and challenging, to investigate.

By using water sample data from over 130 Swedish streams stretching all the way back to 1990, this study looked at both the amount and the character of DOM. How this character was studied was through different tools, or variables, called CDOM, sVISa and $OMCD_{5.6}$. These tools helped determine colour, acidity and charge density at pH 5.6.

What this study found was that although DOM has increased in Swedish surface waters, its chemical character has also changed. In detail, these findings suggested that DOM is less dissociated with fewer groups that are acidic, such as carboxylic acids. A shift like this could be caused by environmental changes, such climate impacts and acidification recovery.

Why do these changes matter? Less DOM that is acidic could influence brownification (this refers to the trend of increasing water colour) in some waters. Such a change may also make it harder to remove in the production of drinking water. Even though these outcomes were not directly tested, they highlight the importance of changes in DOM character. Moreover, this study emphasizes an interesting perspective by introducing $OMCD_{5.6}$ as a measure of DOM character. This new measure helps reveal how the chemistry in Swedish surface waters may be changing, and how these changes could affect ecosystems and ecosystem services related to water management.

Appendix 1

Table A 1: Unit harmonization and conversion of water chemistry variables from the MVM database

Final Variable	Relevant Variable	Units in Title (Original)	Conversion Equation
Alkalinitet/Acid	Alk_Acid_mekvl	mekv/L	1 mekv/L = Direct
Alkalinitet/Acid	Alk_Acid_mmoll	mmol/L	1 mekv/L = 1 mmol/L
Alkalinitet/Acid	Alk_mekvl	mekv/L	1 mekv/L = Direct
Alkalinitet/Acid	Alk_mmoll	mmol/L	1 mekv/L = 1 mmol/L
Alkalinitet/Acid	Acid_mekvl	mekv/L	1 mekv/L = Direct
Alkalinitet/Acid	Alk_mg.HCO3l	mg HCO3/l	1 mekv/L = Alkalinitet/Acid mg HCO3/l x 0,016388069
Aluminium (Al)	Al_µgl	µg/L	Al (µg/L)
Aluminium (Al)	Al_F_µgl	µg/L	Al (µg/L)
Aluminium (Al)	Al_s_µgl	µg/L	Al (µg/L)
Aluminium (Al)	Al_ICPKJB_µgl	µg/L	Al (µg/L)
Aluminium (Al)	Al_ICPAES_µgl	µg/L	Al (µg/L)
Aluminium (Al)	Al_NI_µgl	µg/L	Al (µg/L)
Aluminium (Al)	Al_ICP_µgl Ali	µg/L	Al (µg/L)
Ammoniumkväve (NH4-N)	NH4_N_µgl	µg/L	NH4-N (µg/L) = Direct
Ammoniumkväve (NH4-N)	NH4_N_µgl.N	µg/L	NH4-N (µg/L) = Direct
Ammoniumkväve (NH4-N)	NH4_N_mgl	mg/L	NH4-N (mg/L) = NH4-N (µg/L) x 1000
Fluorid (F)	Fluorid_mekvl	M (mol/L)	F (mg/L) = F (mekv/L) × 19
Fluorid (F)	Fluorid_mgl	mg/L	F (mg/L) = Direct
Kalcium (Ca)	Ca_mgl	mg/L	Ca (mg/L) = Direct
Kalcium (Ca)	Ca_F_mgl	mg/L	Ca (mg/L) = Direct
Kalcium (Ca)	Ca_mekvl	mekv/L	Ca (mg/L) = Ca (mekv/L) x 20,04
Kalium (K)	K_mgl	mg/L	K (mg/L) = Direct
Kalium (K)	K_F_mgl	mg/L	K (mg/L) = Direct
Kalium (K)	K_mekvl	mekv/L	K (mg/L) = K (mekv/L) x 39,1
Klorid (Cl)	Cl_mgl	mg/L	Cl (mg/L) = Direct
Klorid (Cl)	Cl_mekvl	mekv/L	Cl (mg/L)= Cl (mekv/L) x 35,45
Löst organiskt kol (DOC)	DOC_mgl	mg/L	DOC (mg/L) = Direct
Löst organiskt kol (DOC)	DOC_mgl.C	mg/L	DOC (mg/L) = Direct
Magnesium (Mg)	Mg_mgl	mg/L	Mg (mg/L) = Direct
Magnesium (Mg)	Mg_F_mgl	mg/L	Mg (mg/L) = Direct
Magnesium (Mg)	Mg_mekvl	mekv/L	Mg (mg/L) = Mg (mekv/L) x 12,155
Natrium (Na)	Na_mgl	mg/L	Na (mg/L) = Direct

Natrium (Na)	Na_F_mgl	mg/L	Na (mg/L) = Direct
Natrium (Na)	Na_mekvl	mekv/L	Na (mg/L) = Na (mekv/L) x 22,99
NH4-N	NH4_N_µgl	µg/L	NH4-N (µg/L) = Direct
NH4-N	NH4_N_mgl	mg/L	NH4-N (µg/L) = NH4-N (mg/L) x 1000
NH4-N	NH4_N_µgl.N	µg/L	NH4-N (µg/L) = Direct
Nitratkväve (NO3-N)	NO3_N_µgl	µg/L	NO3-N (µg/L) = Direct
Nitratkväve (NO3-N)	NO3_N_mgl	mg/L	NO3-N (µg/L) = NO3-N (mg/L) x 1000
Nitratkväve (NO2+NO3-N)?	NO2_NO3_N_µgl	µg/L	NO2+NO3-N (µg/L) = Direct
Nitratkväve (NO2+NO3-N)?	NO2_NO3_N_mgl	mg/L	NO2+NO3-N (µg/L) = NO2+NO3-N (mg/L) x 1000
Nitratkväve (NO2+NO3-N)?	NO2_NO3_N_µgl.N	µg/L	NO2+NO3-N (µg/L) = Direct
Sulfat (SO4)	SO4_mgl	mg/L	SO4 (mg/L) = Direct
Sulfat (SO4)	SO4_IC_mgl.SO4	mg/L	SO4 (mg/L) = Direct
Sulfat (SO4)	SO4_IC_mgl	mg/L SO4	SO4 (mg/L) = Direct
Sulfat (SO4)	SO4_IC_mekvl	mekv/L	SO4 (mg/L S) = SO4 (mekv/L) x 16,035
Sulfat (SO4)	SO4_mgl.SO4	mg/L	SO4 (mg/L) = Direct
Sulfat (SO4)	SO4_mekvl	mekv/L	SO4 (mg/L S) = SO4 (mekv/L) x 16,035
Sulfat (SO4)	SO4_mgl.S	mg/L	SO4 (mg/L) = Direct
Tot. org. kol (TOC)	TOC_mgl	mg/L	TOC (mg/L) = Direct
Tot. org. kol (TOC)	TOC_mgl.C	mg/L C	TOC (mg/L) = Direct
Iron (Fe)	Fe_mgl	mg/L	Fe (mg/L) = Direct
Iron (Fe)	Fe_µgl	µg/L	Fe (mg/L) = Fe (µg/L) ÷ 1000
Iron (Fe)	Fe_F_mgl	mg/L	Fe (mg/L) = Direct
Iron (Fe)	Fe_F_µgl	µg/L	Fe (mg/L) = Fe (µg/L) ÷ 1000
Silicon (Si)	Si_mgl	mg/L	Si (mg/L) = Direct
Silicon (Si)	Si_F_mgl	mg/L	Si (mg/L) = Direct
Silicon (Si)	Si_µgl	µg/L	Si (mg/L) = Si (µg/L) ÷ 1000
Abs_F 420	Abs_F420_5cm	/5cm	Abs_F 420 = Direct
Abs_F 420	Abs_OF420_5cm	/5cm	Abs_F 420 = Direct

Summarized table with all used variables from the MVM database (*Table A 1*). The table highlights original variable names, associated units and equations used to convert them into standardized formats matching SLU standards.

Appendix 2

Table A 2: Number of unique stations and samples for TOC in each period

period	n_stations	n_samples
1990-1997	54	1322
1998-2012	123	15451
2012-2024	136	19218

Overview on how many unique stations and number of samples in the dataset used for the results on TOC in each period (*Table A 2*)

Table A 3: Number of unique stations and samples for CDOM in each period

period	n_stations	n_samples
1990-1997	54	1322
1998-2012	123	15406
2012-2024	133	19191

Overview on how many unique stations and number of samples in the dataset used for the results on CDOM in each period (*Table A 3*)

Table A 4: Number of unique stations, samples, 25th,50th and 75th percentile for sVISa in each period

period	n_stations	n_samples	p25	median_sVISa	p75
1990-1997	54	1322	0.01192231	0.01606677	0.01940383
1998-2012	123	15406	0.01456052	0.01853874	0.02152730
2012-2024	133	19191	0.01367142	0.01766792	0.02027892

Overview on how many unique stations number of samples in the dataset used for the results on sVISa in each period with its 25th, 50th and 75th percentiles (*Table A 4*).

Table A 5: Number of unique stations, samples, 25th,50th and 75th percentile for $OMCD_{5.6}$ in each period

period	n_stations	n_samples	p25	median_$OMCD_{5.6}$	p75
1990-1997	54	1322	-8.271222e-06	-6.618456e-06	-5.373542e-06
1998-2012	123	15451	-8.169491e-06	-6.919758e-06	-5.864811e-06
2012-2024	136	19240	-7.367244e-06	-6.503881e-06	-5.613867e-06

Overview on how many unique stations number of samples in the dataset used for the results on $OMCD_{5.6}$ in each period with its 25th, 50th and 75th percentiles (*Table A 5*).

Appendix 3

Q-Q plots on the four key water chemistry variables to assess whether their data is normally distributed or not. *Figure A 1* displays TOC data, which shows moderate deviations from normality, particularly in the upper tail, indicating slight right-skewness. *Figure A 2* displays CDOM data, which also shows deviations in the upper tail. *Figure A 3* displays sVISa data, who additionally indicates deviations from normality, not as pronounced as previous variables, but the upper tail highlights a slight right-skewness. *Figure A 4* displays $OMCD_{5.6}$ data, which is the variable showing most similarities to a normal distribution, though minor deviations are visible. These plots support the choice of non-parametric statistical methods in the analysis.

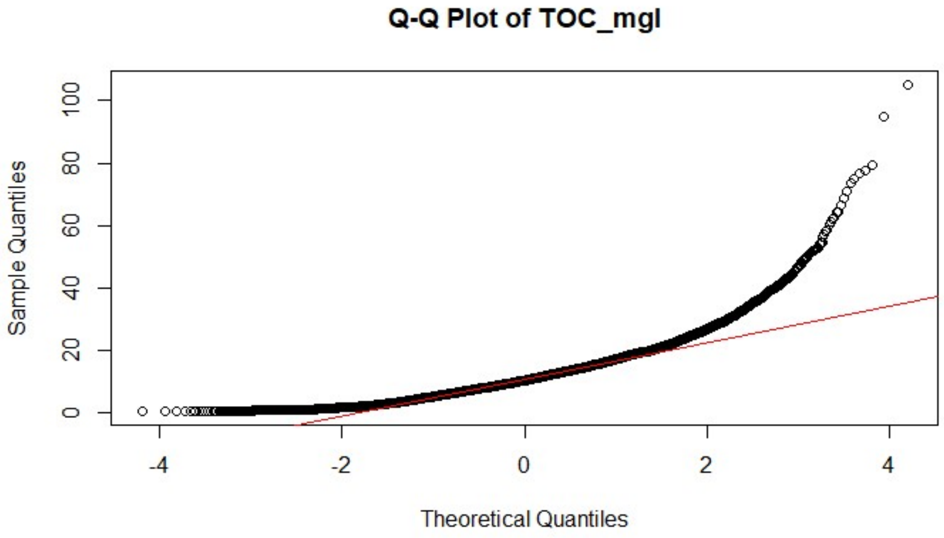


Figure A 1: Q-Q plot comparing the TOC data to a normal distribution

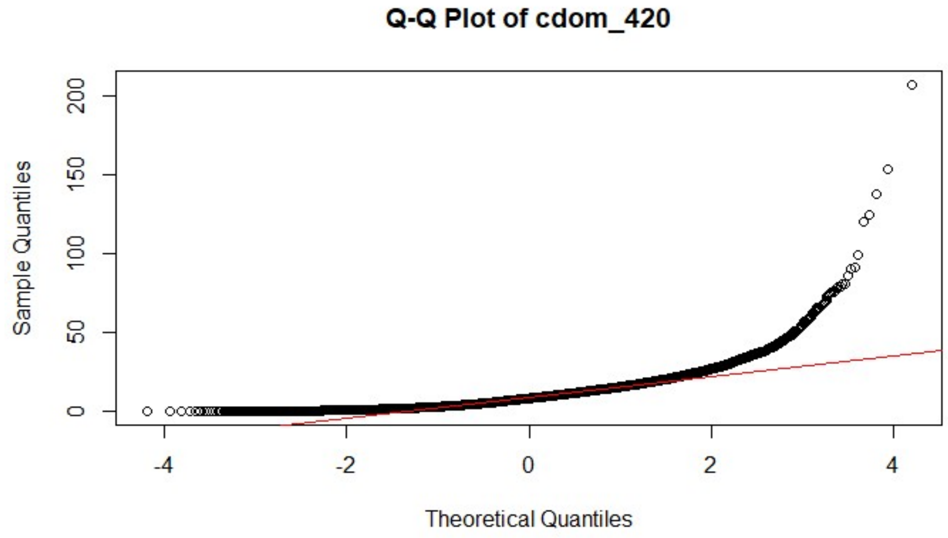


Figure A 2: Q-Q plot comparing the CDOM data to a normal distribution

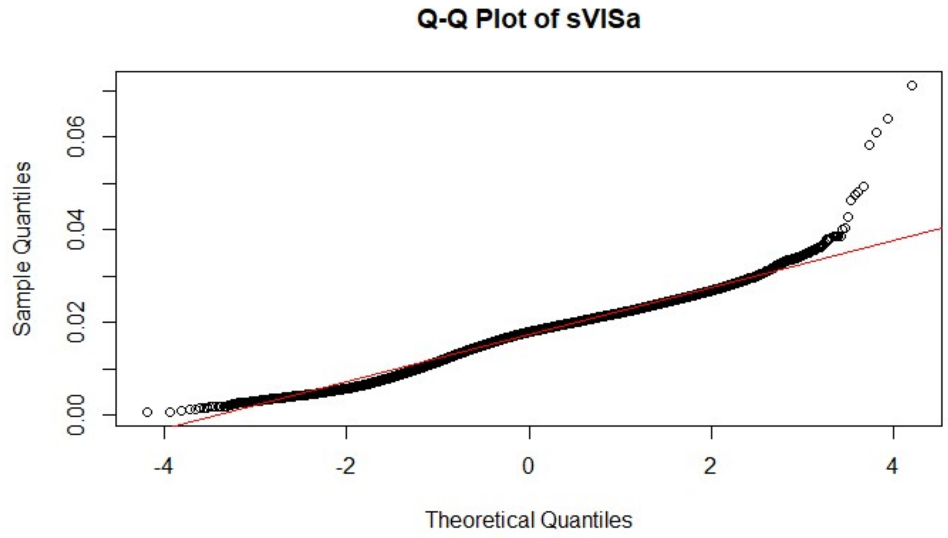


Figure A 3: Q-Q plot comparing the sVISa data to a normal distribution

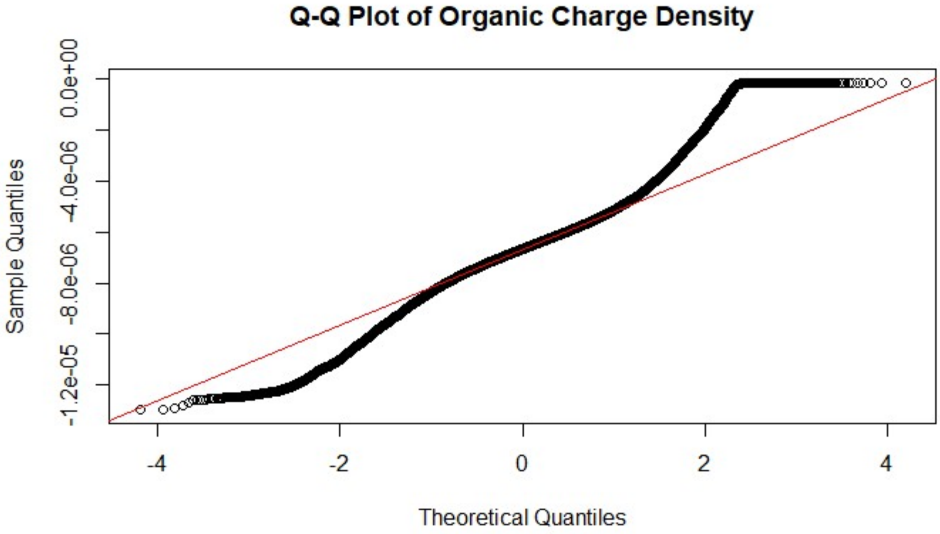


Figure A 4: Q-Q plot comparing the $OMCD_{5.6}$ *data to a normal distribution*

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