RESEARCH ARTICLE

Seasonally variable interactions between dissolved organic matter and mineral particles in an agricultural river

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Abstract

Streams and rivers form an important link in the global carbon cycle by transporting and transforming large amounts of carbon imported from terrestrial ecosystems to the oceans. Since streams in agricultural areas often experience increased concentrations of suspended mineral particles from soil erosion, they are important sites where dissolved organic carbon (DOC) may be adsorbed to particles and retained in the sediment. As the extent of adsorption varies with the molecular composition of dissolved organic matter (DOM), which is seasonally variable, we expect also the fraction of organic material that adsorbs to mineral particles to fluctuate over time. We sampled the agriculturally impacted River Fyrisån (Sweden) monthly during 1 year, and measured DOC concentration and DOM composition based on several optical properties. At each sampling occasion, we estimated the potential for adsorption by exposing the samples to a reference clay. The potential for adsorption was greatest when riverine DOM had the most terrestrial character, as this fraction of the DOM pool was selectively adsorbed to clay surfaces. The extent of adsorption was negatively related to the concentration of base cations, most notably calcium. We suggest that the observed relationships between the potential for adsorption, DOM composition and base cations are linked by discharge. A bioavailability test at one sampling occasion suggested that DOM remaining after exposure to clay particles was more biodegradable. This implies that adsorption may alter the degradation potential of DOM remaining in solution, which could have far reaching effects on the fate of organic carbon.

Keywords Dissolved organic carbon · Adsorption · Seasonality · River

Introduction

The inland water continuum transports large amounts of carbon from terrestrial to marine systems, and is additionally an important site for the transformation of carbon (Cole et al. 2007). A recent estimate suggests terrestrial export of 5.1 Pg C yr^{-1}, out of which only 0.95 Pg C yr^{-1} reaches the oceans (Drake et al. 2018). The majority of terrestrial input of dissolved organic carbon (DOC) is thus removed by microbial and/or photochemical degradation (Molot and Dillon 1997; Algesten et al. 2003), resulting in substantial emissions of CO_2 (Raymond et al. 2013) and CH_4 (Bastviken et al. 2011) to the atmosphere, or is re-directed and stored in the sediment (von Wachenfeldt and Tranvik 2008). Global estimates of carbon burial rates in freshwater sediments vary

between 0.2 and 6 Pg C yr^{-1} for lakes, ponds and reservoirs (Cole et al. 2007; Tranvik et al. 2009), and up to 1.6 Pg C yr^{-1}, if sedimentation in floodplains is also included (Regnier et al. 2013). The large uncertainty in these values also stems from an uneven geographic coverage, with a bias towards data from northern latitudes, and the value of 0.6 pg C yr^{-1} is most commonly used, in spite of the uncertainty (Drake et al. 2018; Regnier et al. 2013). One mechanism by which organic carbon can be directed to the sediment is adsorption to mineral particles and subsequent settling. Understanding the processes and conditions related to carbon burial, together with geographically representative data on carbon burial rates, is necessary to improve our understanding of the carbon cycle and to constrain its fluxes and stocks on a global scale.

The process of dissolved organic matter (DOM) adsorption is relatively well studied in soils, estuaries and marine systems (e.g. Hedges and Keil 1999; Kaiser et al. 1996; Kalbitz et al. 2005; Keil et al. 1994), but has received less attention in inland waters. High sediment loads do

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occur in certain situations, and especially running waters can carry large amounts of suspended mineral particles (Hay et al. 1998). Examples include land clearance and land use change, leading to erosion and eroded particles ending up in the water (Walling and Fang 2003), river bank erosion, whether from natural causes or navigation-induced wave erosion (Gabel et al. 2017) and permafrost thaw (Lafrenière and Lamoureux 2019), e.g. retrogressive thaw slumps, where melting ground ice leads to the collapse of the land surface, which increases the sediment load in nearby streams and rivers (Kokelj et al. 2013). Streams draining an agricultural landscape may be the most prevalent systems that experience high sediment loads. These streams therefore present particularly interesting study cases for the adsorption of DOM to mineral particles. Agricultural practices often cause soil erosion, so that mineral particles end up in neighbouring ditches and streams (Bakker et al. 2008), especially at high runoff (Glendell and Brazier 2014). In case of heavy rainfall or floods, lack of natural vegetation results in more suspended sediment export to streams in agricultural catchments compared to forested catchments (García-Ruiz et al. 2008; Haddadchi and Hicks 2020). Once exported to streams, the eroded mineral particles might serve as a substrate for DOM adsorption.

A previous study showed that the potential for DOM adsorption to particles is widespread and highly variable across boreal waters, as 22–75% of the total DOC pool was removed to clay particles in batch adsorption experiments (Groeneveld et al. 2020). The fraction of DOC that could be adsorbed was related to the DOM composition of the samples, as well as water chemistry parameters (such as pH and base cations), which varied widely across the studied sites, in agreement with other studies on DOM adsorption (e.g. Day et al. 1984; Kaiser 2003; Kothawala et al. 2012; McKnight et al. 2002; Tipping 1981). While environmental characteristics and corresponding response in DOM adsorption properties vary across a broad geographical region (Groeneveld et al. 2020), it is also relevant to consider the extent to which the potential for adsorption at one site might vary over time. Seasonal variability in environmental characteristics within a single site might be more constrained than across multiple sites, which raises the question whether controls on DOM adsorption potential across a broad geographical area are comparable to the controls across a temporal scale at one site. Knowledge of the temporal variability could also help to determine whether adsorption is an important process in regulating DOM dynamics throughout the year, or whether it is likely to be more important at certain times.

For this study, we follow seasonal fluctuations in DOM composition and adsorption potential to a reference clay during the course of 1 year in the River Fyrisån. As a river draining an agricultural landscape, Fyrisån occasionally experiences high turbidity, possibly as a result of suspended sediment that is imported from the surrounding agricultural fields. Long-term monitoring data from the study site show that historically, turbidity is systematically higher in spring and autumn (Fig. S1a, Miljödata-MVM, 2020; Fölster et al. 2014). During the growing season, vegetation cover protects the soil from erosion by reducing runoff and increasing infiltration of water into the soil matrix (Gyssels et al. 2005; Durán Zuazo and Rodríguez Pleguezualo 2008). In spring, the lack of biomass in combination with snow melt may increase erosion, particularly if this coincides with tillage on the fields, while in summer, plant biomass helps to hold the soil together. In autumn, after the end of the growing season, the decrease in biomass in combination with autumn rains once again makes the soil more susceptible to erosion. Total organic carbon (TOC) for the River Fyrisån does not show a clear seasonal pattern (Fig. S1b, Miljödata-MVM 2020), but different organic carbon sources and removal processes may contribute to apparently stable riverine TOC levels at different times of the year. For example, in the period from autumn to spring, leaf litter and soil organic matter from the previous growing season may be degraded and leached from soils, while in summer, the contribution of autochthonous carbon may be greater. Together with photobleaching, this could be an explanation for the decrease in water colour (absorbance at 420 nm) during this period (Fig. S1c, Miljödata-MVM 2020). Variation in organic matter composition can be seen in long-term observations of the specific absorbance at 420 nm, which is generally higher in winter and spring, and lower in summer and early autumn (Fig. S1d, Miljödata-MVM 2020). Since we have indications from historical trends that both DOM composition and turbidity are temporally variable, we hypothesize that adsorption potential varies seasonally.

At any given time, DOM present at the river mouth prior to draining to the sea differs from the DOM imported from terrestrial ecosystems, since DOM is transformed during downstream transport. Extensive processing during transit through inland water has the potential to reduce DOM bioavailability (Catalán et al. 2016). In other rivers at similar latitudes, only 2–8% of the DOC was readily available for microbial consumption (Asmala et al. 2014; Reader et al. 2014). Since adsorption to mineral particles is one of the processes that can alter the composition of the carbon flowing downstream, we studied how adsorption affects DOM bioavailability at one time point. A study on stream DOM adsorption onto iron oxyhydroxides predicted the adsorbed DOM to be less bioavailable since it is mostly composed of aromatic fulvic acids (McKnight et al. 2002). Since adsorption to a reference clay also selectively removed aromatic compounds in boreal waters (Groeneveld et al. 2020), we hypothesize that bioavailability of the DOM

remaining after adsorption might be higher compared to that of the unaltered DOM pool.

The main aim of this study is to explore the seasonal variability in the potential for DOM to adsorb. We determined adsorption potential in monthly samples in laboratory experiments by exposing the samples to a fixed amount of clay particles. By relating the adsorption potential to DOM composition parameters and environmental variables, this study shows when or under which circumstances adsorption may be especially prevalent in the river system. In addition, we tested whether selective DOM adsorption affects bioavailability of the remaining DOM.

Methods

Site description

River Fyrisån, in the region Uppland, Sweden, was sampled at Klastorp (59°53′11.3″N 17°34′42.0″E), approximately 4 km northwest of Uppsala. The catchment area upstream of Klastorp is 1194 km^2, of which 633 km^2 (53%) is forest and 286 km^2 (24%) agricultural fields (Fig. S2). The agricultural fields are situated closer to river, while the forested areas are more towards the periphery of the catchment. Long-term averages (1999–2018, monthly samples, Miljödata-MVM 2020) show that the river is nutrient rich (51 µgL^{-1} total phosphorus and 1.8 mgL^{-1} total nitrogen) as a consequence of the prevalence of agriculture in the catchment. The river is further characterized by a mean pH of 7.6, a good buffering capacity (2.9 meqL^{-1} alkalinity), and fairly high conductivity (40 mSm^{-1} at 25 °C). On average, water temperature is 8.5 °C, oxygen concentration 9.7 mgL^{-1}, total organic carbon concentration 17 mgL^{-1} and suspended matter 9 mgL^{-1}. The catchment soils of Fyrisån are characterized by glacial and postglacial sediments with a high clay content (40–70%), which is calcium rich (10–30% CaCO$_3$) (Möller 1993).

Sampling and storage

The river was sampled once per month between April 2017 and April 2018 at Klastorp. Conductivity, pH, and water temperature were measured in situ with a field probe (Hanna HI991300). The water samples were filtered (approximately 500 mL per filter, 47 mm diameter) over pre-combusted, pre-weighed, and pre-rinsed 0.7 µm Whatman GF/F filters within an hour of sampling and stored at 4 °C in the dark for up to 2 months when the batch adsorption experiments were performed. The filters were dried at 60 °C and stored in Petri dishes in a desiccator and saved for the determination of particulate matter. Muffled 0.7 µm glass fiber filters (GF/F) were used since they hold advantages over the use of 0.2 and

0.45 µm membrane filters. The 0.7 µm GF/F filters allow for a wider and more representative fraction of the DOM pool, possibly including larger colloids. However, studies comparing the effect of filter size on DOM have shown minor effects on descriptors such as DOC concentration, δ13C, and optical characteristics (Baker et al. 2007; Denis et al. 2017; Nimptsch et al. 2014). Storage of the water samples was found to have a small effect on DOC concentration and DOM composition, which was negligible in comparison to the seasonal variation and treatment effect (see Supplementary Information, Supplementary text and Table S1).

Hydrology and meteorology

Temperature and precipitation data were obtained from the Swedish Meteorological and Hydrological Institute (SMHI, https://www.smhi.se/data/utforskaren-oppna-data/, accessed January 18, 2019) for the weather station at Uppsala airport (1.3 km from the sampling site Klastorp). Temperature was reported as the daily average and precipitation as the daily sum. Discharge data were calculated from the rating curve based on water level at a stream gauge 5 km downstream of Klastorp (www.fyris-on-line.nu). Data were collected at an hourly interval, but converted to daily averages. No other major stream branches join Fyrisån between Klastorp and the gauging station, so discharge at the station is expected to be highly representative of discharge at the sampling point. Discharge, air temperature, and precipitation are shown in Fig. 1.

Adsorption experiments

Batch adsorption experiments were performed on each of the collected water samples (once per month during a period of 13 months). On the day of the experiment, the stored water samples were filtered again over GF/F filters and subsamples taken in triplicate for measurements of DOC concentration, anions and cations, and for DOM composition by absorbance and fluorescence spectroscopy. Triplicates of 100 ml sample were transferred into 250 ml glass bottles, and 0.5 g clay (5 gL^{-1}) was added together with a magnetic stirring rod. The clay (IPT 32 "Plastic Clay", Bureau of Analysed standards, UK) consists mainly of SiO$_2$ (51.8%), Al$_2$O$_3$ (28.5%) and Fe$_2$O$_3$ (3.46%) and is composed of approximately 80% kaolinite, 10% quartz, 5% illite, 5% feldspar, and a trace of smectite (Hosterman et al. 1987). The samples were stirred for 20 h at 4–13 °C (depending on available temperature-controlled rooms during the course of the year) in the dark. Afterwards, the samples were transferred into centrifuge bottles and centrifuged for 30 min at 9000 RCF at 13 °C. The supernatant was filtered over GF/F filters and divided into subsamples for DOC
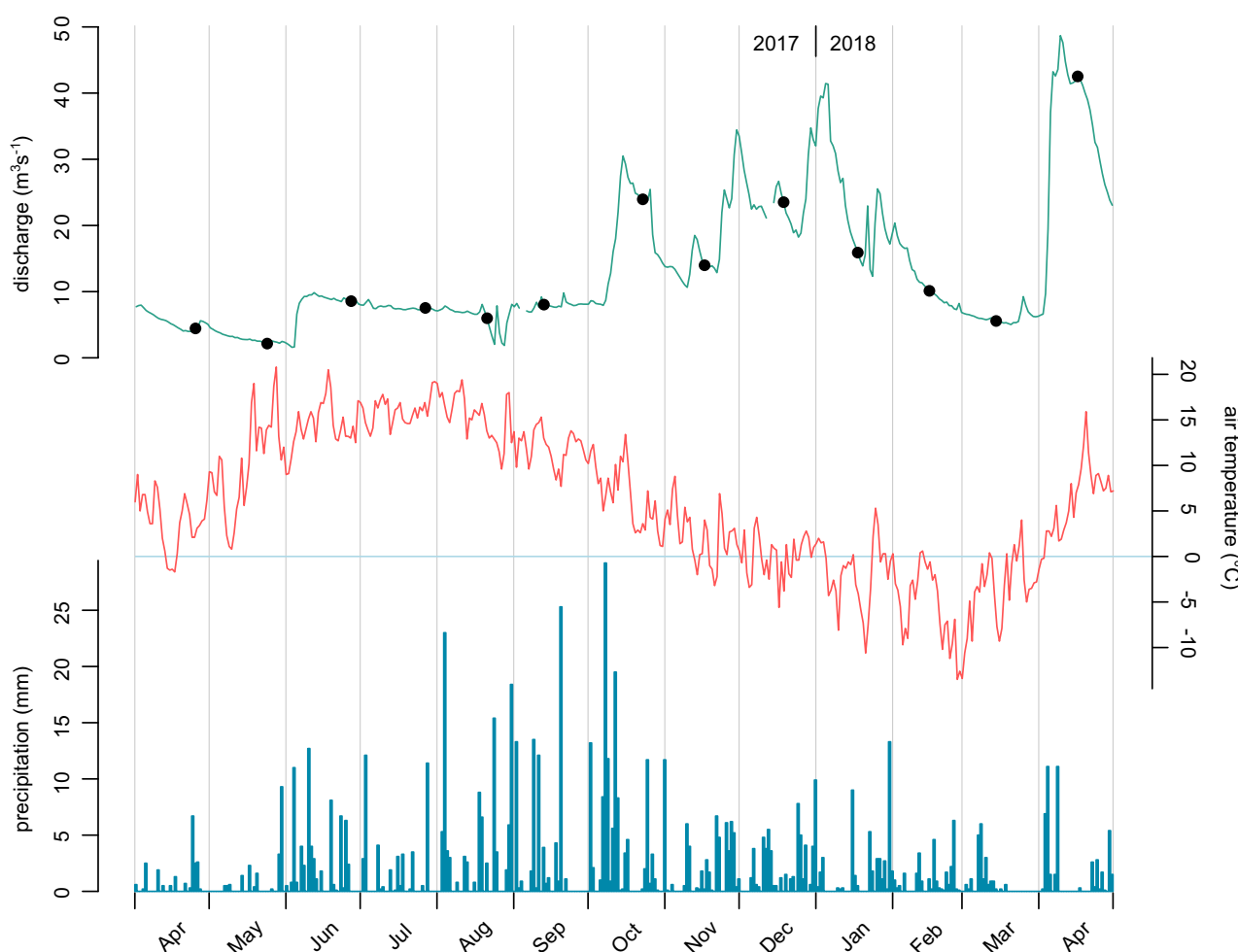
Fig. 1 Mean daily discharge, mean daily air temperature, and daily precipitation during the study period. Sampling occasions are indicated with black dots. In the temperature graph, 0 °C is indicated with a light blue line

and ion concentrations and DOM composition. Procedural blanks of 5 g L^{-1} clay in Milli-Q water were included for all analyses to measure any desorption of pre-existing organic matter from the clay. These clay blanks showed measurable DOC desorption of approximately 0.5mg C L^{-1} and an absorbance signal which at 250 nm contributed at most 7% to the absorbance spectra of the samples (Fig. S3). The concentration of particles was chosen to allow substantial changes in DOC concentration and DOM composition to be observed and to be able to compare the results with a previous study (Groeneveld et al. 2020). All plastic bottles were acid washed (5–10% HCl) and all glassware was acid washed (10% HCl) and combusted (4 h at 450 °C) before use.

Biodegradation experiment

The effect of adsorption to mineral particles on DOM bioavailability was tested on the sample from April 2018 by

comparing DOC loss during a bio-incubation for the original sample and the sample after the adsorption experiment. For this test, the sample was filtered through a 0.2 µm Supor 200 filter to reduce the bacterial abundance. Half the sample was kept as a control, while the other half was exposed to clay particles as described above, centrifuged to separate the clay particles from the water sample, and re-filtered through a 0.2 µm filter. Both the adsorption sample and the control received an inoculum (the same Fyrisån water sample filtered through a Whatman GF/C filter, pore size 1.2 µm) that comprised 10% of the total sample volume and subsamples were taken for DOC and optical measurements at the start of the incubation. Triplicate samples were incubated in 40 ml vials at 20 °C in the dark for 53 days, after which DOC and optical properties were measured again.

Water chemistry analyses

DOC concentrations were determined on a Shimadzu total carbon analyser (Shimadzu TOC-L, Shimadzu Corporation, Kyoto, Japan, as non-purgeable organic carbon (NPOC, with EDTA as a quality check), except the sample from April 2017, which was measured on a Sievers M9 total organic carbon analyser (GE Analytical Instruments, Boulder, Colorado, USA). Samples for anion and cation concentrations were filtered over pre-rinsed 0.2 μm Supor (Pall Laboratory) filters (cation samples were acidified with 20 μl 0.1 M HNO_3 per 1 ml sample), stored frozen, and measured on a Metrohm IC system (883 Basic IC Plus and 919 Autosampler Plus). Anions (F^-, Cl^-, NO^{3-}, PO_4^{3-} and SO_4^{2-}) were separated on a Metrosep A Supp 5 analytical column (150 × 4.0 mm) fitted with a Metrosep A Supp 4/5 guard column at 0.7 ml min^{-1} using a carbonate eluent (3.2 mM Na_2CO_3 + 1.0 mM $NaHCO_3$). Cations (Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) were separated on a Metrosep C4 column (250 × 2.0 mm) with a Metrosep C4 guard column with an eluent of 1.7 mM nitric acid and 0.7 mM dipicolinic acid and a flow rate of 0.2 ml min^{-1}. The GF/F filters obtained after sampling (see Sect. 2.2) were acidified with 1 M HCl to remove carbonates (Nieuwenhuize et al. 1994), dried, cut into quarters, and analysed for N and C to obtain POC/PN ratios on an Elemental Combustion System (Costech Instruments, Cernusco s/Nav., Italy), using acetanilide as a standard and EDTA to check the calibration curve.

Absorbance and fluorescence spectrometry

UV–Vis absorbance spectra (250 to 600 nm) of filtered water were measured in a 1 cm quartz cuvette using a Lambda35 UV–Vis Spectrometer (PerkinElmer Lambda 25, Perkin Elmer, Waltham, USA). The specific UV absorption coefficient at 254 nm ($SUVA_{254}$; L mg C^{-1} m^{-1}), a proxy for aromaticity (Weishaar et al. 2003), was calculated as the ratio between A_{254} and the DOC concentration (mg C L^{-1}). For analyses where A_{254} was not available, the specific absorbance coefficient at 420 nm was calculated (SA_{420}; L mg C^{-1} m^{-1}). The 250/365 absorbance ratio was used as a proxy for non-aromatic and low molecular weight compounds (Peuravuori and Pihlaja 1997), where high values indicate a low degree of aromaticity and low molecular weight, and low values denote a high degree of aromaticity and high molecular weight. The absorption spectral slope ratio S_R (the slope at 275–295 nm divided by the slope at 350–400 nm of log-transformed spectra) was used as a proxy to track changes in molecular weight, for example as a result of photochemistry or microbial alterations (Helms et al. 2008). Total absorbance (A_{tot}) was calculated as the integrated absorbance between 250 and 600 nm.

Fluorescence scans were obtained using a FluoroMax-4 Spectrofluorometer (FluoroMax-4, Jobin Yvon, Horiba, Kyoto, Japan), at excitation wavelengths 250–445 nm with 5 nm increments and emission wavelengths 300–600 nm with 4 nm increments. The excitation–emission matrices (EEMs) were corrected for instrument biases, a water blank (Milli-Q water run on the same day as the samples) and inner filter effects and normalised to Raman units (Lawaetz and Stedmon 2009; Kothawala et al. 2013). Since a clear peak shift (i.e. a shift in the location of the maximum fluorescence intensity in the peak A and peak C area) was observed in the original samples across the seasons and as a result of the adsorption treatment, we refrain from picking peaks at specific wavelength pairs and PARAFAC modelling. Instead, we focus on following the intensity and location of the fluorescence peaks in the peak A and peak C areas. These wavelength locations were determined within Ex 250 nm, Em 350–500 nm for peak A and Ex 300–400 nm, and Em 392–500 nm for peak C. In addition, three commonly used indices were calculated to serve as proxies for DOM composition (fluorescence index (FI; Cory and McKnight 2005), humification index (HIX; Ohno et al. 2002), and freshness index (FRESH; Parlanti et al. 2000)). All fluorescence corrections and calculations of the indices were performed using the FDOMcorr toolbox (Murphy et al. 2010) for MATLAB (Mathworks, Inc., Natick, MA).

Data analyses

We performed a partial least squares (PLS) analysis to determine which DOM characteristics and environmental parameters can help to explain the variability in DOM adsorption potential, expressed as the relative loss in DOC (ΔDOC%). The PLS algorithm extracts uncorrelated latent components from the multivariate data space of the explanatory variables to maximally explain the variance in the percentage DOC lost. The model loadings indicate how different explanatory variables load onto latent components. PLS analysis was especially suitable for this data set, as it is insensitive to correlations between the predictor variables. Predictor variables were checked for skewness (skewness > 2.0 and/or min./max. ratio < 0.1), but none of the variables needed to be transformed, while the response variable was arcsine transformed to increase model performance. All variables were mean centred and scaled to unit variance prior to analysis. The number of variables was reduced by taking the sum of all cations (Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) and anions (F^-, Cl^-, NO^{3-}, PO_4^{3-} and SO_4^{2-}), respectively, with their individual molarities weighted by charge. Discharge was represented as mean daily discharge during 30 days preceding the sampling

date (Q_{30}). The use of mean daily discharge for 1, 10 and 30 days preceding the sampling date gave similar results in the analysis, but the 30-day average was chosen, as this time period allows for the effect of both the water residence time in the river and transport from the catchment to the river. Seasonality was included as smoothed mean daily air temperature (T°C), using Friedman's SuperSmoother in R, which applies a bivariate regression (time vs. temperature) smoother based on local linear regression with adaptive bandwidths. The importance of predictor variables on the model is given by the variable influence on projection (VIP) scores, where VIP scores ≥ 1 were considered highly influential, $1 > VIP \geq 0.8$ moderately influential, and < 0.8 less influential (see Table S2). Cross-validation was performed to assess the predictive power of the model (Q^2Y) and random permutation testing (999 permutations) of the response variable indicated the statistical significance of the estimated predictive power (Eriksson et al. 2013). PLS modelling was done in SIMCA 16.0 (Umetrics AB, Umeå, Sweden).

Based on the results of the PLS, we constructed a multiple linear regression model that predicts the relative loss in DOC ($\Delta DOC\%$) by adsorption to clay particles using two predictor variables with high VIP and assessed their interaction. The multiple linear regression model was subsequently applied to long-term monitoring data (Miljödata-MVM 2020) to predict the potential for adsorption to clay particles on a monthly basis during the years 1993–2002 and 2017–2018 (during which all required variables were measured). The seasonal trend in predicted adsorption potential for the long-term monitoring data was visualized using a generalized additive model (GAM). GAM is a nonlinear regression technique that uses smoothed spline functions to model the relationship between two variables, while the shape of the relationship between the variables does not have to be specified a priori. As such, the model helped to discern the seasonal pattern in the predicted relative DOC loss by adsorption across the long-term monitoring data. The GAM model was applied using the mgcv package in R. Taken together, the multiple linear regression model and the GAM model can give us a more general idea of the temporal variability in adsorption capacity in the river throughout the year.

Results and discussion

Seasonal variation

Seasonal variation in DOC and discharge

DOC concentrations varied from 10.5 mgL^{-1} in May 2017 to 26.4 mgL^{-1} in November 2017 (solid circles in Fig. 2).
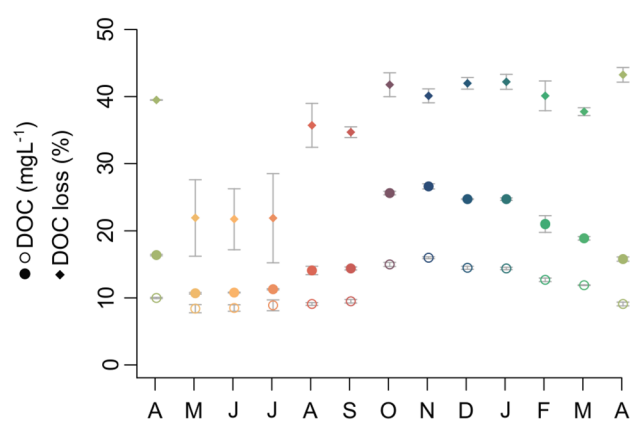

Fig. 2 Absolute and relative DOC loss between April 2017 and April 2018. Solid circles denote ambient samples, and open circles denote samples after adsorption. Diamonds represent the relative loss in DOC concentration by adsorption. The colour gradient of the data points denotes the sampling month and is consistent throughout the figures. The error bars denote standard deviations based on three replicates

A gradual change can be observed with low DOC in spring and summer and high DOC in late autumn and winter. The most abrupt change at the resolution of monthly samples was observed from September to October, when DOC increased from 14.2 to 25.4 mgL^{-1}. This coincides with an increase in discharge as a result of heavy rainfall in early October (Fig. 1). The largest peak in the hydrograph for the study period occurred in April, indicating the spring freshet. This discharge peak is not accompanied by any increase in DOC concentration. High discharge as a result of rainfall or snow melt is often associated with an increase in DOC concentrations (Hope et al. 1994). For instance, a study of seven catchments in northern Sweden showed that TOC concentrations in forested catchments correlated well with discharge during the spring flood (Laudon et al. 2004). In catchments where precipitation is dominated by rainfall, extreme events can be responsible for the majority of the carbon export (Dalzell et al. 2005). However, in catchments with snow being a substantial fraction of the total precipitation, dilution of DOC concentrations may occur at a high proportion of wetland cover, when water from the snow melt is exported over ice and frozen peat rather than through the (forest) soil (Laudon et al. 2004; Raymond and Saiers 2010). Since wetland cover in the Fyrisån catchment is small ($< 5\%$), this is not likely to be the explanation here. We suspect that DOC concentration in this system is affected by both export, which is related to discharge and snow melt, and the carbon stock in the soil, which is available for export. We speculate that the majority of the organic material that can be flushed out of soils and as overland runoff has been exported during autumn and winter, so that the snowmelt in spring mostly had a diluting effect. This mechanism has also
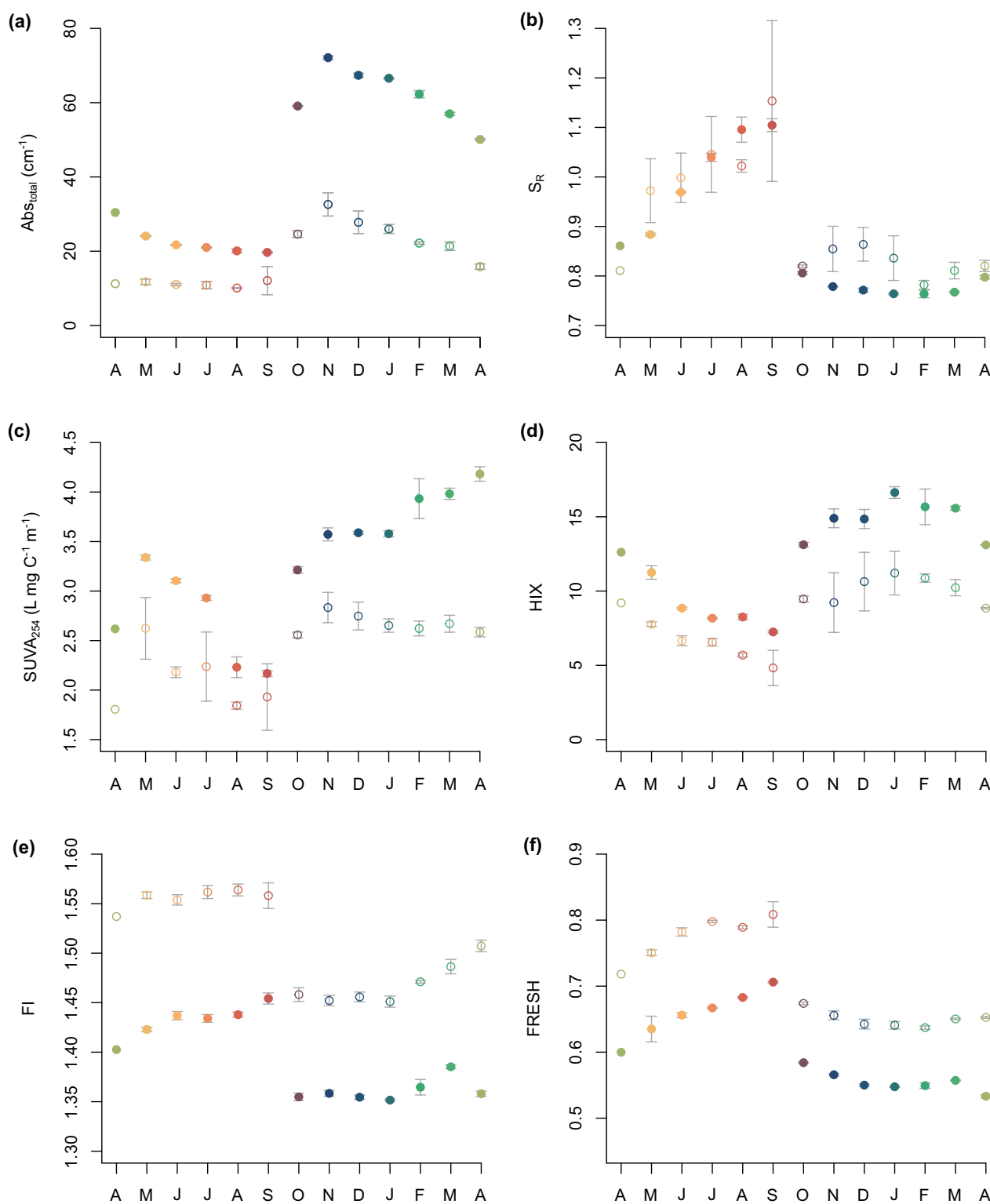
Fig. 3 **a** Total absorbance, **b** spectral slope, **c** SUVA$_{254}$, **d** humification index, **e** fluorescence index, and **f** freshness index between April 2017 and April 2018. Ambient samples are depicted as solid circles, and samples after adsorption are depicted as open circles. The error bars denote standard deviations based on three replicates (the first time point did not have replicates)

been suggested for a northern Swedish river, where TOC export was thought to be limited by the TOC pool in the soil during spring, but not in other seasons (Ågren et al. 2008).

Seasonal patterns in DOM composition

Total absorbance decreased slightly between April and September, increased sharply in October and November, and then decreased again between December and April (Fig. 3a). Not only was the DOC concentration higher in autumn and winter, but also the DOM was relatively more intensely coloured in autumn and winter than in spring and summer (as indicated by Abs_{tot} divided by DOC, not shown). The spectral slope ratio (S_R) increased between April and September (Fig. 3b), suggesting a decrease in molecular weight, possibly as a result of photochemical changes (Helms et al. 2008). It dropped sharply in October and remained approximately stable until April in the next year, suggesting an addition of high molecular weight DOM (Helms et al. 2008) during this period. $SUVA_{254}$ did not show a smooth trend throughout the seasons (Fig. 3c), although the lowest aromaticity was found in September, the largest increase occurred between September and October and the highest value was recorded in April. The humification index showed a gradual decrease between April and September, a sharp increase in October after which it remained high throughout the winter (Fig. 3d). Higher HIX values indicate the presence of more condensed molecules with lower H/C ratios and the emission spectra shifted towards longer wavelengths (Zsolnay et al. 1999), characteristic of terrestrial DOM. The fluorescence and freshness index, both indicators of newly produced, autochthonous DOM (Cory and McKnight 2005; Parlanti et al. 2000), show the opposite pattern with

a gradual increase throughout spring and summer, a sharp drop in October, and continued low values throughout autumn and winter (Fig. 3e, f). Taken together, the optical parameters give the general impression of less coloured, more autochthonous, and photodegraded material being present in spring and summer, and an increase in highly coloured terrestrial, higher molecular weight material in autumn and winter.

Following the pattern observed for the optical parameters described above, maximum fluorescence intensity also increased markedly in October and was higher in autumn and winter compared to spring and summer (Fig. 4a). Maximum fluorescence intensity, which always occurred in the peak A region (Ex 250 nm, Em 420–460 nm, Coble et al. 1990), varied between 1.8 R.U. in September and 4.4 R.U. in November. Simultaneously, a shift in the position of the maximum fluorescence intensity was observed (Fig. 4b), with higher fluorescence intensities occurring at higher emission wavelengths. The emission wavelength of the maximum fluorescence intensity varied between 432 nm in August 2017 and 456 nm December 2017 (for comparison, the maximum intensity in the peak A area was between 428 and 480 nm with a median of 456 nm in a study on > 500 lakes from all over Sweden, Kothawala et al. 2014). The fluorescence intensity in the peak C area (Ex 320–360 nm, Em 420–460 nm) displayed the same seasonal pattern as peak A. In this temporal data set, both the intensity and the position of the peak provide information about the DOM character. A higher fluorescence intensity in the peak A area indicates a larger abundance of 'humic-like' material during the period from late autumn to early spring (Fig. 4a). Fluorescence at high emission wavelengths, which characterizes the EEMs in late autumn through
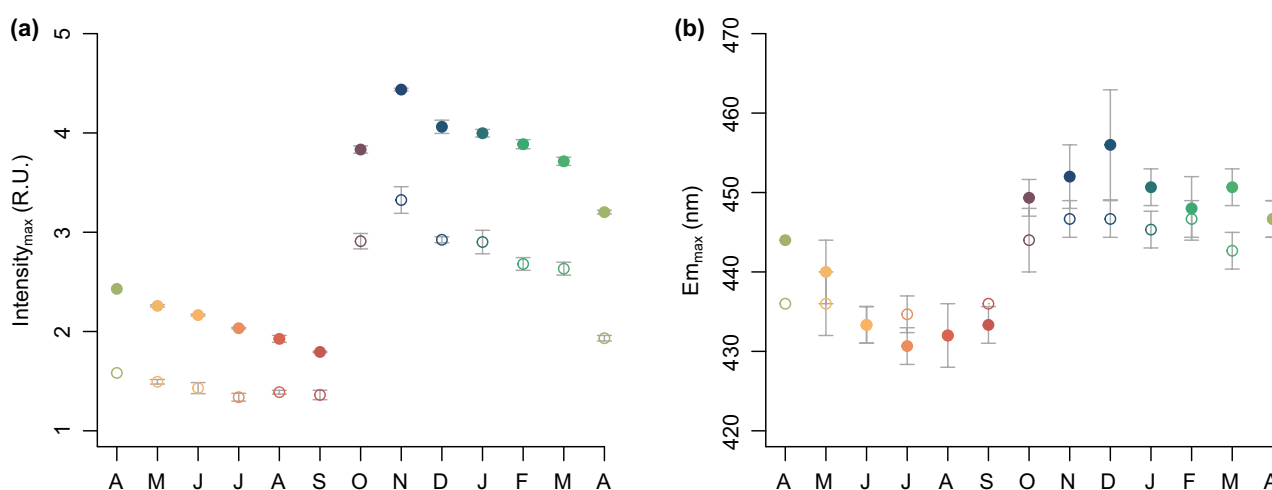

Fig. 4 a Maximum fluorescence intensity in Raman units (R.U.) and **b** emission wavelength in nm at the maximum fluorescence intensity (Em_{max}) at Ex 250 nm between May 2017 and April 2018. Solid circles denote ambient samples, and open circles denote samples after adsorption. The error bars denote standard deviations based on three replicates (the first time point did not have replicates)

early spring, originates from compounds characterized by aromatic rings, conjugated bonds in a chain structure, and carbonyl, hydroxyl, and amine functional groups (Chen et al. 2003; Senesi 1990; Zsolnay et al. 1999), as well as higher molecular weight (Her et al. 2003). These molecular structures and functional groups are typically features of terrestrial organic matter that has accumulated on land as biomass during the growing season and is brought to the soil and eventually to the river at the end of the growing season. A steady decrease is observed in some parameters (total absorbance (Fig. 3a), fluorescence intensity (Fig. 4a) and wavelength at maximum intensity (Fig. 4b)) from autumn to spring, suggesting a continued though decreasing export of terrestrial organic matter from the soils to the river during this period. Fluorescence at lower emission wavelengths, which characterizes the EEMs in late spring through early autumn, is associated with a lower abundance of these functional groups and lower molecular weight. Low emission wavelength fluorescent DOM, together with an increase in the freshness and fluorescence index and the spectral slope ratio, is indicative of autochthonous organic matter, which becomes more apparent in the DOM signature of the river in late spring through early autumn as a result of in situ organic matter production.

In summary, DOM composition as determined by absorbance and fluorescence spectrophotometry showed seasonal fluctuations with a more terrestrial signature dominating in late autumn through early spring, and a more autochthonous signature in late spring through early autumn.

Adsorption to clay particles

Terrestrial DOM is more susceptible to adsorption

Adsorption to 5 gL^{-1} mineral particles removed 2.3–10.5 mgL^{-1} DOC, which corresponds to 22–42% of the initial DOC (diamonds in Fig. 2). This temporal variation within one site covers a substantial fraction of the span across 30 widely different sites (22–75%) in a previous study (Groeneveld et al. 2020). The largest absolute and relative effects of adsorption were found between October and February, whereas the DOC was least affected between May and July. The concentration of PO_4^{3-}, which has a strong adsorption capacity and potential to compete with DOM for binding sites, was measured before and after exposure to clay particles. No systematic change in the PO_4^{3-} concentration was observed, indicating that PO_4^{3-} did not interfere with the adsorption potential of DOM to the reference clay. Adsorption selectively removed DOM of a terrestrial origin that is coloured and with high molecular weight, as indicated by a decrease in total absorbance, SUVA$_{254}$, and humification index and an increase in the spectral slope ratio and fluorescence and freshness indices (Fig. 3).

Analysis of the EEMs showed that DOM adsorption to clay particles also led to a decrease in fluorescence intensity in the humic-like region (Fig. 4a), as well as in the emission wavelength at maximum fluorescence intensity (Fig. 4b. The decrease in fluorescence intensity and the emission wavelength at maximum fluorescence intensity was most apparent for samples with an initially long emission wavelength at maximum fluorescence intensity (in late autumn through early spring, when the DOM has a more allochthonous character), and more ambiguous for samples starting out at shorter emission wavelengths (late spring through early autumn, when the DOM has a more authochthonous character). These results show that organic matter fluorescing at longer emission wavelengths is preferentially adsorbed, causing blueshift in the EEM (the peak maxima of the humic-like compounds shift to a shorter emission wavelength). This blueshift may be caused by a decrease in the number of aromatic rings, conjugated bonds in a chain structure, and carbonyl, hydroxyl, and amine functional groups (Chen et al. 2003; Senesi 1990). Even though not all fluorescent compounds can be analysed with mass spectrometry and vice versa, inferences can be made about the composition of DOM by studying correlations between long emission wavelength FDOM and unsaturated compounds identified by mass spectrometry (Kellerman et al. 2015; Stubbins et al. 2014). A previous study that used mass spectrometry to study the change in DOM composition as a result of adsorption to the reference clay found a preferential loss of low H/C and high O/C compounds, indicative of a loss of oxygen-containing functional groups (Groeneveld et al. 2020). Taken together, this suggests that the fluorescent compounds lost to adsorption contain
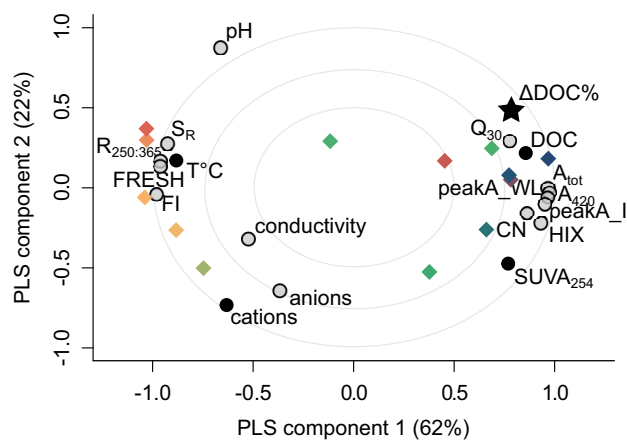

Fig. 5 PLS biplot showing the scores (with 13 samples shown as diamonds, coloured as in previous figures) and loadings (explanatory variables, circles). Highly influential explanatory variables with VIP > 1 are represented in black, and moderately influential variables with 0.8 < VIP < 1 are in grey. The response variable (ΔDOC%) is indicated with a star

functional groups that cause them to fluoresce at longer emission wavelengths and allow them to adsorb to the clay particles. These functional groups are supplied by DOM of terrestrial origin, so that the adsorption effect (% DOC adsorbed, Fig. 2) is largest in autumn through early spring. During this time, terrestrial biomass that has accumulated during the growing season finds its way into the soil and eventually gets exported to the river as terrestrial DOM.

Partial least square (PLS) analysis was performed to see which variables may cause or predict the relative change in DOC concentration after adsorption (Fig. 5). The first component explains 62% of the variation in the relative change in DOC and is mostly associated with a more aromatic, terrestrial DOM character versus a more aliphatic, aquatic-like DOM character. DOM variables indicating a more aromatic, terrestrial character with a highly positive loading on the first component are DOC concentration, total absorbance (A_{tot}), water colour (A_{420}), humification index (HIX), POC/PN index (CN), and the maximum fluorescence intensity in the 'peak A' region (peakA_I) as well as the emission wavelength of this maximum (peakA_WL). DOM variables indicating a more aliphatic, aquatic-like character with a highly negative loading on the first component are the freshness index (FRESH), fluorescence index (FI), absorbance spectral slope ratio (S_R), and absorbance ratio ($R_{250-365}$). This DOM gradient also coincides with discharge (Q_{30}, highly positive loading on the first axis) and seasonality as illustrated by temperature (T°C, highly negative loading). Taken together, we surmise that periods of high discharge, especially at the end of the growing season, result in a large input of terrestrial DOM that is susceptible to adsorption. Large inputs of reactive DOM at the end of the growing season are transported from the soils to the river. This transport flux is reflected in an increase in discharge as a result of periods with high rainfall. Based on its chemical properties, freshly imported DOM has a large potential for processing (Hutchins et al. 2017), although the influence of sunlight and microbes is decreasing at this time of year with lower temperatures and less daylight hours and light intensity. Therefore, there is a large potential for adsorption if a suitable substrate is available.

Water chemistry affects DOM adsorption

The second component of the PLS (Fig. 5) explains an additional 22% of the variation in the relative change in DOC and is associated with pH and cations. However, pH (displaying little variation with values between 6.8 and 7.5) does not show a clear univariate relationship with the relative decrease in DOC after adsorption. Cations, on the other hand, show a negative relationship with the relative change in DOC. That is, with a higher concentration of positively charged ions, a smaller proportion of the DOC gets adsorbed. Although all ions are generally correlated with each other, Ca^{2+} is likely to be the most influential in this scenario. Divalent cations are known to cause flocculation (Eckert and Sholkovitz 1976) or aid adsorption by forming cation bridges between negatively charged mineral surfaces and DOM molecules and thus reducing electrostatic repulsion (Day et al. 1984; Preston and Riley 1982; Tipping 1981). Both Mg^{2+} and Ca^{2+} were measured, but we focus here on Ca^{2+} as this has been shown to have the strongest effect on DOM removal (Eckert and Sholkovitz 1976; Preston and Riley 1982) and is the most abundant cation that we measured. At high Ca^{2+} concentrations, a smaller fraction of DOC is adsorbed onto clay particles (Fig. 6a, linear regression $R^2 = 0.53$, p-value $= 0.0044$). This might be because some of the DOM prone to adsorb has already flocculated out of solution prior to sampling, or because there is less 'adsorbable DOM' present in the system at the time of high Ca^{2+} concentrations. In the second case, our hypothesis is that relatively lower runoff from land and through the deeper soil layers leads to lower terrestrial DOM input to the river, while allowing for a relatively larger groundwater contribution, which brings in base cations. In support of this hypothesis, we find that high Ca^{2+} concentrations are associated with low discharge (Fig. 6b, linear regression $R^2 = 0.38$, p value $= 0.0196$). Base cations such as Ca^{2+} are known to decrease in concentration in streams at high discharge, while higher concentrations may be found at baseflow conditions, indicating a larger influence of shallow groundwater to the total inflow (Halliday et al. 2012; Ledesma et al. 2013; van Gaelen et al. 2014). In our study system, we suspect that a deeper flow path with groundwater inflow from the subsoils and substratum at low discharge supplies base cations. High discharge, especially at the end of the growing season, brings in substantial amounts of terrestrial DOM from surface runoff and through the upper soil horizons, while at low discharge, this terrestrial supply is diminished, as is exemplified by the positive trend observed in the relationship between discharge and $SUVA_{254}$, a proxy for the terrestrial fraction of the DOM (Fig. 6c, linear regression $R^2 = 0.24$, p value $= 0.0595$). While this relationship (which is only based on 12 data points) is statistically not significant and should therefore be considered with some caution, the trend of higher $SUVA_{254}$ with higher discharge can be observed from the plot. High $SUVA_{254}$ values are typically associated with the upper layers of the soil (Jaffrain et al. 2007), from which the DOM is exported to streams in case of a high water table or at high discharge (Schuster et al. 2008; van Gaelen et al. 2014; Wallin et al. 2015). The hypothesized connections between discharge, terrestrial input and base ion concentrations are summarized in Fig. 6d. Shallow layers of the soil export more aromatic DOM, while deeper layers
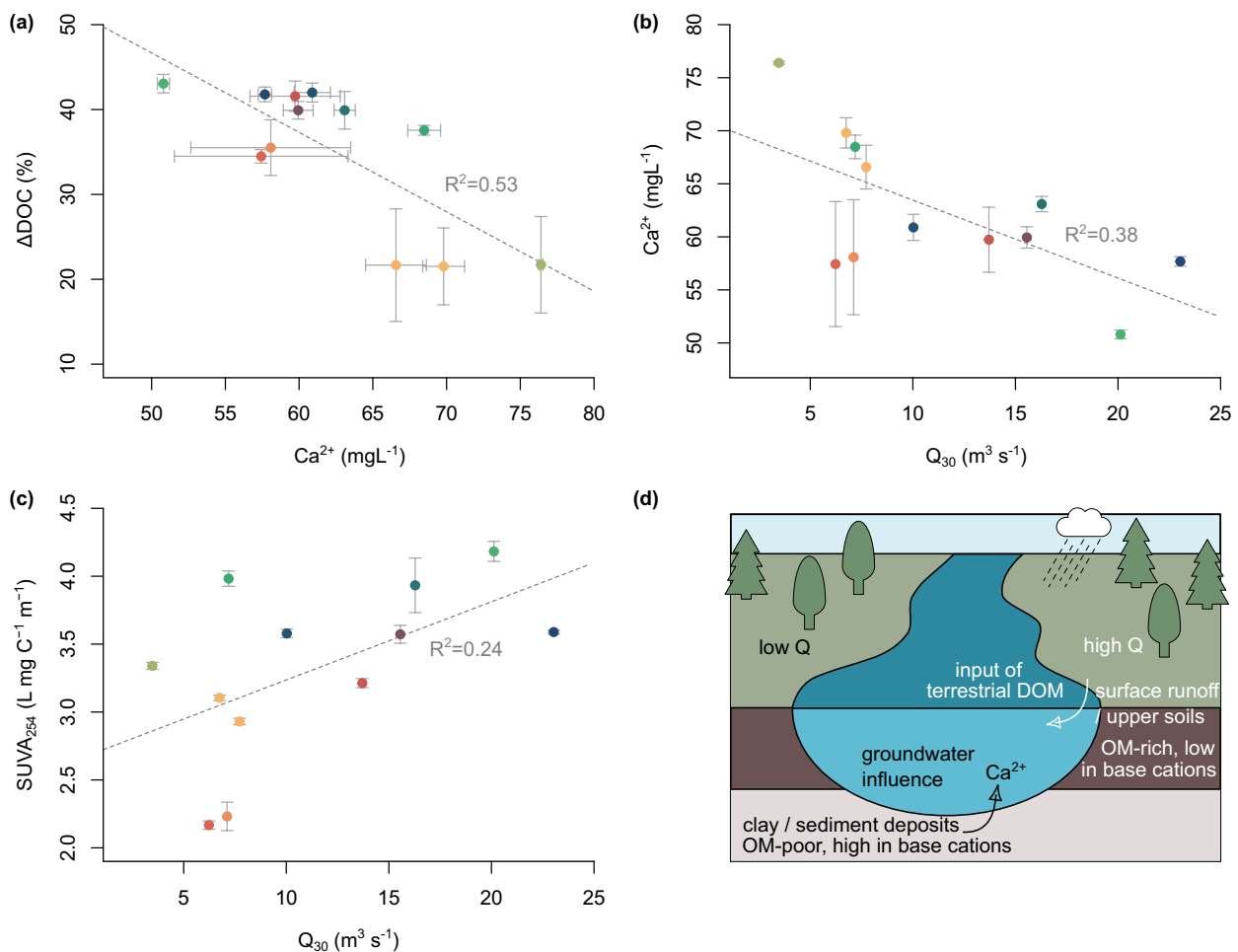
Fig. 6 **a** Relative DOC loss resulting from adsorption to clay particles relative to Ca^{2+} concentration, **b** Ca^{2+} concentration relative to discharge, **c** $SUVA_{254}$ relative to discharge and **d** conceptual sketch of the hypothesized connections between discharge, input of terrestrial DOM and base cations. The left side of the river depicts low discharge conditions, the right side high discharge conditions. In b and c, discharge is given as mean daily discharge during 30 days prior to the sampling date. Colours in a, b and c as in previous figures, the error bars denote standard deviations based on three replicates. The R^2 values are the coefficients of determination from simple linear regression (dashed line)

export higher concentrations of cations. This is consistent with the findings of Barnes et al. (2018)

Ca^{2+} and specific UV absorbance predict adsorption to clay particles

Multiple linear regression was used to investigate whether DOM composition and Ca^{2+} concentrations combined could explain the relative DOC loss to adsorption on clay particles. Specific absorbance at 420 nm (SA_{420}) was used as a proxy for terrestrial DOM, which, in the next step, allowed us to apply the model to the long-term monitoring data which does not include absorbance at 254 nm as required to calculate $SUVA_{254}$. Together, Ca^{2+} and SA_{420} explained 92% of the variation in the percentage DOC adsorbed. The equation for the model is as follows:

$$\Delta DOC\% = 163.27 - 2.29 * Ca - 335.22 * SA_{420} + 6.43 * Ca * SA_{420},$$

where Ca is the concentration of Ca^{2+} in mgL^{-1} and SA_{420} in $L\ mg\ C^{-1}\ m^{-1}$ is absorbance at 420 nm (path length = 1 cm) divided by the TOC concentration in mgL^{-1} and multiplied by 100. The significant interaction (Ca * SA_{420}) term indicates that the effect of Ca^{2+} ions varies with the level of SA_{420}. At low SA_{420}, a small change in Ca^{2+} has a strong effect on percent DOC adsorbed, whereas at higher SA_{420}, the effect of Ca^{2+} is weaker. While the model performs well for the data at hand ($R^2 = 0.92$, $n = 12$, residuals between 0.1 and 4.2 percentage points, i.e. of $\Delta DOC\%$), it is limited by the fact that the percentage DOC adsorbed was either relatively low (21.5–21.7%) or relatively high (34.5–43.0%), leaving a gap in the data between 22 and 34% DOC absorbed. Experiments on samples collected on
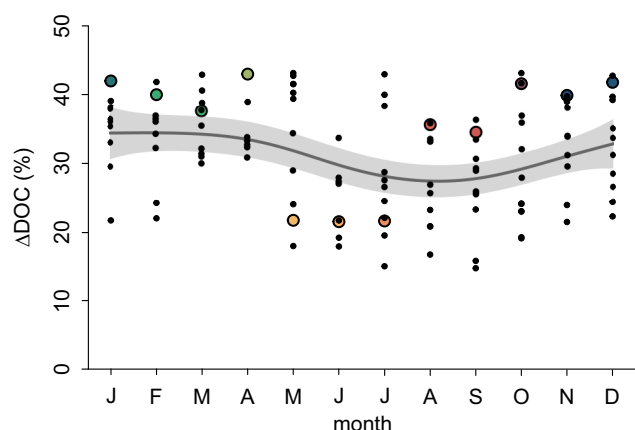
Fig. 7 DOC adsorption predicted by the multiple linear regression model, trend visualized by a GAM model (the fitted spline and its 95% Bayesian credible intervals). Black dots are predicted values based on long-term data; the larger, coloured dots are the experimentally determined values

a monthly basis did not provide a high enough resolution to capture the transitions between low and high adsorption potential that occurred between April–May and July–August, respectively. Increased temporal resolution could improve model robustness.

The model was applied to the long-term monitoring data (Miljödata-MVM, 2020) from the same sampling site (Fyrisån Klastorp) during the period 1993–2002 and 2017–2018 ($n = 145$ observations for which all required variables were available), and limited to the samples ($n = 112$) where both SA_{420} and Ca^{2+} were in the range of the data used to construct the model (SA_{420}: 0.112–0.346 L mg C^{-1} m^{-1}, Ca^{2+}: 50.7–76.4 mgL^{-1}). In the absence of DOC data, TOC was used as a proxy for DOC when calculating SA_{420}, since the values are generally very similar for this system. For the months when both TOC and DOC were available ($n = 36$), the median difference between the values was 0.65 mgL^{-1}, or 3%. The predicted percentage DOC adsorbed when exposed to the clay particles used in this study varies between 15 and 43%. The GAM model shows that the predicted potential for adsorption was generally lower in summer and early autumn and higher in winter and early spring (Fig. 7). This pattern is highly similar to the seasonal pattern in the experimentally determined potential for adsorption (coloured circles in Fig. 7), suggesting that the seasonal pattern in experimental results obtained during one year is similar to in situ conditions across different years. In River Fyrisån, turbidity is generally higher in spring and autumn (Fig. S1a). In both these seasons, increased turbidity coincides with an enhanced potential for adsorption (compare Fig. S1a and Fig. 7), suggesting that adsorption may occur in situ as well. It is important to note that the application of the GAM model to the long-term data, as

well as the experimental results of this study, are limited to the specific adsorbent used. In reality, mineral particles that end up in the river, e.g. from eroding river banks, agriculture or forestry in the catchment, or resuspended sediment, are likely to be less efficient adsorbents, although other coagulants are also likely to result in DOM removal by flocculation, such as bi- and trivalent cations (e.g. calcium, magnesium, iron, and aluminium). In the case of Fyrisån, it might be that $CaCO_3$ originating from the (post)glacial sediments deposited in the area (Möller 1993) is one of the compounds that acts as a sorbent for organic matter (Suess 1973).

Adsorption affects DOM bioavailability

We tested DOM bioavailability after adsorption for one sample (April 2018). Adsorption to clay particles decreased DOC from 18.4 to 12.6 mgL^{-1} (5.8 mgL^{-1} or 32% removed). During the bio-incubation of water that had been exposed to clay, a further 3.6 mgL^{-1} DOC (29%) was removed, compared to a 2.9 mgL^{-1} (16%) DOC loss in the control that was not subjected to any clay adsorption (Fig. 8). This result suggests that more DOC can be microbially degraded after a certain fraction of the DOM has been removed by clay adsorption. Adsorption to clay particles selectively removed DOM that was highly coloured and of aromatic, 'humic-like' character (Fig. 4), which is generally not seen as readily bioavailable (Kalbitz et al. 2003; Fellman et al. 2008; Hansen et al. 2016). Through the removal of this 'recalcitrant' material, the remaining DOM appears to have become more available, or accessible, to the microbial community. Alternatively, adsorption may have resulted in the removal of substances that hinder microbial
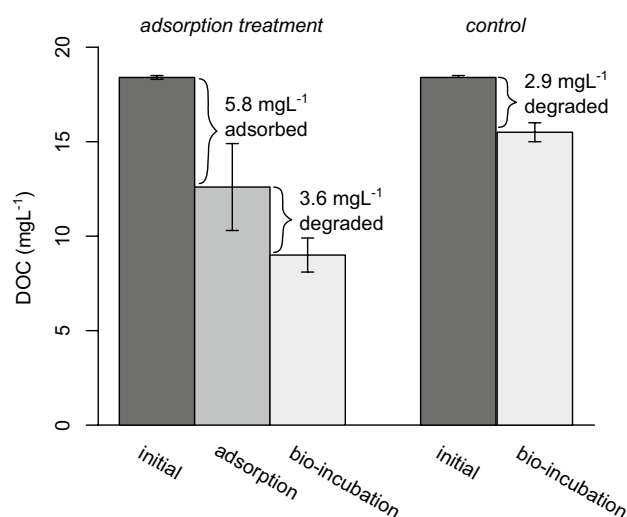

Fig. 8 DOC concentration during the bioavailability test. Error bars indicate the standard deviation around the mean of triplicates

metabolism, such as tannins that cause enzyme inhibition through complexation with microbial enzymes (Kraus et al. 2003). Increased bioavailability after selective adsorption is also illustrated by the $SUVA_{254}$ values. Selective DOM adsorption resulted in a decrease in $SUVA_{254}$ from 3.7 to 2.2 L mg C^{-1} m^{-1}. In the control, $SUVA_{254}$ increased from 3.7 to 4.1 L mg C^{-1} m^{-1}during the bio-incubation. After adsorption to clay particles, $SUVA_{254}$ increased from 2.2 to 2.9 L mg C^{-1} m^{-1} during the bio-incubation. This shows that adsorption to clay particles decreases $SUVA_{254}$, but that microbial degradation increases $SUVA_{254}$, which has been established by previous studies (e.g. Cory et al. 2015; Hansen et al. 2016). An increase in $SUVA_{254}$ with biodegradation was larger after adsorption compared to the control, just as more DOC was degraded after a fraction of the DOM has first been removed by adsorption to clay particles.

The results suggest that adsorption indeed increased DOM bioavailability, which has implications for the carbon budget. Adsorption is generally thought of as a way to re-direct DOC to the sediment, bound to mineral particles and thereby protected from biodegradation. If the remaining DOM (that is, the fraction that does not get adsorbed) has an increased bioavailability in comparison to the total DOM pool, enhanced biodegradation offsets part of the carbon sink caused by sedimentation. Thus, the question to what extent adsorption enhances carbon burial is not easily answered and merits further investigation. For example, the result found here is contrary to a similar study where polyvinylpyrrolidone resin was used to selectively remove coloured phenolic compounds, after which bioavailability was assessed (Mostovaya et al. 2016). After the pre-treatment (which decreased the average $SUVA_{254}$ from 3.5 to 2.5 L mg C^{-1} m^{-1}), the remaining DOM was as bioavailable as the DOM in the control in two lakes, and less bioavailable in one lake. This suggests that removal of 'recalcitrant' DOM does not automatically lead to increase bioavailability of the remaining DOM, and that a mechanistic understanding would be required to predict bioavailability after selective DOM removal by different adsorbents. We suggest that the effect of adsorption on DOM bioavailability should be studied in more detail and in a wider context, as it likely varies with DOM composition and mineral particle characteristics.

Conclusions

The yearlong study of DOM adsorption potential in the River Fyrisån showed a strong influence of seasonality. DOC concentrations were lower in late spring and summer and higher in late autumn and winter. Optical measures of DOM composition showed that DOM was less coloured, more autochthonous and photodegraded in spring and summer, and more intensely coloured, terrestrial, of higher molecular weight material in autumn and winter. Exposure to clay particles at a concentration of 5 gL^{-1} removed 22–42% of the DOC, which is narrower than the range found for 30 sites across Sweden (22–75%, Groeneveld et al. 2020). The percentage DOC adsorbed was highest at times when the DOM had the most terrestrial character, as it was this fraction of the DOM that was selectively removed. In addition to DOM composition, the concentrations of cations, most notably Ca^{2+}, also affected adsorption. We speculate that the relationships between adsorption, DOM composition and Ca^{2+} are linked by discharge. At high discharge, especially at the end of the growing season, substantial amounts of DOM that are prone to adsorb are brought into the river from surface runoff and through the upper soil horizons. At low discharge, especially in late spring and summer, this terrestrial supply is diminished, and groundwater contribution becomes relatively more important, bringing higher Ca^{2+} concentrations. High Ca^{2+} concentrations might have caused terrestrial DOM to be retained in the soil before export to the river or to have flocculated in situ, and we find lower DOC removal in the adsorption experiments. Based on a multiple linear regression model where Ca^{2+} and SA_{420} predict percentage DOC adsorbed, we found that the potential for adsorption in Fyrisån was generally lower in summer and early autumn and higher in winter and early spring for a 12-year data set. A bioavailability test on one sample suggested that the remaining DOM was more available to microbial degradation after a fraction of the DOM had first been removed by adsorption. Since the DOM composition, and with that the percentage DOC likely to adsorb, varies seasonally, the effect of selective DOM adsorption on bioavailability can be expected to vary as well. The process of adsorption, its effect on DOM composition, and the effect of adsorption on bioavailability in streams and lakes have hitherto received little attention and should be investigated further to improve our understanding of the carbon cycle in inland waters. Further experimental studies are important to obtain mechanistic understanding, but adsorption and its consequences should also be studied in the field to quantify the importance of this process in nature.

Declarations

Conflict of interest The authors have no competing interests to declare that are relevant to the content of this article.

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