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Flocculation of Allochthonous Dissolved Organic Matter – a Significant Pathway of Sedimentation and Carbon Burial in Lakes

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Abstract

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Inland waters receive substantial amounts of organic carbon from adjacent watersheds. Only about half of the carbon exported from inland waters reaches the oceans, while the remainder is lost en route. This thesis identifies flocculation as an important and significant fate of carbon in the boreal landscape. Flocculation reallocates organic carbon from the dissolved state into particles which are prone to settle. Thus, flocculation relocates organic carbon from the water column to the sediment.

The dissolved organic carbon (DOC), mainly originating from terrestrial sources, in a set of Swedish lakes was found to determine the extent of sedimentation of particulate organic carbon. A major fraction of the settling particles were of allochthonous origin. This implies that allochthonous DOC was the precursor of the settling matter in these lakes. The gross sedimentation was of the same magnitude as the evasion of carbon dioxide to the atmosphere.

Sunlight, especially in the photosynthetically active region, stimulated flocculation of DOC. The effect of light appeared to involve a direct photochemical reaction. Iron was involved in the flocculation but it could not be unravelled whether the iron catalyzes the flocculation or just co-precipitates with the settling matter. Microbial activity was identified as the main regulator of the flocculation rates. Accordingly, alteration of temperature, oxygen concentration and pH did not affect flocculation only indirectly, via their effects on microbial metabolism.

A comparison of fluorescence characteristics of organic matter collected in sediment trap and in the sediment surface layer revealed that autochthonous organic carbon was preferentially lost in the sediments while allochthonous matter increased. The recalcitrant nature of the flocculated matter could favour sequestration of this matter in the lake sediment. Hence, the lakes will act as sinks of organic carbon due to a slower mineralization of the flocculated matter in the sediments.

Keywords: flocculation, dissolved organic carbon, allochthonous, carbon sequestration, carbon cycle, boreal lakes

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Abbreviations

Chl <i>a</i>	Chlorophyll a
CO ₂	Carbon dioxide
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
EEM	Excitation emission matrix
PAR	Photosynthetically active radiation
PARAFAC	Parallel factor analysis
PLS	Partial least square regression
POC	Particulate organic carbon
<i>p</i> CO ₂	Partial pressure of carbon dioxide
Pg	Petagram (10 ¹⁵ g)
TOC	Total organic carbon
UV	Ultra violet

Introduction

Background

Large amounts of organic carbon enter boreal lakes. Three major fates of this organic carbon in lakes are: mineralization, sedimentation, and export via rivers. Boreal lakes are great in numbers (Downing et al. 2006) and hold a substantial amount of carbon in the water (Sobek et al. 2007) as well as in the sediment (Kortelainen et al. 2004). The carbon entering a lake with incoming water represents a size continuum of molecules, colloids, and particles (Figure 1). It is operationally divided into dissolved organic carbon and particulate organic carbon (POC) where these two fractions are separated by filtration (using filters ranging from 0.2 to 0.7 μm) (Thurman 1985, Tranvik 1998). Most of the organic carbon of natural waters consists of dissolved organic carbon (DOC) constituting 90-95 % of the TOC (total organic carbon) (Wetzel 2001, Kortelainen et al. 2006), where humic matter comprise the major part of DOC in boreal lakes (Thurman 1985, Münster and de Haan 1998).

Mass balances calculations show that as much as 30-80% of the organic carbon entering boreal rivers and lakes is mineralized or buried in sediments, and hence withdrawn from export to coastal areas (Algesten et al. 2003, Cole et al. 2007). The majority of the lakes in the world appears to be a net source of CO_2 to the atmosphere (Kling et al. 1991, Cole et al. 1994). The emission rate from a lake depends on the input as well as the internal mineralization of terrestrial organic carbon (Kling et al. 1991, 1992, del Giorgio et al. 1997, Sobek et al. 2003). Some of the DOC is mineralized in the water column by bacteria (del Giorgio et al. 1997, del Giorgio and Cole 1998) and photochemical reactions, including complete photochemical mineralization as well as photochemically enhanced bacterial mineralization (Bertilsson and Tranvik 2000). However, the bioavailability of the DOC in the water column is limited. The polymeric and colloidal substances that constitute DOC cannot be directly incorporated into bacteria, thus exoenzymes are needed before the larger molecules can be utilized (del Giorgio and Cole 1998). The loss of dissolved organic matter (DOM) increases with increasing residence time within a lake (Curtis 1998) implying a half-life of DOM of several years in lakes. Coagulation, flocculation and subsequent sedimentation may relocate some DOC from the water column into POC which end up in the sediment (Molot and Dillon 1997) and may be buried (Einsele et al. 2001).

There is little known about flocculation of DOC in lakes and flocculation is not even considered as a flux of carbon in conceptual models of carbon cycling (Hanson et al. 2004). It is poorly known to what extent sediment processes contribute to the mineralization or preservation of organic carbon imported to lakes. The rate and extent of flocculation of the dissolved organic matter will influence whether the mineralization takes place in the water column or in the sediments. Accordingly flocculation and subsequent sedimentation along with the mineralization of flocculated material may be very important for the carbon metabolism in lakes.

The microbial activity and mineralization rate in the sediments are high and the sediments often account for a higher proportion of mineralization than the water column (Den Heyer and Kalff 1998, Jonsson et al. 2001). Still, Algesten et al. (2005) report higher values for mineralization in the pelagial than in the sediments. The origin and the fate of this newly formed settling organic carbon are currently unknown. Hence, flocculated organic carbon ending up in the sediments could be buried to a greater extent than if it would have remained dissolved in the water column. Accordingly, knowledge of flocculation processes is important for the complete understanding of the carbon cycle in boreal lakes, which generally receive high loads of terrestrial dissolved organic matter and where previously no estimates or calculations of flux or pathways of flocculated carbon have been considered. This thesis emphasizes flocculation as an important link in the lake carbon cycle and a possibility of carbon sequestration in the sediments.

Estimates of transport and retention of carbon

There is no question that boreal lakes can work as carbon sinks (Molot and Dillon 1996, Algesten et al. 2003, Cole et al. 2007), both on regional and global scales (Kortelainen et al. 2004, Cole et al. 2007). Recently, Cole et al. (2007) reported that $0.75 \text{ Pg C yr}^{-1}$ evades into the atmosphere from inland waters and $0.23 \text{ Pg C yr}^{-1}$ is buried in the sediments. Consequently the lakes retain 1 Pg C yr^{-1} resulting in an estimated 1.9 Pg C yr^{-1} entering the inland waters instead of 0.9 Pg C yr^{-1} when processes in inland waters are not taken into account. Reservoirs and lakes dominate the sediment storage (0.18 and $0.05 \text{ Pg C yr}^{-1}$, respectively) and thus trapping the carbon before entering the oceans (Cole et al. 2007).

Even if lakes and impoundments cover a small area of the land surface, the organic carbon storage of all world lake sediments during the Holocene is estimated to be 820 Pg C (Einsele et al. 2001) which is a considerable amount compared to the organic carbon in terrestrial soils and biomass (1855 Pg C) (Post et al. 1982, Raich and Schlesinger 1992). Lakes, ponds and impoundments cover about 3% of the land surface (Downing et al. 2006) which is about twice as much as previous suggestions (Kalff 2001). The increase in

numbers is due to previous underestimates of small lakes and ponds (Downing et al. 2006). The immense carbon stocks in the sediments enroll lakes, especially small ones, as important carbon sinks in the landscape. Although small lakes ($< 10 \text{ km}^2$) cover one-third of the total lake area in Finland, they represent two-thirds of the carbon storage of all Finnish lakes (Kortelainen et al. 2004). Within Finland, the stock of carbon per ecosystem type is estimated to be second largest for aquatic ecosystems (19 kg C m^{-2}) after peatlands (72 kg C m^{-2}) and exceed the stocks in forest soils (uppermost 75 cm; 7.2 kg C m^{-2}) and woody biomass (3.4 kg m^{-2}) (Kortelainen et al. 2004). In this thesis, I suggest that flocculation of DOC is an important process leading to this large store of carbon.

Constituents and factors causing flocculation

Colloids

A colloid (Figure 1) is an entity large enough to have supramolecular structures and properties (e.g. a possibility of conformational changes for organic colloids or an electrical surface field for inorganic colloids) but small enough to remain in suspension in absence of aggregation (Buffle et al. 1998). Colloidal organic carbon ($1.5 \text{ nm} - 0.45 \mu\text{m}$) may comprise a substantial part of the DOM in some wetlands (Thurman 1985). Colloids exhibits Brownian motion.

Three classes of common organic aquatic compounds possess colloidal properties: rigid biopolymers, fulvic compounds and flexible biopolymers (Buffle et al. 1998). The rigid biopolymers include fibrillar polysaccharides and peptidoglycans released from plankton as exudates or cell wall components. They comprise 10-30% (depending on season of the year) of the DOM in lake surface waters (Buffle et al. 1998). Colloidal constituents that are frequently observed include: microorganisms and biological debris, iron oxyhydroxide, CaCO_3 clays, amorphous silica, polysaccharides or organic fibrillar material, gel-like organic material, soil-derived fulvic compounds (Buffle and Leppard 1995) and humic substances (Filella and Buffle 1993). Humic substances comprise a substantial fraction of the DOM. Humic substances (HS) are complex compounds that can be found everywhere in terrestrial and aquatic ecosystems and are defined as refractory decomposition products of biological material (Thurman 1985). The aquatic HS can be divided into three classes; fulvic acids (FA) which are soluble in acid and base, humic acids (HA) which are soluble in base and humin that is insoluble in base and acid. The HA is yellow to black in color, and have moderate to high molecular weight (McKnight and Aiken 1998). In general the humic acids is a major constituent (up to 70-80 %) of DOM in natural waters (Wetzel 2001). Fulvic compounds are chemically heterogeneous compounds that

comprise 40-80% of DOM in freshwaters and are often of terrestrial origin. The fulvic compounds have low molecular mass (~1 kDa) and a high charge density. Soil-derived humic acids generally have higher molecular mass and lower charge density compared to fulvic compounds.

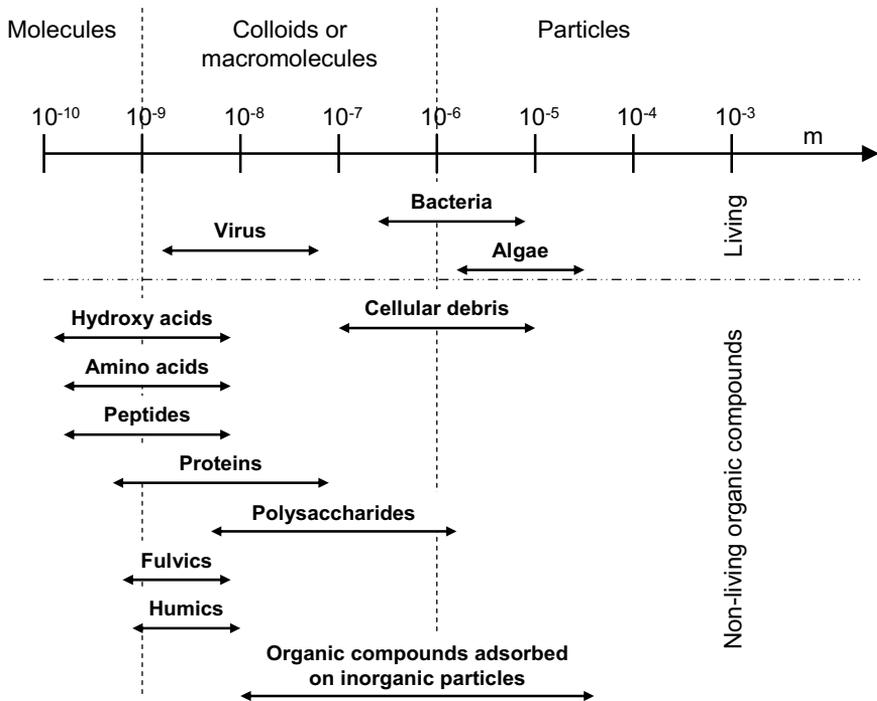


Figure 1. Size spectrum of solutes, colloids and particles. Modified from Stumm and Morgan (1996).

DOM (Buffle et al. 1998, Abbt-Braun and Frimmel 1999), including fulvic substances (Wilkinson et al. 1997), and humic substances (Filella and Buffle 1993) appear to stabilize inorganic colloids through a modification of the surface potential. In contrast, colloidal aquagenic carbon (especially chain-like structures) tend to favor the increase of coagulation and consequently the sedimentation (Wilkinson et al. 1997).

Flexible biopolymers include three main groups: aquagenic refractory matter, polysaccharides and proteins (Buffle et. al. 1998). Aquagenic refractory matter is composed of compounds produced in the water and consists primarily of degradation products of microbial cells. Compared to fulvic compounds the aquagenic refractory matter has slightly less charge density

and molar mass (~800 Da). In small rivers and lakes the aquagenic matter comprises a minor fraction of natural organic matter. However, in large lakes and the ocean the fraction can amount to 90%.

Aggregation

Aggregation is a two-step process where molecules, colloids or particles first collide and then stick together (Kepkay 1994). The collision may lead to aggregation depending on the strength of the energy barrier of their interaction including an attractive energy due to van der Waals force and a repulsive due to negative electric charges (Gregory 1989, Buffle and Leppard 1995). Providing external energy to the system by raising the temperature or stirring will overcome the energy barrier resulting in aggregation (Buffle and Leppard 1995). The formation is related to the origin of the organic matter, to the organisms producing it and conditions of deposition and resuspension (Eisma 1986). Coagulation and sedimentation of colloidal matter depends both on physical properties (e.g. size, density, compactness, rigidity) and chemical properties of the surfaces (Liang and Morgan 1990). The size of particles susceptible to flocculation processes may be initially small (colloidal range) ranging up to a size of around 1 mm (Gregory 1989). Polymers adsorbed to particles can both promote flocculation by bridging mechanisms and they can also work antagonistic as a repulsive force (Gregory 1989).

The hydrophilicity and hydrophobicity of the colloids is important for the stability of formed aggregates. Hydrophilic molecules are water-soluble (e.g. polysaccharides, proteins) and because of their solubility they are thermodynamically stable, but they can be induced to aggregate or precipitate by changing the solvency conditions (by changing temperature or ionic concentrations). In contrast, the hydrophobic compounds are not soluble in water and are thermodynamically instable but can be kinetically stable by repulsion, preventing them to form aggregates (Gregory 1989).

The aggregation of small colloids (< 0.2 μm), the most abundant particles in seawater, is common in ocean waters, leading to aggregates of several microns in size. Two morphologies of the aggregation have been described: Diffusion-limited colloid aggregation (DLCA or DLA), which is limited by the encounter rate of particles. This is a rapid formation that forms open, tenuous structures. For reaction-limited colloid aggregation (RCLA or RLA) to occur, a significant repulsive force has to be overcome by thermal activation. These aggregates form more slowly than DLCA and result in a more condensed structure (Wells and Goldberg 1993). It is not unraveled whether these processes take place in freshwater as well.

Model simulations demonstrate that colloids in river water with a size of 10 nm may coagulate and form stable aggregates with a size of 100-300 nm within 2 hours. However, particles with an initial size of 200 nm undergo slower coagulation and form larger aggregates within days (Newman et al.

1994). This suggests that the rate of increase in particle size due to aggregation decreases with increasing initial size of the precursors of the aggregation

Mechanisms of collisions

A number of mechanisms that contribute to collisions of suspended particles have been described in marine systems (Kepkay 1994) and it is likely that these mechanisms are important in freshwater as well (Figure 2). Mechanism 1-3 below have been attributed to particle formation in river systems (Newman et al. 1994).

1. Brownian motion (thermal effects): Particles in the colloid size range (less than a few μm) experience a random multi-directional motion due to the impact of solute molecules. The motion has an effect on particles in the colloidal size range.

2. Shear (flow effects): Particles follow streamlines and/or eddies which cause collision between particles. This type of collision is important for particles larger than a few μm in diameter.

3. Differential settling (gravity effects): Settling of particles at different velocities can lead to interception of particles. The density of the particles and the density of the surrounding water influence the mechanisms for collisions and settling velocities.

4. Diffusive capture: A diffusion-limited boundary layer is established around the surface of a settling particle and outside this layer the main transport mechanism of particle transport is advection. Within this layer, diffusion is of major importance, where smaller particles can be captured.

5. Surface coagulation: Colloids aggregate at the air-water interface and especially on rising air bubbles.

6. Filtration: Macroaggregates possess a porous structure with capability to capture settling particles through interception or size exclusion.

7. Microbial motility:

Swimming microbes collide with colloids inducing aggregation.

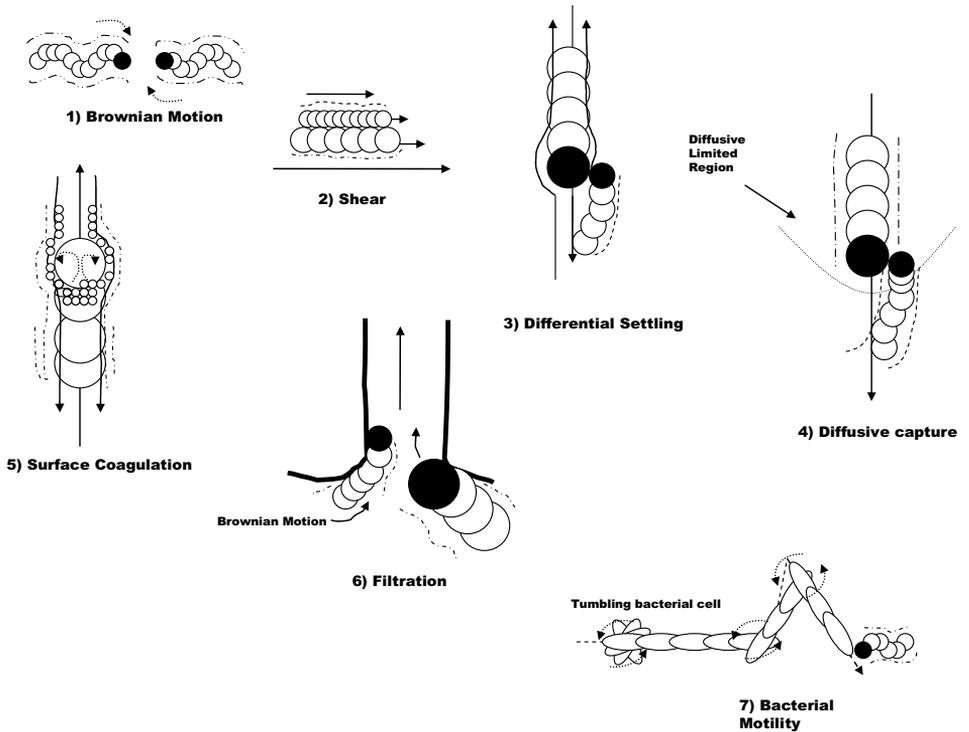


Figure 2. Collision mechanisms causing aggregation of dissolved organic matter. Modified from Kepkay (1994).

Flocs

Flocculated fine-grained sediment is a physically unstable complex heterogeneous matrix of microbial communities, organic material and inorganic material (Droppo and Ongley 1994, Droppo et al. 1997). The majority of the organic material in the floc is not differentiable but in general it consists of decaying detrital matter, diatoms and bacteria (Droppo and Ongley 1994). The fractal structure of the flocs will include void pores and the surface tension of the flocs will govern the ability to trap or replace pore water and decide the density and settling characteristics (Liss et al. 1996). Cells and extracellular fibrils have also been observed within the floc. Thus, these polymeric fibrils can work as a bridge between organic and inorganic constituents and may be of a dominant material for development and stabilization of flocculated material (Liss et al. 1996, Droppo et al. 1997). Factors affecting settling velocity of flocs are longest dimension, width and shape (Li and Ganczarzyk 1987). Settling velocity and porosity increase with floc

size while the density decreases (Li and Ganczarczyk 1987, Droppo et al. 1997). Most of the colloids are in dispersed phases and are hydrophobic by having an electric double layer which causes repulsion between particles upon approach. Hydrophilic colloids (hydrated macromolecules) stay in solution because their ionic or non-ionic polar groups are strong enough to overcome the van der Waal's cohesive force between polymer segments (Filella and Buffle 1993).

Aims of the Thesis

I hypothesize that allochthonous dissolved organic carbon in boreal lakes is flocculated, followed by sedimentation and carbon sequestration in the sediments. Moreover, I investigate the quantitative importance of these processes in the carbon cycle, as well as possible changes in their importance with a changing climate.

The following specific issues are addressed:

1. The origin of flocculated organic carbon in boreal lakes
2. The importance of flocculation in the boreal carbon flux
3. Environmental factors affecting the rate of flocculation in lake water
4. The possibility of sequestration of flocculated and subsequently relocated flocculated organic carbon in sediments
5. The role of flocculation in a changing climate

Methods

Lake description

The studied lakes are all low productive and located in two different regions of Sweden (Småland and Bergslagen). They are representative of Swedish boreal lakes, ranging in annual average DOC concentrations from 4.4 to 21.4 mg C L⁻¹. The lakes receive different input of allochthonous DOC from the catchments, which affects the DOC concentrations as well as water color and spectral properties.

Acquisition of data

To study allochthonous DOC and flocculation, sedimentation was monitored in 12 lakes in boreal Sweden distributed in two different regions (Paper I). Sediment traps were deployed for 3-week periods at four different seasons throughout a year. The gross sedimentation was measured along with characteristics of both the settling matter and lake water parameters.

To study the effect of light upon flocculation of DOC we performed an *in situ* enclosure study (Paper II). Water from a humic lake and water from an adjacent mire which drains into the lake was filtered and incubated in gas-tight UV-transparent enclosures. The enclosures were incubated under different light regimes in a clear water lake to obtain a smooth light gradient. Samples were taken initially and at the end of the experiment to analyze the change in DOC, POC, Iron (TOT-Fe), spectral properties, etc. Sediment traps were deployed to independently gauge the possible contribution of flocculation to sedimentation in the lake.

In order to discern some possible mechanisms (microbial activity, pH and oxygen regime) as regulators of flocculation we performed a series of laboratory experiments (Paper III). Lake water was filtered and incubated in gas-tight flasks and we measured particle formation, respiration, and loss of DOC.

Fluorescence characteristics were studied to determine if organic matter of a certain source is preferentially degraded and if allochthonous organic matter is sequestered in the sediments. Particles retained in sediment traps and sediment were extracted and fluorescence in the extracts was measured (Paper IV). To detect a preferential degradation the fluorescence characteristics of the sediment trap material were compared to the upper sediment layer (0-3 cm).

Quantification of particle organic carbon and its origin

Flocculated matter and sediment were collected on precombusted, pre-weighed glass fiber filters. Filters were stored frozen until analysis and freeze-dried before weighing and analysis for C, N, and Chl *a*.

To discern the origin of settling organic carbon an allochthonous end member of -27 ‰ was used which is representative for Swedish lakes (Jonsson et al. 2001). An autochthonous end member of -35‰ was used which was derived from the representative data set. The estimation of the origin was validated against a fluorescence index, i.e. the ratio of emission at 450 and 500 nm at an excitation at 370 nm. A low fluorescence index (<1.4) indicates a terrestrial origin while a high index is indicative of an endogenous origin (McKnight et al. 2001).

Measurements of mineralization and respiration

Loss of organic carbon in the sediment traps by mineralization was measured by incubation of enclosed traps and measuring of CO₂ production. Water samples were acidified and equilibrated with atmospheric air and the gas phase was measured on a gas chromatograph. Partial pressure of CO₂ in the lake water was equilibrated with atmospheric air and measured on an infrared gas analyzer.

Spectroscopical characterization

All water samples and extracted samples for spectroscopical analysis were filtered. Fluorescence intensity on the extracted and diluted DOC was measured at room tempered samples on a fluorescence spectrophotometer acquiring an excitation emission matrix (EEM).

The EEM's were corrected for Raman scattering, lamp spectral properties (McKnight et al. 2001) and inner filter effects (Mobed et al. 1996, McKnight et al. 2001). Sample EEM's were corrected on a daily basis by normalizing to integrated Raman area (excitation 350 nm) for MilliQ-water (Stedmon et al. 2003). EEM's were also corrected against an EEM from MilliQ-water.

Parallel factor analysis, PARAFAC

The excitation emission matrices (EEM) were analyzed with parallel factor analysis (PARAFAC), a multi-way dimensional mathematical approach (Bro 1997). The PARAFAC model has been shown to be well suited for analysis of multidimensional matrices of fluorescence data (Bro 1997, Stedmon et al. 2003, Stedmon and Markager 2005a). The EEM's are built from a series of emission spectrums at different excitation wavelengths. The PARAFAC model assumes that there are several independent components contributing to the feature of each EEM. In the model all EEM's are analyzed together and the linear superposition give the fluorescent intensity of each component. The intensity of the EEM's is given by (eq. 1),

$$x_{ijk} = \sum_{f=1}^F a_{if} + b_{jf} + c_{kf} + \varepsilon_{ijk} \quad (\text{eq. 1})$$

Where x_{ijk} is the fluorescence intensity for sample i at emission wavelength j and excitation wavelength k . a_{if} is proportional to the fluorescence (alternatively concentration) of component f in sample i . b_{jf} is the vector for the emission spectrum of j and component f , and c_{kf} is the vector for the excitation spectrum for component f . The PARAFAC models the number of components with emission and excitation spectra in order to minimize the sum of square of residue ε_{ijk} for the number of components (Bro 1997).

PARAFAC was applied to the measured EEM's in this study and the extracted samples (flocculated and sediment matter) were analysed in the same PARAFAC analysis. Fluorescence intensities are reported in relation to the fluorescence maxima F_{\max} for each component in the analysis (Stedmon and Markager 2005b) and normalized to DOC concentration of the extract (flocculated and sediment matter) (Wickland et al. 2007). The exact structure of each fluorophore is unknown so the concentration can not be calibrated to actual concentration. Instead, the component score obtained from the model was multiplied with the loadings from the excitation and emission and reported in Raman units, normalized to DOC concentration of the extract (Stedmon and Markager 2005b).

Results and discussion

DOC and sedimentation of carbon

Annual sedimentation of particulate organic carbon which originated from allochthonous sources was related to lake water DOC concentrations (Paper I) (Figure 3). This implies that allochthonous DOC was a precursor of the settling matter in these lakes. Accordingly, a large share of the settling matter originated from allochthonous sources as derived from isotopic signatures (Paper I).

Allochthonous DOC was shown to be a precursor for settling allochthonous organic carbon both in situ (Paper I and IV) and in experimental studies (Paper II and III). The allochthonous origin of the flocculated matter was supported by ^{13}C data (Paper I), C:N ratios (Paper I and IV), and by simultaneous loss of allochthonous DOC (Paper II and III). Furthermore, the fluorescence characteristics of the settling organic matter (Paper IV) supported the allochthonous origin.

Lake water DOC concentration was correlated to both allochthonous sedimentation of organic carbon as well as partial pressure of CO_2 ($p\text{CO}_2$) in the water (Paper I). Allochthonous DOC has been found to be the driver of the CO_2 efflux in lakes by mineralization processes making these lakes net heterotrophic (Sobek et al. 2003, Sobek et al. 2005). Hence, import of DOC from the watershed into lakes may result in lakes simultaneously acting as sources of atmospheric carbon dioxide, and as sinks via burial in the sediment.

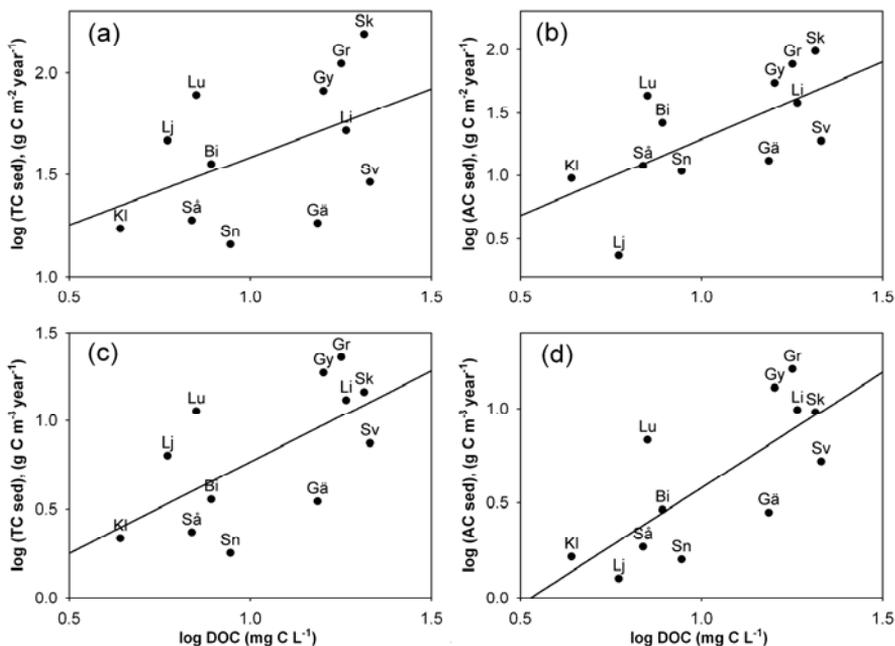


Figure 3. Relationship between annual sedimentation of organic carbon (OC) and DOC concentration in 12 oligotrophic lakes in Sweden: (a) total OC ($R^2 = 0.22$, $p = 0.13$), (b) allochthonous OC ($R^2 = 0.42$, $p = 0.025$), (c) total OC normalized to lake water depth ($R^2 = 0.41$, $p = 0.025$), (d) allochthonous sedimentation normalized to lake water depth ($R^2 = 0.58$, $p < 0.005$) (Paper I).

DOC, mainly of terrestrial origin, was suggested to be the precursor of the formed flocs in the solar exposed enclosures containing lake water from Skärshultsjön and an adjacent mire (Paper II). Up to 22 % of the DOC loss could be accounted for by particle formation in the enclosures. The remaining 78% of the DOC loss was probably caused by mineralization.

Sedimentation in Skärshultsjön was monitored from May to September in 1994 (Paper II) and the accumulated sedimentation amounted to 1.4 mg C L^{-1} while sestonic POC fluctuated with no clear trend over time. During the same period DOC was lost (2.5 mg C L^{-1}) in relation to the accumulated sedimentation of POC, further supporting DOC as a precursor of POC. Hence, if all the settling matter would originate from DOC, the settling matter could account for 56 % of the lost DOC. This is higher compared to the estimation derived from the enclosures (22 %), however, turbulence in the lake could enhance the flocculation (Figure 2) (see also: “the role of light and flocculation section” further below).

The retention time of water may also be a factor that contributes to flocculation within lakes. There was low precipitation in 1994 (Paper II) and now visible inflow of water to the lake, enhancing the retention time for this period compared to normal conditions. Hence, the DOM will reside within

the lake for an extended time period and the chance of flocculation increases. This could explain the relatively low sedimentation rates in Svarttjärn (Paper I) which had the highest DOC among the studied lakes. The short turnover time of water in Svarttjärn could have resulted in a rapid transport of the water through the lake, allowing only limited flocculation.

The export of DOC from the catchments into lakes is increasing (Clair et al. 1999, Tranvik and Jansson 2002, Hongve et al. 2004) and the DOC in Skärshultsjön almost doubled in a ten-year period 1994-2005 (Figure 4) (Paper II). The lake water color increased as well which implies that the increase was mainly due to colored DOC derived from terrestrial sources. During the same period gross sedimentation increased exponentially to the increase in DOC. Incoming solar radiation did not change throughout this period nor did the phytoplankton biomass. Accordingly, the concentration of DOC seems to have an effect on the magnitude of flocculation.

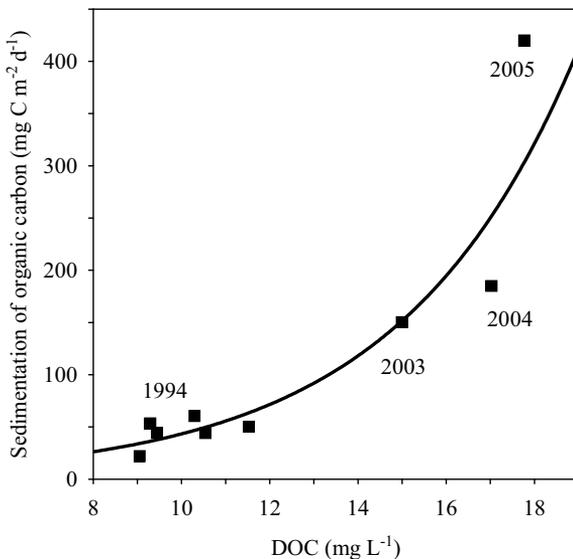


Figure 4. Sedimentation of POC vs. lake water DOC concentrations in Skärshultsjön for 1994 and 2003-2005 (Paper II).

Increasing DOC lake water concentration increased the allochthonous sedimentation in the twelve lakes (Figure 3) (Paper I). From a PLS model we could conclude that annual sedimentation of total organic carbon was correlated to chlorophyll a concentration in the lakes, a measure of phytoplankton biomass (Paper I). Sinking phytoplankton is a source of settling organic matter and is coupled to primary production (Bloesch and Uehlinger 1990,

Baines et al. 1994). However, in the boreal lakes studied here, most of the settling organic matter was allochthonous. The positive relationship between autochthonous and allochthonous matter (PLS-model) may suggest that phytoplankton play a regulatory role in sedimentation of allochthonous matter, although their quantitative contribution to sedimentation is minor. Possibly, transparent polymeric substances (TEP) from phytoplankton could bridge the colloidal and DOM fraction together, a mechanism well-known from marine waters (Passow et al. 2001, Passow 2002, Engel 2004). In the enclosure experiment (Paper II) where the light effect upon flocculation was tested, the phytoplankton did not thrive in the enclosures and could not sustain or induce the measured flocculation. All bottle experiments (Paper III) which were performed to discern heat, pH and oxygen effects upon flocculation, were incubated (Paper III) in the dark allowing no phytoplankton growth. Possibly, TEP's could have increased the aggregation and flocculation of dissolved and colloidal organic carbon further under *in-situ* conditions, as compared to the experiments (Paper III).

Carbon flux

Annual gross sedimentation was monitored in twelve lakes in an annual sediment trap survey (summer, autumn, winter, spring). The lakes were oligotrophic with different DOC and were located in two different regions in Sweden. The annual gross sedimentation (Paper I) was of similar magnitude as the evasion of CO₂ to the atmosphere (Figure 5). The loss of carbon from lakes via evasion to the atmosphere has been studied thoroughly during the recent decades (Kling et al. 1991, Cole et al. 1994, Sobek et al. 2003, Sobek et al. 2005). Our results corroborates with previous findings (Sobek et al. 2003, Sobek et al. 2005, Sobek et al. 2007) where the CO₂ efflux during the open water season is positively correlated to DOC concentration of lakes (linear regression, $R^2=0.51$, $p < 0.001$) (Paper I).

Increasing loading of DOC to the lakes also resulted in increasing sedimentation of allochthonous organic carbon. If mineralization of flocculated organic carbon that reaches the sediment is slower than the mineralization of the precursor DOC in the water column, flocculation and sedimentation may shift the fate of organic carbon in lakes from evasion to the atmosphere, to sequestration in the sediment.

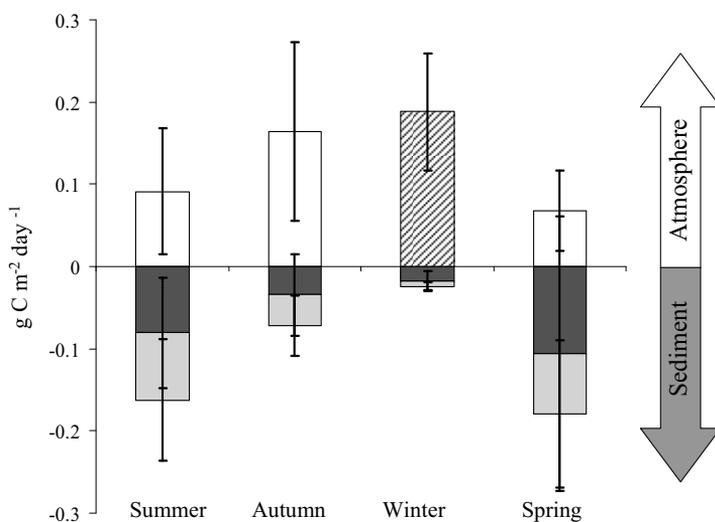


Figure 5. Carbon flux as CO₂ to the atmosphere (white bars) compared to gross sedimentation of allochthonous carbon (black bars) and autochthonous OC (grey bars). Striped bars represent the build-up of CO₂ under the ice at winter season. (Error bars denotes standard deviation) (Paper I).

Hence, in terms of the carbon budget at the lake scale, relocation of organic carbon to the sediments could counteract the epilimnetic mineralization, hence reducing the CO₂ efflux to the atmosphere (see preferential sequestration section below).

Depth integrated flocculation derived from enclosures experiments (Paper II) containing water from Lake Skärshultsjön was 14.7 mg C m⁻² d⁻¹ expressed per unit lake area down to the depth of 3.6 m (average depth of the lake). Epilimnetic photochemical mineralization in this lake has been reported to be 50 mg C m⁻² d⁻¹ (Granéli et al. 1996) and total epilimnetic mineralization 186 mg C m⁻² d⁻¹ (Sobek 2005). Thus, flocculation (Paper II) was 29% and 8 % of the photochemical and total epilimnetic mineralization respectively. Hence, flocculation is an important pathway in the carbon flux in this lake.

The role of light for the flocculation of DOC

Light has multitude effects on dissolved organic matter by e.g. changing the structure and molecular weight (Bertilsson and Tranvik 2000) or inducing cleavage into a variety of photoproducts and inorganic carbon (Mopper et al. 1991, Moran and Zepp 1997, Bertilsson and Tranvik 2000). Irradiation of DOC has also been reported to induce POC formation (Backlund 1992, Gao and Zepp 1998). To study light effects upon flocculation of allochthonous DOC we incubated both lake and mire water in UV-transparent enclosures. The enclosures were positioned in a clear water lake to obtain a smooth light gradient. Particles were formed in the enclosures in all light regimes and in the dark treatments as well. There was a relationship with flocculation and incoming level of photosynthetically radiation (PAR) (Figure 6). Simultaneously with the formation of particles, absorbance at 250 nm and DOC concentration decreased with increasing light levels.

Flocculation in the mire water was five times higher than in the lake water, while the initial DOC was only 72% higher in the mire water. The mire water had recently not been exposed to light and may therefore be more susceptible for light induced flocculation, suggesting a higher reactivity for DOC entering the lakes.

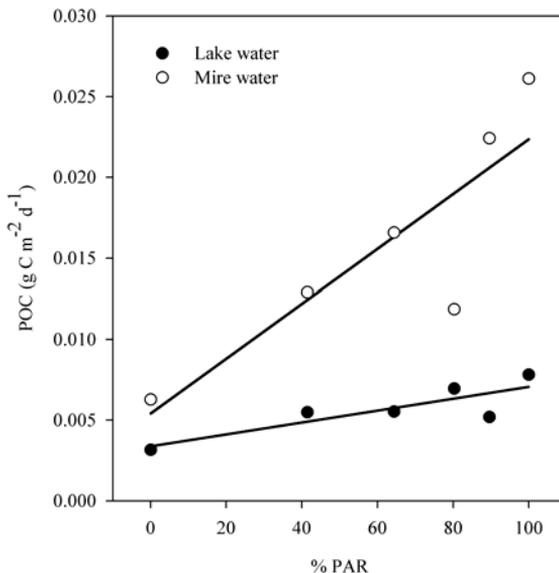


Figure 6. Particle formation in enclosures of lake ($R^2 = 0.72$, $p < 0.05$) and mire water ($R^2 = 0.74$, $p < 0.05$) exposed to different levels of light (PAR, photosynthetically active radiation) (Paper II).

Light-induced flocculation represented 70% of the flocculation integrated down to the average depth of the lake (Paper II). Still, 30% of the flocculation in this lake was independent of light. The enclosures minimized turbulence, an inducer of flocculation (Kepkay 1994) and thus we may have underestimated the flocculation. Phytoplankton did not grow in the mesocosms and their biomass could only support $\ll 1\%$ of the increase in POC.

Light, especially in the PAR region increased the flocculation (Paper II) in the enclosures. Previously light, especially in the UV-region, has been shown to induce particle formation via the Fenton's reaction involving iron (see iron section below). The observed light independent flocculation (Paper II and III) could account for a higher proportion of the overall flocculation in a deep lake and in lakes dominated by allochthonous DOC which attenuates light rapidly. Hence, mixing will not only enhance flocculation by increasing the collision frequency of the molecules (Figure 1) (Kepkay 1994, Newman et al. 1994). Mixing and mixing depth will also be important whether the molecules will be brought up to the surface and be exposed to light.

The role of iron for the flocculation of DOC

Iron in combination with light has been proposed to be a catalyst in particle formation as dissolved organic matter was irradiated (Gao and Zepp 1998). In the enclosures (Paper II), total dissolved iron settled out with the flocs as the dissolved iron decreased with increasing flocculation. The more light the enclosure received (PAR), the greater both the production of POC and the loss of dissolved iron (Paper II) suggesting either that iron played an active role as a catalyst (Gao and Zepp 1998) or was a co-precipitant. In oxic waters, Fe (III) forms a complex with DOM which stays in solution. As the Fe (III)-DOM complex is exposed to UV-light the complex dissociates into colloidal DOM and Fe (II). Fe (II) is oxidized by photochemically produced H_2O_2 and the redox cycling is complete (Fenton's reaction). Possibly, the DOM is stabilized by Fe (III) and as the complex dissociates, DOM becomes more susceptible for aggregation.

By creating either reduced or oxidized conditions in a bottle experiment (Paper III) we hypothesized an increase in flocculation under oxidized conditions by complex-binding of Fe (III) and DOC (see Paper II, Fe and Fenton reaction) Flocculation in the constant oxic or anoxic regimes did not differ. Perhaps a repeated redox cycling of Fe (II) and Fe (III) could have caused another outcome such as for the photochemically induced Fenton cycle. Irradiation of water with added Fe resulted in a substantial conversion of the iron into particles and some of this particle formation can be attributed to conversion of DOC to particulate organic carbon (POC) (Gao and Zepp 1998).

Iron oxides occur naturally, and the iron is chemically interactive with various aqueous dissolved compounds (Liang and Morgan 1990). Humic substances have been found to accumulate by co-sedimentation with iron-oxide particles (Tipping and Woof 1983) and total iron is correlated to sediment carbon burial (Kortelainen et al. 2006). Thus, iron is most probably highly involved in flocculation and sedimentation processes.

The role of temperature and microbial activity

Both heat and microbial activity have been proposed to induce particle formation in marine waters and rivers (Figure 1) (Kepkay 1994, Newman et al. 1994). To discern the effect of heat and microbial activity we performed a bottle experiment (Paper III) where increasing temperatures increased flocculation and addition of glucose increased flocculation further. The addition of glucose stimulated the bacterial metabolism and activity further by providing them an easily accessible source of carbon. Respiration followed particle formation, and respiration increased with increasing temperatures. Bacterial biomass made up a minor fraction of the formed POC (1.1-7.7%) and could not be an exclusive source of the particulate matter. Simultaneously as POC was formed, DOC and absorbance (250 nm) decreased. Thus, similar to the solar irradiated enclosures (Paper II), DOC was found to be the precursor of the flocculated matter.

Aggregation of humic substances has been suggested to be regulated by pH, especially at high concentrations of protons (Maignan 1983, Abate and Masini 2003). At high pH the humic substances become negatively charged and repulsive forces reduce the aggregation. Decreasing the pH in the experiment did not result in increased flocculation as expected (Paper III). Instead the highest flocculation occurred at in-situ pH. As pH deviated in any direction from the in situ pH the flocculation was less pronounced. Similar to the temperature and glucose experiment, formation of particles were related to microbial respiration, again pointing out the role of bacterial activity as a facilitator of flocculation. The tested pH interval in this study ranged from 3.5 to 7.3 and is within the normal range for boreal lakes.

When lake water from the humic lake Svarttjärn was incubated at different oxygen regimes (Paper III), flocculation was again related to respiration regardless of oxygen conditions. No relationship could be detected in the moderately humic lake Stora Snesharen but in this case respiration was lower compared to the more humic lake. Thus, the lower respiration and lower activity could have impeded our ability to detect flocculation.

Bacteria have previously been associated with particle formation in marine waters and are often found to be an integral part of flocculated matter (Droppo and Ongley 1994). Low salt concentration in freshwater allows a wider electrochemical double layer around colloids and fine particles, which

enhances the repulsive forces between the negatively charged humic substances. These repulsive forces will be weakened in marine waters with high concentrations of salts. Thus larger flocs will potentially be formed in marine environments. The production of extracellular mucopolysaccharides by bacteria (del Giorgio and Cole 1998) could have a bridging effect and be a plausible explanation for the flocculation observed in the experiment. Sticky polymeric fibers and extracellular polymeric substances excreted by bacteria are believed to be an important stabilizing factor for the flocs and be the dominant factor for aggregation of flocs in freshwaters (Droppo and Ongley 1994). Possibly, bacterial exudates and excretion products from bacteria bridge and stabilize the flocs of allochthonous organic carbon that were produced in the experiments presented here. Bacterial mobility (Figure 2) could also contribute.

Preferential sequestration of allochthonous organic matter in boreal lake sediments

The imported allochthonous DOM has a complex structure and consists of both low and high molecular weight compounds originating from e.g. decaying vegetation, soil, and litter (Thurman 1985, McKnight and Aiken 1998). Fluorescence has been used to characterize the source of humic matter in natural waters (Coble 1996, Mobed et al. 1996, McKnight et al. 2001, Klapper et al. 2002) as well as in sediments (Wolfe et al. 2002). The sedimentation of settling organic matter in lakes is typically studied using sediment traps. However, the material in the sediment traps may not be representative for the material being buried in the lake sediments due to selective mineralization in surface sediments. Hence, comparison of organic matter characteristics in sediment traps and surface sediments yields information about the extent of transformation in surface sediments.

Allochthonous matter was prevalent in the settling matter of twelve boreal lakes (Paper I). The dominance of the allochthonous organic matter in the settling matter increased with increasing load of terrestrial DOC to the lakes. A comparison between the sediment surface and the settling matter captured in the sediment traps revealed a decline in the contribution of autochthonous characteristics to the total fluorescence of organic matter in the surface sediments as compared to the settling matter (Paper IV). Hence, autochthonous organic carbon appeared to be preferentially degraded in the sediment. Thus, the relative contribution of allochthonous matter to the total sediment increases during sediment diagenesis, and ultimately it may dominate the sequestration of carbon in the sediment.

The lakes constituted a gradient in the relative contribution of terrestrial components to the DOC, as indicated by the DOC-specific absorbance (McKnight and Aiken 1998, Tranvik and Bertilsson 2001). Along this gradient, the allochthonous fluorescent components of extracted sediment trap matter increased (Figure 7). This corroborates the results from previous studies (Paper I, II and III) suggesting that flocculation of allochthonous dissolved organic carbon is a major source of sedimentation.

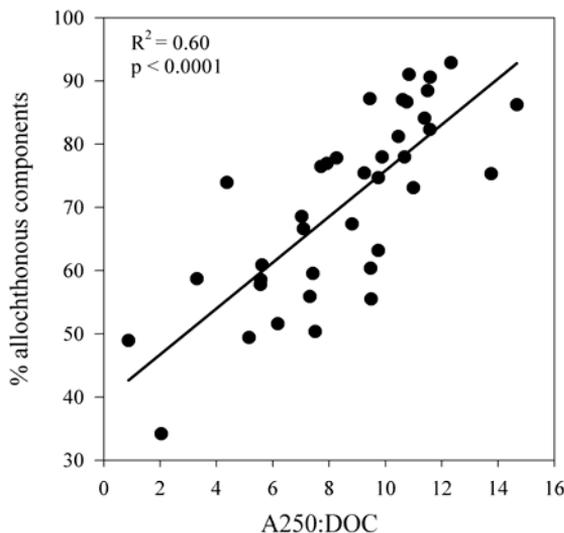


Figure 7. Relationship for A250:DOC in the lake water and the total contribution of the allochthonous components to the total fluorescence in each extracted sediment trap samples (Paper IV).

Allochthonous compounds represented a larger share of the total fluorescence in sediments than in settling matter. This suggests a preferential preservation of allochthonous organic carbon in the sediments, while autochthonous organic carbon was more rapidly degraded. Although the degradation of allochthonous DOC in the water column is substantial, facilitated by photochemical reactions, it may be more recalcitrant than autochthonous organic matter in the sediments, where photochemical reactions are absent, and anoxia hampers the activity of enzymes that are important in the degradation of complex organic matter (Bastviken et al. 2004). Thus, the quite recalcitrant nature of allochthonous compared to autochthonous matter in the sediment results in preferential sequestration of allochthonous organic carbon (Figure 8). This was also reflected in higher C:N ratios in the upper sediment layer compared to the sediment trap matter (Paper IV).

All of the studies indicate (Paper I-IV) indicate a recalcitrant nature of the settling matter and flocs originating from allochthonous DOC, and as estimated in paper II, the sediment organic carbon burial efficiency in a humic lake is 70-90%. This suggests a strong connection between import of DOC and sediment carbon burial in boreal lakes.

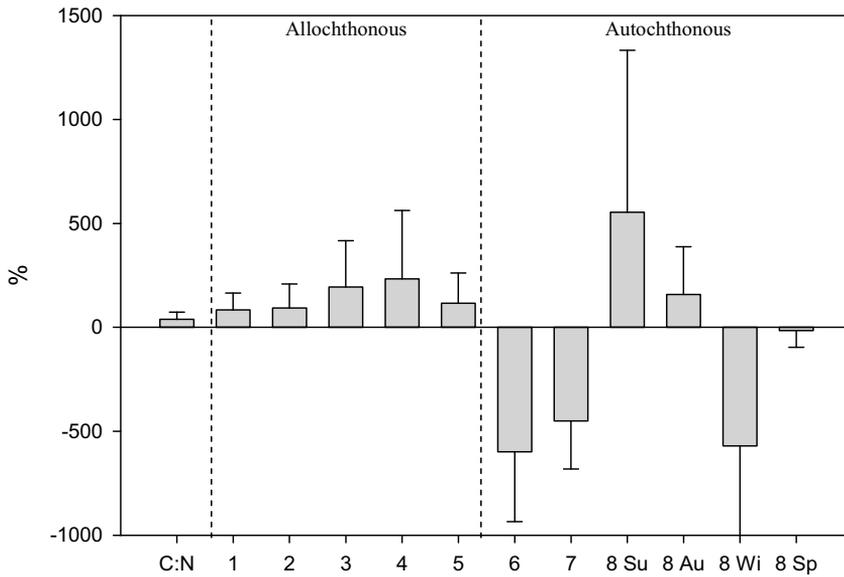


Figure 8. Difference (%) in C:N ratio and contribution of specific fluorescence components of allochthonous and autochthonous origin between extracted sediment and extracted sediment trap matter (Paper IV). The bars represent annual averages except for fluorescent component 8 where summer (Su), autumn (Au), winter (Wi), and spring (Sp) seasons are presented. Positive values indicate higher values in sediment than in traps, i.e. preferential sequestration.

Future perspectives

Climate is subject to change (IPCC 2007) and as a result of global warming, a warmer and wetter climate is to be expected. Precipitation patterns will change and precipitation is predicted to increase in the studied region (Palmer and Ralsanen 2002). During a 10-year period, DOC increased with 21% for 2152 lakes in Sweden (National Survey of Swedish Lakes; 1995, 2005). Increased export of DOC from the catchment through increased runoff could be a possible explanation (Clair et al. 1999, Tranvik and Jansson 2002, Hongve et al. 2004). As DOC increases in the lakes, this thesis suggests that flocculation will increase, along with an enhanced relocation of organic carbon from the water to the sediment. On the other hand, increasing DOC is expected to result in increased CO₂ efflux from lakes (Sobek 2003 and 2005). Therefore, a key question that remains to be elucidated is whether the elevated DOC followed by increased flocculation and subsequent sedimentation exceeds the expected increase in CO₂ emission. In conclusion of the results in this thesis a fraction of the allochthonous carbon entering the sediments is likely to be buried over a geological timescale. Thus, flocculation may counteract to increasing CO₂ evasion to the atmosphere as DOC levels rise and reduce the effect of the CO₂ efflux as climate changes.

Conclusions

This thesis demonstrates that:

1. Allochthonous dissolved organic matter, where humic matter is a major constituent, is a precursor of flocculation in the water column. The origin is supported by ^{13}C (Paper I), fluorescence (Paper I and IV), C:N ratios (Paper I), and by loss of allochthonous DOC corresponding to the appearance of POC (Paper II and III).
2. Flocculation is an important link in the sedimentation of allochthonous organic carbon, of similar magnitude as CO_2 evasion to the atmosphere (Paper I).
3. Increasing concentrations of lake water DOC enhance the sedimentation of allochthonous organic carbon (Paper I).
4. Light, especially in the photosynthetically active region (PAR), stimulates flocculation (Paper II).
5. Iron affects the flocculation process, but whether iron acts as catalyst or a co-precipitate still remains unraveled (Paper II and III).
6. Microbial activity enhances the flocculation of DOC (Paper II), although the contribution of microbial biomass to the flocs is negligible.
7. The relative increase in allochthonous fluorescence in the sediments compared to the settling matter captured in sediment traps demonstrates that autochthonous organic carbon is preferentially lost in the sediments while allochthonous matter is preserved (Paper IV).
8. The recalcitrant nature of the allochthonous flocculated matter enables burial of this newly formed particulate carbon in the sediments. (Paper I–IV).
9. DOC levels are increasing in large regions, and it is forecasted that even more DOC will be exported from catchments as climate becomes warmer and wetter. Increasing DOC will result in an increased flocculation and subsequent relocation of the organic carbon from the water column to the sediments. This relocation could counteract the expected increase in CO_2 emission derived from mineralization.

Lakes have recently been identified as “hot spots” as regulators of carbon flux from land to the ocean. Previously, lakes were considered as “neutral pipes” transporting carbon from terrestrial environments to the oceans. A lot of attention has been paid to the evasion of carbon as CO₂ to the atmosphere. There has been less focus on sedimentation processes, in particular the link between allochthonous organic carbon and sediments. This thesis highlights this link, and demonstrates how it can be made possible by flocculation of DOC. Flocculation relocates the dissolved organic carbon, which to a large extent originates from allochthonous sources, into particles which are prone to gravitoidal settling. The flocculation of allochthonous DOC enhances the role of carbon processing at the land-water interface and augments the role of lakes as regulators of carbon at the boreal landscape level. The quite recalcitrant nature of the flocculated matter favours a sequestration of this newly formed settling matter in the lake sediments. Hence, the lakes will act as sinks of organic carbon due to a slower mineralization of the flocculated matter in the sediments. Changing climate due to global warming resulting in elevated lake water DOC levels will in the future most likely enhance the role of flocculation as an important link and as a regulator of carbon in the boreal landscape.

Summary in Swedish

Flockulering av löst organiskt kol av alloktont ursprung – En viktig faktor för sedimentation och fastläggning av kol i sjöar

Ingen har nog kunnat undgå debatten om växthuseffekten och den globala uppvärmningen. Det råder numera inga tvivel om att människan ligger bakom ökningen av växthusgaser i atmosfären genom utsläpp av t.ex. koldioxid som bildas vid förbränning av fossila bränslen. Sjöar har fram tills för ett par år sedan ansetts inte ha någon inverkan på det globala kolkretsloppet. Flödet av organiskt kol mellan landområden och hav har närmare liknats vid ett rör där ingenting fastnar. Nyligen gjorda studier har visat att inlandsvattnen har en betydande roll i landskapet där ungefär hälften av det organiska kol som exporteras från land till hav försvinner antingen till atmosfären eller fastläggs i sjösedimenten. Merparten av det kol som avgår till atmosfären gör det i form av koldioxid och omfattningen är kopplad till koncentrationen av löst organiskt kol som finns i sjöarna. Mikrobiell och fotokemisk mineralisering omvandlar det lösta organiska kolet till koldioxid. Majoriteten av det organiska kol som finns i sjöar i Sverige kommer från omgivande markområden och brukar kallas alloktont organiskt kol. Typiskt för dessa kolföreningar är att de har en komplex struktur och att de har en karakteristisk whisky-liknande brun färg. Nästan allt (90-95%) av det organiska kol som finns i svenska sjöars vatten är i löst form och kan därmed inte sjunka till sedimenten utan vidare.

Den här avhandlingen visar att desto högre koncentration av organiskt kol en sjö har, desto högre var sedimentationen av organiskt partikulärt kol. En betydande andel av det organiska kol som faller till sjöbotten var av alloktont ursprung. Följaktligen har en betydande andel av det kol som sedimenterar nybildats i sjön genom att partiklar bildats av löst organiskt kol av alloktont ursprung.

Detta visar att det lösta organiska kolet har en förmåga att bilda partiklar genom så kallad flockulering. De partikulära flockarna som bildas växer sig så stora att de sjunker av sin egen tyngd. Därmed sker en omvandling och förflyttning av det lösta organiska kolet i sjövattnet till partikulärt kol som följaktligen hamnar i sjösedimentet. Det finns således en stark koppling mellan sjöars kolbalans och interaktionen mellan terrestra och akvatiska miljöer där koncentrationen av alloktont löst organiskt kol spelar betydande roll.

Solljus visade sig ha en positiv inverkan på flockulering speciellt vid våglängerna för synligt ljus. Halten av löst järn spelade också en roll vid flockuleringen där mängden järn visade sig att minska i samma omfattning som partiklar bildades. Antingen inducerar järnet flockuleringen eller så binder det bara till partiklarna som sedimenterar.

Avhandlingen visar att sedimentationen av organiskt kol i boreala sjöar är av samma storleksordning som koldioxidavgången till atmosfären. En fråga man då måste ställa sig är om det organiska kolet fastläggs i bottenarna eller om det i stället kommer att brytas ned där i stället för i sjöns vattenpelare. Tidigare studier har visat att mineraliseringen i boreala sjöar med efterföljande emission av koldioxid främst sker i vattenpelaren. Detta tillsammans med att alloktont kol bryts ner mycket långsamt i sedimentet talar för att kolet kommer att fastläggas under mycket lång tid.

Fluorescensspektra mättes på extraherat organiskt material som fångats i sedimentfällor för att reda på materialets ursprung och vilken förändring det genomgår i sedimentet. Resultatet styrker att det nedfallande materialet till stor del hade ett alloktont ursprung. Vid en jämförelse mellan materialet från sedimentfällorna och det översta sedimentskiktet visar det sig att det terrestra kolets andel ökar i sedimentet medan kol som härstämmer från växplankton bryts ner i snabbare takt.

Ett troligt framtidsscenario är att årsmedeltemperaturen kommer att öka samt att nederbörden kommer att öka i vissa områden. Den ökade nederbörden leder till en ökad avrinning som leder till att mer löst organiskt kol sköljs ut i till sjöarna. De ökade mängderna av löst organisk kol kommer resultera i att koldioxidemissionen till atmosfären kommer att öka ytterligare. Som ett motvikt till detta, som påvisas i den här avhandlingen, så kommer även flockulering följt av sedimentationen att öka. Flockulering kan därmed motverka en ökande emission av koldioxid till atmosfären. Det flockulerade organiska kolet kan potentiellt fastläggas i sedimenten och begravas där för en lång tidsperiod.

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