Effect of advective pore water flow on degradation of organic matter in permeable sandy sediment

- A study of fresh- and brackish water

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Abstract
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Keywords  Advective pore water flow, chamber experiment, CO₂, fresh- and brackish water, linear regression
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Abstract
The carbon metabolism in costal sediments is of major importance for the global carbon cycle. Costal sediments are also subjected to physical forcing generating water fluxes above and through the sediments, but how the physical affect the carbon metabolism is currently poorly known. In this study, the effect of advective pore water flow on degradation of organic matter in permeable sandy sediment was investigated in a laboratory study during wintertime. Sediments were collected from both brackish water (Askö) and from a fresh water stream (Getå Stream). In two chamber experiments, with and without advective pore water flow, the degradation of organic matter was measured through carbon dioxide analysis from water and headspace. In Askö sediments mineralization rates ranged from 3.019 - 5.115 mmol C m$^{-2}$ d$^{-1}$ and 3.139 mmol C m$^{-2}$ d$^{-1}$ with and without advective pore water flow, respectively. Those results correspond with results from earlier studies of carbon mineralization rates in sediment in the North Sea and the Baltic Sea. There were no significant differences between the two groups in the Askö sediment. In Getå Stream sediments mineralization rates ranged between 4.059 mmol C m$^{-2}$ d$^{-1}$ and 6.806 mmol C m$^{-2}$ d$^{-1}$ with and without advective flow, respectively. The mineralization rates for Getå Stream correspond with earlier studies of carbon mineralization rates in a stream in New Hampshire.
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1 Introduction

1.1 The global carbon cycle and the importance of mineralization in coastal sediment

Oceans contain the largest part of the active global carbon pool, about 38,000Gt, the total carbon pool involved in the global carbon cycle is 55,000Gt (Smith and Smith, 2001). About 1 % of the global inorganic carbon, which is easily accessible, is transformed every year through biological processes (Warfvinge, 1997). Microorganisms and particularly bacteria perform most of the mineralization in aquatic environments (Fenchel et al., 1998). Shallow coastal waters receive large amounts of the organic matter settling in the sea (Rusch et al., 2000). A large part, or almost 44%, of the world’s continental shelf is covered with permeable sediment (Riedle et al., 1972 in Rusch et al., 2000). Pore water in permeable sediment is circulated by waves and currents. Circulation of water through the sediment pores may enhance the mineralization rate of both dissolved and particulate organic matter. Thereby mineralization processes in permeable shelf sediment can have an important role in the global carbon cycle (Shum and Sundby, 1996).

1.2 Factors that can affect mineralization in sediment

There are many factors potentially affecting mineralization rates. Well known such factors are pH and temperature affecting all biological activity. Molecular oxygen (O2) is also believed to play a key role in the mineralization of organic compounds in marine sediment. It is energetically the most valuable electron acceptor used in microbial degradation (Ziebis et al., 1996). Another important factor that can affect mineralization is the supply of carbon. Many of the above factors are affected by the physical location in the sediment and by water turbulence above the sediments. The mineralization processes takes place particularly at the sediment-water interface, and the oxidation is mediated by benthic micro and macro organisms (Anderson et al., 1986). Waves generates water movements (Horne and Goldman, 1994) which bring fresh supplies of dissolved oxygen, dissolved organic matter (DOM) and particulate organic matter (POM) to the interstitial biological community. At the same time, waves remove products of community metabolism (Shum and Sundby, 1996). Hence, water movements above and through the surface sediment should enhance mineralization rates. In turn, the characteristics of these water movements are affected by water velocities induced by waves and currents and the grain size and permeability of the sediment (Huettel and Rusch, 2000).

1.3 Advective pore water flow

A phenomenon called advection occurs when waves and currents generate horizontal movements in the water (Horne and Goldman, 1994). If the sediment is permeable enough, the surface roughness in the millimeter scale can cause pressure gradients and thereby water inflow in the sediment (Huettel and Rusch, 2000). The magnitude of the advective pore water exchange depends on sediment permeability, near bottom flow velocities and on the bed topography (Precht and Huettel, 2004). When the sediment permeability exceeds 1 x 10^-12 m² the pore water flow increases (Huettel and Rusch, 2000). Scultz and Zabel (2000) describe advection as motions of water coupled to a pressure gradient. Three possible causes leads to this pressure gradient and thereby to advective flow. The first is compaction of sediment and the flow of water towards the sediment. The second cause is when warm currents at one area produce upward directed water flow, which corresponds with water flows directed downwards at another area. The last cause is when bottom water currents make pressure differences at the ripples troughs and flanks (or of any rough patches) on the sedimentary surface.
1.4 Water movements are common in large areas – potentially great large impacts of advective pore water flow on organic matter mineralization

Permeable sediment contains small amounts of organic material, but it seems like pore water circulation is an effective mechanism to bring organic material into the top sediment (Shum and Sundby, 1996). A few previous studies have indicated an increased carbon mineralization in permeable sediment subjected to advective pore water flow (e.g. Ehrenhauss et al., 2004a; Ziebes et al., 1996; Huettel and Rusch, 2000). These studies have been based on sediment from intertidal areas and oceanic waters like the North Sea, both field studies and laboratory experiments have been performed. The studies have focused on e.g. transport and decomposition of diatoms in permeable sediment, degradation of diatoms and phytoplankton, but also on fluxes of oxygen in permeable sediment. There have been measurements of nutrients in pore water, O₂ penetration depth into sediment, Chl a content in sediment and measurements of diatoms in sediment. In some laboratory studies have results from measurements in flumes and chambers affected with advective flow been compared to results from flumes and chambers without affection of advective flow. In a field study of the North Sea sediment Rusch et al., (2001) found a carbon mineralization rate of 42 – 265 mg C m⁻² d⁻¹ (3.497-22.065 mmol C m⁻² d⁻¹) during winter (Mars). Natural waves and currents had affected the sediment in their study.

However, the effect of advective pore water flow on the degradation process of organic matter and formation of carbon dioxide and methane through the mineralization process in the north Baltic Proper (brackish water) and in freshwater have, to my knowledge, not been studied. There is a lot of permeable sediment in the Baltic Sea area that can be affected by advective pore water flow (Gelumbauskaite et al., 1999). Absence of studies concerning advective pore water flow in the north Baltic Proper and in freshwater makes even small differences, of some mmol C m⁻² d⁻¹, in the mineralization rates between sediment affected by pore water flow compared to sediment not affected by pore water flow interesting. Since continental shelf sediments can play an important role in the oceanic carbon cycle may even small differences have influences on the global carbon cycle, and as mentioned above there is a lot of permeable sediment covering the world’s continental shelf. Therefore, the present study focuses on how advective flow affect organic matter mineralization rates in brackish and freshwater sediments, and to include all mineralization processes the formation of carbon dioxide and methane was used to estimate mineralization.

1.5 The aim of this study

The aim of this study was to investigate the mineralization rate in permeable sandy sediments in chambers affected by advective pore-water flow in a laboratory study during wintertime. The primary aim was to investigate if there were any differences in the mineralization rate between sediments with and without advective pore water flow. Sediment was collected both from brackish water and from a fresh water stream.
2 Method

2.1 Sediment collection

2.1.1 Sediment collection Getå Stream
Sediment was collected in the middle of January 2005 from The Getå Stream in Norrköping. The Getå Stream is situated in a pine-forest area. It is a meandering humus colored fresh water stream. The sediment was collected from meanders where the water flow was intensive and the sediment had ripples. The water temperature was 2.8°C. The water depth was 0.10 – 0.20 m. Machine washed and MilliQ-water rinsed acrylic (PMMA) cylinders with an inner diameter of 80 mm were pressed down into the sediment and the top of the chambers were plugged with stoppers. The cylinders were pulled up from the sediment and the bottoms were plugged with stoppers (Para rubber) while the cylinders were still submerged. The stoppers had been washed, leached in ethyl alcohol and stored in humic lake water before the final rinse with MilliQ-water. More water had to be added to the chambers immediately after the sediment collection was carried out, since the water was shallow at the collecting place and the water height in the chamber (i.e. the cylinder) only reached 10 cm.

2.1.2 Sediment collection Askö
The sediment collection was carried out in Mars 2005 at Sand Strand, Askö (longitude E 17° 41´04 and latitude N 58° 48´04). Askö is situated in the Trosa Archipelago south of Stockholm, Sweden. The sediment was collected at a depth of 0.80 m where the bottom had ripples. The water had a temperature of 2°C. The collection was made with same equipment as the sediment collection in the Getå stream. Askö sediment collection followed the same procedure as Getå Stream collection.

2.2 Experiment set up
In all experiments in this study, except the dye experiment with Rhodamine (see below), the degradation of organic matter was measured through carbon dioxide analysis.

The height of the sediment in the experiment was chosen according to earlier studies of the penetration depth of oxygen and algae into permeable sediment affected by advective flow in flumes and the pressure distribution at the sediment-water interface in a stirred chamber (Huettel and Rusch, 2000). Between the lid (a stopper made of Para rubber) on top of the chamber (400 mm height, 80 mm inner diameter and 90 mm exterior diameter) and the water surface was a headspace of 6-10 cm left to permit gas exchange (see Figure 1.). The water inside some of the chambers was stirred (advective pore water flow) by an acrylic horizontal disk (60 mm diameter), rotating approximately 10 cm above the sediment surface. The size of the space between the disk and the chamber walls was chosen according to earlier studies of advective water flows in chambers (Glud et al., 1996; Huettel and Rusch, 2000; Ehrenhauss and Huettel, 2004; Ehrenhauss et al., 2004a; Ehrenhauss et al., 2004b). Broström and Nilsson (1999) showed that a stirrer of small radial extent gives a constant solute concentration at the sediment surface, which is not desirable in this study and therefore stirrers of larger radius were chosen. A machine washed and MilliQ-rinsed acrylic (PMMA) axis (30cm height, 11 mm inner diameter and 15 mm exterior diameter) from each stirred chamber was operated by an electric motor (VWR Power Max Dual Shaft Mixer), to rotate the disk at 20 rounds per minute (rpm) for the Getå Stream experiment and 40 rpm for the Askö experiment. In a study of Ehrenhauss et al., (2004a) has 20 rpm been used, since 20 rpm gives a radial pressure
gradient which develop and causes advective pore water flow on smooth sedimentary surfaces. 40 rpm for Askö were used to ensure a larger radial pressure gradient. The axis was enclosed in a machine washed and MilliQ-rinsed acrylic (PMMA) tube (20cm height, 16 mm inner diameter and 20 mm exterior diameter) which was submerged in the water phase and thereby functions as water trap. In Figure 1. chambers with sediment and rotating discs can be seen. During experiments the chambers were incubated in the dark to prevent photosynthesis and at in situ water temperature (4°C).

2.2.1 Experiment set up with sediment from the Getå Stream

The experiment set up was based on 4 stirred and 4 unstirred chambers (see Figure 1.). Each chamber was filled with 8-10 cm sediment with a mixed grain size between > 8000 – < 125μm, 20 cm of water from the sediment collecting place, and 7.6 - 10.4 cm headspace. Water samples for carbon dioxide, oxygen and methane analyses were taken from all the chambers, through a tube into the water. In addition headspace samples were withdrawn from the unstirred chambers, through an injection needle. Trapped water in the sampling tube was exchanged before sampling of water. This made the samples more representative, since it homogenized the water column and decreased the gradients that may arise during the incubation. The experiment ran for 7 days. During this period samples were taken from both stirred and unstirred chambers at time intervals of 24 h for 5 days and approximately 48 h between the sixth and the seventh sampling-occasion.

In the stirred chambers samples were retrieved from the water only (due to leakage of air into the headspace upon water sampling), while both water and headspace were sampled in the unstirred chambers. To replace the withdrawn headspace and water samples in the unstirred chambers the same quantity of air from the room was injected after the samplings had been performed. To the stirred chambers the leakage of air to the chambers compensated for the reduced headspace pressure upon water sampling and thereby corresponded to the withdrawn water volume.

2.2.2 Experiment set up with sediment from Askö

The experiment set up was based on 6 stirred and 7 unstirred chambers (see Figure 1.). Each chamber was filled with 7.9 - 12.3 cm sediment (with a mixed grain size between >8000 – < 125 μm), depending on how deep the chambers could bee pushed down into the sediment. On top of the sediment was 18 cm of water from the sediment collecting place. The experiment ran for 11 days. During this time period water and headspace samples for carbon dioxide, oxygen and methane analyses were taken with a syringe from both stirred and unstirred chambers at 0, 15, 37, 61, 83, 136, 179 and 251 hours from experiment start.

The sampling procedure differs at some points from the Getå Stream experiment. Headspace samples were taken first followed by water samples at every sampling occasion. The sampled quantity of headspace and water was replaced with gas (air from the room where the chambers were placed) and water from the collecting place (water was stored in a can which was bubbled with air) after every sampling occasion. Air from the room and water from the can were sampled and analyzed to correct for additions when replacing sampled volumes.
Figure 1. Chambers with sediment, water and headspace. The axis for the rotating disc, water sampling tubes and headspace sampling needles are passed through the lids of the chambers. A block with a driving belt is placed around a block fixed at the axis; the driving belt is coupled to another block which is driven by an electric motor to rotate 20 rpm in the Getå stream set up and 40 rpm in the Askö set up.

2.3 Dye experiment

A dye experiment was conducted prior to both the Getå Stream and the Askö experiment to evaluate if advective flow would exchange pore water in sediment with a grain size of 500 - 1000µm in a stirred chamber. The experiment set up was made according to the experiment set up with sediment from Getå Stream and Askö. Dry sediment was dyed with Rhodamine dissolved in water. The water on top of the sediment was not dyed initially. The water phase in the chamber was stirred (20rpm) and the upwelling dyed pore water from the sediment (dyed) was observed. The observations were made to get knowledge about at what rate water penetrated into the sediment. The dye experiment ran as long as upwelled dyed water was visible. The experiment showed that the highest water pressure was generated along the outer rim of the chamber where water was forced into the sediment. The pressure was lowest at the centre of the chamber and Rhodamine dyed water was forced out of the sediment surface as a convolution (or spiral) which can be seen in Figure 2. and Figure 3.
2.4 Sediment and water characterizations

Analyses of sediment characterizations were; porosity, grain size, water content and organic matter content. Water content and organic matter content (Loss on ignition, Loi) was calculated according to SS 02 81 13 (SIS, 1981). The whole sediment sample core for each chamber was dried in 105°C for at least 24h and heated at 550°C for 2h. Analyses of the organic matter content for sediment collected in Askö were taken at the beginning of the experiment and when the experiment was finished, while the Getå Stream organic matter content only was taken at the beginning of the experiment.

Grain size was analyzed at the end of both the experiments. Grain size was determined by sediment sieving. Porosity was calculated at the beginning and at the end of the experiment with Askö sediment, and at the end of the per-experiment with sediment from the Getå Stream. Porosity was calculated according to; wet sediment – dry sediment (reduced weight in gram)/ sediment volume (cm³).

Water characterizations which were conducted at the sediment collecting place in Askö were salinity and temperature. Salinity was measured with TB 4610E0300002 sensor and TB 84-EC module; the measurements were made by Askö laboratories. Measurement of water pH was made according to SS 02 81 22 (SIS, 1979) with a Radiometer Copenhagen PHM 93, buffer solution 4.005 and 7.000. The measurement was performed at laboratory for both the Getå Stream experiment and the Askö experiment.
2.5 Preparation of samples

2.5.1 Preparation of water samples before analysis of carbon dioxide, methane and oxygen concentrations

For water samples, 5 ml water in the Askö experiment and 10 ml water in the Getå Stream experiment was withdrawn with a syringe and transferred to a 60 ml syringe. The water samples in the 60 ml syringe were acidificated by the addition of 0.5 ml sulphuric acid (5 M) through a 3-way luer-loch valve. 40 ml nitrogen gas was added to the syringe to get a headspace. Finally was the syringe shaken 30 seconds, and after 30 minutes shaken another time for 30 seconds. The acidification was made to get a pH< 1, which convert carbonates to CO₂ that equilibrates between the water and the headspace according to Henry’s law. The acidification was made according to Hargrave and Phillips (1981) in Anderson et al., (1986). The headspace in the syringe was transferred by an injection needle to a machine washed, rubber plugged and aluminium caps secured, and evacuated vial (30ml). The samples were stored cold and dark until analysis.

2.5.2 Preparation of gas samples before analysis of carbon dioxide, methane and oxygen concentrations

For headspace samples 5 ml in the Askö experiment and 15 ml in the Getå Stream experiment gas from the headspace was withdrawn with a syringe and transferred to evacuated vials (30 ml for Getå and 13 ml for Askö) by an injection needle. Thereafter 20 ml (Askö experiment) or 30 ml (Getå Stream) nitrogen gas was added to the vials to get overpressure in the vials making later withdrawals of gas easier and as a precaution against contamination of surrounding air. The samples were stored at a cold and dark place until analysis.

2.6 Analyses

2.6.1 Analysis of carbon dioxide, methane and oxygen concentrations

The main analysis in this study has been the measurement of carbon dioxide from both water- and headspace in the chambers. Carbon dioxide production is a measure of the total benthic mineralization process, since the mineralization process has carbon dioxide as end product (Anderson et al., 1986). Carbon dioxide from the vials was analyzed by a gas chromatograph (Shimadzu GC–8A) with a thermal conductivity detector (TCD). Helium is used as carrier gas (30ml/ minute). The column temperature was 60°C and the injector and detector had a temperature of 100°C.

Methane has also been measured from both water and headspace. The measurement of methane was of importance in the control of an aerobic degradation process. Methane is end product of an anaerobic degradation process, and presence of methane in the water headspace indicates a shift in the sediment from aerobic to anaerobic conditions (Madigan et al., 2000). Methane from the vials was analyzed by a gas chromatograph (Chrompack CP 9001) with a flame ionization detector (FID). Nitrogen gas was (30ml/minute) used as carrier, the colon is 2.5 m x 2 mm Haye-Sep 80-100 Mesh colon. The injector and detector had a temperature of 150°C, and an oven temperature of 125°C. Oxygen, which is essential for aerobic life within the sediment (Ziebis et al., 1996), was measured as a complement to methane measurements to ensure oxic conditions. Headspace from the vials was analyzed by a gas chromatograph (Shimadzu GC–8A) with a thermal conductivity detector (TCD). Argon was used as a carrier (30ml/min).
The analysis of carbon dioxide, methane and oxygen was conducted in following way. A syringe with an injection needle was used to withdraw 0.5 ml of gas from the sample vials. Gas was injected twice into the gas chromatograph. Standards with known concentrations of carbon dioxide, methane and oxygen were analyzed at the same time as the analysis of water and headspace. The standards were made in one series with three known concentrations (one low, one in the middle and one high). A graph was produced from a linear equation obtained from the standards. The equation was used to calculate the partial pressures of carbon dioxide, methane and oxygen in the vials from both water and headspace samples. The laboratory temperature and barometric pressure were recorded every sampling day and when the analysis was performed, the recorded values were used to calculate the formation of carbon dioxide, methane and oxygen.

2.6.2 Calculations of amount carbon dioxide, methane and oxygen in the water and headspace

Areas from gas chromatograph analyses of carbon dioxide, methane and oxygen were obtained from an integrator (Perkin – Elmer LCI – 100 Laboratory Computing Integrator). The amount of carbon dioxide, methane and oxygen in the sample vials calculated according to The Ideal Gas Law formula; \[ p \times V = n \times R \times T \]. Where \( p \) is the partial pressure in Pascal given by the GC measurements; \( V \) is the volume in the vial (m\(^3\)); \( n \) is the mole of gas present; \( R \) is the molar gas constant 8.314 (J/mol*K) and \( T \) is the temperature in Kelvin (Fifield and Haines, 1995). The amount of gas in the headspace and water of the chambers was then obtained from calculations of sampled volume proportions and subsequent dilution during sample preparation.

Henry’s law was used when the amount of carbon dioxide, methane and oxygen in the water phase was calculated. Henry’s law states that the concentration of a gas dissolved in a liquid is proportional to the partial pressure of the gas (Ekbom et al., 1997). The equation of Henry’s law is \( C_{(aq)} = K_H \times p \), where \( C_{(aq)} \) is the concentration of gas dissolved in water phase (in mol/l), \( K_H \) is Henry’s constant for the given gas and temperature, \( p \) is the partial pressure of gas (in atm) (Stumm and Morgan, 1996). \( K_H \) for carbon dioxide and methane varies with temperature and salinity. Correction for salinity hasn’t been made since the salinity was low. Temperature corrected \( K_H \) values for carbon dioxide and methane were obtained according to Butler (1991) and Wiesenburg and Guinasso (1979) respectively.

2.7 Statistical analyses

The amount of CO\(_2\) was transferred by calculations to inorganic carbon (mmol C m\(^{-2}\) d\(^{-1}\)) before the statistical analyses was performed. To enable comparison with other studies the mineralization rates were normalized to the surface area of the sediment in the chamber. To estimate initial formation of inorganic carbon, linear regression was calculated based on all sampling-occasions in each chamber (0, 15/20, 37/44, 61/67, 83/91, 136/114, 179/172 and 251 h after incubation start). The slope of this linear regression (if significant; i.e. \( p < 0.05 \)) represents the respiration rate (see Figure 4 and 5). The respiration rate is synonymous with the mineralization rate. To test if there were any differences in total mineralization rate between stirred and unstirred chambers (with and without advective pore water flow), the corresponding rate estimates (regression coefficients for significant chambers) were used in a Mann-Whitney test in SPSS 11.5 for windows. A significance level of 5% was chosen.
3 Results

3.1 Results from experiment with sediment collected in the Getå stream and Askö

3.1.1 The Getå Stream water and sediment characterization

Start values
pH was measured in one sample, and the result was pH 6.82. The mean water content was 19.86 ± 1.25 % (n = 6) for sediment from the Getå Stream. Loi mean value was 0.59 % ± 0.07 % (n = 6).

End values
At the end the pH was 6.68 ± 0.14 (n = 8), which means no drastical change during the experiment time. The decrease was consistent in all chambers regardless of the treatment. The mean water content was 20.40 % ± 1.29 % (n = 8). The mean porosity was 40.1 % ± 1.8 % (n = 8). Grain size characteristics showed that the largest part of the sediment was in the 125 - 1000µm fraction, (76.2 %) while the rest of the sediment was in the fractions < 125 (11.0 %) and > 1000µm (12.6 %).

3.1.2 Askö water and sediment characterization

Start values
The mean pH was 7.77 ± 0.08 (n = 7). The salinity was 6‰. The mean water content was 37 % ± 0.88 % (n = 2). Loi was 0.61% ± 0.01 % (n = 2). Porosity mean value was 29.18 % ± 2.22 % (n = 2).

End values
The mean pH was 7.80 ± 0.06 (n = 13). The mean water content was 13.00 % ± 1.21 % (n = 13). The mean Loi was 0.51 % ± 0.001% (n = 11). The porosity mean value was 28.46 % ± 2.31 % (n = 13). The grain size for 10 out of 13 chambers shows that the largest part of the sediment will be found in an area of 125 - 1000µm and the lowest part in < 125µm. One chamber has the largest part of the sediment in > 1000µm and the lowest part in < 125µm. for all chambers was < 1 % of the sediment found in grain size < 125µm, > 57 % was found in grain size of 125 - 1000µm and approximately 40 % was found in > 1000µm.

3.2 Change in carbon concentrations over time

3.2.1 Getå Stream experiment

During almost the whole incubation time, all stirred chambers (water phase and headspace measurement depict formation of inorganic carbon in sediment) seem to have an increase in inorganic carbon concentration, but all chambers have also a dip in the concentration between day one and day two. The concentrations seem to increase after day two and continue to increase almost the whole incubation time (see Figure 4. where stirred chambers is marked with A). The unstirred chambers follows the same pattern of inorganic carbon concentration as the stirred chambers during almost the whole incubation time, a dip between the first and the second day, and then an increase after the second day (see Figure 4. where unstirred chambers is marked with B).
Figure 4. Getå Stream experiment. Y-axis shows concentration of inorganic carbon in sediment cores (mmoles m$^{-2}$) and x-axis show time in days. (A) Stirred chambers (with advective pore water flow) (B) Unstirred chambers (without advective pore water flow). Linear regression curves are given for the entire 9 day incubation for 7 chambers, for one stirred chamber is the linear regression given for 6 days. The regression coefficients are shown in the right corner of each chamber diagram.
3.2.2 Askö experiment

There seems to be an increase in the concentration of inorganic carbon in all stirred chambers (water phase and headspace measurement depict formation of inorganic carbon in sediment) in the Askö experiment over time (see Figure 5, where stirred chambers is marked with A). For the unstirred chambers was the situation almost the same as for the stirred chambers, increased inorganic carbon concentrations over time (see Figure 5, where unstirred chambers is marked with B). Dips in inorganic carbon concentration occurred in some stirred and some unstirred chambers (more frequent) in the beginning of the experiment.
3.3 Mineralization rates

The slope of the linear regressions regarding carbon concentrations over time using all samples in each chamber was to estimate mineralization rates (respiration). The mineralization rates (regression coefficient) are expressed as mmol C m$^{-2}$ d$^{-1}$.

3.3.1 Getå Stream experiment

The results from the analysis of linear regression showed that one regression slope for stirred chambers and one regression slope for unstirred chambers in the Getå Stream experiment was significant. The results from the linear regression analysis are shown in Table 1. There are increases of inorganic carbon concentrations and thereby of mineralization rates in chambers with significant regression slopes. Chambers without significant regression slopes show no
significant mineralization rates. The linear regression curves for each chamber can be seen in Figure 4. For the stirred chamber with a significant regression slope was the p-value 0.038 (bold figure) and for the unstirred chamber with a significant regression slope was the p-value 0.005 (bold figure), both values were < 0.05. The regression coefficients (mineralization rate) in mmol C m$^{-2}$ d$^{-1}$ for significant chambers show positive values (see Figure 4. and Table 1.). For the significant stirred chamber was the mineralization rate 4.059 mmol C m$^{-2}$ d$^{-1}$ and the standard error was ± 1.455. For the significant unstirred chamber was the mineralization rate 6.806 mmol C m$^{-2}$ d$^{-1}$ and the standard error was ± 1.391. $R^2$-values for significant chambers were not close to 0.

Mann-Whitney was not conducted for Getå Stream experiment, since there were only two significant regression slopes.

<table>
<thead>
<tr>
<th>Getå Stream experiment</th>
<th>Regression coefficient (mmol C m$^{-2}$ d$^{-1}$) and standard error</th>
<th>p-value</th>
<th>$R^2$-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stirred chambers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>6.677(± 3.089)</td>
<td>0.097</td>
<td>0.539</td>
</tr>
<tr>
<td>2</td>
<td>2.741(± 1.151)</td>
<td>0.063</td>
<td>0.531</td>
</tr>
<tr>
<td>3</td>
<td>2.548(± 1.147)</td>
<td>0.077</td>
<td>0.497</td>
</tr>
<tr>
<td>4</td>
<td><strong>4.059 (± 1.455)</strong></td>
<td><strong>0.038</strong></td>
<td><strong>0.609</strong></td>
</tr>
<tr>
<td>Unstirred chambers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2.410(± 1.525)</td>
<td>0.175</td>
<td>0.333</td>
</tr>
<tr>
<td><strong>2</strong></td>
<td><strong>6.806 (± 1.391)</strong></td>
<td><strong>0.005</strong></td>
<td><strong>0.827</strong></td>
</tr>
<tr>
<td>3</td>
<td>3.398(± 2.053)</td>
<td>0.159</td>
<td>0.354</td>
</tr>
<tr>
<td>4</td>
<td>3.906(± 1.714)</td>
<td>0.072</td>
<td>0.509</td>
</tr>
</tbody>
</table>

### 3.3.2 Askö experiment

The results from the linear regressions for the Askö experiment are shown in Table 2. The result showed four significant regression slopes for stirred chambers and one significant regression slope for unstirred chambers. There are increases of inorganic carbon concentrations and thereby of mineralization rates in chambers with significant regression slopes. The linear regression curves for each chamber can be seen in Figure 5. For the stirred chambers with significant regression slopes was the significant p-value = 0.019, 0.022, 0.015 and 0.019 (bold figure) and for the unstirred chamber with significant regression slope was the p-value = 0.010 (bold figure), all values were < 0.05. The statistically significant regression coefficients (mineralization rates) in mmol C m$^{-2}$ d$^{-1}$ show positive values (see Figure 5. and Table 2.). For the stirred chambers (with significant regression slopes) the mineralization rates ranged between 3.019 and 5.115 mmol C m$^{-2}$ d$^{-1}$ and the standard errors ranged between ± 0.942 and ± 1.599. The unstirred chamber (with significant regression slope) showed a mineralization rate of 3.139 mmol C m$^{-2}$ d$^{-1}$ and the standard error was ± 0.841. The chambers without significant regression slopes show no mineralization rates. $R^2$-values for significant chambers were not close to 0.
Since there was only one significant value for the unstirred chambers and four significant values for stirred chambers, the Mann-Whitney test was performed by assigning mineralization rates corresponding to 0 (zero) for chambers with non-significant regression slopes. The result from the statistical Mann-Whitney test for Askö sediment showed a p-value = 0.051. There were no significant differences found between the two groups (with and without advective pore water flow) in the Askö experiment, since p > 0.05.

Table 2. Results from the linear regression analysis for the Askö sediment. The regression coefficient (mineralization rate) for each chamber is presented in mmol C m$^{-2}$ d$^{-1}$ together with standard error (±). The p-values and R$^2$-values for each chamber is also presented in the table. Bold values are statistically significant.

<table>
<thead>
<tr>
<th>Askö experiment</th>
<th>Regression coefficient (mmol C m$^{-2}$ d$^{-1}$) and standard error</th>
<th>p-value</th>
<th>R$^2$-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stirred chambers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>3.019(± 0.942)</td>
<td>0.019</td>
<td>0.631</td>
</tr>
<tr>
<td>2</td>
<td>4.232(± 1.375)</td>
<td>0.022</td>
<td>0.612</td>
</tr>
<tr>
<td>3</td>
<td>5.221(± 2.813)</td>
<td>0.113</td>
<td>0.365</td>
</tr>
<tr>
<td>4</td>
<td>2.116(± 1.216)</td>
<td>0.133</td>
<td>0.335</td>
</tr>
<tr>
<td>5</td>
<td>3.985(± 1.173)</td>
<td>0.015</td>
<td>0.658</td>
</tr>
<tr>
<td>6</td>
<td>5.115(± 1.599)</td>
<td>0.019</td>
<td>0.630</td>
</tr>
<tr>
<td>Unstirred chambers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.178(± 1.155)</td>
<td>0.347</td>
<td>0.148</td>
</tr>
<tr>
<td>2</td>
<td>3.139(± 0.841)</td>
<td>0.010</td>
<td>0.699</td>
</tr>
<tr>
<td>3</td>
<td>2.488(± 1.823)</td>
<td>0.221</td>
<td>0.237</td>
</tr>
<tr>
<td>4</td>
<td>2.300(± 1.605)</td>
<td>0.202</td>
<td>0.255</td>
</tr>
<tr>
<td>5</td>
<td>2.373(± 1.582)</td>
<td>0.184</td>
<td>0.273</td>
</tr>
<tr>
<td>6</td>
<td>4.006(± 3.455)</td>
<td>0.290</td>
<td>0.183</td>
</tr>
<tr>
<td>7</td>
<td>1.375(± 1.823)</td>
<td>0.322</td>
<td>0.162</td>
</tr>
</tbody>
</table>

Oxygen and methane analyses confirmed that oxic conditions prevailed in the water and the headspace during both the Getå Stream and the Askö experiment (i.e O$_2$ was always present and methane absent.)
4 Discussion

The dye experiment showed that the pressure was highest in the outer rim of the chamber where water was forced into the sediment. The lowest pressure took place in the centre of the chamber where the water was forced out of the sediment. Huettel and Gust (1992) describe the same phenomenon in a study 1992. Hence, the experiment with Rhodamine showed that there was advective pore water flow in the stirred chambers. In addition oxic conditions prevailed during the experiment. Altogether this indicates that the experimental setup was successful.

In the Askö sediment experiment four out of six stirred chambers showed significant regression slopes and the carbon mineralization rate in mmol C m⁻² d⁻¹ for these chambers ranged between 3.019 and 5.115 mmol C m⁻² d⁻¹. One out of seven unstirred chamber showed a significant regression slope and this chamber had a mineralization rate of 3.139 mmol C m⁻² d⁻¹. Rusch et al., 2001 studied permeable interstitial coarse sediment using a field study approach during a year (1997-1998) in the North Sea, and they found a carbon mineralization rates ranging between 1.665 mmol C m⁻² d⁻¹ in winter and 48.210 mmol C m⁻² d⁻¹ in summer. The carbon mineralization rates in Mars were ranging between 3.497 - 22.065 mmol C m⁻² d⁻¹ as mentioned in the introduction. Mineralization rates of the North Sea and Baltic Sea have been measured to range between 0.333 to 46.211 mmol C m⁻² d⁻¹ (Rusch et al., 2001 and references therein). The results from the Askö sediment mineralization rates in this study corresponds with the results from the North Sea study made by Rusch et al., 2001, and with the mineralization rates in fine sandy sediment of the North Sea and the Baltic Sea (Rusch et al., 2001 and references therein).

In the Getå Stream sediment experiment showed one out of four chambers a significant regression slope in both the stirred and unstirred treatment. The mineralization rate for the significant stirred chamber was 4.059 mmol C m⁻² d⁻¹ and for the significant unstirred chamber 6.806 mmol C m⁻² d⁻¹. The results in this study corresponds with the results from the study of a fresh water stream in New Hampshire where the mineralization rates ranged between 2.2 and 28.4 mmol C m⁻² d⁻¹ (Hedin, 1990 in den Heyer and Kalff, 1998).

The statistical Mann-Whitney test in this study showed that there was no significant difference between the two groups (with and without advective pore water flow) for the Askö experiment. No statistical Mann-Whitney test was made for Getå Stream sediment, since there was only one significant regression slope for stirred chambers and one for unstirred chambers. It was surprising that there was no difference between the two groups, since both theory (see introduction) and some previous results suggest that advective flow should affect mineralization. A laboratory study made by Ehrenhauss and Huettel (2004) showed that carbon mineralization rates were significantly higher in stirred chambers compared to unstirred chambers. They used cultured diatoms, sediment from the Wester river estuary and seawater from the North Sea to investigate the carbon mineralization rate. In the Askö experiment four out of six stirred chambers had significant regression slopes, and an increased mineralization rate. Just one out of seven unstirred chambers had a significant regression slope and an increased mineralization rate. With some more replicates (both stirred and unstirred) in the Askö experiment it had probably been possible to see a difference between the two groups. The p-value for the Mann-Whitney test was 0.051 which is very close to < 0.05, however the difference was too small to be significant.
Maybe the absence of difference between the two groups is related to quantity of the organic matter in my experiments. Sediments were collected during late winter. According to Hagström et al., (2001) the supply of carbon is low in the Baltic Sea during October to Mars but the supply increases from April when the algae production increases. However, the ice break-up was late in spring 2005; the ice sheet had broken only one week before the sediment was collected. A consequence of the late break-up was probably that the water and sediment contained very small amount of easy degradable organic carbon, since the phytoplankton production had not yet increased. Water content of total organic carbon hasn’t been measured in this study, but the low supply of carbon during winter as mentioned above may have an influence on the result.

There was not much organic matter in the Askö sediment; Loi mean value was 0.61 % in the beginning and end mean values was 0.52 %. Coarse-grained sandy sediments don’t contain much organic matter (Shum and Sundby, 1996). The organic matter content found in this study corresponds relatively well with organic matter content in earlier studies of permeable sediment. Ziebis et al., (1996) found an organic matter content of 0.8 % in permeable sediment in the Mediterranean Sea during May to August. However, the high mineralization rates (in chambers with advective pore water flow) found in Askö sediment also support the hypothesis of relatively high mineralization rates in coarse sediments in spite of low organic matter content.

In the Getå Stream experiment was the water coloured brown by humus, so there was a lot of organic matter in the water. Low amounts of organic matter content in the sediment was also found in the Loi analyses of sediment for the Getå Stream, it was only 0.59 % and that is within the same amount as Askö sediment. Such low sediment organic matter contents along with the refractory character of humus may be a reason to the few significant mineralization rates found in the Getå Stream sediment and the absence of differences between treatments. The Getå experiment was in progress for 9 days and the Askö experiment was in progress for 12 days, which may be another reason to the fact that there were more significant regression slopes for stirred chambers in the Askö experiment.

The inorganic carbon concentration continues to increase during the whole experiment time for both Getå Stream experiment and Askö experiment. The carbon increase seems to be largest the first 7 days in the Askö experiment for both stirred and unstirred chambers, and at the end of the experiment the carbon concentration seems to be more constant in the unstirred chambers (see Figure 4. and 5.). A potential reason for the difference between the experiments is that there was a greater disc rotation velocity in the Askö experiment (40 rpm) than in the Getå Stream experiment (20 rpm). Hence, the advective flow was most likely more extensive in the Askö experiment. The differences in terms of mineralization rates between experiments corresponds with the hypothesis that advective flow is important for mineralization rates even though previous studies indicate that 20 rpm should be enough. Ehrenhauss et al., (2004b) used 20 rpm in their experiments, since 20 rpm develop and gives a radial pressure which causes advective pore water flow on smooth sedimentary surface. According to that, 20 rpm ought to be fast enough to get an increase in the mineralization rates. Ehrenhauss and Huettel (2004) studied diatoms and how fast they were penetrating into permeable sediment in chambers with a stirrer rotating 20 rpm. During the first 24 hours had almost all diatoms penetrated into the sediment. In another study with diatoms, chambers and a rotating disc (20 rpm) made by Ehrenhauss et al., (2004b) was the trapped diatoms released as dissolved organic carbon after the third incubation day. According to these studies the concentrations ought to increase most in the beginning of the experiments with sediment from Getå Stream.
and Askö, however for the Getå Stream experiment was the carbon concentration increasing during the whole incubation time that may depend on the fact that humus is hard to degrade (Tranvik, 1998), or that the experiment was in progress for shorter time than the Askö experiment.

Oscillations in the inorganic carbon concentrations may depend on the fact that the sediment is brought into lab from its natural environment. Naturally, new fresh water penetrating the sediment of streams or seas, while in a laboratory experiment the water is not exchanged in the same way. During this experimental set up, new water was only added to the chambers when water samples were taken. The consistent dip in concentrations during day 2 in the Getå Stream experiment may also be due to some unidentified systematic error, e.g. regarding the sample dilution in the sample vials.

The absence of large effects from advective flow in my experiments using sediments retrieved during winter, along with contradicting results in studies using additions of fresh organic matter to sediments, indicate that the impact of advective flow may differ between seasons. Hence, further studies are needed both to evaluate if there are any increase in inorganic carbon concentrations and thereby in mineralization rates in stirred chambers compared to unstirred chambers. Those studies ought to be performed later in spring time or in summer time when the Baltic Sea and Getå Stream contains more organic matter. More replicates are also needed to get a larger difference between the two groups. To get knowledge about how much organic carbon the water contains, measurements of total organic carbon (TOC) are needed in further studies.

As mentioned above, the statistical Mann-Whitney test showed no differences between the two groups (with and without advective pore water flow) in the Askö experiment, but if calculating the results from the significant regression slopes to mmol C m$^{-2}$ y$^{-1}$ it will show mineralization rates in the north Baltic Proper for a whole year. For stirred chambers with significant regression slopes there will be a mineralization rate ranging between 1101.935 and 1866.975 mmol C m$^{-2}$ y$^{-1}$, which are as much as 13.23 - 22.42 g C m$^{-2}$ y$^{-1}$. Calculating the results for the unstirred chamber with a significant regression slope it will be a mineralization rate of 1145.735 mmol C m$^{-2}$ y$^{-1}$, which is 13.760 g C m$^{-2}$ y$^{-1}$. Considering that the mineralization rates are calculated on measurements made in winter time, the mineralization rates may be higher if calculated on measurements made during a whole year. Since almost 44% of the world’s continental shelf is covered with permeable sediment (Shum and Sundby, 1996) and about 1 % of the global inorganic carbon, is transformed every year through biological processes (Warfvinge, 1997), the effect of advective pore water flow in this study brings a discernible quantity of inorganic carbon to the global carbon cycle yearly, compared to sediment not affected by advective pore water flow.

There has been an increase in wave height during the last 30 years in the North Atlantic (Gulev and Hasse, 1999), and the same tendency is discernible for the Baltic Sea according to Alexandersson et al., (2000). The storm frequency increased between the 1960’s and 1990’s. Hence, the magnitude of advective flow may increase in the future due to climate change making future studies of how advective flow affects mineralization processes both interesting and important.
5 References


