

Carbon Cycling in Baltic Sea Sediments

– In situ investigations with benthic landers

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Doctoral Thesis



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Abstract

Coastal seas, estuaries and continental shelves are the connection between land and the open ocean, and due to high productivity and strong influence from land a majority of the marine organic carbon (OC) cycling and preservation in sediments occurs in these areas. Sediments are hotspots in the C cycle also since they constitute a link between the biogeochemically active C pool and the C pool that cycles on much longer timescales, and benthic processes will thus have an effect on atmospheric CO₂ levels. To accurately predict future atmospheric CO₂ levels it is of great importance to understand how C is recycled and preserved in sediments of coastal seas and estuaries.

This thesis investigates benthic OC cycling in the Baltic Sea with emphasis on understanding and quantifying the recycling and preservation of OC. The investigations were made in situ using advanced benthic chamber landers that incubate an area of sediment and overlying water. By discrete water sampling or continuous measurements by sensors it is possible to detect the concentration change of a solute over time resulting from early diagenetic processes in the sediment. Dissolved inorganic carbon (DIC) fluxes were measured in the incubation chambers and used as a proxy for OC oxidation. Moreover, the vertical distribution of OC in the sediment solid phase together with sediment accumulation rates were used to quantify the OC preservation or burial.

It was found that OC recycling rates in Baltic Sea sediments are much larger and burial rates lower than previously thought. In total 96 % of the OC that deposits on the sea floor is recycled back to the water column. However large variations between the different Baltic Sea sub-basins were observed as well as between different bottom types. The highest OC recycling rates ($\sim 32 \text{ mmol m}^{-2} \text{ d}^{-1}$ on average) were observed in the deep accumulation areas of the Baltic Proper, where also the lowest burial efficiency (burial rate/deposition rate) was found (2.5–3.5 %). OC recycling rates in general tended to increase with increasing water depth, and so did the OC oxidation efficiency, i.e. the DIC flux per available OC in the reactive sediment surface layer. This was largely explained by focusing of fresh labile OC along the depth gradient within the basin. It was estimated that nearly half of the OC that deposits on shallow bottoms in erosion-transportation areas of the Baltic Proper is resuspended and redistributed to deeper calmer accumulation parts of the basin. Oxygen in

the overlying water had no significant effect on the OC recycling rates as found from observations before and after a so-called major Baltic inflow.

During the thesis work the benthic chamber landers have been updated with regard to control of quality and performance of the sediment-water incubations. The measured benthic fluxes can now be determined with higher accuracy and reliability of chamber functioning, and still enable an efficient full lander deployment-incubation-recovery cycle in one day. One major step forward was the installation of conductivity sensors to determine chamber volume from the dilution of salinity resulting from a small injection of MQ water. The benthic landers used in this work are considered to be one of the most suitable systems available in the field today. The outcome of this in situ study improves the understanding of the carbon cycle and its dynamics in the Baltic Sea.

Populärvetenskaplig sammanfattning

Kustnära grunda hav är de områden som förbinder land med öppna oceanen. I de här områdena är primärproduktionen (d.v.s. tillväxt av växtplankton eller mikroalger) och därav bildningen av organiskt material extra hög på grund av hög tillförsel av näringsämnen från land. Organiskt material tillförs även kustområden direkt via floder. Organiskt material består till största delen av kol i organisk form. Detta innebär att kustnära hav är områden med hög omsättning av organiskt kol och de är därför extra viktiga i den globala kolcykeln.

Sedimenten i grunda havsområden tillförs stora mängder organiskt kol som antingen kan brytas ner av mikroorganismer och sedimentlevande djur, eller begravas under långa tidsskalor. Sedimenten utgör därför en viktig plats där kol bortföres genom begravning från den oceana biogeokemiska cirkulationen, vilket påverkar atmosfärens innehåll av koldioxid på lång sikt. Sedimenten utgör också en viktig plats för nedbrytning av organiskt kol till löst oorganiskt kol som återcirkulerar till vattenmassan.

Den här avhandlingen fokuserar på sedimenten i Östersjöns som är ett grunt, kustnära innanhav starkt påverkat av omkringliggande länder. Det övergripande målet har varit att bestämma hur mycket kol som begravs i Östersjöns sediment och hur mycket som återvänder (eller återcirkulerar) i löst oorganisk form till vattenmassan på grund av nedbrytningen av organiskt material. Det visade sig att så mycket som 96 % av det kol som tillförs sedimenten bryts ner och återcirkuleras till vattenmassan. Nedbrytningen av organiskt material i sedimentet kan påverkas av flera faktorer och i denna studie har målet också varit att identifiera vilka av dessa faktorer som är av betydelse för sedimenten i Östersjön. Ett exempel är att vi undersökt effekterna av ett stort syrerikt vatteninflöde som då och då sker till Östersjön som förnyar eller byter ut åldrat syrefritt vatten ur Östersjöns djupaste delar. Den här studien visade att nedbrytningen av organiskt material i sediment inte verkade påverkas av ett sådant syrerikt inflöde. Vi fann istället att de höga nedbrytningshastigheterna av organiskt kol kunde förklaras av omfördelning av sedimentpartiklar från grunda bottnar till djupa bottnar. Denna omfördelning av partiklar/material ger upphov till en anrikning av färskt organiskt material som är extra lättnedbrytbart och således ökar nedbrytningshastigheterna i de djupa bottenarna.

I studien har sedimenten undersökts med hjälp av avancerad mätteknik, så kallade bottenlandare, som kan utföra kammarinkubationer av sedimentytan och på så sätt mäta nedbrytningsprocesserna in situ, dvs. under verkliga förhållanden nere på havsbotten. Detta är en viktig aspekt eftersom sediment lätt påverkas om de studeras ex situ, dvs. ombord på fartyget eller i ett laboratorium på land. Användandet av bottenlandare är ofta tekniskt krävande och metoden utvecklas ständigt. Under den här studien har flera förbättrande åtgärder gjorts för att få en högre kvalitet och bättre kontroll över mätningarnas tillförlitlighet.

Den här studien har visat att sedimenten i Östersjön begraver (långsiktigt lagrar) betydligt mindre kol än vad man tidigare har trott. Denna kunskap kan leda till att prognoser om kustnära havs betydelse för att långsiktigt ta upp koldioxid från atmosfären kan behöva revideras.

Utfallet av studien bidrar till en ökad förståelse för Östersjöns kolcykel, och till att befintliga modeller för Östersjöns kolomsättning kan förbättras.

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Part II: Papers

Paper I

Nilsson, M., Kononets, M., Ekeroth, N., Viktorsson, L., Hylén, A., Sommer, S., Pfannkuche, O., Almroth-Rosell, E., Atamanchuk, D., Andersson, J. H., Roos, P., Tengberg A. and Hall, P. O. J.

Organic carbon recycling in Baltic Sea sediments – An integrated estimate on the system scale based on in situ measurements.

Marine Chemistry, submitted

Paper II

Nilsson, M., Ekeroth, N., Kononets, M., Hylén, A., Viktorsson, L., Almroth-Rosell, E., Roos, P., Tengberg, A. and Hall P. O. J.

Particle shuttling and oxidation efficiency of organic carbon – In situ sediment observations in contrasting brackish marine environments.

(Manuscript)

Paper III

Kononets, M., Nilsson, M., Tengberg, A., Ekeroth, N., Hylén, A., van de Velde, S., Blomqvist, S. and Hall, P. O. J.

In situ incubations with a benthic chamber lander system: Performance, quality control and capabilities with recommendations for a best practice

(Manuscript)

Paper IV

Hall, P. O. J., Almroth-Rosell, E., Bonaglia, S., Dale, A. W., Hylén, A., Kononets, M., Nilsson, M., Sommer, S., van de Velde, S. and Viktorsson, L.

Influence of natural oxygenation of Baltic Proper deep water on benthic recycling and removal of phosphorus, nitrogen, silicon and carbon

Frontiers of Marine Sciences (2017) 4:27, doi: 10.3389/fmars.2017.00027

Publication not included in thesis

Viktorsson, L., Ekeroth, N., Nilsson, M., Kononets, M. Y. and Hall, P. O. J.

Phosphorous recycling in sediments of the central Baltic Sea

Biogeosciences (2013) 10:6, doi: 10.5194/bg-10-3901-2013

Author's contribution

Paper I

Designed the study together with PH, NE, MK and SS. Contributed to the coordination of sediment sampling and to the lander deployments. Participated on expeditions and processing of samples. Made most of the calculations, statistical analyses and evaluation of data. Did most of the writing of the manuscript.

Paper II

Designed the study together with PH, NE and MK. Contributed to the coordination of sediment sampling and to the lander deployments. Participated on expeditions and processing of samples. Made most of the calculations, statistical analyses and evaluation of data. Did most of the writing of the manuscript.

Paper III

Contributed to the improvement of the benthic landers. Implemented the new technique to determine chamber volume together with AT. Participated on expeditions, and in processing of samples and flux determinations. Made many of the calculations, statistical analyses and evaluation of data. Contributed to the writing of the manuscript.

Paper IV

Contributed to the coordination of sediment sampling and to the lander deployments. Participated on expedition and processing of samples. Contributed to calculations, and evaluation of data. Contributed to writing of the manuscript.

Part I

Carbon Cycling in Baltic Sea Sediments

- In situ investigations with benthic landers

Aims

The main aim with this thesis was to study organic carbon (OC) cycling in sediments of the Baltic Sea and compare the patterns observed between the different sub-basins, which differ in terms of for example nutrient load, trophic status, salinity and oxygen regime (i.e. different oxygen levels in the overlying bottom water). Another aim was to quantify, on a Baltic Sea system scale, the deposition of OC on the sea floor and compare this estimate with known sources of OC.

The rates of mineralization and preservation of OC and the factors that can influence or control these processes were also investigated. The investigations were performed with benthic chamber landers, an advanced in situ technique which results in high quality measurements of the sediment biogeochemical processes with minimal disturbance of the sediment-water interface.

Paper I of this thesis had the main goal to quantify the carbon recycling and burial in Baltic Sea sediments and to construct a basin-specific, benthic carbon budget on the system-scale

Paper II investigates what factors control or influence the sediment recycling and burial rates of OC in the Baltic Sea. In this context OC oxidation efficiency, i.e. oxidation rate per available OC, is presented as a parameter to explain variability of OC recycling rates within and between basins.

During my PhD studies there has also been work on developing and improving the benthic landers and how to optimize this in situ method. This work is discussed in **Paper III**.

Nature gave us the opportunity to study the effects of a natural oxygenation of long-term anoxic bottoms. This oxygenation was due to a large intrusion of oxygenated salty water into the Baltic Proper, a so-called major Baltic inflow, which started at the end of 2014. The effects of this natural oxygenation event on benthic recycling of OC and other biogenic elements are discussed in **Paper IV**.

1. Introduction

1.1 Carbon in the marine and brackish water environments

Carbon (C) is an element that has an important role in regulating the global climate. In the marine environment C is present in both organic form (total organic carbon, TOC) and inorganic form (total inorganic carbon, TIC). The TOC and TIC consist of both a particulate (POC and PIC) and a dissolved (DOC and DIC) fraction. POC and PIC is the C associated with living or dead biomass (e.g. detritus, fecal pellets and shells), whereas DOC and DIC are released during degradation of POC or dissolution of PIC. By operational definition POC is separated from DOC as the particle size fraction that does not pass through a 0.2–1.0 μm filter (Middelburg et al., 1993). However the scale from dissolved organic species to particles is continuous and extremely small particles, colloids and aggregates may pass through the filter and are thus operationally defined as dissolved (Linders et al., 2018 and references therein).

Some marine phytoplankton produce hard shells, some of which are made of calcium carbonate (CaCO_3). These structures define the PIC fraction and contribute to DIC and alkalinity production upon dissolution. The DIC species are present in equilibrium with each other and form the marine carbonate system:



Subsequent hydration and dissociation reactions:



(Eq. 1)

The DIC or total carbonate (C_T) is the sum of the dissolved inorganic carbon species and includes carbon dioxide (CO_2), carbonic acid (H_2CO_3), bicarbonate ion (HCO_3^-) and carbonate ion (CO_3^{2-}) in aqueous form (Eq. 2). Bicarbonate and carbonate are the dominant forms in sea water. The $\text{CO}_2(\text{aq})$ and the H_2CO_3 (which exists in very low concentrations) are often combined and referred to as CO_2^* (Eq. 3).

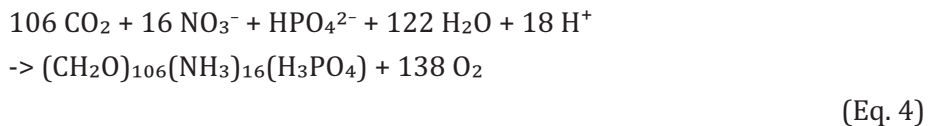
$$DIC \text{ or } C_T = [\text{CO}_2(\text{aq})] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (\text{Eq. 2})$$

$$DIC \text{ or } C_T = [\text{CO}_2^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (\text{Eq. 3})$$

In a typical marine water mass below the photic zone, the dominant form of carbon is DIC. The higher concentration compared to the photic zone is mainly resulting from degradation of organic matter in the water column and sediments.

1.2 Primary production and benthic pelagic coupling

Particulate organic matter is formed during primary production with a stoichiometric composition of carbon and (macro) nutrients according to the Redfield ratio (C:N:P of 106:16:1) (Redfield, 1958):



When light and nutrient conditions are favorable, phytoplankton growth and primary production are stimulated.

During primary production, CO_2 or HCO_3^- is assimilated through photosynthesis and transformed to POC in biomass. Some of the POC (the export production) sinks through the water column and is degraded and mineralized in the water column into DIC. The reverse form of the formula for photosynthesis (Eq. 4) represents respiration (i.e. organic matter degradation). The fraction of sinking POC that escapes pelagic mineralization deposits on the sea floor. This drawdown of C from the ocean surface to the deeper layers and sediments is known as the 'biological C pump' (Fig. 1).

Other sources also contribute to the vertical particle flux, especially in coastal seas where land derived POC is transported to the sea via rivers (Elmgren, 1984; Gustafsson et al., 2014), and in estuaries where mixing of fresh and saline waters results in aggregation or flocculation of DOC (Asmala et al., 2014 and references therein).

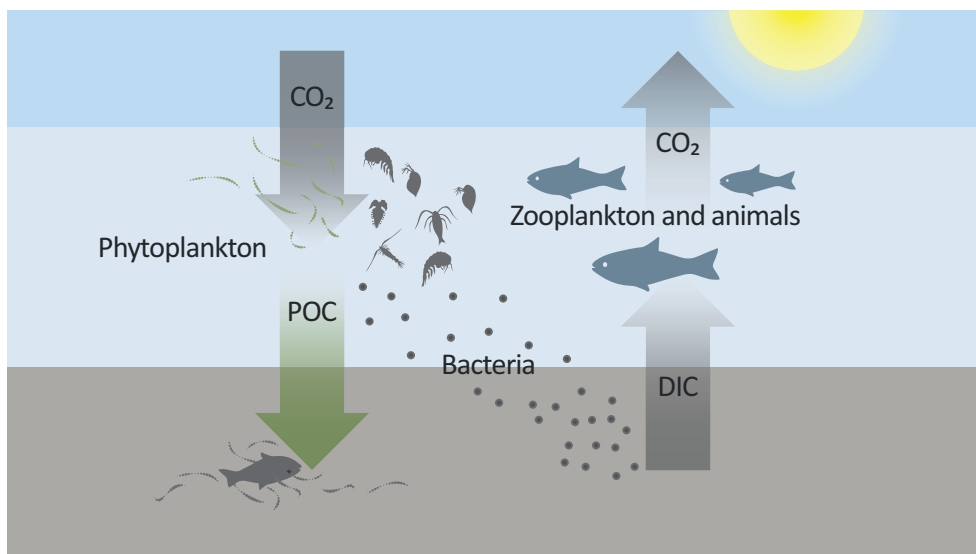


Figure 1 Biological C pump and examples of coupling between pelagic and benthic processes

The vertical POC flux thus consists of both of sinking marine POC (mPOC), terrestrial POC (tPOC) and aggregates or flocs of DOC.

1.3 Early diagenesis and sediment-water fluxes of carbon

As organic matter settles on the sea floor it will be degraded by microbes and fauna. The structure of the benthic community is determined by the physicochemical factors at the sea floor e.g. water hydrodynamics (bottom-stress), depositional conditions, light, temperature and nutrient availability (Deming and Baross, 1993; Köster and Meyer-Reil, 2001). The biological, chemical and physical processes affecting the composition and quantity of organic matter within the sediment after deposition is called diagenesis. Early diagenesis refers to the most recent processes that take place in the upper layer of the sediment (Berner, 1980; Henrichs, 1992).

The pool of organic matter in the sediment and pore water system consists of a mixture of different fractions of OC and IC. The generally largest pool in coastal and continental margin sediments is POC and only a few percent is DOC and biomass carbon (BMC) (Köster and Meyer-Reil, 2001). However, in several deep-sea sediments, such as calcareous ooze sediments, the major C component is PIC (e.g. Ståhl et al., 2004b). The different OC sources are often

classified according to their reactivity with respect to mineralization processes, going from labile (short lived, most reactive) to refractory (long lived, least reactive) (Hansell, 2013). Among the more refractory materials are terrestrial OC, which can be transported long distances from its origin. On the other end of the spectra is the more labile marine OC.

When OC arrives at the sediment surface as POC it must first be transformed to DOC before it can be used as an energy source by bacteria. This transformation can occur both through grazing by benthic fauna or by hydrolyzation with extracellular enzymes by microbes. DOC can be protected from microbial degradation by adsorbtion to particles (Borch and Kirchman, 1999; Keil et al., 1994). Bacteria gain energy from oxidation of OC with different oxidants, such as oxygen, nitrate (NO₃⁻), manganese and iron oxides (MnO₂ and Fe(OH)₃), and sulfate (SO₄²⁻). The different diagenetic pathways, their reactions and energy yields (ΔG⁰) are described in Table 1. The most energetic reaction is favored until the corresponding electron acceptor is fully depleted, then the next most efficient reaction starts. However, the interactions between the different pathways are more complex as discussed in e.g. Canfield et al. (1993). The net effect of early diagenetic processes in terms of carbon is the conversion of POC to DOC, DIC and methane (CH₄).

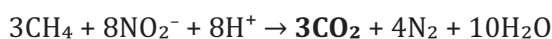
Table 1 Diagenetic pathways of oxidation of organic carbon in marine sediments (Canfield, 1993). Marked in bold are the C species that contribute directly to the DIC formation in sediments according to Eq. 3.

| Diagenetic pathway | Reaction | ΔG ⁰ |
|---------------------|--|-----------------|
| Aerobic respiration | CH ₂ O + O ₂ = CO₂ + H ₂ O | -475 |
| Denitrification | CH ₂ O + 4/5NO ₃ ⁻ = 4/5HCO₃⁻ + 1/5CO₂ + 2/5N ₂ + 3/5H ₂ O | -448 |
| Manganese reduction | CH ₂ O + 3CO ₂ + H ₂ O + 2MnO ₂ = 2Mn ²⁺ + 4HCO₃⁻ | -349 |
| Iron reduction | CH ₂ O + 7CO ₂ + 4Fe(OH) ₃ = 4Fe ²⁺ + 8HCO₃⁻ + 3H ₂ O | -114 |
| Sulfate reduction | CH ₂ O + 1/2SO ₄ ²⁻ = 1/2H ₂ S + HCO₃⁻ | -77 |
| Methanogenesis | CH ₂ O = 1/2CH ₄ + 1/2CO₂ | -58 |

The mineralization of organic matter has traditionally been, and is still often quantified as the loss of oxygen or as the increase of hydrogen sulfide (H₂S). This approach is not representative for total mineralization rates since several other oxidants (not only oxygen and sulfate) are used to oxidize OC during early diagenesis (Table 1). In fact oxygen is seldom the main direct oxidant

in sediments with high sediment accumulation rates and high OC contents, which often only have a few mm depth of oxygen penetration, or lack oxygen completely (eg. Bohlen et al., 2011; Canfield et al., 2005). In sediments that underlie anoxic waters it is of course impossible to estimate mineralization of organic matter by measuring oxygen consumption.

By contrast, OC oxidation estimated from the release of DIC from the sediments captures the net result from all oxidation steps, provided that carbonate dissolution and methanogenesis is negligible. If there is a large contribution from carbonate dissolution it can lead to an overestimate of organic matter mineralization, since the process will yield carbonate ions (Eq. 3). Also, if the sediment has a high rate of methanogenesis, a large amount of methane is produced. A fraction of it can be lost in dissolved form or as gas bubbles to the overlying water with the potential risk of underestimating the OC oxidation rate. However, most of the produced methane is oxidized in the upper sediment layer with nitrate, nitrite (NO_2^-) or sulfate to DIC (e.g. Iversen and Jørgensen, 1985):



The effect on measured DIC fluxes of processes of calcium carbonate dissolution and methanogenesis can be corrected for by simultaneous measurements of alkalinity or methane flux. Determining organic matter mineralization from DIC flux measurements from the sediment is for the reasons mentioned above preferable when working in organic rich sediments in low oxygen or anoxic environments.

1.4 Burial or preservation of OC

The fraction of OC that escapes mineralization, either because of its chemical structure or the environmental conditions, will be buried for long timescales. The burial of marine OC will thus have an effect on the ocean's capacity to take up atmospheric CO_2 on these timescales (Bernier, 2004; Burdige, 2007; Hedges and Keil, 1995).

Burial is expected to increase as the deposition rate of OC increases (Henrichs and Reeburgh, 1987; Müller and Suess, 1979; Stein et al., 1986) since the available oxidants (primarily oxygen) get depleted fast due to the intensified OC oxidation (Canfield, 1993), and anoxic oxidation of OC is slower and less efficient than aerobic (Hulthe et al., 1998).

Burial efficiency, which is the ratio of C burial rate and the carbon deposition rate to the sediment surface, can be used to compare preservation rates between areas of different productivity and sedimentary deposition. Several factors are suggested to influence the OC burial efficiency of a sediment; 1) The sediment accumulation rate (e.g. Aller, 2014; Canfield, 1994 and references therein). 2) The composition and reactivity of the organic matter. Marine organic matter is preferentially degraded compared to terrestrial organic matter (Burdige, 2006). 3) The dominant oxidant and time of exposure to oxygen (Hartnett et al., 1998). Fresh labile organic matter is degraded equally fast in oxic and anoxic sediments, however old and refractory organic matter is degraded slower in anoxic than in oxic sediments (Hulthe et al., 1998). It has also been observed that repeated exposure of old and refractory organic matter to oxygen and anoxia (facilitated e.g. by bioturbating animals) stimulates degradation (Hulthe et al., 1998; Aller, 2014 and references therein). 4) Degradation protection by adsorption to mineral surfaces (Hedges and Keil, 1995; Mayer, 1994).

Marine sediments can have a total organic carbon (TOC) content from less than 0.0025 % C of sediment dry weight (% dwt) in open ocean sediments to about 20 % dwt, in coastal sediments (Burdige, 2007 and references therein). Burial efficiencies (OC burial rate/OC deposition rate) often exceed 10–20 % in sediments with high sediment accumulation rates in normal marine settings. However, the burial efficiencies of marine OC tend to be lower in muddy deltaic sediments with marine organic matter being more efficiently remineralised than terrestrial organic matter (Burdige, 2006).

2. The Baltic Sea

The Baltic Sea (392 978 km², Fig. 2) is the world's largest continental brackish-water sea (Snoeijs-Leijonmalm et al., 2016), with a mean depth of 54 m and a volume of 21 205 km³ (Leppäranta and Myrberg, 2009).

The Baltic Sea is divided into a number of sub-basins. The Baltic Proper and two major gulfs, the Gulf of Bothnia and the Gulf of Finland are considered in this thesis.

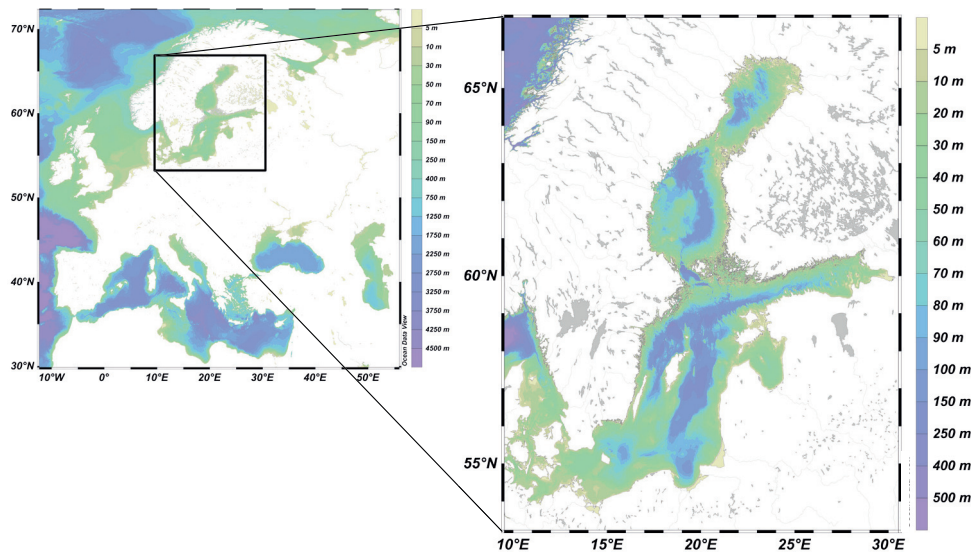


Figure 2 Map of the Baltic Sea.

The main basin (64 % of total water volume) is the Baltic Proper, where the greatest depth (the Landsort deep, 459 m) is found (Snoeijs-Leijonmalm et al., 2016). Another deep site in the Baltic Proper is the Gotland deep (249 m) located in the Eastern Gotland Basin where several stations of this study are located. The Baltic Proper is connected to the Gulf of Bothnia in the north and to the Gulf of Finland in the east.

The sills ('Southern Quark', 70 m) and the shallow Archipelago Sea between the Baltic Proper and the Gulf of Bothnia limits the water exchange between them. However, there is no sill that define the border between the Baltic proper and the Gulf of Finland (Snoeijs-Leijonmalm et al., 2016) making it possible for a closer interaction between these two systems. The Gulf of Finland is the most

shallow system with an average water depth of 37 m, whereas the maximum water depth is 123 m (Leppäranta and Myrberg, 2009).

The Gulf of Bothnia has a mean depth of 54 m and is further sub-divided into the Bothnian Sea and Bothnian Bay with maximum water depths of 293 and 146 m, respectively. The sill between them is only 25 m ('Northern Quark') (Leppäranta and Myrberg, 2009).

The Gulf of Bothnia has a mean depth of 54 m and is further sub-divided into the Bothnian Sea and Bothnian Bay with maximum water depths of 293 and 146 m, respectively. The sill between them is only 25 m ('Northern Quark') (Leppäranta and Myrberg, 2009).

2.1 Water supply and exchange

The Baltic Sea can be seen as a large semi-enclosed brackish water estuary with a mean salinity of 7.4 (Leppäranta and Myrberg, 2009), with a large (on average $500 \text{ km}^3 \text{ yr}^{-1}$) riverine inflow of freshwater in the northern and eastern part. In the southern part the Baltic Sea is connected to the North Sea via the Danish straits and Öresund through which denser more saline water enters the system along the seafloor.

The ten largest rivers (according to their drainage area) that discharge into the Baltic Sea (summarized in Table 2) account for 55 % of the total freshwater inflow.

The inflow from rivers and the exchange through the straits are important processes that affect the physical, biogeochemical and ecological state of the system. The outflow of brackish water is balanced by an inflow of denser saline water resulting in a net outflow through the straits of $500 \text{ km}^3 \text{ yr}^{-1}$ (Gustafsson, 2010). The inflowing water does not have the same salinity as the North Sea water, which indicates that the inflowing water is a mixture of old Baltic Sea water and North Sea water.

During certain weather conditions a so-called major Baltic inflow can occur. A longer period (weeks) of strong easterly winds can push the Baltic Sea water out of the system with a resulting decrease in sea level. If the winds then change direction to the west, the sea level in the Kattegat will rise. The sea

Table 2 The ten largest rivers according to drainage area feeding into the Baltic Sea region (BACC Author Team, 2015; Kulinski and Pempkowiak, 2011). The Göta river is draining into the Kattegat, which is sometimes included into the Baltic Sea region.

| River | Country | Drainage area (km ²) | Mean annual discharge (m ³ s ⁻¹) | % of total river inflow to the Baltic Sea | Run off (L km ⁻² s ⁻¹) | TIC (Gg yr ⁻¹) | TOC (Gg yr ⁻¹) |
|--------------|------------------|-------------------------------------|---|---|--|-------------------------------|-------------------------------|
| Neva | RUS/FIN | 281 000 | 2460 | 17.6 | 8.8 | 1295 | 1209.5 |
| Vistula | POL/UKR/BY/SLK | 194 400 | 1065 | 7.6 | 5.5 | 1168.1 | 175.6 |
| Odra | POL/GER/CZR | 118 900 | 573 | 4.1 | 4.8 | 431 | 75.5 |
| Nemunas | BY/LIT/RUS | 98 200 | 632 | 4.5 | 6.4 | 609 | 123.4 |
| Daugauva | BY/LV/LT/EST/RUS | 87 900 | 659 | 4.7 | 7.5 | 1068 | 210.7 |
| Narva | EST/RUS | 56 200 | 403 | 2.9 | 7.2 | 384 | 190.9 |
| Kemi | FIN | 51 400 | 562 | 4.0 | 11.0 | 1.3 | 2.1 |
| Göta | SWE | 50 100 | 574 | 4.1 | 11.5 | 63.8 | 80.5 |
| Torne | SWE/FIN | 40 100 | 392 | 2.8 | 9.8 | 28.9 | 102.4 |
| Kymi | FIN | 37 200 | 338 | 2.4 | 9.1 | 21.9 | 46.2 |
| Total | | 1 015 400 | 7658 | 55 | 8.2 | 5073.5 | 2427.5 |

level difference between the Kattegat and the Baltic Sea may then result in a large inflow of dense salty seawater along the sea floor into the Baltic Sea. In the northernmost basin, the Bothnian Bay, the circulation and renewal of deep water take place in winter when surface water is cooling and thus gets heavier and sinks towards the sea floor.

2.2 Eutrophication and hypoxia

The drainage area of the Baltic Sea is 1.74 million km² and it is inhabited by approximately 150 million people of which 80–90 million live in coastal areas (BACC Author Team, 2015; Leppäranta and Myrberg, 2009; Snoeij-Leijonmalm et al., 2016). The 10 largest rivers (Table 2.) contribute with nearly 70 % of the total C (10.9 Tg C yr⁻¹, (Kulinski and Pempkowiak, 2011) load to the Baltic Sea region. The fraction of OC load is around 40 % (4.09 Tg C yr⁻¹) of this total C load (Kulinski and Pempkowiak, 2011). The northern parts of the basin are characterized by less populated areas and rivers drain the boreal zones resulting in a river load enriched in carbon, but low in nutrients. The low nutrient input to the Gulf of Bothnia makes this ecosystem oligotrophic, especially in the Bothnian Bay (Humborg et al., 2003; Lundberg et al., 2009). The large rivers draining the eastern Baltic states results in a large nitrogen and phosphorous load. The largest load is found in the Gulf of Finland where the river Neva delivers around 17 % of the total inflow of water to the Baltic Sea. Rivers contribute with approximately 70 % of the annual phosphorous and 50 % of the annual nitrogen input to the Baltic Sea (Wulff et al., 2001).

In an enclosed system, like the Baltic Sea, the long renewal time of the water masses (30–40 years) (Snoeij-Leijonmalm et al., 2016) makes the system especially sensitive to land and human activities. This means that carbon and associated nutrients are recycled several times before they get buried or leave the system through water exchange with the sea outside. If the balance between the sources and sinks of a system is disturbed it can have consequences on the ecosystem, such as eutrophication and spreading of oxygen depleted (hypoxic) or anoxic areas.

The use of industrial fertilizers increased during the 1950s and led to increased amounts of bioavailable nutrients (nitrogen and phosphorous) and eutrophication in the Baltic Sea. The total external supply of nitrogen and

phosphorous has increased by a factor of two and three, respectively, during the last century (Savchuk et al., 2008). This has led to an enhanced net production of organic matter (Schneider and Kuss, 2004).

If the supply of organic matter is large enough, and especially when water renewal is infrequent, the degradation of organic matter, both in the water column and at the sea floor, can lead to depletion of oxygen in the water mass. Hypoxia is common in areas with limited new supply of oxygenated water and a pronounced stratification of the water column, which is the case in parts of the Baltic Sea. The Baltic Sea has experienced hypoxia occasionally since its formation (Bianchi et al., 2000; Zillén et al., 2008). Since the 1950s hypoxia has increased, both in intensity and in spatial coverage (Conley et al., 2009b). The area with hypoxic waters in recent years is about four times larger than in the 1960s (Jonsson et al., 1990), and covered an area averaging 49 000 km² in the period 1961–2000 (Conley et al., 2009a). The mean areal extent of hypoxia and anoxia was in 2017 estimated at around 46 % of the Baltic Proper area (Hansson et al., 2017).

The increase of hypoxic areas in the Baltic Proper has led to a less efficient phosphate retention in the sediments. The phosphate that is released from the sediments reaches the surface waters during winter mixing or upwelling during summer and will give a lower nitrogen to phosphorous ratio, which are one of the main drivers for cyanobacteria blooms in the Baltic Sea (Vahtera et al., 2007). These organisms have the capability to fix dissolved nitrogen gas (N₂) and they are therefore not limited by nitrogen as other phytoplankton organisms. The magnitude and frequency of these cyanobacteria blooms have increased since the 1960 (Finni et al., 2001).

2.3 Sediments

Sediments in the Baltic Sea are important zones for degradation and recycling of OC. Due to the shallowness of the Baltic Sea, a relatively large proportion of the primary production is expected to escape degradation in the water column and deposit at the sediment surface where oxidation and recycling of OC will continue. The primary production during spring bloom is dominated by diatoms and dinoflagellates in the Baltic Sea. Diatoms have higher sinking rate and are considered to constitute the major transport pathway of organic material to the

sea floor (Blomqvist and Heiskanen, 2001 and references therein; Heiskanen and Kononen, 1994). Despite their high abundance, the cyanobacteria biomass is not believed to contribute to a large extent to the deposition of organic matter to the sediments (Heiskanen and Kononen, 1994; Olli and Heiskanen, 1999), but its presence is indicated by cyanobacteria specific pigments found in sediment (Poutanen and Nikkilä, 2001).

With increasing organic matter production due to eutrophication it is also believed that burial of OC in sediments have doubled during the last century (Emeis et al., 2000). In contradiction to this, sediment accumulation rates appear to not have changed during the past 100 years (Hille, 2006).

Organic matter deposition to sediments is not homogenous; sedimentation patterns are instead closely related to basin topography and level of bottom-stress. A large part (~75%) of the Baltic Sea is shallow (<70 m), which makes the system largely influenced by resuspension induced by wind and bottom currents (Snoeijs-Leijonmalm et al., 2016). It is not clear if this resuspension have direct effects on the degradation rates of organic matter (Almroth et al., 2009; Ståhlberg et al., 2006). Moreover, the vertical transport of particles to deep less energetic areas (Almroth-Rosell et al., 2011) and its effect on OC recycling rates is not known. Approximately 30–40 % of the seafloor in the Baltic Sea is of accumulation type (Carman and Cederwall, 2001), thus it is important to understand how this vertical transport of particles will affect burial and recycling efficiencies.

The sediment response to eutrophication and hypoxia in terms of carbon burial and recycling thus remains unclear. To resolve the role of sediments, the spatial distribution and burial of carbon in Baltic Sea sediments has received considerable attention (Emeis et al., 2000; Hille, 2006; Leipe et al., 2011; Winogradow and Pempkowiak, 2014). However, benthic recycling of OC is often overlooked and much less studied (Kulinski and Pempkowiak, 2012; Winogradow and Pempkowiak, 2014), signifying the need for investigations, preferably in situ, of Baltic Sea sediments and their role in the C cycle.

3. Methods

3.1 Benthic Landers to study early diagenetic processes in situ

The Gothenburg benthic landers used in this study are advanced in situ instruments that can sink to the sea floor and perform biogeochemical measurements in the bottom water and sediment. Different modules can be mounted on the landers for different purposes (e.g. planar optodes, incubation chambers, micro electrodes). During this study both the big (Fig. 3) and small Gothenburg landers were used equipped with 4 and 2 incubation chambers respectively. The big lander is fully autonomous and can sink to the sea floor and perform incubations of the sediment water interface without any connection to the surface. The small lander must have a rope attached for deployment and recovery.



Figure 3 The big Gothenburg benthic lander at recovery (left) and a close up of the chamber module and attached syringes (right).

After the instrument has landed on the sea floor and equilibrated to surrounding bottom water conditions (i.e. ventilation phase) the chambers are gently inserted into the sediments. Another ventilation phase is made with chambers inserted to assure that no water from above is left inside and then the lids

are closed and the incubation begins. Each chamber is connected to a set of 1 injection and 9 sampling syringes that take water samples at pre set times. The injection syringe is used to inject a tracer or MQ water to be able to detect the incubated water volume, which has to be known in order to calculate solute fluxes. The volume of the incubated water will differ between incubations since the penetration depth varies.

The solute concentration change over time inside the chamber is monitored either by sensors or by discrete water sampling made by syringes connected to the chamber. The benthic solute flux is derived from the concentration change of the solute over time, the area of the incubated sediment and the volume of the incubated water.

The great advantages of this approach is that a relatively large area of the sediment (400 cm² for the chambers on the Gothenburg benthic landers) is incubated in situ with minimal disturbance resulting in a good representation of the natural flux between the sediment and overlying water (Tengberg et al., 1995).

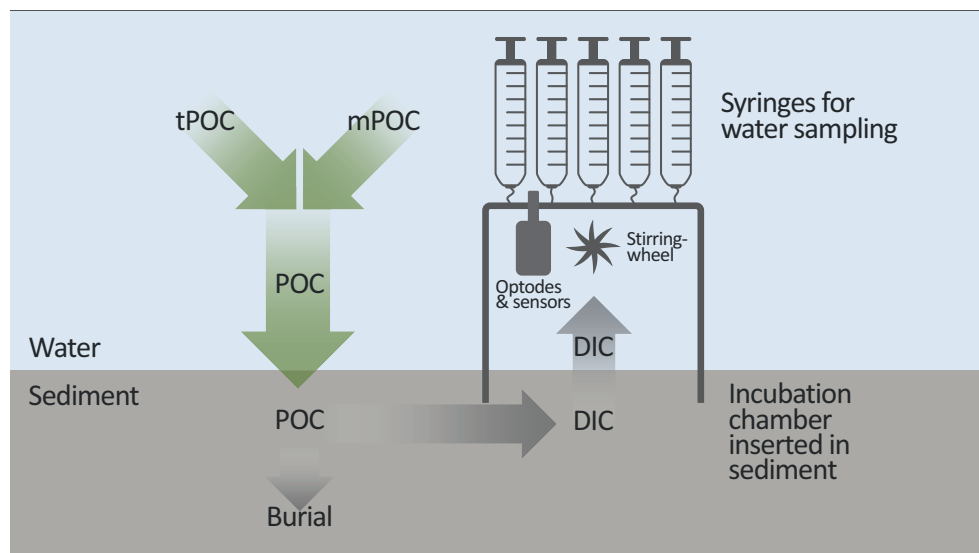


Figure 4 Basic principles to study early diagenetic processes in the sediments with chamber incubations performed with benthic landers. The total deposition of POC consist mainly of a terrestrial part (tPOC) and a marine part (mPOC). The transformation of POC to DIC are described in section 1.3.

The basic principle of chamber incubations to study the process of OC degradation in sediments during early diagenesis is depicted in Fig. 4. Deposition of POC (marine (mPOC) and terrestrial (tPOC)) to the sediments will be partly buried and partly hydrolyzed and further oxidized to DIC (described in section 1.3). The production of DIC during oxidation of OC results in a flux of DIC out of the sediment, which can be determined in chamber incubations. As mentioned in section 1.3, calcium carbonate dissolution can contribute to the production of DIC. However, carbonate dissolution is considered negligible in Baltic Sea sediments (Leipe et al., 2011; Schneider et al., 2002), which is also suggested from results in this study (PIC<1% dwt). Furthermore, C loss in terms of bubble emission of methane are not found to be important in Baltic Sea sediments (Sawicka and Brüchert, 2017).

Thus, we expect that on a large Baltic Sea system scale, the processes of calcium carbonate dissolution and methanogenesis will have a negligible net effect on our estimates of OC recycling rates, i.e. we consider the DIC flux being equal to total OC oxidation.

Sediments overlaid by oxygenated bottom water are inhabited by benthic fauna that make burrows and re-work the sediment. They have an important influence on OC degradation and can enhance the benthic flux of solutes several-fold through bioturbation (e.g. Aller, 2014). The influence of benthic animals on the benthic flux is included during chamber incubations. In sediments with few but large animals, however, the measured flux may not be representative on a larger spatial scale unless a large number of chamber incubations are made. Typically the macrofauna contribution to the overall respiration has been estimated to be 40–75 % (Glud et al., 1998; 2003). The incubated sediment can be sieved for animals after incubation to get a first estimate of bioturbation effects.

3.2 Sediment cores to study OC burial or preservation

A multiple corer (MUC, first described by Barnett et al., (1984) Fig. 5) was used to sample short sediment cores (<50 cm) for obtaining vertical distribution of C in recent sediment. The MUC can retrieve up to eight cores in one deployment. Only sediment cores of high quality were used. Sediments were sliced in 0.5–2 cm depth intervals with highest resolution in the upper part of the core.

Each slice was sampled and analyzed for particulate C species (POC and PIC). Example of a sediment profile of POC is seen in Fig. 6. The OC concentration decreases with sediment depth as a result of the OC oxidation, which decreases the sediment OC content over time.



Figure 5 Multiple corer (left) that can take up to eight sediment cores (right). Tubes are 55 cm in length and 9.9 cm in inner-diameter.

The layer where the steepest decline of OC occur with sediment depth, i.e. where the major part of OC oxidation occurs, is defined as the *reactive layer* (indicated by the shaded area in Fig. 6) in this thesis. The total amount of OC in this reactive layer is termed the POC inventory. The POC inventory can be seen as a measure of the total available OC pool that can undergo oxidation on the time-scale that is reflected in the total DIC flux measured by the lander.

At a certain sediment depth the OC concentration reaches a stable low concentration, i.e. only OC of lower quality, which does not easily undergo further oxidation, is left. This stable low OC concentration is defined as the OC *burial concentration* (indicated by the dashed line in Fig. 6). The rate of OC burial was estimated from the OC burial concentration and the sediment accumulation rate (SAR).

The main focus of this thesis work has been to describe differences and quantify process rates for different depositional regimes that are present in the Baltic Sea. For this purpose the Baltic Sea have been divided into accumulation areas

and erosion/transportation areas. The classification into accumulation and erosion/transportation areas was made based on the sediment water content in the top centimeter of the sediment after recommendations in (Håkanson and Jansson, 1983). In general, sediments with water contents higher than 75 % were classified as accumulation type sediments. However, additional characteristics such as OC content and the shape of the sediment profile of OC were also used to classify the sediments in this investigation.

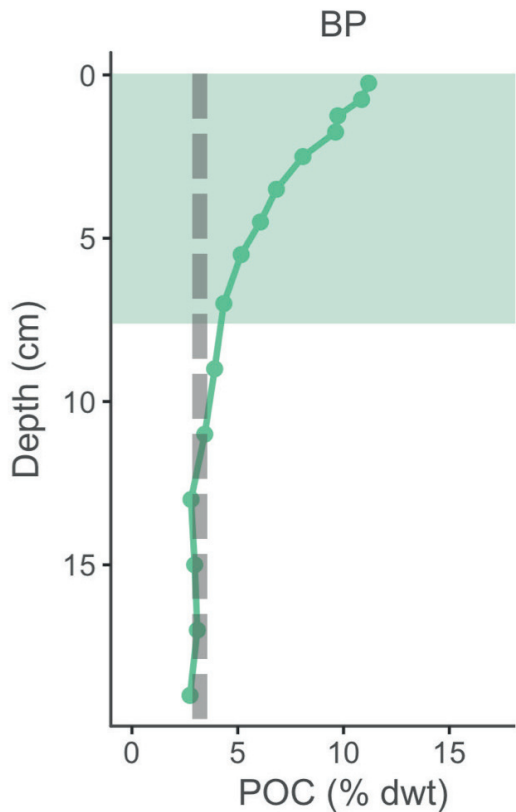


Figure 6 Vertical distribution of OC (% C of sediment dry weight) in the top 20 cm of sediment in the Baltic Proper accumulation area. The shaded area indicates the active zone of early diagenesis and is called the reactive layer. The dashed line indicates the stable concentration reached with depth, which is defined as the burial concentration in this thesis.

4. Main findings and discussion

4.1 OC recycling and burial in Baltic Sea sediments

The Baltic Sea sediments are subject to intense deposition of organic matter as found in **Paper I**. In total, we found that nearly 23 Tg OC deposits at the sea floor each year (Fig. 7). 96 % (22 Tg) of this OC is recycled back to the water column in the form of DIC due to OC oxidation.

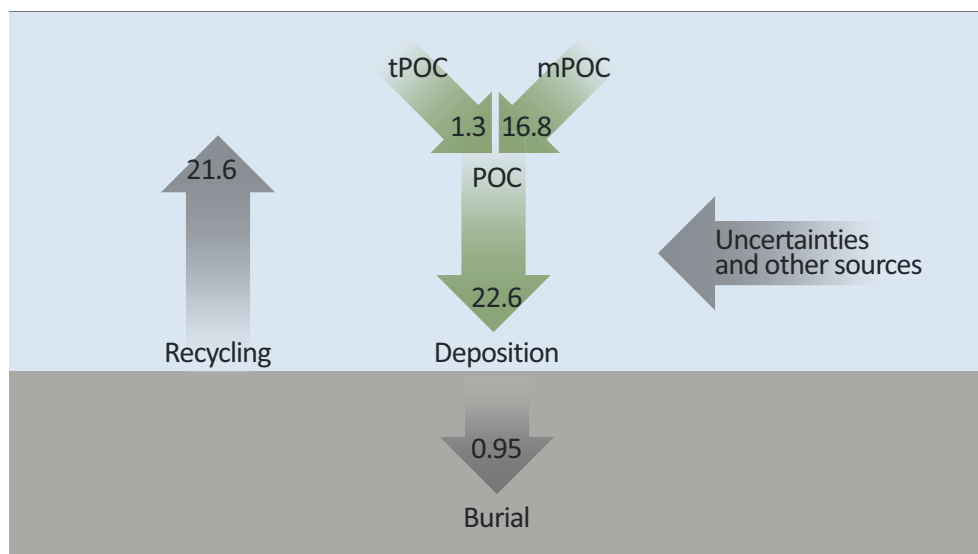


Figure 7 Benthic OC mass balance for the Baltic Sea as developed in Paper I. All numbers in Tg yr⁻¹.

The total burial for Baltic Sea sediments of 0.95 Tg found in this study is lower or in the same range than previous studies (ranging from 1.2–3.5 Tg C yr⁻¹, (Gustafsson et al., 2014; Kulinski and Pempkowiak, 2011; Leipe et al., 2011; Winogradow and Pempkowiak, 2014))

Moreover, the burial efficiency on the Baltic Sea system scale is in the lower (4 %) range when compared to other marine systems (Table 3, (Hartnett et al., 1998; Martens et al., 1992; Ståhl et al., 2004a, 2004b, 2004c), but large variations between the Baltic Sea sub-basins were observed (2.5–11 %). Burial efficiencies in the Baltic Sea have previously been found to range from 18–57 % (Canfield, 1993 and references therein). Our burial efficiencies are much

lower (6–16 % for accumulation areas and 2.5–11 % on a total basin-scale, i.e. including erosion/transportation areas, which have no net burial)

Table 3 Benthic OC process rates ($\text{mmol m}^{-2} \text{ d}^{-1}$) and burial efficiencies (BE, burial rate/deposition rate) found in other seas (Ståhl et al., ¹2004a, ²2004b, ³2004c), ⁴(Hartnett et al., 1998); ⁵(Martens et al., 1992).

| | Deposition | Recycling | Burial | BE (%) |
|--------------------------------------|------------|-----------|--------|--------|
| N. Aegean Sea ³ | 3.6 | 3.5 | 0.1 | 1.7 |
| Porcupine Abyssal Plain ² | 1.2 | 1.2 | 0.03 | 2.5 |
| Baltic Proper (This study) | 17.2 | 16.8 | 0.4 | 2.5 |
| Gulf of Bothnia (This study) | 2.81 | 2.58 | 0.24 | 8.4 |
| Gulf of Finland (This study) | 2.53 | 2.25 | 0.28 | 11 |
| Washington shelf ⁴ | 21.2 | 18 | 3.2 | 15 |
| Washington slope ⁴ | 11.2 | 8.7 | 2.5 | 26 |
| Mexican shelf ⁴ | 6.4 | 5.0 | 1.4 | 23 |
| Mexican slope ⁴ | 4.2 | 2.5 | 1.7 | 38 |
| Skagerrak ¹ | 21 | 9.2 | 12 | 57 |
| Cape Lookout Bight ⁵ | 452 | 130 | 321 | 71 |

In **Paper IV** the effects of the large inflow of oxygenated salty water that occurred in the Baltic Sea at the end of 2014 are investigated. The in situ measured benthic DIC fluxes in the Eastern Gotland Basin during 2008–2010, when the water column below about 100 m depth was anoxic, was compared to measurements conducted in early July 2015, less than four months after the inflow reached the Eastern Gotland Basin.

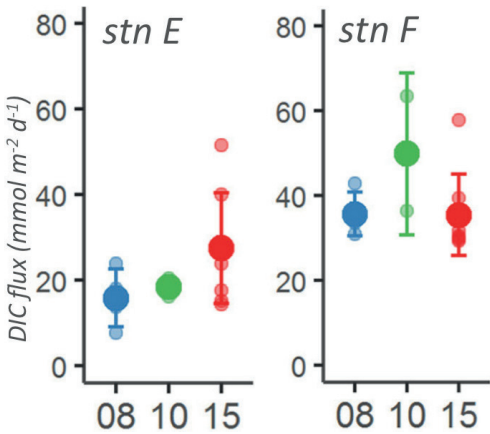


Figure 8 DIC fluxes before (2008 and 2010, blue and green dots) and after (2015, red dots) the major Baltic inflow.

The benthic ammonium, silicate (not shown) and DIC fluxes (Fig. 8) did not change significantly during the oxygenation event compared to the fluxes under anoxic conditions in 2008-10. However, the phosphate fluxes became lower or turned into an influx in 50 % of the chamber incubations.

Measurements of OC recycling rates in this study were made over several years (2001–2017) and included different seasons (April, July, August, Fig. 9). We found no significant seasonal variations.

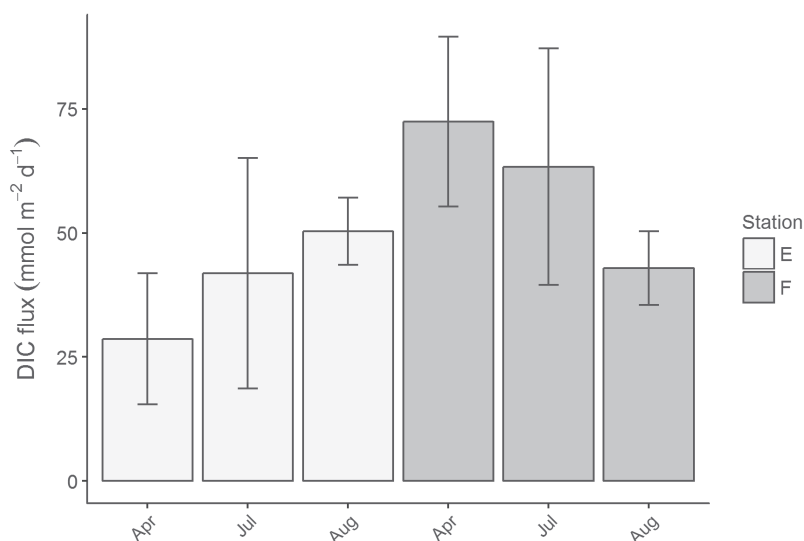


Figure 9 Seasonality at the two deepest stations (E and F) of the Eastern Gotland Basin.

We hypothesize that the sediment pool of OC is so large that any potential seasonal variation in POC deposition to the sediment do not influence the DIC fluxes significantly. Our estimates of OC recycling rates can therefore be looked upon as resembling the average annual rate at present time. However, uncertainties exist due to spatial heterogeneity.

4.2 OC recycling efficiency and factors influencing benthic OC recycling

Deep sediments in the Baltic Proper and Gulf of Finland release large amounts of DIC as a result of intensive OC oxidation. In **Paper II**, the observed increase

in OC recycling rates with normalized water depth is discussed. The term normalized water depth (i.e. actual water depth/maximum water depth of the basin) was introduced in order to compare accumulation bottoms between basins with different maximum water depth.

It was found that sediments in deep accumulation areas are more efficient in mineralizing OC, as suggested from the increase of the DIC/OC inventory ratio (here called the OC oxidation efficiency) with normalized water depth. However a few stations (A, H, U and V) located in permanently oxygenated ET areas of the Baltic Proper showed the highest efficiencies. The OC oxidation efficiency at these sites ($0.5\text{--}1\text{ yr}^{-1}$) also indicates that within a time period of less than one year the major part of the OC in the reactive layer of the sediment is recycled to overlying waters.

The OC and the chlorophyll-a inventories (Chl-a, an indicator for fresh labile material) also increased with normalized water depth. However, the DIC flux was not explained by the increased amount of available OC or fresh labile material (i.e. did not correlate with these inventories; $p>0.05$, $R^2<0.2$, no significant correlation between DIC flux and POC inventory or Chl-a inventory in sediment).

Resuspension and redistribution of OC is needed to balance the measured OC recycling and burial rates within the Baltic Proper. The results suggest that about 4.8 Tg of C is redistributed from ET areas and is redeposited at deeper calmer accumulation areas in the Baltic Proper (Table 4). Deposition of OC in deep accumulation areas of the Baltic Proper is 12 Tg C yr^{-1} according to our estimates. We can estimate that marine primary production delivers approximately half of this material (5.7 Tg C yr^{-1}). The rest is likely resulting from redistribution of sediment particulate material from ET areas. This redistribution of 4.8 Tg C yr^{-1} does not fully compensate for the deficit (-6.3 Tg C yr^{-1}) in deposition observed in A-areas. But when also taking into account riverine input (around 0.2 Tg C, Gustafsson et al., (2014)) and other point sources as well as uncertainties of the estimates, the numbers are considered to match (Table 4).

Table 4 Local OC budget (Tg C yr⁻¹) for the Baltic Proper suggest that approximately 4.8 Tg C yr⁻¹ is redistributed from shallow erosion/transportation areas and is redeposited in deeper, less energetic accumulation areas.

| | ET | +/- | A | +/- |
|------------------------------------|------------|-------------|-------------|------------|
| Recycling | 4.8 | 2.4 | 11 | 4.8 |
| Burial | 0 | | 0.4 | 0.2 |
| Deposition | 4.8 | 2.4 | 12 | 4.8 |
| Marine PP | 9.6 | 0.003 | 5.7 | 0.002 |
| Diff (Marine PP-Deposition) | 4.8 | 2.37 | -6.3 | 4.8 |

4.3 Improvement of benthic landers

When studying sediment, water fluxes in situ investigations are preferable since they are considered to give the highest quality data (e.g. (Glud et al., 1994; Hall et al., 2017; Sundby et al., 1986; Tengberg et al., 1995)). One difficulty of using benthic lander is that they are technically challenging and need continuous service and maintenance to keep optimal performance. As for all field sampling and measurements technical instruments and methods have to be improved and developed to obtain as high quality data as possible. **Paper III** describes work that has been made with the Gothenburg benthic landers during the past twelve years to improve this system with the aim to share our experience from the more than 250 deployments made in total. This has not been described for this type of system, since the early lander review that was published more than 20 years ago (Tengberg et al., 1995). **Paper III** also demonstrates that many possibilities exist to manipulate the natural system in situ to target specific sedimentary processes, for example injections of tracers or introducing physical stress by increased stirring speed (Almroth-Rosell et al., 2012).

One major improvement of our benthic lander system has been in measuring the incubation volume to determine the incubated water height needed for flux calculations. Originally the height was determined from camera observation of a ruler mounted inside the chamber, and later on by injection of a non-reactive tracer (bromide) and subsequent analysis of the dilution in the proceeding water samples. Today conductivity sensors are installed inside the chambers that can determine very small changes in salinity. By injection of milli-Q water the incubation volume can be determined from the observed change in salinity.

The salinity data also let us detect if there is a leakage during the incubation. This new method is very time-efficient and gives a more accurate determination of the volume; the incubated volume can now be measured with an accuracy of $1 \pm 4 \%$.

This is an important step forward for in situ chamber incubation measurements since a 10 % error in the volume determination results in a 10 % error in the calculated flux. Furthermore, since the volume detection is now made by sensors rather than by discrete water sampling, no valuable sample volume is lost for this purpose and can be used for analysis of other solutes of interest. The method also has the advantages of providing the results right after recovery and download of the data. In this way we can quickly determine if the incubations were successful and discard chambers that show signs of leakage or any other problems. This saves time and efforts in further analysis of syringe samples.

It is not only crucial to find the exact volume of the incubated water, it is also important to identify that syringes are released at the time they are supposed to in order to get high accuracy in the flux calculations. Even if the syringes are pre-programmed they can be delayed or pre-released due to mechanical dislocations in the trigger system or get released upon impact with the water surface during the deployment. To be able to detect exactly when the syringe samples are taken a pressure sensor has been installed and tested successfully.

5. Conclusions

The benthic landers used in this study allow for high quality measurements of sediment-water fluxes of DIC and we now have a substantial tool-box for evaluating and controlling the functionality and reliability of the lander chamber incubations. The in situ measurements of benthic DIC fluxes conducted in the Baltic Sea during this thesis work are unique and have enhanced the understanding of OC cycling in the Baltic Sea.

It was found that the intensive OC oxidation in Baltic Sea sediments results in an annual DIC release from sediments on the order of 22 Tg C; about three times as large as the riverine input of TIC (6.8 Tg C yr^{-1} ; Kulinski and Pempkowiak, (2011)) and one order of magnitude larger than previous estimates of benthic release of DIC in the Baltic Sea (Gustafsson et al., 2014; Kulinski and Pempkowiak, 2011). The effect on the benthic OC recycling rates of deep water oxygenation after a major Baltic inflow was insignificant. This was probably due to a combination of the high amount of reduced substances in the sediment, which consume oxygen rapidly resulting in a minimal penetration of oxygen into the sediment, and the large pool of OC.

Despite similar inventories of OC in the sediment reactive layer, OC oxidation rates were significantly lower in the oligotrophic Gulf of Bothnia than in the mesotrophic/eutrophic Baltic Proper and Gulf of Finland, suggesting differences in the oxidation efficiency of OC. For the eutrophic system, the OC oxidation efficiencies were largely influenced by the location in relation to the maximum water depth of the basin (i.e. normalized water depth as a proxy for basin topography). A similar dependence with basin topography was seen for the OC and Chl-a inventories. However, the OC recycling rates could not be explained by the POC inventory or Chl-a inventory (no significant correlation between DIC flux and POC inventory or Chl-a inventory). Instead, the age of the surficial sediment had a main influence on OC recycling, since the OC oxidation efficiency decreased with increasing age (DIC flux/POC inventory vs sediment age showed a negative trend). It was found that the surface layer of the sediments in deep A-areas consisted of younger and thus more labile material compared to sediments in ET-areas. This accumulation of young and fresh material resulted in a more efficient OC oxidation (i.e. oxidation rate per available OC in the sediment). These results demonstrate the importance of

lateral transport of particulate material within the Baltic Sea basin system, with focusing of OC along the bathymetric continuum as a major factor controlling OC oxidation efficiencies in the system.

6. Future outlook

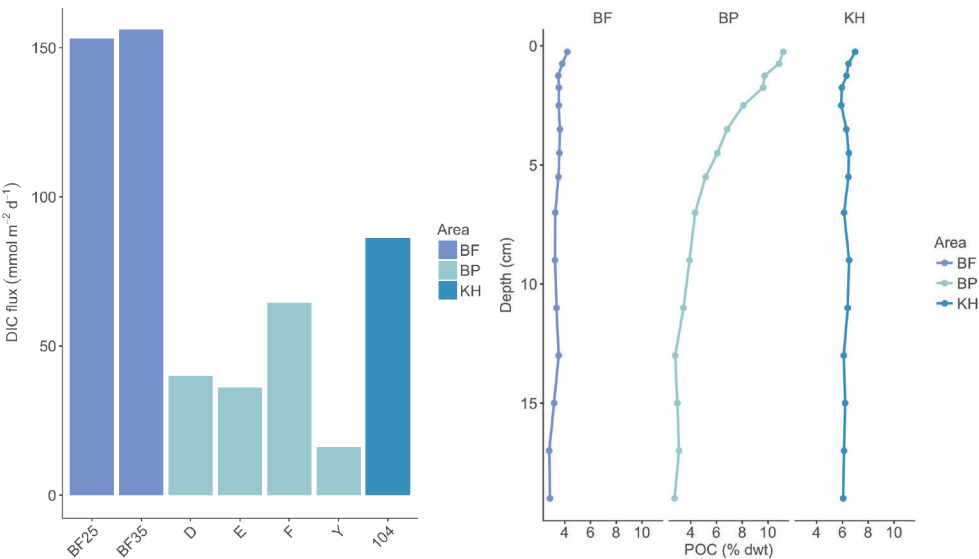


Figure 10 In situ measured DIC fluxes at two sites compared to Baltic Proper (BP) A-areas of this study (left), and corresponding sediment profiles of OC (right). Kanholmsfjärden (KH) is a coastal basin located in the Stockholm archipelago and Byfjorden (BF) is a small estuarine fjord on the Swedish west coast.

Our experience with sampling of sediments in anoxic and extremely organic rich sediments have led to the question whether regular sediment core slicing methods are suitable when working in sediments with a pronounced ‘fluffy layer’ at the sediment surface, since it can be very difficult to determine exactly where the sediment-water interface is.

In both Kanholmsfjärden (Ekeröth et al., 2016) and Byfjorden (unpublished results) we measured even higher OC recycling rates than in the deep accumulation areas of the Baltic Proper (Fig. 10). However, sediment profiles of OC did not seem to match these high rates (Fig. 10).

A simple budget calculation taking into account possible sources of OC to sediments in Byfjorden suggests that our measured DIC fluxes are compatible with expected OC deposition to the sediment surface (Fig. 11).

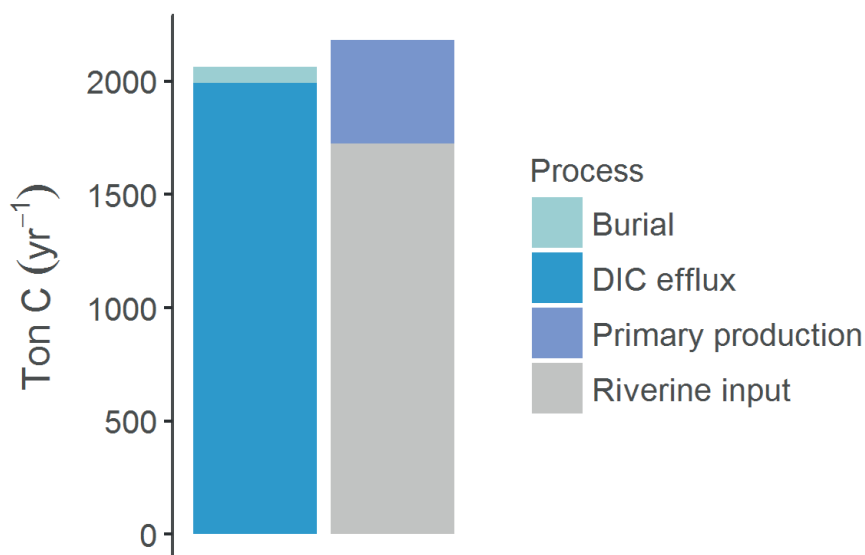


Figure 11 Estimated POC deposition to sediments (left) from our measurements in Byfjorden compared to sources of POC (right) estimated from riverine input of TOC from Båveån and marine primary production (from SMHI monitoring program).

It seems like a layer of organic rich material is lost through the current sampling and slicing methods. Both Kanholmsfjärden and Byfjorden sediments are characterized by extremely high water contents (>90 %) in several centimeters of the surface sediment in contrast to the Baltic Sea sediments in this study, which had high water contents in the top 0–1 cm. These extremely high water contents in Byfjorden sediments made it difficult to sample the uppermost sediment layer.

We hypothesize that benthic landers incubate the natural fluff layer and fluxes measured with landers should thus include DIC produced in the fluff layer, whereas a large part of the OC in this layer is lost during regular sampling and slicing procedures. This may explain the very high benthic DIC fluxes measured in Byfjorden and Kanholmsfjärden without correspondingly high sediment OC inventory.

In coming expeditions to the Baltic Sea, we will test a new method for sampling this fluffy layer. The aim is to investigate different sampling methods and find the ‘missing carbon’. The method is adopted from water column measurements of POC, where a known volume of water is filtered through a 0.7 µm glass fiber

filter, the whole filter is then packed into capsules and analyzed for the different C species.

We believe that this method will be a step forward measuring actual OC concentrations at the sediment-water interface.

One aspect that was not discussed in this work was the contribution of degradation of OC originating from cyanobacteria biomass. Unpublished results from measurements of cyanobacterial specific pigments suggest that organic matter originating from cyanobacteria is also accumulating in the deep accumulation sediments of the Baltic Sea (Fig. 12). It would be interesting to find out the contribution of organic matter originating from cyanobacteria to the overall benthic OC recycling rates and efficiencies in the Baltic Sea.

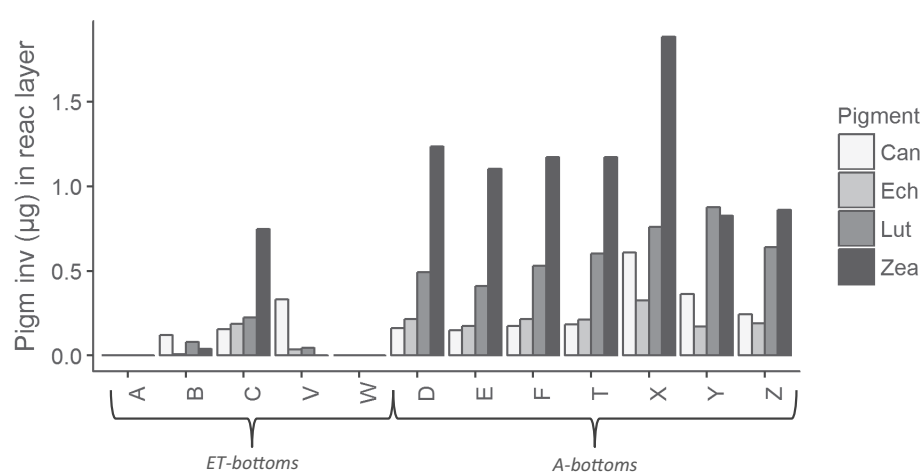


Figure 12 Inventory of cyanobacteria specific pigments found in the sediments of the Eastern Gotland Basin. Inventories were highest in deep A-areas. Cantaxanthine (Can), Echinenone (Ech), Luteine (Lut) and Zeaxanthine (Zea) are all specific carotenoid pigments associated with cyanobacteria.

7. Acknowledgements

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