Organic carbon dynamics in the Baltic Sea
A modelling perspective

Filippa Fransner

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Abstract
Coastal seas constitute a link between land and the open ocean, and therefore play an important role in the global carbon cycle. Large amounts of carbon, of both terrestrial and marine origin, transit and are transformed in these waters, which belong to the more productive areas of the oceans. Despite much research has been done on the subject, there are still many unknown factors in the coastal sea carbon cycling.

This doctoral thesis investigates the carbon dynamics in the Baltic Sea, with a focus on the production and fate of marine and terrestrial organic carbon and its influence on the air-sea CO₂ exchange in its northernmost part, the Gulf of Bothnia. The main approach is the use of a coupled 3D physical-biogeochemical model, in combination with a long series of measurements of physical and biogeochemical parameters.

A new coupled 3D physical-biogeochemical model, which includes the stoichiometric flexibility of plankton and organic matter, is set up for the Gulf of Bothnia. It is found that phytoplankton stoichiometric flexibility in particular, with non-Redfieldian dynamics, is key to explaining seasonal pCO₂ dissolved organic carbon (DOC), and nutrient dynamics. If the Redfield ratio is instead used to predict organic carbon production, as done in most biogeochemical models currently in use, the uptake of atmospheric CO₂ is reduced by half. Furthermore, it is shown that the organic carbon production needed to reproduce the summer pCO₂ drawdown is larger than measured estimates of primary production. This discrepancy is attributed to a substantial production of extracellular DOC, which seems not to be captured by measurements.

The dynamics of terrestrial dissolved organic carbon (tDOC) is studied by the use of a passive tracer released from rivers into the physical model of the Baltic Sea. It is found that 80% of the tDOC released in the Baltic Sea is removed, and the rest is exported to the North Sea. Two different parameterisations of tDOC removal are tested. In the first one a decay rate with a timescale of 1 year applied to 80% of the tDOC, and the remaining 20% is assumed to be refractory. In the second one a decay rate with a timescale of 10 years applied to 100% of the tDOC. Trying these parameterisations in a full biogeochemical model shows that only the one with the faster decay is able to reproduce observations of pCO₂ in the low-salinity region. A removal rate of one year agrees well with calculated removal rates from bacterial incubation experiments, indicating that bacteria have the potential to cause this remineralisation. It is not only remineralisation of tDOC that affects the pCO₂; it is also suggested that a strong tDOC induced light extinction is needed to prevent a too large pCO₂ drawdown by phytoplankton in the low salinity region.

Keywords: carbon cycle, organic carbon, primary production, remineralisation, terrestrial DOC, extracellular DOC, flexible stoichiometry, Redfield ratio, air-sea CO₂ exchange, pCO₂, coupled 3D physical-biogeochemical modelling, Gulf of Bothnia, Baltic Sea.

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Department of Meteorology

Stockholm University, 106 91 Stockholm
ORGANIC CARBON DYNAMICS
IN THE BALTIC SEA

Filippa Fransner
Till mamma och pappa
Sväll härligt, sköna segel, sväll i vindens dust
Flyg fram med fröjd mot vågens fjäll i stundens högsta lust!

from "Till Havs" by Jonatan Reuter
Abstract

Coastal seas constitute a link between land and the open ocean, and therefore play an important role in the global carbon cycle. Large amounts of carbon, of both terrestrial and marine origin, transit and are transformed in these waters, which belong to the more productive areas of the oceans. Despite much research has been done on the subject, there are still many unknown factors in the coastal sea carbon cycling.

This doctoral thesis investigates the carbon dynamics in the Baltic Sea, with a focus on the production and fate of marine and terrestrial organic carbon and its influence on the air-sea CO$_2$ exchange in its northernmost part, the Gulf of Bothnia. The main approach is the use of a coupled 3D physical-biogeochemical model, in combination with a long series of measurements of physical and biogeochemical parameters.

A new coupled 3D physical-biogeochemical model, which includes the stoichiometric flexibility of plankton and organic matter, is set up for the Gulf of Bothnia. It is found that phytoplankton stoichiometric flexibility in particular, with non-Redfieldian dynamics, is key to explaining seasonal pCO$_2$, dissolved organic carbon (DOC), and nutrient dynamics. If the Redfield ratio is instead used to predict organic carbon production, as done in most biogeochemical models currently in use, the uptake of atmospheric CO$_2$ is reduced by half. Furthermore, it is shown that the organic carbon production needed to reproduce the summer pCO$_2$ drawdown is larger than measured estimates of primary production. This discrepancy is attributed to a substantial production of extracellular DOC, which seems not to be captured by measurements.

The dynamics of terrestrial dissolved organic carbon (tDOC) is studied by the use of a passive tracer released from rivers into the physical model of the Baltic Sea. It is found that 80% of the tDOC released in the Baltic Sea is removed, and the rest is exported to the North Sea. Two different parameterisations of tDOC removal are tested. In the first one a decay rate with a timescale of 1 year applied to 80% of the tDOC, and the remaining 20% is assumed to be refractory. In the second one a decay rate with a timescale of 10 years applied to 100% of the tDOC. Trying these parameterisations in a full biogeochemical model shows that only the one with the faster decay is able to reproduce observations of pCO$_2$ in the low-salinity region. A removal rate of one year agrees well with calculated removal rates from bacterial incubation
experiments, indicating that bacteria have the potential to cause this remineralisation. It is not only remineralisation of tDOC that affects the pCO₂; it is also suggested that a strong tDOC induced light extinction is needed to prevent a too large pCO₂ drawdown by phytoplankton in the low salinity region.
Sammanfattning

Kustnära hav länkar samman land och oceanner, och spelar därför en viktig roll i jordens kolcykel. Stora mängder kol, av både terrestert och marint ursprung, passerar och omvandlas i dessa vatten som är en av de mer produktiva delarna av världshaven. Trots att det finns många mätningar och att det har bedrivits mycket forskning i kustnära hav, så är stora delar av dess kolcykel fortfarande dåligt förstådd.

Den här doktorsavhandlingen behandlar Östersjöns kolcykel, med ett fokus på produktionen av marint organiskt kol och det öde terrestert organiskt kol går till mötes i havet, samt hur detta påverkar utbytet av koldioxid med atmosfären. Den största delen av forskningen har fokuserat på Östersjöns nordligaste del; Bottniska viken. Tredimensionell fysik-biogeokemisk modellering har varit det huvudsakliga verktyget, och modelldata har jämförts med flera år av mätningar av fysiska och biogeokemiska parametrar.


Genom att använda en passiv tracer som representerar terrestert löst organiskt kol (tDOC) och som släpps ut från floder i den fysiska modellen för Östersjön och Nordsjön, undersöks vad som händer med detta kol i havet. Vi kommer fram till att 80% av det tDOC som kommer till Östersjön på något sätt försvinner, och att 20% exporterar till Nordsjön. Vi föreslår två olika parameteriseringar för att simulera tDOC-sänkan. I den första appliceras en linjär nedbrytningstakt med en tidsskala på ett år på 80% av tDOC, och den resterande andelen antas vara refraktionär. I den andra parameteriseringen appliceras en nedbrytningstakt med en tidsskala på 10 år på 100% av tDOC. När dessa parameteriseringar testas på en full biokemisk modell visar det sig att bara
Résumé

Les mers côtières établissent une connexion entre les surfaces continentales et les océans. Elles jouent donc un rôle important dans le cycle global du carbone. Des grandes quantités du carbone marin et terrestre transitent, et sont transformées, dans ces eaux peu profondes, lesquelles sont parmi les plus productives de l’océan global. Malgré de nombreuses recherches sur le sujet, il reste de grandes incertitudes concernant le cycle du carbone des mers côtières.

Cette thèse de doctorat examine le cycle du carbone dans la mer Baltique, en particulier la production du carbone organique marin et le destin du carbone organique terrestre, ainsi que l’effet de ces transformations sur l’échange de CO₂ avec l’atmosphère. La recherche se concentre sur la baie du Bothnie, la partie Nord de la mer Baltique. La modélisation physique biogéochimique 3D a été l’outil principal, et des simulations ont été comparées à des mesures des paramètres physiques et biogéochimiques.

Un nouveau modèle 3D physique-biogéochimique, qui prend en compte la variabilité de la stœchiométrie des planctons et des matières organiques, a été appliqué dans la baie de Bothnie. Nous démontrons que la stœchiométrie variable du phytoplancton est nécessaire pour comprendre les variations saisonnières du pCO₂, du carbone organique, et des nutriments. Si le ratio de Redfield est utilisé pour calculer la fixation de carbone du phytoplancton, comme dans la plupart des modèles couramment utilisés, l’absorption du CO₂ atmosphérique est réduite de moitié. De plus, nous démontrons que la production de carbone organique nécessaire pour reproduire la baisse de pCO₂ estivale est beaucoup plus grande que celle mesurée in situ. Ce biais est relié à une grande production du carbone organique dissous extracellulaire, qui ne semble pas être capturée par les mesures.

La dynamique du carbone organique dissous terrestre (tDOC) est étudiée par l’utilisation d’un traceur passif libéré par les rivières dans le modèle physique de la mer Baltique et la mer du Nord. On trouve que 80% du tDOC apporté dans la mer Baltique est retiré, et le reste est exporté vers la mer du Nord. Deux paramétrisations différentes de l’élimination de tDOC sont essayées. Dans le premier cas, un taux de décroissance avec une échelle du temps d’une année est appliqué à 80% du tDOC, et les 20% restants sont supposés réfractaires. Dans le second, un taux de décroissance avec une échelle de temps de 10 ans est appliqué à 100% du tDOC. L’étude de ces paramétrisations dans un modè-
le biogéochimique complet montre que seul celui qui a la décroissance la plus rapide est capable de reproduire les observations de pCO₂ dans la région de faible salinité. Un taux de décroissance avec une échelle du temps d’un an s’accorde bien avec les taux d’élimination calculés à partir des expériences d’incubation bactérienne, indiquant que les bactéries ont le potentiel pour provoquer cette reminéralisation. Ce n’est pas seulement la reminéralisation du tDOC qui affecte le pCO₂, on trouve également qu’une forte extinction de la lumière induite par le tDOC est nécessaire pour entraver un prélèvement de pCO₂ trop important par les phytoplanctons dans la région de faible salinité.
List of Papers

The following papers, referred to in the text by their Roman numerals, are included in this thesis.

PAPER I:  
**Tracing terrestrial DOC in the Baltic Sea – A 3-D model study**


DOI: 10.1002/2014GB005078

PAPER II:  
**Non-Redfieldian dynamics explain seasonal pCO$_2$ drawdown in the Gulf of Bothnia**


DOI: 10.1002/2017JC013019

PAPER III:  
**Remineralization rates of terrestrial DOC as inferred from CO$_2$ supersaturated waters**


PAPER IV:  
**Nemo-Nordic: A NEMO based ocean model for the Baltic and North Seas, research and operational applications**


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Author’s contribution

The idea of paper I was developed in discussions with me and my supervisors. I came up with the idea of dividing the DOC into two pools of different reactivity (2POOL simulation). I constructed the simple decay-model within the TOP interface of NEMO and performed all the simulations. I did all the data-analysis and was responsible for the main part of the writing and review process, with input and comments from the co-authors.

The idea of paper II was originally my own. In the beginning of my PhD I read a paper that made me think that flexible stoichiometry may be the answer to the modelling problems in the Northern Baltic Sea. The story of the paper was then developed in discussions between me and the co-authors. I did all the simulations and data-analysis. I was responsible for the main part of the writing and review process with inputs and comments from the co-authors. The work in this paper does not only contain a scientific story, but also the setup and tuning of a new physical-biogeochemical model configuration for the Gulf of Bothnia. The setup of the physical part was done together with Robinson Hordoir. Then I did all the tuning. For the biogeochemical part I did all the technical work and the tuning process, with the guidance mainly from Letizia Tedesco, Marcello Vichi and Erik Gustafsson. Ivan Kuznetsov and Magnus Mörhth provided me with atmospheric and river load data, respectively.

The idea of paper III was developed between me and my supervisors. I did all the simulations and the data-analysis. I also did the main part of the writing, with help and comments from co-authors. Agneta Fransson provided me with the pCO2 measurements.

Paper IV is a technical paper describing the physical model used in all papers in this thesis. My main contribution is on the vertical thermohaline structure and the surface currents (sections 3.2.1, 4.2.1 and 4.3.1), as well as figures 7 and 8. I have also been responsible for the editing process, i.e. in putting everything together, making the text fluent, and correction reading.
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## Abbreviations

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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>BFM</td>
<td>Biogeochemical Flux Model</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>DIC</td>
<td>Dissolved inorganic carbon</td>
</tr>
<tr>
<td>DIN</td>
<td>Dissolved inorganic nitrogen</td>
</tr>
<tr>
<td>DIP</td>
<td>Dissolved inorganic phosphorus</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved organic carbon</td>
</tr>
<tr>
<td>mDOC</td>
<td>marine dissolved organic carbon</td>
</tr>
<tr>
<td>mOC</td>
<td>marine organic carbon</td>
</tr>
<tr>
<td>mPOC</td>
<td>marine particulate organic carbon</td>
</tr>
<tr>
<td>NEMO</td>
<td>Nucleus for European Modelling of the Ocean</td>
</tr>
<tr>
<td>OC</td>
<td>organic carbon</td>
</tr>
<tr>
<td>pCO₂</td>
<td>CO₂ partial pressure</td>
</tr>
<tr>
<td>POC</td>
<td>Particulate organic carbon</td>
</tr>
<tr>
<td>TA</td>
<td>total alkalinity</td>
</tr>
<tr>
<td>tDOC</td>
<td>terrestrial dissolved organic carbon</td>
</tr>
<tr>
<td>tOC</td>
<td>terrestrial organic carbon</td>
</tr>
<tr>
<td>tPOC</td>
<td>terrestrial particulate organic carbon</td>
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</tbody>
</table>
Acknowledgements

I can’t believe it’s finished. I have learned so much, and got to know so many people, it has been a real adventure!

First of all I want to thank my main supervisor Jonas Nycander. You have been very supportive and have always given me time when I needed. Especially there was a time where my thesis work took quite a turn and I was hesitating, and I’m very grateful that you believed in me and encouraged me to take the path I took. I also want to thank you for speeding up the innebandy (floorball) games on Thursdays! Many thanks also to my co-supervisor Christoph Humborg for all your support, and for giving me the perspective of a biogeochemist in this interdisciplinary science! What I have learned especially from you is how to find the story and how to sell it, although there is still a long way to go there. I’m grateful to Erik Gustafsson for all your time and your patience! I much enjoyed coming over to your department for a cup of coffee and to discuss all kinds of modelling issues!

I want to give a big warm thanks to Letizia Tedesco for everything you have done and for teaching me about everything from sea-ice to phytoplankton to sediments, and helping me understanding to me a very complex model. It has been very nice to collaborate with you and I enjoyed coming to Helsinki to work with you and your colleagues! Thanks to Kristian Spilling for nice discussions about stoichiometry! I’m also very grateful to Marcello Vichi. I’m glad that I went to that winter school in Cochin, my PhD would have ended quite differently if I didn’t. I want to thank you for all your support (although it has been remote it has worked perfectly fine!), for finding interesting things in my results that I thought were not that good, and all the Skype meetings that took me several days to process afterwards!

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I want to thank Magnus Mörh, for always being so optimistic about my
work, and Agneta Fransson, for your quick response and for seeing me in Tromsø, and all my co-authors that have not yet been mentioned for their contribution to the work in this thesis! Markus Meier is thanked for taking part in the supervision the beginning of the thesis.

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In the last rows I wish to thank my family. First I want to thank my mum and my dad for always, since I was a kid, saying that studies are good (studier lönar sig), and see now where it ended! I want to thank Oscar and Isolde for being my bother and ma belle sœur and all that comes with that! Oscar, it has been fun to compete with you about who will be the first Dr. Fransner! Thanks to my grandparents (mormor och morfar och farmor) and moster, and all my relatives, for all your encouragement and for always asking how things are going!

À la fin, I want to thank Robinson for your endless support, and for sharing my passion for the sea (...and food)!
1. Introduction and background

Carbon has a profound effect on Earth’s climate and is an essential building block of life. Studying the fluxes and transformations of carbon in the environment is therefore fundamental from both a climatic and ecological perspective.

The oceans play an important role in the global carbon cycle as they constitute the largest carbon reservoir on Earth and exchange substantial amounts of carbon with the atmosphere and land [45]. About half of the global net primary production, a process where inorganic carbon is fixed into organic carbon, takes place in the marine environment (Chavez et al. [17], and references therein). Coastal seas belong to the more productive areas of the oceans; despite their relatively small area it has been estimated that their contribution to the oceanic primary production is as large as 30% [10]. Due to this large productivity, coastal seas are generally considered as sinks of atmospheric CO2 [14]. However, these waters also receive relatively large amounts of terrestrially derived carbon, both in inorganic and in organic form, the latter providing bacteria with an additional source of carbon. Inner parts of coastal seas, especially estuaries, are often heterotrophic, i.e. sources of atmospheric CO2, as a result of remineralisation of tOC and input of CO2 supersaturated waters [10; 13; 14]. Inputs of terrestrial organic matter can also hamper primary production by making the waters turbid, further reducing the carbon uptake [94].

With climate change, it has been anticipated that the loads of organic carbon to high latitude coastal seas will increase [78]. Questions have been put forward on how these increased carbon loads, as well as reductions in ice extent and a warmer climate in general, might influence the bacterial versus the primary production, the carbon cycling, and the air-sea CO2 exchange in these waters [6; 77; 94]. The fate of carbon in present day coastal seas is, however, poorly constrained [10], which also makes it difficult to understand how it would change with a warmer climate.

The aim of this thesis is to contribute to the understanding of the contemporary carbon cycling in one of our most well-observed coastal seas, the Baltic Sea, by investigating the dynamics of both terrestrial and marine derived organic carbon. The main approach has been coupled 3D physical-biogeochemical modeling, which has been combined with measurements of physical and biogeochemical parameters. A descent representation of the physics in the physical model is required before any further steps into biogeochemical
questions can be taken, which is validated in paper IV. When it comes to biogeochemical model, one major concern has been that there is no good model parameterisation of primary production in the Baltic Sea. All existing large-scale models of the Baltic Sea use a Redfield approach [22; 24; 35; 53], which mostly is adapted for open the ocean. I therefore had to apply a new model in order to understand the marine carbon production.

The research in this thesis is structured as follows: i) I first investigate tDOC removal in the Baltic Sea by means of a 3D tracer approach with various decay functions. The results show that the Northern Baltic Sea, the Gulf of Bothnia, is the most interesting place when it comes to tDOC dynamics (paper I). ii) I then focus on the Gulf of Bothnia, and adopt a non-Redfieldian approach to parameterise primary production, and it is demonstrated that it adequately simulates nutrient and carbon dynamics (that do not follow Redfield dynamics) and the marine carbon production (paper II). iii) Finally the parameterisations of tDOC removal and non-Redfieldian primary production is combined, together with high resolution underway measurements of pCO₂, to investigate the influence of tDOC on the carbon cycling in the Gulf of Bothnia (paper III).
1.1 Carbon cycling in the marine environment

1.1.1 Inorganic carbon

Inorganic carbon exists in marine waters as carbon dioxide, carbonic acid, bicarbonate and carbonate ions. These species together are called dissolved inorganic carbon (DIC):

\[ DIC = [CO_2(aq)] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \quad (1.1) \]

The amount of DIC that can be held in seawater, and its speciation, depends on the temperature, salinity and total alkalinity of the seawater, the pressure, as well as the atmospheric content of CO\(_2\).

The total alkalinity (TA), is defined as the buffering capacity of seawater, i.e. its capacity to neutralise H\(^+\) ions:

\[ TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [SiO(OH)_3] + [NH_3] + [HS^-] - [H^+] - [HSO_4^-] - [HF] - [H_2PO_4] + [Organic alkalinity] \quad (1.2) \]

This expression comes from Dickson [19], with the addition of organic alkalinity by Ulfsbo et al. [88]. The higher the alkalinity is, the higher the pH, and the more DIC can be contained in the seawater.

\( pCO_2 \) and air-sea CO\(_2\) exchange

The sum of the CO\(_2(aq)\) and the H\(_2CO_3\) are together called CO\(_2^*\), and determines the CO\(_2\) partial pressure (pCO\(_2\)) of seawater:

\[ pCO_2 = \frac{[CO_2^*]}{K_0} \quad (1.3) \]

where \( K_0 \) is the CO\(_2\) solubility constant.

The air-sea exchange of CO\(_2\) is primarily driven by the pCO\(_2\) difference between the atmosphere and the seawater (\( \Delta pCO_2 \)), and can be expressed as:

\[ F = kK_0\Delta pCO_2 \quad (1.4) \]

where \( k \) is the gas transfer velocity, which is dependent on the physical state of the sea surface. The more turbulence and waves, the larger is the gas transfer velocity. The gas transfer velocity is therefore often expressed as a function of wind speed. In presence of sea-ice, the air-sea exchange is dampened. It has
been observed that the dampening is proportional to the sea-ice concentration [65]. This is applied in the model used in paper II and III.

In absence of processes other than air-sea exchange, sea water would be in equilibrium with the atmospheric CO$_2$ content, and its CO$_2$ partial pressure would equal that of the atmosphere. Processes that either produce or remove DIC in the surface waters, or reduce/increase the solubility of CO$_2$, lead to an increase/decrease in the pCO$_2$. The resulting disequilibrium drives an outgassing/uptake of CO$_2$ to/from the atmosphere. Changes in surface water pCO$_2$ can also come a result of upwelling and physical mixing that bring deep water oversaturated in CO$_2$ to the surface. Measurements of pCO$_2$ can therefore give clues about carbon transformations and fluxes that take place in the seawater, and are used in paper II and III.

1.1.2 Organic carbon

Where does it come from?

Inorganic carbon is transformed to organic carbon through carbon fixation, a process where the carbon is reduced and bound into organic molecules. There is a large variety of organic molecules ranging from simple amino acids, lipids and sugars, to more complex molecules such as polysaccharides, lignin and humic substances (e.g. Repeta [72]). Organic carbon is often separated into particulate organic carbon (POC) and dissolved organic carbon (DOC).

**Autochthonous organic carbon**

In the marine environment the primary producers of organic carbon are phytoplankton (Figure 1.1). When they fix carbon the DIC concentration in the seawater decreases, leading to a drop in the seawater pCO$_2$ (paper II). Except for inorganic carbon, phytoplankton also need sunlight, water and nutrients for their growth. Nitrogen and phosphorus belong to the more limiting nutrients in the marine environment [58]. A simplified expression for marine organic matter production is as follows:

$$106CO_2 + 16NO^-_3 + HPO_4^{2-} + 122H_2O + 18H^+ \Rightarrow (CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138O_2$$ (1.5)

This expression in based on the work of Redfield [69, 70]; Redfield et al. [71], who observed that the average C:N:P ratio in organic matter in the ocean is 106:16:1. This ratio, called the Redfield ratio, has thereafter been widely used in budget calculations and marine biogeochemical models to estimate organic
matter production [75]. However, in reality there are a large variety of organic compounds and molecules with different composition, and the stoichiometry of living phytoplankton is known to be able to deviate far from the Redfield ratio [31]. Variations of C:N:P ratios in phytoplankton can come as a response to nutrient availability, as well as variations in the composition of the cellular machinery of phytoplankton, which can vary across taxa and as a response to growth strategy/growth phase, temperature, light and nutrient conditions [60]. Low nutrient conditions can not only lead to elevated carbon:nutrient ratios within phytoplankton cells. It can also result in carbon overflow (exudation), a process where phytoplankton release recently fixed carbon as extracellular DOC [15]. It has been shown that this extracellular release can constitute a large part of the total primary production [47; 62; 66; 81]. Engel [25] further showed that the production of transparent exopolymer particles (TEP), which is believed to be a result of the production of extracellular DOC, can cause a substantial drawdown of the pCO₂. In paper II we show that flexible stoichiometry and carbon overflow is crucial for understanding the carbon and nutrient cycling in the Northern Baltic Sea.

Allochthonous organic carbon
In coastal waters a large part of the organic carbon can be of terrestrial origin (tOC), which arrives into coastal waters via river discharge (Figure 1.1), erosion and to some extent ground water leakage [10; 67]. It has been estimated that 0.45 PgC y⁻¹ of tOC arrives to coastal seas via rivers globally [10]. With global warming there has been a rising concern for increasing river discharge at high latitudes [78], and especially the release of organic carbon frozen into the permafrost, which is estimated to contain more than twice as much as the atmospheric content of carbon [45; 84]. Allochthonous organic carbon can have a large influence on the biogeochemistry of coastal seas as it constitutes an external sources carbon for heterotrophic bacteria, which can lead to a decoupling of the bacterial and primary production [94]. Many inner estuaries have been observed to be net heterotrophic, which often is related to the remineralisation of tOC [13; 14]. Additionally, tOC contains large amounts of humic matter that has a strong capacity to absorb light [48]. Inputs of tOC can therefore hamper the growth of photosynthetic organisms [40].

Where does it end up?
Organic carbon can be removed from coastal waters through bacterial and photochemical remineralisation, transforming it back to inorganic carbon, through sinking and subsequent burial in sediments, or by simple advection, where it is brought to the open ocean by water currents [10; 15; 20; 57], (Figure 1.1).
Figure 1.1: **Organic carbon dynamics** - Simplified scheme of processes affecting organic carbon cycling in coastal seas, and how it influences the air-sea CO₂ exchange.
definition, sinking only affects the POC. DOC can however through aggregation processes attach to or form POC [10; 15; 46]. Bacterial and photochemical remineralisation can interplay [1; 59]. For example, it has been observed that organic matter can become more available to bacteria after exposition to sunlight [1; 59]. Remineralisation processes produce CO₂ and lead to an increase in the pCO₂. Waters oversaturated in CO₂ are for example observed close to river mouths and in deep waters where there is a relatively large degradation of organic carbon.

Due to the large variety of organic molecules, the fate of organic carbon in the marine environment is poorly constrained. Depending on the OC’s reactivity with respect to remineralisation processes, where the turnover time can stretch from seconds to millennia, the OC is often separated into different classes of lability (labile, semi-labile, semi-refractory, refractory etc.) [15; 38]. The more refractory parts of organic carbon are more affected by water movements and advection, and can be transported long ways from where it was produced. Terrestrial organic carbon is considered to be more refractory than marine produced organic carbon [10; 27; 51] due to its more complex molecular structure [11; 27]. Based on conservative mixing of tDOC with salinity it has been debated whether it undergoes any removal at all [20]. However, other research has shown that a substantial removal takes place [26; 68]. In paper I and III, the fate of terrestrial DOC in the Baltic Sea is investigated.

The way the organic carbon is removed influences the CO₂ exchange between the coastal seas and the atmosphere (Figure 1.1). Remineralisation of terrestrially derived organic carbon can turn coastal seas into net heterotrophic systems. Burial of marine produced organic carbon (“the biological pump”), increases the capacity of the area to take up atmospheric CO₂, and can remove carbon from the active carbon cycle on geological time scales. Export of organic carbon to the open ocean also increases the CO₂ uptake capacity (if the exported carbon is subject to some form of remineralisation), but then what happens to the exported carbon in the open ocean is another question.
1.2 The Baltic Sea

The Baltic Sea (Figure 1.2) is a semi-enclosed sea stretching from temperate climate in the South in to subarctic climate in the North [80]. During cold winters it can be almost completely ice-covered, while during mild winters the sea ice only covers the northernmost part, the Bothnian Bay [33]. Due to the many rivers draining into the area, and the relatively large precipitation, the Baltic Sea has a positive freshwater balance. This implies that there is a general outflow in surface waters and a general inflow in the deep (estuarine circulation). Due to the positive freshwater balance and the narrow connection to the North Sea, Baltic Sea is brackish and vertically stratified. The surface salinities range from close to zero in the northernmost part to slightly below 20 PSU in the Danish straits, and there is a permanent halocline at about 50-60 meters of depth. The vertical stratification slows down the mixing between deep and surface waters. In the Southern parts of the Baltic Sea, where the haline stratification is the strongest, the deep waters are in general anoxic, partly as a result of eutrophication. These waters, and its oxygen, are only renewed by occasional intrusions of saline water from the Skagerrak-Kattegat (so called major Baltic Inflows).

1.2.1 Primary production in the Baltic Sea

The average net primary production in the Baltic Sea has been estimated to 112 gC m$^{-2}$ y$^{-1}$ [80]. It is, however, not clear whether the estimated average production only considers the production of mPOC (and biomass), or also includes the production of mDOC and extracellular release. The institutes measuring primary production in the Baltic Sea use different methods, where some measure both the mPOC and mDOC production, while others only measure mPOC production [5]. The observed accumulation of DOC during summer in the Baltic Sea has in some cases been related to authochtonous processes and could thus be a result of carbon overflow and the production of semi-labile extracellular DOC.

There is a strong North-South gradient in the estimated net primary production in the Baltic Sea, from 17-28 gC m$^{-2}$ y$^{-1}$ up to 67-163 gC m$^{-2}$ y$^{-1}$. The lower production in the North is partially due to the lower insolation [80]. In the Gulf of Bothnia there are also less available nutrients compared to the rest of the Baltic Sea [80]. This is a result of lower concentrations of mineral
nutrients in the rivers [82] and the almost limnic characteristics of the Bothnian Bay that results in a strong retainment of phosphorus in the sediments [12]. Additionally, large inputs of anthropogenic nutrients [37] have lead to an increase in the productivity in the Southern parts of the Baltic Sea [16]. This eutrophication has further resulted in a spreading of anoxic bottom waters and an augmented presence of cyanobacteria in the Baltic Proper [80].

The phosphorus problem

Nitrogen is the most limiting nutrient for phytoplankton in almost the whole Baltic Sea, except for in the Bothnian Bay where the phytoplankton are phosphorus limited [4; 32; 36]. The nitrogen limitation in the Southern basins favors the growth of cyanobacteria in summer, which can fix gaseous nitrogen when the dissolved inorganic nitrogen (DIN) has been depleted [75]. In the Bothnian Bay, the low salinity favors the formation of phosphorus-iron complexes that retain phosphorus in the sediments [12], which results in very low dissolved inorganic phosphorus (DIP) concentrations and high N:P ratios in the winter water (paper II). Although these low amounts of DIP are quickly consumed in the beginning of the productive season, observations show that there is a continuous drawdown of pCO₂ and DIN [54], indicating that phytoplankton are active also in absence of DIP. This cannot be explained with the Redfield model, and has been called the "phosphorus problem", as no Baltic Sea models have been able to explain it. In paper II it is shown that it can be explained by considering flexible stoichiometry of phytoplankton. It is also shown that a large part of the fixed carbon ends up as DOC due to carbon overflow, which seems not to be captured by the conventional techniques to measure primary production.

1.2.2 Terrestrially derived organic carbon

The Baltic Sea receives large amounts of terrestrially derived organic carbon. For the whole Baltic Sea the yearly tOC input comprises about 10% of the estimated annual net primary production [30; 80]. In the Northern parts its relative importance is larger and the input is of the same order as estimated yearly net primary production. Of the total DOC pool in the Baltic Sea it has been estimated that 40–90% is of terrestrial origin [3; 18], with higher and lower percentages in the northern Bothnian Bay and the Baltic Proper, respectively. The fate that the tDOC meets in the waters of the Baltic Sea is, however, enigmatic, and one goal of this thesis is to increase the understanding of tDOC dynamics. Several studies has shown that a relatively large removal of tDOC takes place. Already Wulff & Stigebrandt [95] showed that about 75% of the the input of humic substances, which is mostly of terrestrial origin, has to be
Figure 1.2: Map of the Baltic Sea - Filled contours are showing bathymetry (depth in meters). Depth contours mark isolines of 50, 100, 150, 200, 300, 400 and 600 meters.
removed within the Baltic. Later separate studies have shown by studying the isotope and molecular composition that more than 50% [18], and 43-51% [79], respectively, of the tDOC is removed. In paper I the removal of tDOC is investigated in a 3D hydrodynamical model. Two parameterisations for the tDOC are proposed, and it is suggested that as much as 80% is removed. The processes behind this large removal are, however, unclear. Studies of phytoplankton and bacterial production suggest that a major part of the tDOC is needed to meet the bacterial carbon demand in the Northern Baltic Sea [73; 96]. On the other hand, incubation experiments suggest a minor availability of tDOC to bacteria [7; 8; 27; 39; 51; 93]. Another possible removal mechanism is aggregation followed by sedimentation and burial, but it has been suggested to be of minor importance in the Baltic Sea [9]. Aarnos et al. [1] proposed that photochemical degradation in the Baltic Sea has the potential to degrade an amount of DOC equal to the terrestrial input, but it has never been shown explicitly. In paper III it is shown that a large remineralisation (with a rate similar to the faster one in paper I) of tDOC is needed in the nearshore areas to explain the observed high pCO2 values. Remineralisation is needed also during winter months and under the sea ice, which argues against photochemical degradation as the main removal mechanism. When calculating degradation rates from bacterial incubations with tDOC, rates of the same order to the one used in the model are obtained. This suggests that the large removal of tDOC can be caused by bacteria.

1.2.3 Air-Sea CO2 exchange

There are several estimates of air-sea CO2 exchange in the Baltic, which have been done with various methods. Based on high resolution underway pCO2 measurements, with a relatively large geographical coverage, Thomas & Schneider [85] and Löffler et al. [54] calculated the air-sea CO2 flux in the Southern Baltic Sea and the Gulf of Bothnia, respectively. They concluded that the Southern Baltic and the Bothnian Sea are sinks of atmospheric CO2 (-900 mmol m$^{-2}$ y$^{-1}$ and -730 mmol m$^{-2}$ y$^{-1}$), while the Bothnian Bay is a weak source (+140 mmol m$^{-2}$ y$^{-1}$). The measurements from Löffler et al. [54] are used for validation of the model in paper II. A nice result is that the simulated air-sea exchange agrees well with their calculated air-sea exchange (which it should as it is determined by the pCO2 difference between the air and water).

Estimates of the air-sea exchange in several Baltic Sea basins have also been done based on pCO2 measured at single stations [2; 92]. Algesten et al. [2] calculated the Bothnian Bay and the Bothnian Sea to release 2600 mmol m$^{-2}$ y$^{-1}$ and 3500 mmol m$^{-2}$ y$^{-1}$ of CO2, respectively. Similarly, Wesslander et al. [92] estimated the East Gotland sea and the Bornholm Sea to be sources...
of CO₂ of 1600 mmol m⁻² y⁻¹ and 2300 mmol m⁻² y⁻¹, respectively, and the Kattegat to be a sink of -1100 mmol m⁻² y⁻¹. However, care should be taken when extrapolating air-sea CO₂ exchanges from single stations to entire basins. As suggested (but not discussed) by the model results in paper III, the central parts of the basins tend to be more heterotrophic, while the coastal rims are more autotrophic. Extrapolating air-sea exchange obtained at stations in the centre of basins could in other words lead to an underestimate of the marine uptake of atmospheric CO₂, and an overestimate of the basin heterotrophy, which could explain the discrepancies between for example Löffler et al. [54] and Algesten et al. [2], as well as Thomas & Schneider [85] and Wesslander et al. [92].

Other studies, where the air-sea exchange has been calculated based on more indirect methods (satellite data and as a closing term in the carbon budget) have estimated the whole Baltic Sea to be a source of CO₂ to the atmosphere amounting to +440 mmol m⁻² y⁻¹ and +230 mmol m⁻² y⁻¹, respectively [50; 64].
2. Methodology - Marine biogeochemical modelling

Marine biogeochemical models are useful tools to put observations and small scale experiments into a larger context, to investigate the influence of the physics on the biogeochemistry, and thus test our understanding of the marine system as a whole. Especially when the time scale of biogeochemical processes exceeds the timescale of incubation experiments, models can be useful (paper I and III). There exist a number of coupled marine physical-biogeochemical models of various complexity, both from a physical and biogeochemical point of view.

2.1 Physical model

The complexity of a physical model is related to the number of dimensions, and the way the physics are resolved. The number of dimensions can range from 0D to 3D, from well mixed boxes to a realistic representation of the physical space. Ocean general circulation models, usually 3D models that solve the primitive equations, belong to the more complex physical models. Coupling a biogeochemical model to a physical model implies that the biogeochemical tracers are affected by the ocean physics. The concentration of a tracer \( C \) in a 3D model is calculated according to the following:

\[
\frac{\partial C}{\partial t} = -\mathbf{u} \cdot \nabla C + \nabla h (K_h \nabla h) C + \frac{\partial}{\partial z} \left(K_z \frac{\partial C}{\partial z}\right) + F \quad (2.1)
\]

where the first term on the right-hand side represents advection, the second term horizontal diffusion, the third term vertical diffusion and the fourth term biogeochemical fluxes.

The use of 3D in this thesis was chosen primarily to be able to study the removal of terrestrial DOC along a horizontal gradient. The physical model used is a NEMO (Nucleus for European Modelling of the Ocean, Madec et al. [56]) configuration for the Baltic and North Seas [43; 44] (paper I and IV), as well as a smaller NEMO configuration for the Gulf of Bothnia (paper II and...
III. It has a horizontal resolution of 2 nautical miles and is therefore eddy permitting. The vertical resolution is 3 meters at the surface, with increasing grid spacing towards the depth. A complete description and validation of the physical model is found in paper IV.

2.2 Biogeochemical model

The complexity of a marine biogeochemical model depends on the number of tracers that is contains, and the amount of biogeochemical processes that are taken into account. An example of the simplest form of a biogeochemical model is found in paper I, which contains only one tracer subject to a linear decay rate. The aim of this paper was only to study removal of terrestrially derived organic carbon, and we therefore did not have to take into account the entire marine carbon system. As a continuation we wanted to see if the removal of the terrestrially derived DOC gives a large signal in the pCO2 in coastal waters. pCO2 is however influenced by many factors, not just remineralisation of terrestrial DOC, and the whole marine carbon system, including the production of autochthonous organic matter, therefore had to be taken into account.

The most common way to model primary production and phytoplankton dynamics is by using nutrient based models, simulating the flux of nutrients between inorganic and organic forms (in phytoplankton and zooplankton). The growth (and thus uptake of nutrients) of the phytoplankton is simulated as a function of sunlight and available nutrients. The models can be made more complex by adding additional tracers, such as other detritus, zooplankton, oxygen, other nutrients, carbon etc. Usually, the uptake of carbon and nutrients are modelled as a function of the uptake of the most limiting nutrient by using the Redfield ratio, and phytoplankton are thus only represented by a single currency. Such models are widely used in regional and global applications as well as in Earth System Models for climate projections.

Biogeochemical modelling for the Baltic Sea started with Stigebrandt & Wulff [83]. They constructed a nitrogen based biogeochemical model solving nutrient and oxygen processes coupled to a horizontally integrated physical model with a high vertical resolution. The aim was to better understand the observed changes in the Baltic Sea related to eutrophication. Their work has lead to several coupled biogeochemical models, such as PROBE [63], SAN-BALTS [74] and BALTSEM [34], SCOBI [23] and ERGOM [61]. SCOBI and ERGOM has been coupled to 3D physical models of the Baltic Sea (NEMO-NORDIC and RCO for SCOBI and MOM for ERGOM, respectively). To these models additional processes and tracers has been added (compared to Stigebrandt & Wulff [83]), for example phosphorus, silicate, cyanobacteria, sedi-
ment processes. Carbon has been added to PROBE, BALTSEM and ERGOM. None of these models have, however, managed to satisfactorily reproduce the biogeochemical dynamics of the Northern Baltic Sea [24], which is the main area of interest in this thesis.

All models descending from Stigebrandt & Wulff [83] are nutrient based, and the cycling of carbon and the less limiting nutrients is therefore not fully resolved (see for example Flynn [28, 29]). It was therefore decided to use a model that simulates the content of carbon and different nutrients in phytoplankton separately, and thus take into account their stoichiometric flexibility. Stoichiometric flexible modelling began with Droop [21], who constructed a mathematical model describing the rate of phytoplankton growth as a function of their intracellular nutrient quota. Several models with flexible stoichiometry have been developed since, but these models have been less applied on large scales than single-currency models. In these models the number of tracers increases fast with the number of nutrient and plankton groups, and they are therefore computationally heavy, especially when coupled to 3D hydrodynamical models. In the Baltic Sea stoichiometrically flexible models have been applied to sea-ice studies [86; 87], and to simulate processes in mesocosms (0D) [76] and at specific stations (1D) [49; 52; 89]. Kuznetsov et al. [52] investigated the role of flexible stoichiometry in cyanobacteria in a 3D model, but it was only validated at one station in the Baltic proper. No attempt with flexible stoichiometry has thus been done on a larger scale in the Baltic Sea.

In paper II we investigate the role of the stoichiometric flexibility for carbon and nutrient cycling in the Gulf of Bothnia. We use the Biogeochemical Flux Model (BFM, Vichi et al. [90, 91], Figure 2.1) coupled to a NEMO configuration of the area. The advantage of BFM in the Gulf of Bothnia is not only the flexible stoichiometry, but also that it contains organic matter of different lability and bacteria and thus explicitly simulates the microbial food web. This model setup is also used in paper III, where the impact of terrestrial DOC remineralisation on pCO₂ is investigated.
Figure 2.1: The Biogeochemical Flux Model - Scheme of pelagic variables in the Biogeochemical Flux Model (http://bfm-community.eu, Vichi et al. [90, 91])
3. Summary of papers

Paper I

In paper I the removal kinetics of tDOC is studied by the release of a passive tracer from the rivers entering the Baltic Sea. Three experiments are performed i) the tracer does not undergo any removal and is simply advected, ii) a linear removal rate is applied to the whole pool of tDOC and iii) the tDOC is divided into a refractory and a labile pool. The results are compared to the tDOC concentrations in the Baltic Sea estimated by Deutsch et al. [18]. It is found that 80% of the tDOC has to be removed in order to reproduce the observed concentrations of tDOC in the Baltic Sea, and that this can be done by either applying a decay rate with a timescale on the order of 10 years to the whole pool of tDOC, or a decay rate with a timescale of the order of 1 year to 80% of the tDOC. In the latter parameterisation the remaining 20% of the tDOC is assumed to be refractory. The parameterisation with a faster decay of 80% of the tDOC results in a more concentrated removal in the nearshore waters. In the next step the idea was to study this in a model with the whole carbon system and compare with pCO₂ data, with the hypothesis that this could maybe give an indication which of the two parameterisations that is more realistic. But when modelling pCO₂ other processes than remineralisation have to be taken into account, in particular primary production. The problem was that no Baltic Sea models had managed to reproduce the primary production in the North.

Paper II

In paper II a coupled physical-biogeochemical model with flexible stoichiometry is set up for the Northern Baltic Sea, with the aim to test if a model like this is able to simulate the biogeochemical dynamics of the Gulf of Bothnia within reasonable stoichiometric bounds. Its performance is compared to a simulation where the phytoplankton stoichiometry is fixed to the Redfield ratio, which is the most common way to model carbon and nutrient uptake in biogeochemical models. In contrast to the fixed-stoichiometry model, the stoichiometrically flexible model is able to reproduce the pCO₂ and nutrient dynamics. As shown by the stoichiometric flexible model, ratios deviating far from Redfield are
required to adequately simulate the seasonal nutrient and pCO$_2$ dynamics. Using the Redfield ratio to predict carbon fixation results in a reduction by half in the atmospheric CO$_2$ uptake. It is also shown that the production of organic carbon needed to reproduce the pCO$_2$ is larger than measurements, which is attributed to a large production of extracellular DOC that seems to be left out in the measurements. The production of the extracellular DOC is responsible for a seasonal accumulation of mDOC in the model, which corresponds well to measurements of DOC concentrations.

Paper III

In paper III the influence of tDOC on the pCO$_2$ dynamics is investigated by comparing underway pCO$_2$ measurements with simulated pCO$_2$ from the model developed in paper II. A suite of experiments is performed to investigate the influence of tDOC remineralisation and light extinction on the pCO$_2$. It is found that the faster remineralisation rate in paper I reproduces the high pCO$_2$ values in the low salinity region, while the slower one does not. The faster rate agrees well with remineralisation rates that are calculated from bacterial incubation experiments, suggesting that bacteria can be responsible for the large tDOC removal in the Baltic Sea. It is also found that a strong tDOC-induced light extinction is needed to reproduce the measured summer pCO$_2$ values. A stronger light extinction in coastal seas leads to a larger export of nutrients to offshore waters, and thus a less efficient "coastal filter", but the overall effect on the carbon cycling in the Gulf of Bothnia is minor.

Paper IV

Paper IV provides a thorough validation of the physical model that is used in papers I-III, including the barotropic and baroclinic dynamics and the thermohaline structure. It is shown that it has an overall good representation of the physical characteristics of the Baltic and the North Seas. Biases are found especially in relation to horizontal saline fronts in the North Sea. In the Baltic Sea, such biases are found particularly in deep waters due to an over ventilation of the halocline. A positive warm bias in SST is related to a warm winter bias in the atmospheric forcing, and too low vertical mixing in the summer as a result from the Galperin parameterisation.
4. Outlook

There are many things that I would have liked to look more into, but for which I didn’t have time during my thesis. Here are some thoughts on what directions the research in this thesis could spin off into:

1. **Stoichiometry**: There are many aspects of stoichiometry that are left untouched in paper II, and that would be interesting to investigate in future research. Measurements of stoichiometry (phytoplankton and/or dissolved and particulate organic matter) would then be needed to compare the model to. One thing I started to look at in my thesis was how phytoplankton uptake of organic nutrients could influence their stoichiometry. The model results showed that it could almost reduce the internal ratios by half during the most nutrient limiting conditions. Measurements of stoichiometry could therefore help to understand whether organic nutrients are used or not. Measurements of chlorophyll:carbon stoichiometry could also be interesting to help understanding the light acclimatisation.

2. **Extracellular DOC**: In paper III it is shown that carbon overflow and production of extracellular DOC is an important part of the carbon cycle in the Gulf of Bothnia. The question is then, where does it end up? Does it aggregate and sink to the sediments, and contribute to the biological pump? Or is it just remineralised in the water column?

3. **Bacteria**: BFM models bacteria explicitly, but in paper II and III they were set to only act as efficient remineralisers. A next step would be to activate them as "real" bacteria, including stoichiometric variability, uptake of inorganic nutrients. A subject that would be interesting to investigate could be for example bacterial competition with phytoplankton. Considering the large amount of nutrient poor organic matter (tDOC and extracellular DOC) in the Gulf of Bothnia, as predicted by the model, one could hypothesise that bacteria would compete with phytoplankton for inorganic nutrients. Again, actual measurements of the C:N:P ratios of organic matter would be useful. Other interesting subjects could be bacterial uptake of tDOC, the influence of C:N:P ratios of the substrate on bacterial growth etc. Before looking at it in the full model setup,
small scale experiments would be suitable to look closer into (and try to model) bacterial dynamics.

4. **A deeper look into tDOC dynamics:** From this thesis it is learned that there are large transformations of tDOC in the Northeastern Bothnian Bay, where large rivers drain into the sea. This area would be ideal for measurements campaigns to learn more about the processes affecting tDOC.

5. **Sea ice:** In both paper II and III it was noticed that the sea ice had quite a large effect on the modelled pCO$_2$. Most literature on the ice influence on the air-sea gas exchange come from Arctic- and Antarctic research, where the ice dynamics are different from those the Baltic Sea. Local measurements would be needed to better constrain this.

6. **Arctic shelf:** It would be interesting to take the knowledge gained in this theses to the Arctic shelves, which receives large amounts of tDOC, and set up a regional model for the area. With dense water formation on the shelves and shorter residence time compared to the Baltic Sea, this would require a more dynamic perspective and deeper analysis of the physical processes.
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