Simulating Transport and Understanding Future Fluxes of Organic Carbon in Rivers Draining into the Baltic Sea

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Abstract

Riverine organic (TOC, Total Organic Carbon) and inorganic (DIC, Dissolved Inorganic Carbon) carbon are the main sources of carbon in the Baltic Sea. While the importance of this contribution has been evaluated, there are currently several gaps in our knowledge of the mechanisms governing organic carbon dynamics in this region, especially for the particulate form, and the impact of future climate change on organic carbon transport. This licentiate thesis addresses this research deficit by (1) developing a model for assessing the flux of particulate organic carbon (POC), and by (2) simulating the potential climate effects on the transport and fate of TOC, both particulate and dissolved organic carbon, in the Baltic Sea environment.

**Study I** developed a novel dynamic model for simulating the generation and transport of POC in all the major rivers discharging into the Baltic Sea. The POC load was assessed using algorithms for the processes governing the input i.e. erosion, litterfall and in-stream primary production. Using daily information on precipitation and temperature, the water discharge from each river was calculated. The total annual POC load from the Baltic Sea drainage basin was predicted within a factor of about 2 and was estimated to be 0.34 Tg POC, or 7-10 % of the annual TOC. The prediction of the timing of the monthly peak loads, however, was hampered by the current lack of field measurements of POC loads to the Baltic Sea.

**Study II** assessed the potential future climate effects on riverine TOC (particulate and dissolved organic carbon, DOC) in the Baltic Sea drainage basin. A small decrease in POC load (-7 %) was predicted and no changes in DOC load on an annual and total basin scale, but the simulations showed significant variations between seasons and across sub-basins by the end of this century. Seasonal total loads were predicted to increase in winter and decrease in summer. Due to counterbalancing increases and decreases in predicted TOC loads in various parts of the Baltic Sea catchment, the impact of climate change on the total carbon budget in this region was limited. However, our simulation results indicated significant differences over time in POC and DOC export across the six Baltic Sea sub-basins, and an altered seasonal pattern in the timing and magnitude of the delivery.

This thesis comprises a first attempt to better describe the mechanisms and dynamics of OC generation and transport in the Baltic Sea catchment and assess the potential climate effects on the transport with a spatiotemporal resolution. The work provides a starting point for further development of the understanding of large scale organic carbon export and how it may be affected in the future. This thesis also discuss the role of riverine organic carbon in biogeochemical processes, food web structures and contaminant transport in inland, coastal and marine waters.
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List of Studies

This licentiate thesis is based on the following studies, referred to as study I and study II.

Study I


This study has been published and the paper (referred to as paper I) was reproduced with the permission from Springer.

My contributions:

1) I developed the POC module and integrated it into the existing CSIM model;
2) I performed the simulations, data treatment and statistical analysis;
3) I led the writing of the paper.

Study II

Strååt, K.D., Mörth, C-M. & Undeman, E. (submitted) Future export of particulate and dissolved organic carbon from land to 1 coastal zones of the Baltic Sea

This study has been submitted to the Journal of Marine Systems and the paper (referred to as paper II) is under revision.

My contributions:

1) I performed the model simulations;
2) I did the data treatment and statistical analysis;
3) I led the writing of the paper.
1. Introduction

*Background*

Organic carbon (OC) is a key component in ecological systems. It is utilized as a source of energy for microorganisms hence influencing the base of many food webs (Allan and Castillo, 2007) and constitutes an important species in the carbon cycle, impacting the CO$_2$ exchange by respiration and sequestration and climate change (Gustafsson et al., 2014, Philippart et al., 2011). Organic carbon also influences physical conditions in the environment (e.g. light penetration and turbidity of water (Dagg et al., 2004)) and, affects the transport and fate of organic and inorganic contaminants (Dachs et al., 2000). Hence, knowledge about the catchment-scale land to sea transport of OC is crucial for our understanding of many fundamental earth system processes. Understanding of how terrestrial inputs (Reader et al., 2014, van Dongen et al., 2008, Kuliński and Pempkowiak, 2011) and in-stream production (Algesten et al., 2006, Andersson and Rudehäll, 1993, Dzierzbicka-Głowacka et al., 2010) influence the carbon cycle is improving. Description of the transport and fate of OC, however, is often limited by a lack of estimates of the input of particulate organic carbon (POC) and its relative importance to the dissolved organic carbon (DOC) fraction. Especially, POC approximations of total catchment-scale discharge and estimates of seasonal dynamics of both OC species have been lacking.

In this licentiate thesis, insights regarding the importance of POC for the total organic carbon budget of the Baltic Sea and the impact of changes in climatic conditions in this region on OC transport, gained by applying a coupled hydrological-biogeochemical model, are presented.

*The carbon cycle*

The biogeochemical cycle where carbon moves through the environment (i.e. is transformed and transported between living organisms and the physical environment) is called the carbon cycle. Historically, carbon is described as being transported between two active boxes, the terrestrial and marine environment, via a third box, the atmosphere (Bolin, 1981, Siegenthaler and Sarmiento, 1993). This view has over time been developed to include more sub-compartments and processes in the biosphere as the understanding of the carbon budget has improved (Cole et al., 2007).

In Figure 1, the key carbon cycling processes between the atmospheric, terrestrial and marine environment are illustrated, and are briefly explained below (IPCC, 2001). There is an inorganic and organic part of the carbon cycle and globally they are about the same in size (Hope et al., 1994). There are two “wheels” in the carbon cycle, organic and inorganic with CO$_2$ in the middle as the connector of the two. Atmospheric CO$_2$ is taken up by plants via photosynthesis and when the biomass is degraded, the carbon enters the detritus and soil OC pool. The terrestrial carbon, both organic and
inorganic, can then be transported to the marine environment via rivers with surface, and to some extent groundwater, runoff. A small fraction of the soil OC can also be converted to inert forms and add to the geological storage, a process which occurs with decadal to centennial turnover time. By weathering, carbonates from these geological storages can also reach the oceans via river transport. Globally, 1.9 Pg C y⁻¹ enter inland freshwater systems and circa 0.9 Pg C y⁻¹ of this is eventually transported to the oceans, half of which is inorganic and half organic carbon (Meybeck, 1982, Meybeck, 1993). The remaining carbon is either buried in sediments or mineralized and evaporated back to the atmosphere (Cole et al., 2007). In the aquatic environment, the mixture of inorganic and organic carbon is affected by several processes. Organic carbon is lost due to the combined influence of microbial degradation (where the OC is utilized as an energy source by heterotrophic organisms) and photochemical oxidation, leading to an outgassing of CO₂, i.e. conversion into inorganic carbon. Other loss processes of OC include sedimentation, scavenging and salinity-induced flocculation (Bauer et al., 2013). Inorganic carbon can be processed by autotrophic primary producers via CO₂ uptake to produce OC. There is a difference in time scale for the organic and inorganic cycles, where the organic part has a much faster turn over time than the inorganic (also called the long and short term carbon cycle) (White, 2013). The ratio between the heterotrophic (OC consumption) and autotrophic (OC production) determines if a receiving estuary is a net carbon sink or source (Cummins, 1974), which also influence the air-sea exchange of CO₂ (Gustafsson et al., 2014).

![Figure 1: Key carbon cycling processes (IPCC, 2001).](image-url)
Organic carbon in rivers

The riverine transport of OC is mainly driven by hydrological factors, climate conditions, land use and population density (Alvarez-Cobelas et al., 2012, Milliman and Syvitski, 1992, Meybeck, 1988). Rather than being a passive transport pipe for terrestrial carbon, research shows that the riverine export is the net result of transformation and loss processes, illustrating the active role river networks play in the carbon cycle (Hope et al., 1994, Billen et al., 1994, Schlünz and Schneider, 2000). In addition to the processes described above and illustrated by Figure 1, OC can also act as a transport vector for organic contaminants and trace metals. For example, many hydrophobic persistent organic pollutants (POPs) deposited from the atmosphere or emitted directly to the terrestrial environment sorb to organic matter which may in turn be transported via surface runoff to rivers and eventually the sea (Agrell et al., 2001, Josefsson et al., 2016).

The OC is composed of detritus from the terrestrial environment (allochthonous input) and material originating from within the river channel by aquatic primary producers (autochthonous input) (Allan and Castillo, 2007). In addition to origin, the riverine OC can be divided into two fractions, dissolved and particulate. The DOC fraction is conventionally defined as the fraction that passes through a 0.45-0.5 μm filter; whereas the POC fraction is defined by what remains on the filter (Hope et al., 1994, Zsolnay, 2003). Terrestrial sources of POC are soil organics, leaf litter and woody debris, that enter the river via overland flow, erosion and direct litterfall (Committee on Flux of Organic Carbon to the Ocean, 1981). The transport is strongly influenced by rainfall intensity (Ludwig et al., 1996) and seasonal changes with the highest amounts being deposited in the spring and autumn (Allan and Castillo, 2007, Swaney et al., 1996). DOC originates from direct deposition of aerosols from the atmosphere, leaching from plants in surface and groundwater runoff, and decomposition and leaching of organic matter from soils, and enters the river channel via drainage waters (Committee on Flux of Organic Carbon to the Ocean, 1981). It is composed of organic compounds including amino acids, peptides, carbohydrates, lipids, lignin and, humic and fulvic substances (Kuliński et al., 2016). The concentration and composition of DOC in rivers is influenced by the amount and type of OC stored in soils (Ludwig et al., 1996).

The ratio between the two OC species in rivers varies between continents and climates. The average DOC/POC ratio is highest in areas with low erosivity, i.e. in polar, tundra and taiga climates where DOC transport exceeds the POC on average by a factor of 4, and lowest in climates with higher erodibility, i.e. desert climate, while in most of the continental area the ratio is close to one (Ludwig et al., 1996). Other studies show a mean DOC/POC ratio of 10:1 in small temperate forest watersheds and close to 1:1 in predominantly grassland areas (Schlesinger and Melack, 1981, Hope et al., 1994), but generally on a global scale DOC is the major fraction (Alvarez-Cobelas et al., 2012).
**Catchment hydrology**

Riverine transport of OC from land to sea is highly dependent on the hydrological conditions in the catchment. A catchment is a geographically confined and topographically defined area that includes all parts of the hydrological cycle (Wagener et al., 2004, Dooge, 1986). A common description of catchment hydrology is that water enters a catchment via precipitation and then either partitions into storage (e.g. as snow, soil moisture or groundwater) or leaves the area via river flow, groundwater runoff or evapotranspiration (Wagener et al., 2007). Catchments with high precipitation have high river runoff and runoff has been attributed to be the main driver for the variability in TOC export (Meybeck, 1982) with peak discharge during high flow events (Bass et al., 2011) and periods with maximum average precipitation (Köhler et al., 2008).

**Climate change and riverine organic carbon transport**

For the delivery of riverine carbon to the coastal zones and ocean, climate is a recognized key driver (Bauer et al., 2013) and the consequences of climate change due to increasing CO₂ concentrations are likely to have an effect on the environmental conditions of the Baltic Sea and its catchment. Predictions of potential impacts of climate change in this region include higher temperatures, more precipitation in the entire region in the winter and in the northern part during summer, and an increased risk of extreme weather events, e.g. flooding and drought (Helcom, 2013). The consequences of these changes are several. Increasing air temperature would result in decreased length of the cold season including a decrease in the extent and duration of snow and ice-cover, and an increased length of the growing season. Also, the projected changes in precipitation and higher air temperatures would affect river runoff by increasing discharges in the north and reducing stream flows in the south (Graham, 2004, Helcom, 2013). Such changes would affect the riverine organic carbon transport.

An increase in river runoff to the northern sub-basins could increase weathering via deeper percolation into the ground or discharge more organic matter from the topsoil (Humborg et al., 2007), where the latter has already been observed in Finnish rivers and led to an increase in TOC flux (Sarkkola et al., 2009). Predictions of the hydrometeorological conditions in the southern region are less divergent than those in the north (Donnelly et al., 2014), but higher temperatures and reductions in precipitation are projected to cause an increase in TOC concentration (Humborg et al., 2007).

**Organic carbon in the Baltic Sea and its drainage basin**

The Baltic Sea is under stress from multiple environmental changes linked to acidification (Omstedt et al., 2012), eutrophication (Andersson et al., 2015) and climate change (Helcom, 2013), all of which impact the large-scale carbon flows. The main flow of carbon to the Baltic Sea is riverine carbon, with about a 38% contribution of organic carbon (Kuliński and Pempkowiak, 2011) and changes in these
flows, both in terms of when and where the export occurs, have complex implications for the coastal and marine environment.

In the southern Baltic Sea, OC is dominated by autochthonous material (Andersson et al., 2015) and is currently suffering from eutrophication. The projected increase in temperature could accelerate the mobility of nutrients, by increasing mineralization, and their release into the water column (Meier et al., 2012). The increased mobility may in turn further fuel primary production and have a negative impact on eutrophication. In the north, allochthonous material dominates the OC pool in the Baltic Sea (Alling et al., 2008). The allochthonous contribution is predicted to increase as a consequence of the increased runoff expected in a warmer climate (e.g. Humborg et al. (2007)). An increase in terrestrial TOC input to coastal zones, due to higher freshwater discharge, may cause a shift towards heterotrophic production by limiting the light availability and deepening the mixing layer (Wikner and Andersson, 2012).

The altered spatiotemporal pattern of riverine OC export in the future may potentially have a large impact on the biogeochemical cycle of the Baltic Sea. However, the large-scale transport of both particulate and dissolved OC to the Baltic Sea from land has not been assessed, nor has the effect of future climate change on this transport in this region. By further developing the Catchment SIMulation (CSIM) hydrologic model developed by Mörth et al. (2007) to simulate land to sea fluxes of nutrients using hydrological simulations and emissions data, an OC transport model linked to external forcings such as land cover, nutrient concentrations and meteorological conditions can be constructed and used to study OC flows on the full catchment scale.

**Aims of the thesis**

The overall aim of this thesis was to fill and identify knowledge gaps regarding large scale movement of OC and the potential future climate effect on that transport.

In **study I**, we further develop the Catchment SIMulation (CSIM) hydrologic model to create a spatially and temporally resolved POC watershed model that calculates POC loadings to the Baltic Sea from the entire Baltic Sea catchment.

In **study II**, using the extended CSIM model, we project the effect of climate change on the export of OC loads to the coastal zones of the Baltic Sea by the end of this century and assess how this impact may vary in different regions and seasons.
2. Methods

Both studies presented in this licentiate thesis were carried out using a hydrological nutrient model as starting point, CSIM (Catchment SIMulation) that simulates hydrological and nutrient fluxes in all the rivers that discharge into the Baltic Sea (Mörth et al., 2007). To quantify the yearly total POC load to the Baltic Sea, a novel modeling tool was assembled and implemented in CSIM for simulations of POC generation and transport in all major rivers discharging into this marine environment. This extended CSIM version was then used to estimate the potential future climate effects on riverine OC, both particulate and dissolved, loads in the Baltic Sea and the consequences for the coastal zone.

*Model development*

Details on the model development can be found in paper I and its supplementary information. Briefly, the CSIM model divides the Baltic Sea drainage basin into 82 catchments and 35 coastal areas and minor catchments. We considered the 75 major catchments for which hydrological data required in CSIM was available (see Figure 1 in paper I and Figure 1 in paper II). Each catchment is further divided into 10 land-use categories (e.g. forest, wetlands, and cultivated areas) for which daily surface and groundwater discharge volumes are estimated based on information on precipitation and air temperature. The model was developed by implementing algorithms for the significant processes generating riverine POC (soil erosion, litterfall and in-stream primary production) in CSIM. Soil erosion was calculated daily for each land class and then aggregated to average monthly loads per catchment. Direct litterfall input was aggregated to average monthly loads using seasonally dependent changes in canopy volume per forested land class. The in-stream primary production contribution to the average monthly POC load was predicted for agricultural land based on estimations of chlorophyll-α (chl-α) concentrations. The POC concentrations were calculated by dividing the POC loads by the total monthly runoff.

The model was calibrated using 107 data points of total suspended solids (TSS) measurements collected during uneven years between 1978-2000 in three rivers; Torne in Sweden, Neva in Russia and Vistula in Poland (UNEP GEMstat, 2006). To compensate for the tendency of CSIM to underestimate high flow events (Lyon et al., 2014) and the event-driven nature of erosion (Ford and Fox, 2014, Oeurng et al., 2010), a calibration was done on the peak runoff rate. To evaluate the model, we used a set of 56 data points of POC measurements in four rivers (Kalix, Lule, Vistula and Oder) and 268 data points of TSS measurements in six rivers (Viskan, Åtran, Nissan, Torne, Neva and Vistula).
**Model application and future scenario simulation**

By forcing the extended CSIM model (developed in study I) using three climate scenarios developed by the Intergovernmental Panel on Climate Change (IPCC), representing low, middle and high carbon dioxide emission scenarios, downscaled for the Baltic Sea, we examined the annual and seasonal changes in riverine POC and DOC loads for the next century in study II. The daily discharge estimations from CSIM were aggregated to annual and seasonal averages (spring=March-May, summer=June-August, autumn=September-November and winter=December-February) for each of the six Baltic Sea sub-basins (BB=Bothnian Bay, BS=Bothnian Sea, BP=Baltic Proper, GF=Gulf of Finland, GR=Gulf of Riga and KT=Kattegat) as well as for the entire drainage basin. The POC module was run as described above except for the in-stream primary production estimates. To predict future total phosphorus (TP) concentrations required to estimate chl-a concentrations from which the contribution of primary production to the POC load is calculated, river specific empirical correlations between TP and chl-a based on monthly historic (1990-2000) were used.

The DOC module in CSIM was developed by Mörl et al. (2007) and is based on the Generalized Watershed Loading Function (GWLF) (Haith and Shoenaker, 1987) where each land class has a fixed concentration of DOC. Dynamic changes in DOC with time were achieved by generating root zone DOC concentrations in the Baltic Sea sub-watersheds for the next century using an adapted LPJ-GUESS model (Smith et al., 2001, Omstedt et al., 2012). The DOC concentration in rivers was calculated by using a fixed retention, i.e. by assuming a constant increase/decrease in root zone DOC concentration compared to the reference period, to alter the type concentration by the same factor for each land class.
3. Results

Study I - POC simulation

The modeling tool developed in study I is, to our knowledge, the first process-based model with the capacity to dynamically model POC loads on a whole Baltic Sea catchment scale, as well as the first attempt to quantify the total POC discharge based on spatially resolved sub-basin characteristics and meteorological data. The simulation results showed that the model has the capability to estimate total annual load of POC and TSS to the Baltic Sea within a factor of 2 compared to field measurements for watersheds of widely different sizes (Figure 1 in Paper I). Despite predicting concentrations in the same range as measurements, the seasonal variations were less well captured as the model in many cases missed the timing of peak flow events and was shown by the low proportion of variation explained in the model (low $R^2$ values) (Table 1 in Paper I).

The results for the large-scale, total riverine POC delivery the model predicted an average annual POC load of 0.34 Tg ($10^{12}$ g year$^{-1}$) and 3.10 Tg of TSS to the Baltic Sea (Figure 2). The predicted POC load agreed well with the 0.59 Tg estimated by Liu et al. (2009) using the Global nutrient export from watersheds model (NEWS) based on correlations between POC, TSS and yearly runoff, and the 0.38 Tg estimated by Gustafsson et al. (2014) using a correlation between nitrogen and POC. Comparing the predicted POC load with estimated TOC loads to the Baltic Sea, our projections make up 7-10% of the total TOC load of about $4.1 \pm 0.77$ Tg TOC year$^{-1}$ (Gustafsson et al., 2014, Kuliński and Pempkowiak, 2011) and thus correspond with the general perception that POC is the minor fraction of
TOC delivered by rivers (Alvarez-Cobelas et al., 2012). The TSS load was lower than estimated 7.5 Tg by HELCOM in the late 1970’s (Helsinki Commission, 1986).

Figure 3 shows the export of POC to the six individual sub-basins, with the size representing the contribution to the average annual total POC load. Also, the relative contribution of soil erosion, litterfall and in-stream primary production to the POC load is illustrated. Our results showed that the POC load and the relative input contribution differed from north to south in the Baltic Sea catchment. In the north the annual average POC load was dominated by eroded soil and litterfall, which correlated to forest being the dominant land cover. This was in contrast to the south, where agriculture land dominate and the POC composition was more diverse between the sub-basins. The correlation between POC composition and land cover has been made before e.g. Howarth et al. (1991), Allan and Castillo (2007). Hagen et al. (2010) even observed that the relative contribution of autochthonous carbon compared to allochthonous increased as agricultural land became more dominant.

**Study II – Projected changes in OC loads**

The simulations of the future climate change effects on transported POC and DOC loads was done by forcing the extended CSIM model with three climate scenarios developed by the Intergovernmental Panel on Climate Change (IPCC) (Nakićenović et al., 2000), representing low (B1), middle (A1B) and
high (A2) CO$_2$ emission scenarios and downscaled for the Baltic Sea (Omstedt et al., 2012). The difference between the three scenarios was evaluated by comparing the predicted annual average loads between 2090 and 2099 (see Figure 2 in Paper II). The statistical analysis did, however, not result in any significant differences (p-value range = 0.051-0.991; Wilcoxon rank sum test) in transported loads of POC or DOC to the entire Baltic Sea drainage basin or the individual sub-basins except in one instance (to GF between scenario a1b and b1, p-value = 0.023; Wilcoxon rank sum test). Hence, the projections of future climate effects in study II continued solely with the business as usual, A1B scenario.

Average annual loads of POC and DOC were simulated over the whole of the current century (2001-2099) and the differences between current (2001-2010) and future (2090-2099) loads were evaluated. The projections of future climate effects on the transport of OC loads performed in study II indicated significant changes in POC and DOC delivery to the different sub-basins under the business as usual scenario. Counteracting increasing and decreasing inputs to the individual sub-basins, however, indicated a low climate effect on the total annual OC load to the Baltic Sea. The results showed a 7% decrease in average annual load and a decreasing trend of POC to the Baltic Sea mainly due to reduced primary production contribution in the southern part of the basin, while the projections of DOC indicated no significant changes or trends on the total basin-scale (Table 1 and Figure 3 in Paper II).

The seasonal projections, however, indicated a more diverse pattern in response to climate change. On an entire catchment scale, the POC loads increased by 46% in winter and decreased by 19% and 8% in spring and summer respectively (Figure 4A). Figure 4B shows the spatial distribution of the seasonal

![Figure 4: Changes in seasonal POC load for A) the entire drainage basin and B) the sub-basins. Only the significant changes are shown. The color of the circles illustrate the season (green=spring, yellow=summer, orange=autumn and blue=winter), the size represent the amount of the load change and the sign indicate if the change was a decrease (-) or an increase (+).](image-url)
changes in POC loads. The results indicated an increase in winter to all sub-basins, except the BP, and was a consequence of more precipitation and an altered snowfall duration. More precipitation led to more runoff and therefore an increased delivery of soil erosion. In the model, no surface runoff occurs during the duration of snow cover, thus a shorter snow season caused POC from litter to be released earlier during the winter season and further increases in erosion was predicted. These shifts in timing of the delivery also explained the decreased POC load in the spring. In summer, reductions in primary production due to decreased total runoff lowered the predictions of TP and caused a reduction in predicted POC loads. This decrease originated from a reduction in delivered loads primarily to the BP (the largest sub-basin) and partly to the GR. The reduction in total runoff was a combination of less precipitation and increased evapotranspiration due to higher temperatures.

For DOC, the average seasonal loads were predicted to increase by 30% in winter and decrease by 21% in summer. These counteracting seasonal results for the Baltic Sea catchment, explained the lack of significant changes on an annual scale. The results for the sub-basins showed increased loads in winter to BB, BS, GF and GR, and decreased loads in summer to BB, BS, GF and BP. In spring the export increased to BB, BS and GR. Results for autumn showed an increase to BB while loads decreased to BP and KT in the same season. Similarly to POC, the projected changes in DOC export was a consequence of changes in runoff and temperature.

Figure 5: Changes in seasonal DOC load for A) the entire drainage basin and B) the sub-basins. Only the significant changes are shown. The color of the circles illustrate the season (green=spring, yellow=summer, orange=autumn and blue=winter), the size represent the amount of the load change and the sign indicate if the change was a decrease (-) or an increase (+).
4. Discussion

The two studies conducted in this licentiate thesis both focused on the dynamics of OC fate and transport in the Baltic Sea drainage basin. The model development project conducted in study I was essential to stimulate the future changes in total OC loads in study II. The total POC load to the Baltic Sea estimated by the model showed that POC, as previously assumed (e.g. Alvarez-Cobelas et al. (2012)), was the smaller fraction of TOC exported by rivers (Figure 2). There was, however, a difference in the relative contribution to the total POC load from the northern compared to the southern regions. The POC export from the northern rivers, i.e. those discharging into the BB and BS sub-basins, barely make up a fifth of the total POC load and only 2% of the total TOC pool, while the main contribution came from the southern part, i.e. the rivers discharging to the GF, BP, GR and KT sub-basins. The reduced input contribution of POC in the north has been seen in Finnish rivers where 94% of the TOC was in dissolved form (Mattsson et al., 2005), while in the south, POC can contribute up to 25% of the TOC (Dzierzbicka-Głowacka et al., 2010).

The accuracy of OC transport estimations is largely dependent on the predictive power of the hydrological model used. During the model development in study I, attempts to assess the in-stream retention and residence time of POC, and capture peak flow events were hampered by a lack of current knowledge and data. In-stream retention varies depending on e.g. the topography and flow rate. Thus in high-gradient streams, i.e. streams with a steep valley formation and rapid flow of water, retention is topographically limited and only occurs during low flow conditions, while in low-gradient streams, i.e. streams with a more level streambed and slower moving water, create a more depositional environment (Battin et al., 2008). Retention of nutrients in river systems is controlled by specific runoff

![Figure 6: The fraction of POC compared to the TOC and the relative contribution from the north and south rivers estimated in study I (Strååt et al., 2016).](image-url)
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\(1 \text{ km}^{-2} \text{s}^{-1}\) and hydraulic load, which is the quotient between mean depth and residence time (Behrendt and Opitz, 1999). The difficulty in assessing in-stream dynamics, however, lead to the retention of nutrients often being estimated as the difference between the sum of all inputs to the river and the observed output (Behrendt and Opitz, 1999, Humborg et al., 2007). But work is ongoing to improve our understanding and better approximate retention e.g. it has been identified it as one of the key research questions in urban stream ecology (Wenger et al., 2009). The consequences of not including retention and residence time of POC in the model development may be a contributing factor to the underestimated values in the low-gradient rivers in the southern region where especially residence time of water is an important factor for capturing the in-stream seasonal dynamics, e.g. onset of phytoplankton growth, the extent of sedimentation and for estimating the base flow concentration. Peak flow events are important for capturing the seasonal POC dynamics as one such event may be responsible for generating the bulk of the annual load (Committee on Flux of Organic Carbon to the Ocean, 1981, Hope et al., 1994), but are often underrepresented in field data e.g. Hope et al. (1997).

As discussed in study I, to more accurately capture the timing of peak flows and include in-stream retention and residence time estimates, we need a more highly spatially-resolved hydrological model and an improved understanding of the relationship between river characteristics and base flow concentrations e.g. via more long-term monitoring of suspended particulate matter. These limitations of the model are expected to have limited impact on study II as the estimations of potential climate changes effects on OC loads were assessed as the difference between average current and future values, i.e. potential errors are the same for all estimates.

The projected changes in exported OC loads in study II was explained by alterations in temperature and runoff. The governance of river runoff patterns on POC transport have been observed in a broad range of streams from alpine headwaters (Smith et al., 2013) to the Amazon river (Johnson et al., 2006) and the Baltic Sea (Andersson and Rudehäll, 1993).

The projections in study II, however, resulted in limited predicted effects due to climate change on the average annual export of POC and DOC because of counteracting changes in future inputs to individual sub-basins. Also, both POC and DOC transport are characterized by large variation between years, seasons, months and even days. Thus for significant changes to occur, rather large differences have to occur and prevail through the noise. But, the spatiotemporal changes in these flows, have implications for the coastal and marine environment in terms of trophic balance (Wikner and Andersson, 2012), the exchange of \(\text{CO}_2\) at the air-water interface (Gustafsson et al., 2014) and, metal and organic contaminant transport (Agrell et al., 2001, Josefsson et al., 2016, Dachs et al., 2002).
5. Conclusions and Future Work

We developed a dynamic model to simulate the contribution of POC in the Baltic Sea in study I and our assessment of riverine POC and its sources showed that OC in particulate form is by no means negligible when looking at the full catchment scale, and our results contributed to new understanding of factors governing land to sea fluxes of POC. By conducting a comprehensive model evaluation, the study illustrated the predictive capacity of the model. This model evaluation comprised of comparisons between modelled and measured concentrations of POC, TSS and chl-\(\alpha\) and further detailed analysis of factors influencing the performance of the model.

Riverine discharge is the largest input source of carbon to the Baltic Sea and the alteration in spatiotemporal pattern in the delivery of POC and DOC projected in this study could impact the coastal habitats in several ways, as discussed in study II e.g. shift the trophic balance in the coastal production from autotrophic to heterotrophic, affect the mineralization and consequently the air-sea exchange of \(\text{CO}_2\), and influence the transport of metals and organic contaminants. Our projections thus imply a potential future impact of climate change on the local ecology and biogeochemistry of coastal areas.

Issues to address in terms of future research within the field of OC dynamics include; the lack of field measurements (especially during peak flow events), a more detailed description of river hydrology, the dynamics and in-stream fate of organic matter e.g. sedimentation, resuspension and retention, and the relationship between POC and DOC within the river channels and in the coastal zones. Suggestions for future work in the Baltic Sea include combining the CSIM model with a marine model, e.g. the Baltsem, to better study the entire carbon flux and provide an important understanding of catchment dynamics in the Baltic Sea. Also, continued development of the POC/DOC-CSIM model with process descriptions for the fate and transport of organic contaminants and metals to better model the land to sea transport of pollutants.
Acknowledgements

Life and work these part years would not have been possible without the support, help and advice of so many people.

First and foremost my supervisor Emma, thank you for you quick replies, insightful and thorough comments, and great support. To Magnus, thanks for staying positive and teaching me that we are in science and not production, and it’s supposed to take time. Thank you Ian for calling it for what it is and all you can do is come in and do your best every day, go home and do the same the next day. Michael, you are the greatest boss a department could have. Anna, thank you for your mentorship, kind words and honest advice, it would have been a lot more of a rough ride without you. Going to work can be tough, but what makes you keep coming back in the toughest times and puts a smile on your face the rest of the time, are the people. Lovely Mel, I found my way through this world thanks to you and came out stronger, better and with a lifelong friendship, thank you. Lisa, Kerstin, Maria, Lara, Berit and Cat – one have to look far to find sweeter chicks – thank you for the celebratory cakes, distracting coffee breaks and reviving dance-offs. Li, you have been an awesome roommate and become a good friend, thank you for our chats, they brightened my days. Lukas, I will miss our standing fika and please, keeping making up words. To Anne, my Baltic Sea ally, thank you for the insightful discussions and you rock the science life. There are so many more, all of you at ACES are part in creating and maintain a workspace you want to keep coming back to day after day, so thank you.

Life of course exist outside work in the company of wonderful friends and family that easily turn your frown upside down in a heartbeat. A big thank you to my family, jag är oändligt tacksam och lyckligt lottad som har er, ni är mina bästa vänner och bästa supportrar. You have always been there to support (and sometimes question) my twists and turns through life, and I know that no matter what, you will be there. Finally and most importantly, Jon you are my present and my future, you keep me grounded and true, without you I would be lost and without a clue.
References


