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Estimating soil organic carbon from soils to the sea

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Abstract

Carbon lateral exports from terrestrial soils to the water conduit have been recently recognized as important components of global C budgets. These fluxes play also a major role in several processes within freshwaters that are important for biodiversity and human health. Swedish boreal forest is of special interest since part of the large amount of C stored within soils is exported as DOC. The export occurs mainly to small headwaters streams that vary greatly in spatial scales. This study attempts to estimate the distribution of TOC for all Swedish headwater streams by using a model that predicts TOC long-term concentrations in headwater streams smaller than $3Km^2$ and that is based on wetland percentage, altitude and precipitation levels. For the purpose all Swedish catchments draining to these streams were identified and exports from the remaining larger streams were divided by a factor of 50%. The results showed that export fluxes in northeast regions had the highest mean values where wetland and forests were predominant. The southeast characterized by the predominance of agricultural soils had the lowest fluxes. Fluxes of TOC for major 43 river mouth basins were found to vary from 2.1 to 7.6 g C m^{-2} yr^{-1}. Losses of C within these basins of C had a mean value of 35% and were found to be mostly related with WRT as C losses increased with longer WRT. Basin with high agricultural fractions gained C which may be related to the inputs of nutrients in freshwaters. C losses in middle basins suggested that the model is capable of estimating mean TOC concentrations but less accurate predictions were found in low and high TOC concentrations. Comparisons with literature revealed good agreement for TOC export estimates and losses, although in different magnitudes. Nonetheless, most studies focused on export estimates based on C transformations within freshwaters which may not correspondent to the amount of C that leaves the soils. Further studies may focus on C exports from agriculture soils and improving the models accuracy to predict low and high TOC concentrations.

Contents

Abbreviations

C	Carbon
CO_2	Carbon dioxide
DIC	Dissolved organic carbon
DOC	Dissolved organic carbon
$Fraction_{for+wet}$	Fraction of forest and wetlands
HW_{model}	Headwaters model
HW	Headwaters
NEE	Net ecosystem exchange
NEP	Net ecosystem productivity
PCA	Principal component analysis
SVAR	Svensk Vatten Arkiv
TOC	Total organic carbon
WRT	Water residence time

Carbon budgets have been gaining significance during the last decades given the role of carbon for global warming (Chapin *et al.*, 2006; Jonsson *et al.*, 2007). The terrestrial biosphere´s capacity of acting as a sink for atmospheric CO_2 has therefore become an object of intense investigation and controversy (Fan *et al.*, 1999; Houghton *et al.*, 1998). This study will focus dissolved organic form of carbon that is released from terrestrial soils to inland waters, which has recently been recognized as an important key for global C budgets. Here is proposed a model that estimates dissolved organic carbon (DOC) long-term concentrations and DOC exports from all Swedish boreal headwater catchments using map information as input data. These estimates attempt to quantify, more accurately, the amount of carbon that is lost laterally mainly by forested and wetland headwater soils and that returns to the atmosphere as CO_2 or sediments in the aquatic conduit or ultimately, moves on into the ocean pool.

1.Introduction

For the last 50 years CO_2 and vapor water exchanges between the biosphere and atmosphere, have been investigated (Baldocchi *et al.*, 2001). The first successful micrometereological measurements done continuously in this domain date from 1980, when CO_2 estimates were presented based on eddy covariance methods (Baldocchi, 2008). A decade later a small number of these research sites, spread along the globe, made possible the first estimates of CO_2 evasion on a global scale by determining vertical exchanges of CO_2 between the vegetation and the atmosphere, i.e. the net ecosystem production (NEP).

Nowadays, more than 400 sites, where surveys are conducted above ground through towers placed on top of forests, are continuously gathering data (Baldocchi, 2008). This methodology has been acknowledged as essential for NEP estimates on terrestrial ecosystems and for the comprehension of spatial and temporal variations of carbon cycling (Baldocchi, 2003). Nonetheless, there are still many uncertainties regarding the fate of the sequestered carbon calculated through these models, in short and long time scales (Luyssaert *et al.*, 2007).

Recently, the importance of carbon export through lateral fluxes occurring between terrestrial and aquatic ecosystems has been highlighted. This flux is now being considered as an important link between oceanic and soil carbon pools (Dawson, 2004; Hope *et al.,* 1994). It has been proved that a significant quantity of terrestrial carbon is released to the aquatic conduit, of which nearly half is lost by sedimentation and mineralization during the transport to the sea (Algesten *et al.,* 2004; Cole *et al.,* 2007). In certain ecosystems inland waters are, in contrast to terrestrial systems, regarded as source of carbon to the atmosphere (Algesten *et al.,* 2004; Cole *et al.,* 2007). Estimates indicate that emissions from the terrestrial aquatic conduit equal the global terrestrial NEP (Cole *et al.,* 2007; Tranvik *et al.,* 2009) and the total carbon export from the terrestrial biosphere to inland waters is estimated to be 2.9 Pg yr^{-1}, as shown in Figure 1.

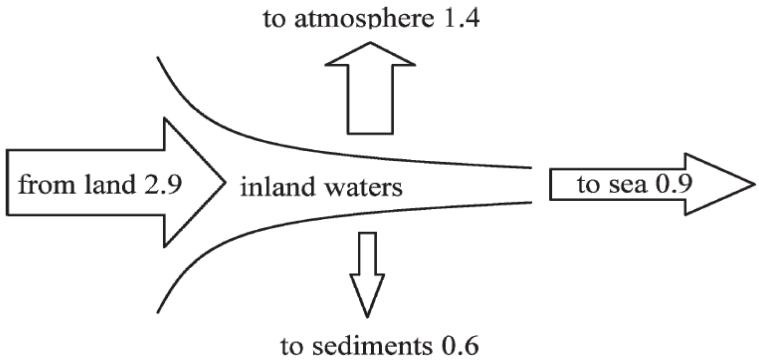

Figure 1. Schematic view of the C global flux (Pg yr^{-1}) in inland waters. Source: Tranvik et al., 2009

Despite the importance of the aquatic conduit, most global C models have ignored lateral fluxes when estimating global terrestrial carbon budgets (Billett *et al.,* 2004; Richey *et al.,* 2002). This fact leads to an overestimation of the true capacity of the terrestrial biosphere to act as a sink (Cole *et al.,* 2007; Gielen *et al.,* 2011), hence the amount of carbon flowing through inland waters is actually accounted as being stored in the terrestrial biomass and soils. When inland waters are taken into account in global carbon models, the purpose has mainly been to include DOC deliveries from riverine systems to the ocean (Cole *et al.,* 2007). However before entering the sea, much of the aquatic

carbon that was fixed by photosynthesis in the terrestrial ecosystem, has already been lost through sedimentation and evasion of CO_2 to the atmosphere (Dalzell *et al.,* 2005).

1.1. DOC in boreal streams

The riverine DOC originating from soils, also known as allochthonous carbon, is divided in two fractions: total organic carbon (TOC) and dissolved inorganic carbon (DIC). The DIC is composed of carbon dioxide (CO_2), bicarbonate (HCO_3^-) and carbonate (CO_2^{3-}; Humborg *et al*., 2010). Whereas TOC is made up of dissolved (DOC) and particulate fractions (POC). The importance of the each of these carbon fluxes is related to catchment features (Dawson *et al.,* 2004). In boreal streams, DOC compromises a major part of the TOC (95%; Bishop and Pettersson, 1996) and downstream DOC fluxes in these ecosystems are in general higher than inorganic carbon fluxes (Cole *et al.,* 2007; Jonsson *et al.,* 2007). Though recent results by Wallin (2011) suggest that DIC fluxes may have been underestimated.

The molecule of DOC is chemically composed by two different groups: a group of humic and fulvid acids, characterized by high molecular weight (MW) of recalcitrant nature (Wood *et al.*, 2011) and a group of low molecular weight labile compounds such as carbohydrates, amino acids, peptides, carboxylic acids and alcohols (Sachse et al., 2005). The high MW molecules are mainly derived from lignin and cellulose decomposition and confer to boreal water bodies their typical brown color. The low MW can be rapidly degraded (Kalbitz *et al.*, 2003) and with turnover rates on the order of two days, contrarily to the lignin compounds which take much longer to be degraded (Roehm et al., 2009). For a determinate DOC pool, the fraction made up by labile compounds can vary significantly (0% to 50%; Meyer, 1994), owing to the fact that chemical structures of DOC molecules vary according to the landscape type. For instance, respiration of DOC with an origin in forested soils is higher than DOC originating from wetlands (Berggren *et al*., 2007) hence wetlands soils derived DOC is considered to be more recalcitrant (Geller, 1986). Nonetheless, relations between the outlet water chemistry with biodegradability of DOC have not been easy to establish (Holmes *et al.,* 2008; Neff *et al.,* 2006).

The terrestrial carbon exported to fresh waters is produced from plant residues and microbial material. The fate of DOC is dependent on biological and chemical processes; DOC can be removed from soil solution by plant uptake and microbial/fungal decomposition or can be sorbed onto soil particles or form complexes with metals. The processes involving DOC, which take place either in soils and waters are, in turn, influenced by abiotic factors such as climate, soil physicochemical properties and atmospheric deposition of inorganic ions (Futter and de Wit, 2008; Kalbitz *et al.*, 2003). DOC concentration can vary widely, especially in boreal headwater streams as demonstrated by Temnerud *et al.* (2007), who found that TOC concentrations spanning 4-66 mg/l. Furthermore, DOC concentrations in boreal streams are mainly determined by the chemistry of the riparian zones and flow water depths (Bishop *et al.*, 2004).

The DOC in surface waters is not only naturally produced in terrestrial ecosystems (allochthonous), but can also be originate within aquatic systems (autochtonous) from algae, bacterial activity (Wood *et al.*, 2011. The autochtonous DOC represents a small flux in natural waters (Gerger *et al.*, 1999). In boreal lakes autochtonous DOC production is smaller compared to other types of lakes.

1.2. Why has DOC been neglected?

One of the reasons for neglecting aquatic allochthonous organic carbon has to do with the small fraction that inland waters comprise of the total global surface area (1%; Battin *et al.*, 2008). The amount of DOC in the aquatic conduit is thus much smaller than what is stored in terrestrial biomass and of little relevance when compared with terrestrial carbon budgets (Curtis *et al.*, 2002; Neff and Asner, 2001). Furthermore, freshwater DOC also makes a modest contribution to the total amount of carbon stored in the oceanic pool, representing only 1.8% (Kalbitz and Kaiser, 2008). The terrestrial organic carbon has also been assumed as not very degradable since experiments with short scale degradation showed that only 10% of total organic carbon is immediately respired (Moran and Hodson 1990). Hence, the simplifying assumptions that allochthonous DOC is transported directly to the ocean pool has generally been made in global carbon budget

calculations (Cole *et al.*, 2007). In addition, most estimates of carbon output along the aquatic conduit start at lakes or larger water courses, where monitoring data are available (Öquist *et al.*, 2009). However, most of allochthonous C enters the aquatic conduit in the capillary network of headwater streams (Bishop *et al.*, 2008). This means that the carbon entering the aquatic conduit is probably being underestimated. Especially in Sweden, where small catchments (< 2 Km2) represent approximately 80 % the length of permanent water systems (Nisell *et al.*, 2007) and have higher DOC concentrations than further downstream (Temnerud *et al.* 2010, Eriksson 1927).

1.3. Importance of DOC for boreal forest carbon budgets

An important step in documenting the importance of the aquatic conduit was made by Algesten et al. (2004), who demonstrated that in Northern Sweden 30-80% of riverine organic carbon was lost by sedimentation/mineralization mostly in lakes with long water residence times. Dawson *et al.* (2001) also showed that approximately 18% of the terrestrial carbon respired is decomposed in first order streams, suggesting that some DOC removal occurs immediately after entering the aquatic conduit. Furthermore, there is also CO_2 in groundwater derived from soil respiration that enters the stream network. This carbon is rapidly evaded (within hours) and may further increase the size of the aquatic conduit (Wallin, 2011). The importance of aquatic carbon losses is further linked with time scales and land use as suggested by Jonsson et al (2006). In ecosystems close to equilibrium, the net ecosystem exchange-NEE, i.e., the difference between sequestered and respired carbon plus the difference between inorganic sinks and sources of CO_2 of local scales (Lovett et al., 2005) is close to zero. In these cases, autotrophic carbon uptake represents a small fraction of the carbon balance and the steady export, through the aquatic conduit, becomes relatively more important (Cole and Caraco, 2001; Öquist *et al.*, 2009). Low terrestrial sequestration of carbon is characteristic of mature ecosystems, at high latitudes, such as the boreal forests (50°N-70°N; Black *et al.*, 2004). Boreal forests play a major role in carbon budgets since they are generally considered to be a carbon sink (Chapin *et al.*, 2000; Janssens *et al.*, 2003). Despite of the quantity of carbon sequestered in the aboveground biomass of these ecosystems being small, their peat soils contain roughly 43% of the total carbon in world´s soils (Dunn, 2006). Due to the NEE of

boreal forests being dominated by the accumulation of carbon in the soil, the consequent export of terrestrial carbon to water systems has a considerable impact when considering catchment net carbon accumulation (Jonsson *et al.,* 2007). For this reason, many researchers have proposed that carbon balances should be investigated at a catchment scale instead at an ecosystem scale (Cole *et al.,* 2007; Jonsson et al., 2007; Tranvik *et al.,* 2009), hence net carbon balances conducted at local scales might potentially modify carbon estimates in a global perspective (Valentini *et al.,* 2000).

1.4. DOC multiple effects

Besides being an essential part of carbon budgets in boreal catchments, the relevance of DOC flux has other dimensions as well, with respect to DOC´s multiple effects on water quality and ecosystem function. Aquatic allochthonous organic carbon controls processes such as complexation, mobility and solubility of metals, ions, nutrients and organic pollutants (Erlandsson *et al.,* 2010; Köhler *et al.,* 2008). Moreover, high concentrations of aquatic carbon also have implications for drinking water treatment, since the disinfection of DOC-rich water with chlorine may lead to the formation of cancerigenous substances (Jennings *et al.,* 2010). DOC has the capacity to attenuate UV-radiation, thus protects aquatic biota and fauna against harmful UV-B radiation (Schindler *et al.,* 1996). The input of organic matter from the terrestrial landscape is also a source of energy for heterotrophic bacteria which supports the food web in streams, wetlands and lakes (Jansson *et al.,* 2000). And lastly, the increase of DOC concentrations lowers the pH and influences the biota (Erlandsson *et al.,* 2010). Improving the prediction of DOC export from headwater streams is thus relevant for water quality as well for improving the understanding of local and global estimates of carbon budgets (Tranvik *et al.,* 2009).

1.5. Headwaters model

For all the growing awareness of DOC´s importance, one weakness in the analysis is actually defining the amount of terrestrial carbon entering surface waters in the capillary network of streams. This is because there are so many small streams and so few representative measurements. But in Finland and Sweden there are small (<3 Km^2) catchments with DOC observations over five years. Rappe (2009) found that these data

were sufficient to create a simple regression model of carbon export to headwaters where TOC can be predicted based on landscape elements. These data are available in a large scale for the whole of Sweden. Based on that information it was possible to upscale the model and to predict the TOC fluxes entering much of the stream network in Sweden.

2. Aim

In this context, the main objective of this thesis is to predict the long-term flux of DOC from soils into the aquatic conduit considering all headwater catchments in Sweden. This will be done using estimates of long term DOC concentrations and water fluxes from each of 17 312 catchments in Sweden.

The study will also investigate catchment-specific characteristics, such as different land uses, precipitation levels, altitude and catchment areas and analyze their influence on TOC export, according to the model.

The results obtained for TOC export from headwaters, will be compared with data monitored further downstream, in the middle and at the outlet of some of Sweden's basins. This approach will permit the understanding and characterization of how much TOC in the aquatic conduit may be lost to mineralization/sedimentation/evasion between leaving the soil in headwater catchments and reaching lakes, rivers or the ocean further downstream.

The estimates for terrestrial carbon exports and the losses or gains of TOC during its riverine transport will be compared with estimates of previous studies based on different approaches. This will be the ultimate step which will provide a more complete characterization of the aquatic conduit.

3. Materials and methods

3.1. The headwaters model

A simple regression model was previously developed to predict TOC exports from headwater forested catchments. The model was based on annual TOC transport data for the period 2001-2007 from 20 catchments, located in Sweden and Finland. The

catchments were dominated by forest and wetlands and drained to small headwater streams (<3Km^2). Flow measurements were also available, in an annual basis, for the same sites for 2001-2006. Based on these data was possible to calculate the volume-weighted concentrations (VWC) for each site and identify TOC long-term concentrations. These were further related to catchment specific characteristics, through a multiple linear regression. Within the 19 variables evaluated, the multivariate statistical analysis showed that altitude, precipitation and wetland coverage were the main TOC determinants. The model performance was an r^2=0.73 and is represented by the following equation:

$$\mathbf{TOC_{VWC} = 0{,}0024\ (wetlands^2) - 0{,}0322\ (altitude) - 0{,}0266\ (precipitation_{long\text{-}term}) + 44{,}27} \quad \mathbf{(1)}$$

where TOC_{VWC} has units of mg/l, wetlands are expressed in %, altitude in m and precipitation series of 30 years in mm.

The data set used for model's calibration spanned on an altitude range from 134 to 454 m, long-term precipitation varied from 523 to 1150 mm, wetland areas ranged 0 to 69% and TOC volume-weighted concentrations spanned 8,0 to 36,4 mg/l. The headwaters model (HW_{model}) was further upscale and TOC long-term concentrations were calculated based on the data available in: National Atlas of Sweden, Swedish land cover data, SLU forest database KNN-Sweden and SMHI. To calculate TOC transport across Sweden runoff data were retrieved from the Svensk Vatten Arkiv (SVAR). This contains runoff data according to a subcatchment division- SVAR catchments. Based on this was possible to calculate the carbon (C) export for a large number of catchments. In total 17 312 SVARs where used, which compromises the majority of the running waters in Sweden. Information regarding all SVARs is presented on Table 1.

Table 1. SVAR data description for 17312 SVAR catchments.

Variable	Units	Min	Q_1	Median	Q_3	Max
Altitude	**m**	**0**	**93**	**226**	**395**	**1444**
Long-term precipitation	**mm**	**450**	**650**	**700**	**850**	**1950**
Total annual runoff	**m^3**	**150**	**300**	**350**	**450**	**1400**
SVAR area	**Km^2**	**$1.0x10^{-3}$**	**7**	**18**	**38**	**7575**
Catchment fraction draining to streams<3Km^2	**%**	**0**	**45**	**59**	**68**	**100**
Forest cover	**%**	**0**	**53**	**73**	**85**	**100**
Wetlands cover	**%**	**0**	**0**	**1**	**9**	**100**
Alpine	**%**	**0**	**0**	**0**	**0**	**100**
Agriculture	**%**	**0**	**0**	**3**	**22**	**100**

Hence the HW_{model} was based on concentrations from catchments draining to small headwaters streams (<3Km^2), these areas had to be distinguished from catchments draining to larger streams. This was done by the VIVAN model (Nisell *et al.*, 2007). VIVAN uses the Swedish national digital elevation model to identify where all the streams flow in Sweden. Streams initiate when upstream accumulated catchment area surpasses a threshold. The threshold is adapted to catchment regions of the country based on the maps of streams. Since these maps are not in a digital form, VIVAN is needed to place the streams in the landscape. In this study, SVAR catchments were divided into 3 Km^2 headwater catchments and areas draining to streams larger than this threshold (>3Km^2). The objective of this distinction was to identify the export from areas draining to headwater streams, which are known for having higher TOC concentrations. This is what the model is calibrated for. In order to estimate what left the soils draining to larger catchments a factor of 50% was arbitrarily applied to the DOC HW_{model} output. This is based on the assumption that soils draining directly to larger water courses have a deeper flow pathway that bring less DOC to the streams but that then is a proportionality between the export to larger streams and that to headwaters within any given SVAR.

3.2. Site and data description

TOC exports were calculated for 17 312 SVAR catchments, compromising an area of approximately 476 356 Km^2. This area includes catchments inside Sweden but also some catchments that have their headwaters outside Sweden. Land-use coverage varied considerably across the studied area. Alpine areas were characteristic in the northwest, whereas forests were predominant in the north and central parts of Sweden. Wetlands occurred in higher percentage in north inlands areas. Land-use changes occurred more abruptly towards the south, where agriculture and urban areas were more pronounced. Agriculture was found as the dominant landscape in the very south of Sweden.

3.2.1. Predictor variables: altitude, precipitation and land use areas statistics

Altitude values varied from 0 m at the coastal areas to 1444 m in alpine areas. Roughly 90% of the catchments were below 600 m (i.e. within the range of model calibration data). Average precipitation annual values were based on data series of 31 years. The values ranged from 450 to 1950 mm, with minimum values occurring in the north and maximums in the alpine catchments located in northwest of Sweden, where altitude values were also higher. The mean annual precipitation value was 752 mm.

Land use area statistics for each SVAR catchment were obtained from National Atlas of Sweden, Swedish land cover data, SLU forest database KNN-Sweden and SMHI´s map data (Rappe, 2009). Land-use data were primarily retrieved in ten specific classes and further aggregated into 5 general groups: forest (forest and clear-cut felled), wetlands, alpine, agriculture (urban, agriculture, fields, limestone pavement and fields) and water (water and sea). Different land-use types were not only divided by the land-use types but also divided according to the stream area they drained to.

The model was also built for forested and wetland headwater catchments, which represent the majority of Sweden's area. Alpine and agriculture exports were set as constant values. The export from mountain areas was set to 4 mg/l and agricultural areas to 11mg/l, which are assumed to be reasonable proxies of what these areas export based on data for these catchment types. A minimum of 7 mg/l was applied to forest exports for

SVARs with values below the range of calibration sites. The functions used for each landscape exports are shown in Table 2.

Table 2. Export functions for each land-use category.

Landscape	Function	
Forest	$TOC_{VWCforests}$ =	44.27–0.0322 (altitude)–0.0266 (precipitation)
Wetlands	$TOC_{VWCwetlands}$ =	68.27–0.0322(altitude)–0.0266(precipitation)
Agriculture	$TOC_{VWCagriculture}$=	11
Alpine	$TOC_{VWCalpine}$ =	4

3.2.2. Annual runoff

Average annual runoff data was gathered from the SVAR archive and used to calculate TOC annual transports. The runoff ensemble varied from 150 to 1400 mm yr^{-1}.

3.2.3. Outlet TOC measurements for river mouth basins

TOC measurements at the outlet of 43 major Swedish river mouth basins were gathered from the Department of Aquatic Sciences and Assessment (September, 2011). TOC samples were taken monthly and the amount of TOC at the river mouth was calculated on an annual basis as the volume-weighted concentration for the years 2001-2007.

3.2.4. Middle basins

TOC data was available at the Aquatic Sciences and Environment database (June, 2011) for the middle part of 26 basins for the period of 2001-2007 (with exception of four basins that had less years of observations). Even tough, at least 4 observations were assured in all basins. The catchments were located throughout Sweden and are shown in Appendix. The basins varied significantly in terms of land uses. Stations linked to land coverage areas outside the model calibration (agriculture and alpine) are also included hence they allow understanding the model application domains.

3.2.5. TOC regional fluxes

The CLEO project from the Swedish EPA has the objective of determining how likely climate change will constrain the accomplishment of Swedish environmental targets. For that purpose Sweden was divided into 7 regions according to different climate change

characteristics. In order to calculate TOC exports for these regions, the SVAR catchments resembling in each region had to be first identified. This was possible by using ArcView GIS 9.0 (ESRI) and matching CLEO regions, available in a digital form, with all SVARs and limiting the SVAR catchments within each region.

3.3. TOC estimates

3.3.1. TOC long-term concentrations for total $SVAR_{tot}$, $SVAR_{under3}$ and $SVAR_{over3}$

The initial calculations had the purpose of mapping TOC long-term concentrations for whole SVARs, for SVAR areas dranning to large streams (>3Km2) and SVAR areas draining to small headwaters streams (<3Km^2). The distinction between SVAR areas draining to headwaters or larger streams was done since the model was made based on TOC concentrations from headwater streams (>3Km^2), which represent the majority of permanent streams in Sweden and are acknowledged for having higher TOC concentrations. A factor of 50% was applied to areas draining to larger streams, where lower TOC concentrations are expected. Firstly, TOC concentrations were calculated for the total SVAR areas by setting Equation 1 as function of wetlands and forested areas. TOC contributions were, in this way, calculated for both land uses categories based on precipitation and altitude values. The result indicated the potential export from those soils and was then weighted by the fraction of each of these land-use coverage within the total SVAR. The same method was applied to calculate exports from alpine and mountain areas by multiplying the potential TOC export of these areas (Table 2) by their fraction in each SVAR. Values for these four categories were summed up, resulting in the TOC long-term estimates of SVAR.

After calculating TOC long-term concentrations for the total SVAR area, these were calculated only for SVAR areas draining to small headwater streams. For that, TOC export of each land-use was multiplied by precipitation and altitude data (forest and wetlands) and by the fraction of areas draining to small streams within the whole SVAR (for all categories). TOC concentration of the whole SVAR and TOC concentrations of

SVAR areas draining to headwaters were multiplied by the total annual runoff (m^3), thus identifying the TOC exports for both areas and for each SVAR.

The export from areas draining to large streams was then calculated by subtracting TOC exports from the SVAR total area by the TOC export from areas draining to small streams. The result was divided by a factor of 50%. TOC export to large streams and the TOC exported for headwaters were summed up and divided by the total runoff of each SVAR. This step allowed to calculate TOC long-term concentrations for each SVAR, based on the assumption that headwaters have the potential of exporting twice as much as areas draining to larger streams. TOC concentrations for the whole SVAR were plotted together with main predictor variables and mapped for the whole of Sweden, together with TOC concentration for areas draining to small headwaters and larger streams.

3.3.2. TOC long-term concentrations for wetlands and forested headwater areas

TOC concentrations were calculated using Equation 1 for the whole of Sweden, considering all SVARs as headwater areas and totally covered with forest. This approach investigated TOC contribution from forested soils in each SVAR catchment according to altitude and precipitation levels. A TOC limit of 7 mg/l was used in order to assure a minimum export concentration from forested soils. The same method was applied to calculate concentrations for wetland soils by assuming each SVAR as totally covered by wetlands. A minimum of 0 mg/l was set for some SVARs in the alpine zone that were outside the range of calibration of the model.

3.3.3. TOC exports and losses for river mouth basins

After calculating TOC exports in terms of mass for each SVAR (section 3.1.1.), TOC exports of SVARs within the same river basin were summed up down to the sea. In this way, it was possible to calculate how much TOC entered the water conduit from the soils at the very beginning in each river basin. The export of TOC was further compared with average TOC exports for the period of (2001-2007) measured at the outlet of 43 basins. The percentage of TOC losses during the transport from headwaters to the sea were found by using Equation 3:

$$TOC\ losses_{\ river\ mouth\ basin}\ (ton) = \frac{TOC_{outlet}\ (ton)}{TOC\ export_{whole\ SVAR}(ton)} \quad \textbf{(2)}$$

Exports and losses for each river mouth were presented in a table together with catchment-specific features. The table contains also fluxes for forested and wetlands headwater areas, areas draining to large streams (>3Km^2), areas draining to first order streams (<3Km^2) and fluxes for the whole river mouth basin. TOC fluxes (g C m^{-2} yr^{-1}) were calculated as described below:

$$Forest_{headwaters\ flux} = \frac{TOC\ 100\%\ forest\ coverage\ (ton)}{Total\ catchment\ area\ (Km^2)} \quad \textbf{(3)}$$

$$Wetlands_{headwaters\ flux} = \frac{TOC\ 100\%\ wetland\ coverage\ (ton)}{Total\ catchment\ area\ (Km^2)} \quad \textbf{(4)}$$

$$Headwaters_{flux} = \frac{TOC\ export\ headwaters\ (ton)}{Headwaters\ area\ Km^2} \quad \textbf{(5)}$$

$$Large\ streams_{flux} = \frac{TOC\ export\ large\ areas\ (ton)}{Large\ areas\ Km^2} \quad \textbf{(6)}$$

$$Whole\ areas_{flux} = \frac{TOC\ export\ whole\ catchment\ (ton)}{Total\ area\ Km^2} \quad \textbf{(7)}$$

A principal component analysis (PCA) was performed in Simca-p 11.0 (Umetrics) on 7 variables related to TOC exports. The variables that were able to explain most of the TOC variability were identified by using variable importance plots.

3.3.4.. TOC exports and losses for middle basins

TOC monitored data were gathered for the 26 basins for the period 2001-2007. Mean TOC transport values were compared with modeled exports. This was done by identifying all SVARs located upstream the measuring points. Losses were further calculated based on Equation 9:

$$TOC\ losses_{middle\ basins}\ (ton) = \frac{TOC_{observed}}{TOC_{exported}} \quad \textbf{(8)}$$

3.3.5. TOC regional fluxes

This approach divided Sweden into 7 regions according with climate change scenarios and identified the SVAR catchments within each region. After this classification TOC exports from all the SVAR catchments belonging to the same region were summed and divided by the total soil area of the region, according to Equation 9:

$$TOC\ regional_{flux} = \frac{TOC\ export_{\ all\ region\ SVARs}\ (ton)}{Total\ region\ area\ (Km^2)} \quad \textbf{(9)}$$

$$TOC\ regional_{\ flux\ forested\ HW} = \frac{TOC\ export_{forested\ HW}(ton)}{Total\ area_{forest\ HW}\ (Km^2)} \quad \textbf{(10)}$$

$$TOC\ regional_{\ flux\ wetland\ HW} = \frac{TOC\ export_{wetland\ HW}(ton)}{Total\ area_{wetland\ Hw}(Km^2)} \quad \textbf{(11)}$$

Equation 9 gives the average flux for the whole regions based on the assumption that areas exporting to small headwater streams contribute twice as much as areas draining to larger streams. Fluxes were further calculated for forested and wetlands headwaters areas. TOC exports from each land-use were summed up for each region and divided by the sum of the total area draining to headwaters according to each land use (Equation 10 and 11). Average fluxes for the three approaches were mapped and presented together with mean land-use coverage for each region.

4. Results

4.1. TOC long-term concentrations in SVAR catchments

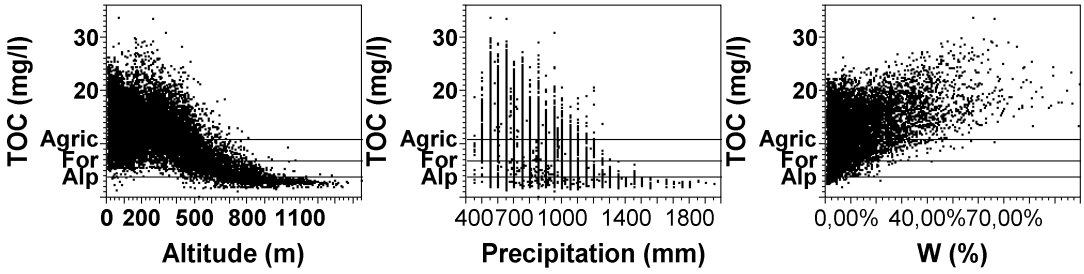

Figure 2. SVAR concentrations (mg/l) dependence on altitude (m), long-term precipitation (mm) and wetlands area (%). Limits for agriculture, forest and alpine are displayed in the figure.

TOC long-term concentrations were calculated for each SVAR catchment based on land use, precipitation and altitude data (Equation 2). Agriculture and alpine coverage were considered as having constant TOC exports potentials (11 mg/l and 4 mg/l, respectively) and a minimum of 7 mg/l was applied to forested soils. Estimates were done differently according to the stream area the catchments drained to and a factor of 50% was applied to the export of SVAR catchments draining to streams >3Km^2. Results were plotted together with main TOC predictors in Figure 2. In general, the increase in altitude and precipitation led to decreases in TOC concentration, whereas high fractions of wetlands were positively related to TOC concentrations that increased with high fractions of wetlands. The maximum TOC long-term concentration value was 35.8 mg/l and the mean 12.0 mg/l.

Figure 3. Distribution of TOC concentrations according to the HW_{model} for: i) headwater catchments, ii) larger streams, iii) whole SVARs (from left to right).

TOC long-term concentrations for each SVAR were further mapped in Figure 3. On the left are shown i) TOC concentrations for areas exporting to headwater streams, followed by ii) a map of the distribution of TOC concentrations of areas exporting to larger streams and iii) TOC estimates for to the whole SVARs. The SVAR areas draining to headwaters streams presented in general the highest concentrations, with maximum values next to the east coast that decreased gradually towards the west, reaching minimum values in mountain areas. TOC long-term values for headwater SVARs varied up to 34.6 mg/l with a mean value of 8.5 mg/l. Catchment areas draining to larger streams had lower TOC concentration values, mostly at the west coast and inland regions. The highest concentrations were found in streams next to the Finish border. TOC long-term concentrations for these areas varied up to 22.8 mg/l with a mean value of 3.6 mg/l. Distribution of long-term concentrations for the whole SVAR had a mean value of 12.0 mg/l. The east coast presented in general the highest exports, followed by inland regions and mountain areas that had the smallest values. The highest TOC concentration of the whole SVAR area (35.8 mg/l) occurred also in the northwest part.

4.2. TOC long-term concentrations in headwater forested areas

The estimates in Figure 4 considered all SVARs as catchments areas draining to streams $<3Km^2$ and entirely covered with forest. This investigated the forest contribution to TOC exports as a function of precipitation and altitude data. A minimum export value for forested soils was set to 7 mg/l. The results showed that the concentrations found followed the same pattern as exports from whole SVARs in Figure 3. Low values were characteristic from northwest zones, whereas inland regions and southeast parts had intermediate TOC concentrations. The east coast had the highest TOC concentrations that spanned on 7 to 30.9 mg/l, with a mean value of 16.8 mg/l.

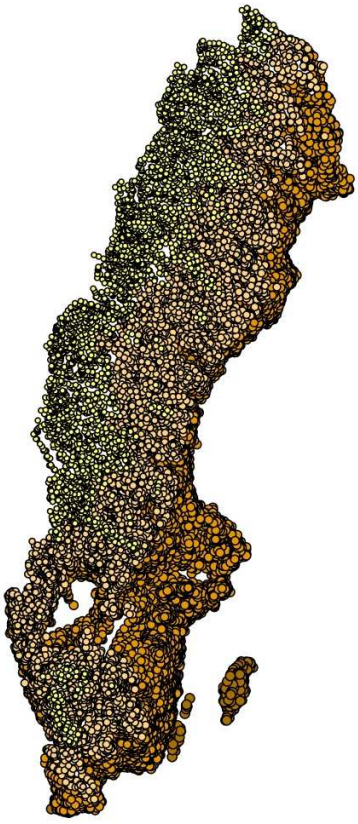

Figure 4. Map of TOC concentrations for forested headwaters calculated based on Equation 2. Minimum concentration value of 7 mg/l was assumed for areas covered 100% by forest.

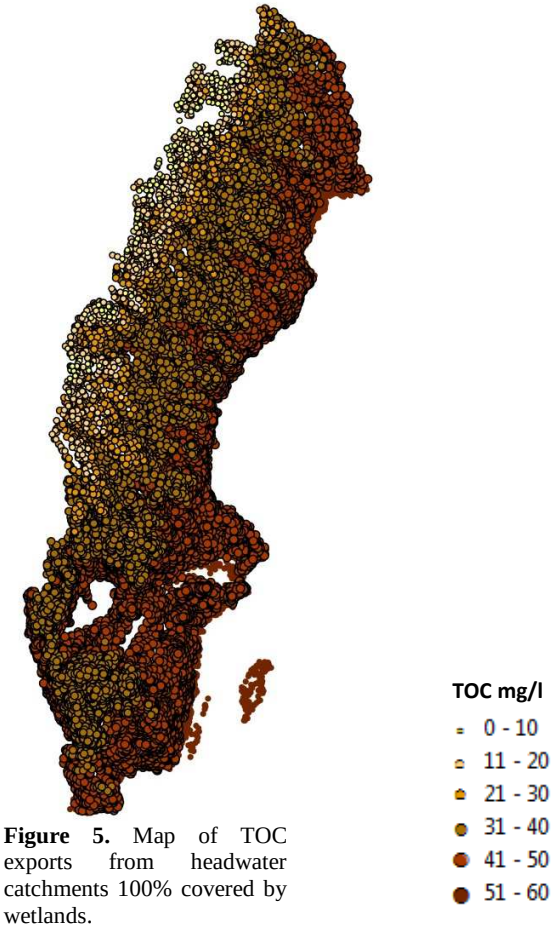

Figure 5. Map of TOC exports from headwater catchments 100% covered by wetlands.

$$TOC_{VWCforests}=44{,}27–0{,}0322(altitude)–0{,}0266(precipitation) \quad (12)$$

$$TOC_{VWCwetlands}=68{,}27–0{,}0322(altitude)-0{,}0266(precipitation) \quad (13)$$

4.3. TOC long-term concentrations in headwater wetland areas

Figure 5 shows potential TOC concentrations in headwater catchments with dependence on altitude and precipitation. Concentration values varied up to 54.9 mg/l, with TOC concentrations reaching generally high values all along the east coast. The south east area was found as a region with higher potential for TOC exports. Some of the mountain areas, which are outside the model calibration range, had to be excluded from the map

hence they presented very low TOC long-term concentrations. The mean potential TOC long-term concentration value for wetland headwater areas was 39.3 mg/l.

4.4. TOC fluxes and losses in river mouth basins

Table 3. Export fluxes, losses and catchment-specific features for river mouth basins.

No.	Basin area (Km^2)	Basin area < $3Km^2$ (%)	Basin areas >600m (%)	WRT (years)	For (%)	Wet (%)	Alp (%)	Agri (%)	For export hw ($gCm^{-2}y^{-1}$)	Wet export hw ($gCm^{-2}y^{-1}$)	Terrestrial TOC export ($gCm^{-2}y^{-1}$)				TOC sea ($gCm^{-2}y^{-1}$)	Losses (%)	Losses w/o factor (%)
											Headwaters	Larger Streams	Whole SVAR	Whole SVAR w/o factor			
1	449	55		0.5	79	16		1	8.2	17.0	9.7	4.7	7.5	9.6	4.1	45	57
2	4207	23		0.5	72	24		1	7.2	15.1	9.1	4.3	5.5	8.8	2.4	56	73
3	1608	62		0.6	82	12		2	5.2	12.6	6.2	3.1	5.0	6.2	3.6	29	42
4	3002	58		0.4	81	14		3	5.3	12.4	6.2	3.1	4.9	6.2	4.1	15	34
5	3442	62		1.3	82	10		2	5.4	13.7	6.3	3.1	5.1	6.3	3.6	29	43
6	459	53		1	82	9		5	8.2	16.7	8.7	4.4	6.7	8.7	4.0	40	54
7	19828	57	29	2.1	76	11	5	4	4.5	11.8	5.1	2.6	4.1	5.2	2.4	41	54
8	1525	47			85	1		9	4.7	10.3	4.7	2.3	3.4	4.6	3.4	1	26
9	376	50			73	13		10	5.9	12.0	6.4	3.2	4.9	6.4	4.6	5	28
10	1649	63		2.1	75	10		6	6.4	14.4	7.2	3.6	5.9	7.2	3.9	34	46
11	12851	69	16	3.8	78	6	5	3	4.8	12.2	5.1	2.6	4.4	5.1	1.9	57	63
12	28954	68	18	3.1	73	10	4	6	4.9	13.8	5.7	2.8	4.8	5.6	2.9	40	48
13	1994	70		8.4	80	2		7	5.8	12.7	5.8	2.8	5.0	5.7	1.8	64	69
14	2686	73			72	9		14	6.0	17.6	7.1	3.4	6.2	7.1	7.7	-25	-9
15	18130	45	18	0.5	63	18	13	2	6.2	14.2	7.0	3.6	5.2	7.1	2.9	45	59
16	2459	60		2.5	76	4		11	6.6	14.8	6.8	3.2	5.4	6.6	3.4	38	48
17	31865	64	21	2.4	70	9	11	2	5.5	15.3	6.2	3.1	5.1	6.2	2.9	43	53
18	810	60			77	2		18	5.0	10.6	4.7	2.3	3.7	4.7	5.0	-33	-6
19	11285	57	25	2.4	68	9	14	1	5.5	14.5	5.8	3.1	4.7	6.0	2.0	57	67
20	758	57			74	1		24	4.2	10.8	3.9	1.8	3.0	3.8	3.4	-13	11
21	4470	56			73	1		20	4.4	10.3	4.1	2.0	3.2	4.0	3.5	-8	13
22	782	75			71	1		19	8.7	24.4	8.6	4.1	7.6	8.5	4.1	46	52
23	26778	57	33	2.0	65	7	18	2	5.2	13.9	5.4	2.8	4.3	5.5	2.4	44	56
24	999	60			72			18	3.9		3.6	1.7	2.9	3.5	2.9	1	17
25	6452	62			59	13		20	5.9	17.1	7.4	3.3	5.9	7.1	5.2	11	27

Table 3. Continued.

No.	Basin area (Km^2)	Basin area < $3Km^2$ (%)	Basin areas >600m (%)	WRT (years)	For (%)	Wet (%)	Alp (%)	Agri (%)	For export hw ($gCm^{-2}y^{-1}$)	Wet export hw ($gCm^{-2}y^{-1}$)	Terrestrial TOC export ($gCm^{-2}y^{-1}$)				TOC sea ($gCm^{-2}y^{-1}$)	Losses (%)	Losses w/o factor (%)
											Headwaters	Larger Streams	Whole SVAR	Whole SVAR w/o factor			
26	40157	35	22	1.4	60	11	21	4	6.4	14.4	6.4	3.2	4.3	6.4	2.4	46	63
27	3342	75			64	6		24	6.1	19.7	7.0	3.3	6.1	6.9	5.2	15	25
28	11731	60	23	5.6	60	10	15	2	4.8	13.3	5.4	2.7	4.4	5.4	2.1	52	61
29	26727	69	28	3.2	61	8	17	4	5.1	14.7	5.7	2.8	4.9	5.7	2.3	52	60
30	1340	74			65	4		27	7.2	20.5	7.5	3.6	6.6	7.5	5.5	16	27
31	2202	74			65	3		26	6.9	21.5	7.3	3.5	6.4	7.2	4.8	24	33
32	3369	53			64	3		21	4.5	10.5	4.3	2.1	3.4	4.3	4.5	-32	-5
33	301	66			62	3		30	6.9	17.4	6.7	3.1	5.5	6.5	6.3	-14	3
34	4724	67			55	7		33	6.1	14.3	5.9	2.6	4.9	5.7	5.2	-7	9
35	50115	55	9	13.5	57	4	4	18	5.7	15	5.7	2.5	4.3	5.4	2.0	53	63
36	22650	55			56	2		31	6.1	14.5	5.4	2.4	4.1	5.1	1.8	56	65
37	3631	64			57	1		29	5.3	10.7	4.4	2.1	3.7	4.4	2.2	40	50
38	25263	50	46	2.6	45	9	34	2	5.5	14	5.6	3	4.3	5.8	1.9	56	67
39	15481	62			51	1		28	4.3	10.9	3.8	1.7	3.1	3.7	1.9	37	49
40	1897	66			45	3		48	6.7	16	6.0	2.7	4.9	5.8	2.2	55	62
41	479	52			40			60	7.4		4.8	2.2	3.5	4.6	2.2	37	52
42	1204	44			14			84	6.3		4.1	1.9	2.9	3.9	2.6	8	33
43	193	13			3			97	6.8		4.1	1.8	2.1	3.7	1.3	39	65

4.4.1. TOC fluxes

Table 3 has focus on 43 river mouth basins spread along Sweden (Appendix 1). Catchment specific features were presented in the table together with different TOC fluxes and losses based on differences between modeled TOC exports and observations at the river mouths. The basins were ordered in the table according with fractions of forest and wetlands ($fraction_{for+wet}$) existent in each basin. Catchments where the model is thought to be better applied are the ones in green, in which $fraction_{for+wet}$>80%. Water residence times (WRT) were taken from Algesten *et al.* (2004) and are available for 21 river mouth basins located in the north and central Sweden. The table also contains catchments with altitude areas outside the model calibration range and basins with considerable alpine and agricultural coverage. These were included in order to achieve a better understanding of the model constrains. TOC all SVAR fluxes (considering different exports to headwaters and larger streams) spanned on 2.1 to 7.6 g C $m^{-2}y^{-1}$. Fluxes concerning small basins varied in a greater extent (2.1 to 7.6 g C $m^{-2}y^{-1}$) than fluxes from larger basins (> 10 000Km^2), which were more evenly distributed (3.1 to 5.2 g C $m^{-2}y^{-1}$). The average flux for the whole SVARs was 4.7 g C $m^{-2}y^{-1}$, whereas a mean flux of 5.9 g C $m^{-2}y^{-1}$ was obtained when considering that areas draining to small and large streams had export potentials (in the table presented as “whole SVAR without factor”).

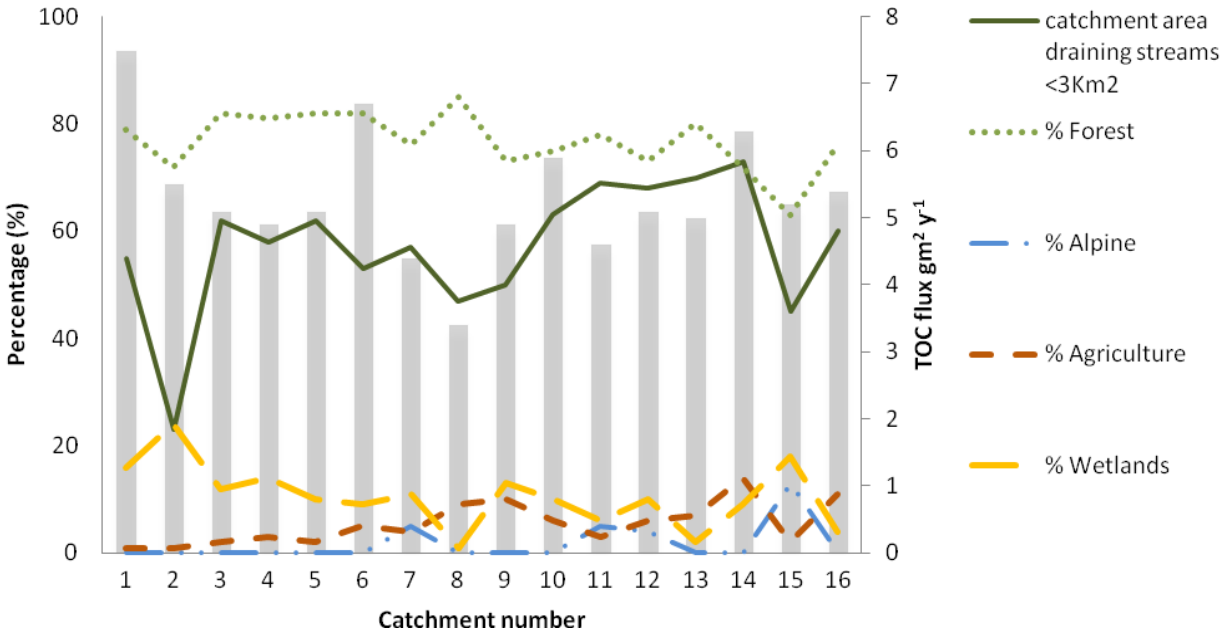

Figure 6. TOC fluxes, for basins where fractionfor+wet >80%, plotted against percentage of catchment area draining to streams <3Km^2 and land-use percentages.

Considering these basins and their catchment-specific features, TOC whole SVAR fluxes seemed to vary mostly with catchment fractions draining to streams <3Km^2 and tended to

increase while the increase of these fraction areas within the catchment (Figure 6). In order to investigate relationships between fluxes and basins where the model is best applied (basin 14 was excluded from the dataset hence resulted in gain or C), a principal component analysis (PCA) was run. This showed that fluxes of TOC were in some extent related to the total area of the catchments followed by wetland and forests fractions within the catchments. These three variables together explained roughly 63% of the TOC variability (Figure 7).

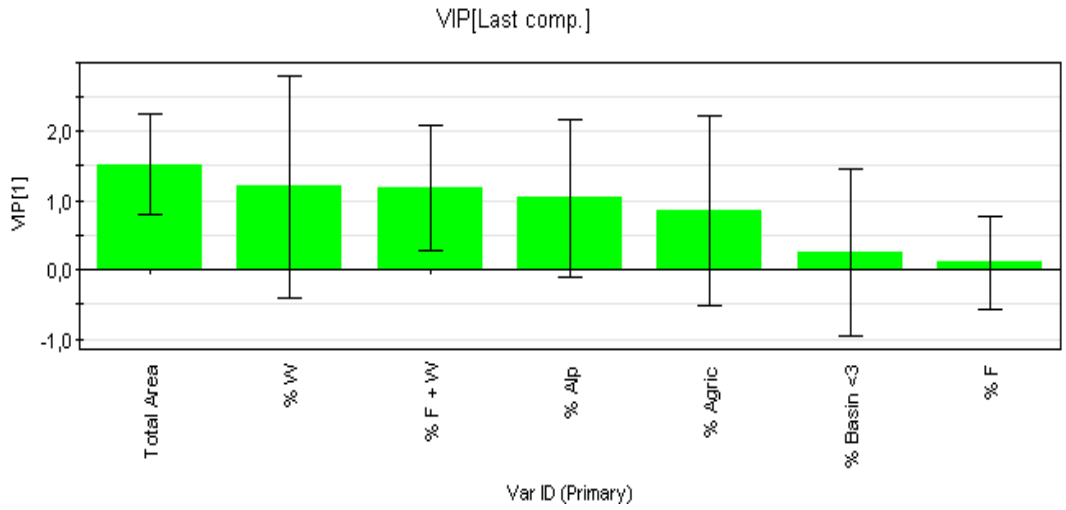

Figure 7. Variable importance plot of catchment specific features to TOC whole SVAR fluxes.

4.4.2. TOC losses

Carbon losses were calculated for the 43 basins by subtracting the observed TOC at the basins outlet from the TOC exports (Table 3). Losses of C spanned on from 1 to 64% when considering different exports for areas draining to small or large streams. Accounting equal exports for both areas resulted in losses of C from 3% to 73%. Average C losses were 38% and 45%, for each case respectively. Gains of carbon took place in some basins where the percentage of agricultural coverage occurred in a more significant extension (>14%).

Losses and catchment area

Basin total area and TOC losses/gains are plotted on Figure 8. The figure says respect to losses that distinguished exports potential areas draining to headwaters or larger streams. Small basins tended to have in general higher variability of TOC losses, irrespective of being the basins where the model is better applied or not. Basins smaller than 10 000Km^2 ranged from carbon gains of 33% to losses of 64%. Whereas larger basins had losses more evenly distributed, ranging from 37% to 57%. The relationship between basins catchment area and

TOC losses had an r^2=0.20. The same predictive power was found for catchment areas and TOC losses considering all areas exporting equally.

Losses and catchment fraction draining to streams <3Km2

Figure 9 shows C losses/gains in relation to the basin fraction draining to small headwater streams. The figure shows that 37 out of 43 basins had at least 50% of catchment areas draining to headwater streams up to 3 Km^2. The smallest catchment area draining to these first order streams (13%) rendered TOC losses of 39%, whereas 75 % of the same variable gave origin to a loss of TOC of 17%. Equal percentages of basin areas draining to small watercourses resulted in significant C losses differences, as for instance 60% of this variable resulted in gains of 1% and 33% and losses of 38% and 52%. A broader analysis of the figure reveals that losses and catchment areas draining to small headwater streams may vary differently and resulted in a very low predictive relationship (r^2=0.01).

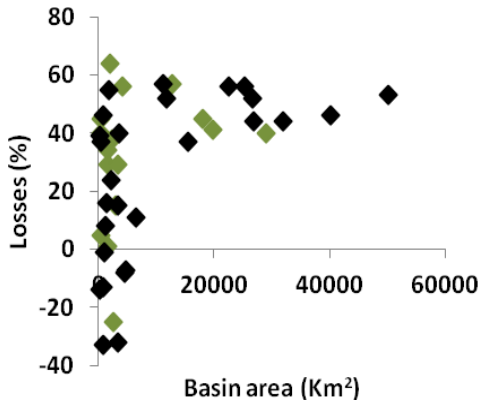

Figure 8. Percentage of TOC losses plotted against basin total areas.

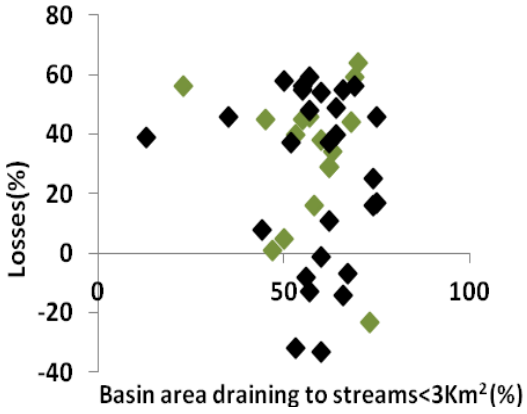

Figure 9. Percentage of TOC losses plotted basins basin fractions draining to small streams (<3 Km^2).

Losses and land use

Land use coverage varied greatly among the investigated catchments. The catchment with the highest percentage of wetlands and forest (95%), rendered a TOC loss of 45%. Equal percentages of wetlands and forest land uses in different basins, as for instance the basins containing a $fraction_{for+wet}$ of 81%, resulted in different TOC losses. Basin 15 with a $fraction_{for+wet}$ of 81% had C losses of 45% and basin 14 with the same $fraction_{for+wet}$ had a gain of C of 23%. TOC losses in smaller basins with high $fraction_{for+wet}$ tended to vary more significantly. The results showed that a variation of 10% within the $fraction_{for+wet}$ in two different basins (basins 19 and 32), resulted in variations of carbon of 89% (-32% to 57%). On

the other hand the smallest fraction$_{for+wet}$, 3%, had still a loss of carbon of 39%. All gains of C occurred in basins where agriculture land use occupied a significant parcel of the catchment(>14%), however some of the basins containing high agriculture percentages resulted in carbon losses (e.g. basin 41 with 60% agriculture land-use). Within all basins containing alpine areas carbon losses were fairly constant varying from 44% to 59%. Thus, C losses seemed to vary with other factors rather than land use coverage.

Losses and water residence time

Water residence times (WRT) were related to C losses considering two different scenarios: i) exports from areas draining to larger streams are considered to be half of what is exported to headwaters (Figure 10) and ii) catchment areas draining to headwaters/large streams have equal C exports potential (Figure 11). Figures 10 and 11 clearly suggested a relationship between the variation between C losses and WRTs, mostly when considering differences between exports to small or large headwater streams (Figure 10). In both figures, losses tended to increase with small WRTs and to reach more constant values with longer WRTs. When relating C losses and WRTs together with catchment features seemed that these were mostly related to the fraction of drainage area draining to small headwater streams.

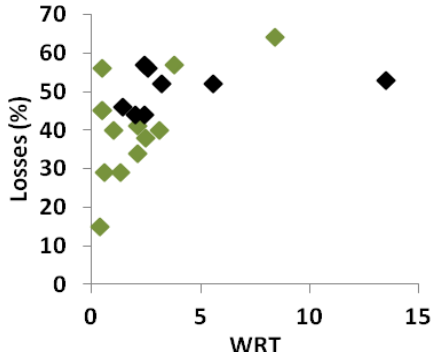

Figure 10. Percentage of C losses plotted against WRTs.

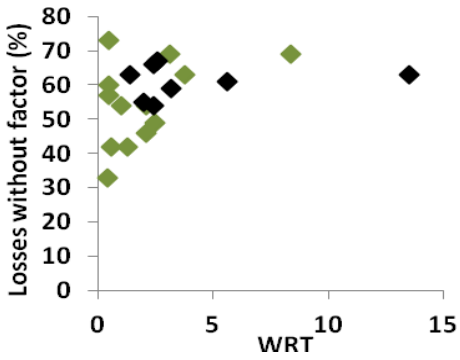

Figure 11. Percentage of C losses considering equal exports to headwaters/larger streams plotted against WRT.

Figure 12 analyses losses and WRTs by different fractions of the areas draining to small streams. Limiting the analysis to basins where the model is best applied and where the basin fraction draining small streams > 58%, resulted in a good predictive relationship between C losses and WRTs with a r^2=0.84. Variables with low fractions of catchment areas draining to streams <3Km^2 had lower correlations with C losses over time. Losses in terms of concentration were also linked to WRT in Figures 13 and 14. The variables presented a small

correlation indicating that losses in terms percentage are better predictors of the variability of TOC losses over WRT.

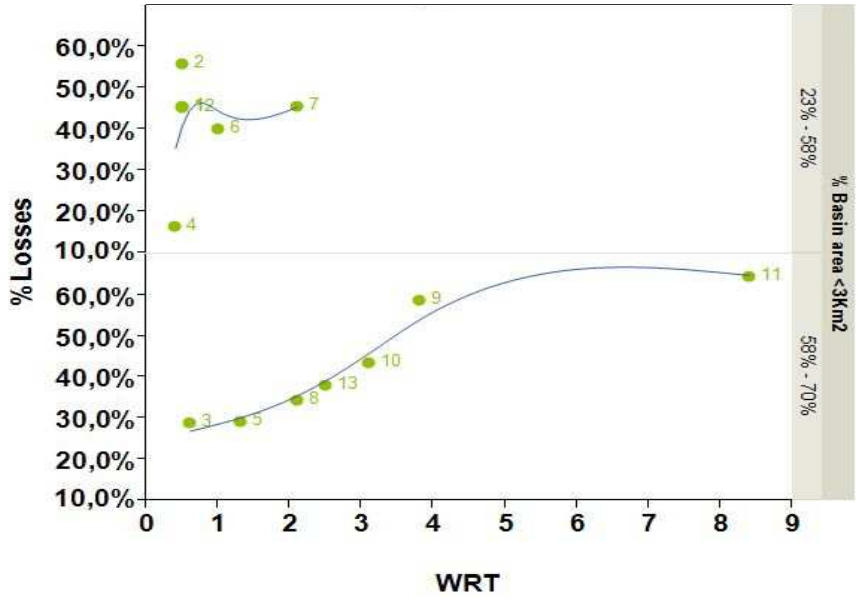

Figure 12. Percentage of TOC losses as a function of WRT by percentage of catchment area draining to small streams. Basin areas draining to streams higher than 58% rendered equation 3: %Toc losses=0.308+0.149 log(WRT).(r^2=0.84; n=7)

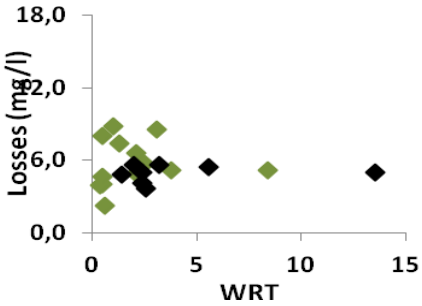

Figure 13. Losses in terms of concentration plotted against WRTs.

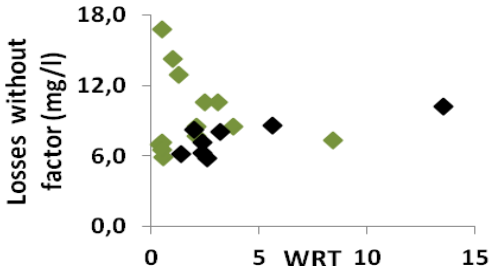

Figure 14. Percentage of losses vs. WRTs by percentage of basin area draining to streams <3Km^2.

4.5. Comparison between modeled TOC and TOC observed in middle basins

Export estimates from headwaters catchments were compared with TOC monitored data along 26 basins. Carbon losses were calculated from headwaters until the measuring sites by subtracting the observed TOC to the TOC export estimates. Results were then plotted on Figure 15 and related to different catchment coverage types and to catchment fractions draining to streams <3Km^2. Losses of carbon occurred in 15 basins and varied from 6 to 59% with a mean loss of 32%. Within C losses (upper part of the *y* axis), agricultural areas had the

biggest influence on the results (r^2=0.22) as losses tended to be smaller with the increase of this land-use fraction. In addition, catchment fraction draining to small streams and basin size showed also some correlation with losses percentage. The C observed and modeled tented to be similar while the increase of catchment areas draining to small streams and the decrease of basins size. Thus, losses tended to be smaller for small areas, areas with high agriculture coverage and for basins with large areas draining to small headwaters streams. Larger basins showed on the other hand a higher difference between the C exported and the C measured at the monitoring sites.

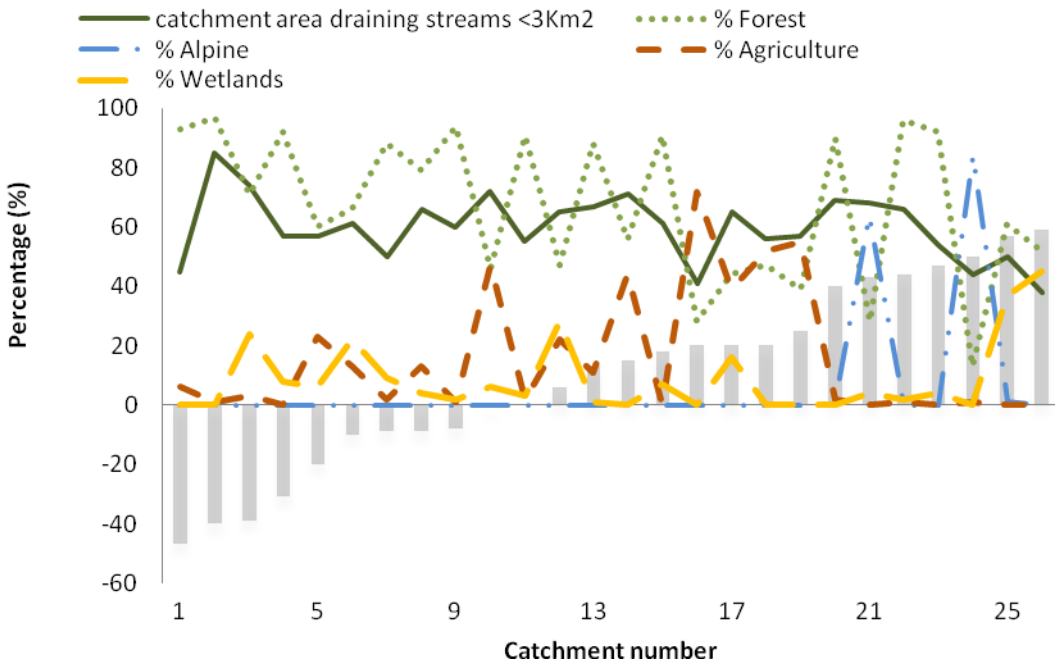

Figure 15. Losses of TOC in percentage plotted against catchment specific features.

C gains occurred in 10 basins and took place mainly in small basins. Agriculture and forest areas seemed to have strongest influence for C gains. The increase of forested areas tended to increase C gains whereas high fractions of agriculture coverage resulted in small gains of C. Besides variations between losses in terms of percentage and catchment features there was also a clear and strong trend between measured C concentrations and differences between modeled and observed values (Figure 16). Differences between concentrations were calculated for estimates considering an equal export from headwaters and large areas and considering differently both catchment fractions by applying a factor of 50% to the export to larger streams.

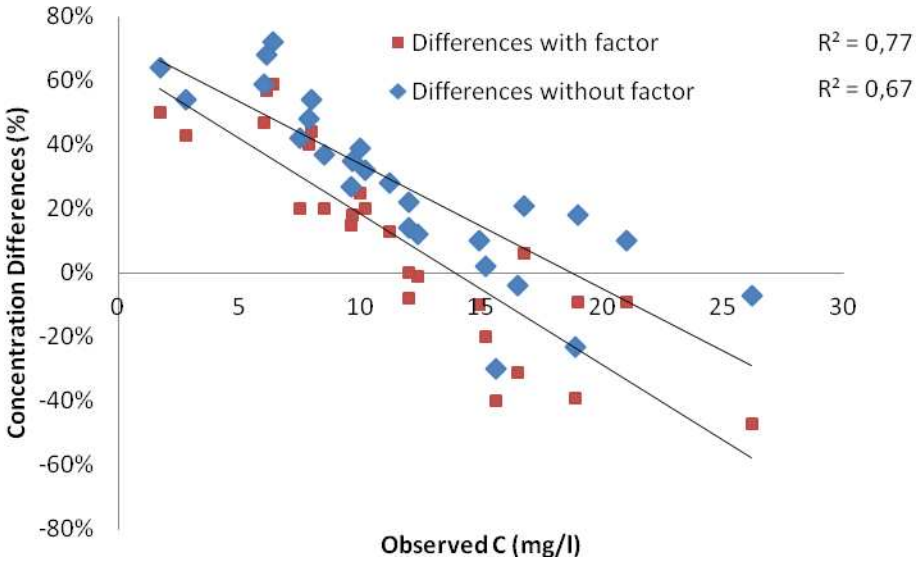

Figure 16. Differences between modeled and observed concentrations in percentage plotted agains TOC observed concentrations.

C exports tended to equal measurements for values ranging approximately 10 to 20 mg/l. Whereas high and low C concentrations resulted in higher differences between modeled and observed values.

4.6. TOC regional fluxes

TOC fluxes were estimated for the whole of Sweden according to 7 different regions. These regions were based on different climate change scenarios. Fluxes were calculated i) assuming that the export from areas draining to small or larger streams were different (i.e., that areas draining to headwaters export a double amount of C), ii) considering catchment areas covered 100% forest soils draining to headwaters and iii) the whole catchments were entirely covered by wetlands and drained to headwaters. Fluxes were mapped and presented on Figure 17 for each case. Table 4 shows land-use statistics for each region as well as estimated fluxes based on different catchment area assumptions. Besides the fluxes mentioned above, fluxes for headwater areas (streams <3Km^2), areas draining to larger streams greater than 3Km^2 and fluxes from all SVAR areas without factor (i.e., considering equal exports to headwaters and larger streams) were also included in the table.

Region 4, located on the northeast part, presented the highest percentage of forest (79%) and the highest values for most fluxes. This was followed by region 1 and 5 that had the next greater fluxes for 3 of the estimated fluxes. Region 1 had the biggest catchment area draining to small streams (62%) and was also the region where agriculture was more abundant (40%). This region presented high forest headwater fluxes (6.6 g C m^{-2} yr^{-1}) as well as the high fluxes

from headwaters and total areas (6.5 and 5.1 g C m^{-2} yr-1). On the other hand, the inland region 5 had the second highest fluxes for wetlands export from headwaters, larger streams and whole SVAR fluxes (13.4, 3.4 and 6.5, respectively). This area corresponded to the region with the smallest areas draining to headwaters (55%) and with the highest percentage of wetlands (15%). The lowest fluxes were found in Regions 2 and 7, where wetland coverage is absent. Region 2, presented a small potential of C export from forested and wetland headwater soils (4.8 and 9.8 g C m^{-2} yr^{-1}, respectively) and a large part of the region is covered by agricultural area (30%). Region 7 represents the 2 biggest lakes in Sweden and is characterized by the lack of wetland areas and a small fraction of forested soils. Carbon fluxes for headwaters, larger streams and whole SVAR without factor had the lowest values for this region (3.9, 1.9 and 3.9 g C m^{-2} yr^{-1}).

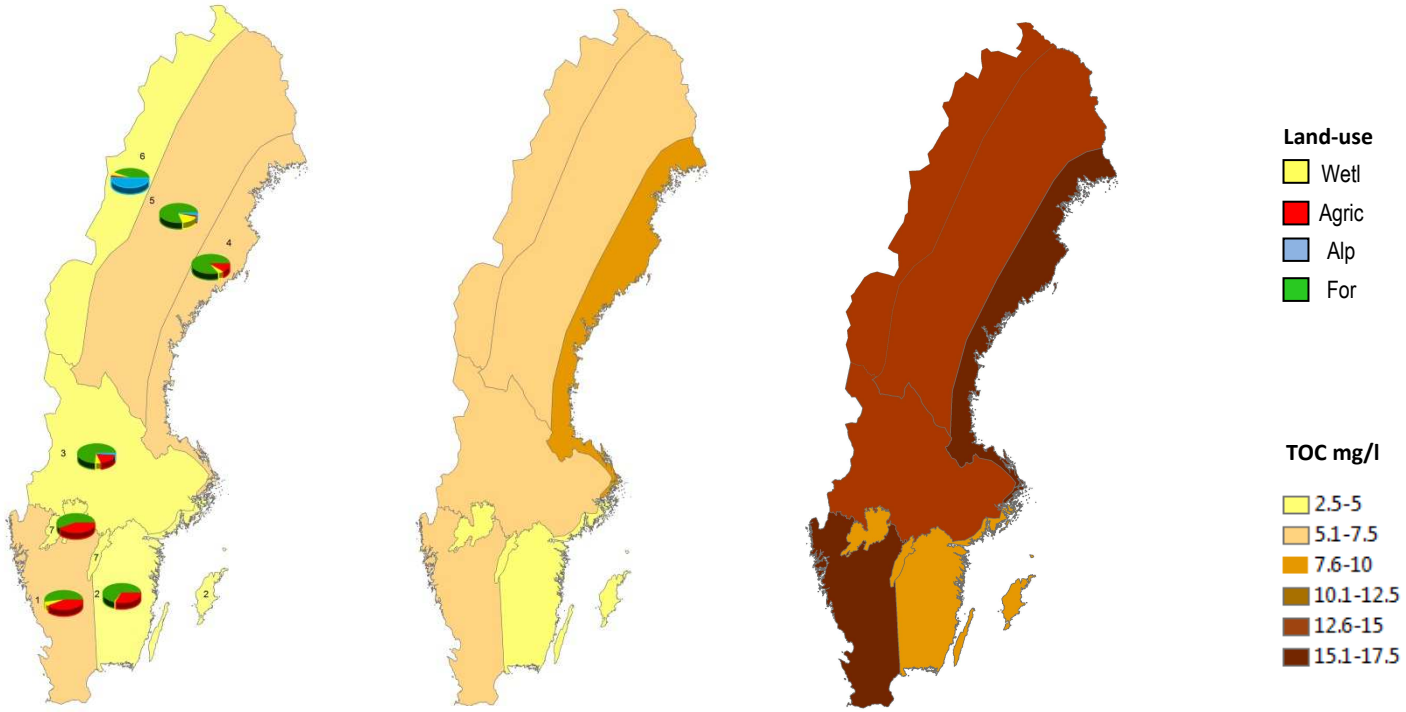

Figure 17. TOC regional fluxes for: i) SVAR catchments, ii) Forested areas draining to streams <3Km^2 and iii) Wetland areas draining to streams <3Km^2.

Table 4. TOC regional fluxes.

Region	Total area (Km^2)	Mean alt (m)	Mean pp (mm)	Mean runoff (mm)	Area <3Km^2 (%)	Areas >600m (%)	For (%)	Wet (%)	Agri (%)	Alp (%)	For export hw (gCm^{-2}y^{-1})	Wet export hw (gCm^{-2}y^{-1})	Terrestrial TOC export (gCm^{-2}y^{-1})			
													Headwaters	Larger Streams	Whole SVAR	Whole SVAR w/o factor
1	49676	113	892	426	62		50	5	40		6.5	16.6	6.5	2.7	5.1	6.0
2	41671	104	668	213	57		63	1	30		4.6	9.8	4.0	1.9	3.2	4.0
3	81961	214	770	353	61	5	67	6	17	1	5.4	13.7	5.6	2.7	4.5	5.5
4	51051	115	699	355	61		79	5	10		7.6	16.0	7.6	3.7	6.1	7.5
5	145822	351	660	354	55	4	75	15	2	2	5.1	13.7	6.2	3.4	5.0	6.5
6	67617	723	901	737	60	76	39	4	2	46	5.0	13.2	4.6	2.3	3.7	4.6
7	10431	122	713	193	61		16		12		4.9	9.9	3.9	1.9	3.3	3.9

4.7. Comparison of headwaters model and literature estimates

4.7.1. Algesten et al. (2004)

Algesten *et al.* (2004) calculated TOC terrestrial exports and losses for 21 catchments located in north and central parts of Sweden. This was done by investigating the correlation between TOC concentrations in lakes and rivers and CO_2 emissions from lakes. Losses were calculated based on with TOC data at the river mouths. According to the study, losses of C occurred mostly in lakes, where mineralization and sedimentation processes led to a carbon loss of 30-80%, depending on WRT and temperature values. Figure 18 compares TOC exports estimates from Algesten and estimates from the headwaters model. The figure shows that Algesten´s study had, in general, higher export estimates for the 21 catchments investigated, with a total TOC estimate of 1.6 Tg C yr^{-1} versus an estimate of 1.4 Tg C yr^{-1} from the HW_{model} (when considering different export to headwaters and larger streams). When considering that areas draining to large streams export the same as headwaters rendered a TOC flux of 1.7 Tg C $yr^{-}1$. Catchments where the headwaters model had greater estimates were placed in higher latitudes, whereas catchments located in central Sweden had lower estimates then Algesten's. After normalizing TOC exports by the catchments area, the differences between TOC fluxes from both methods were related to catchments specific features in Figure 19. This showed that differences in TOC fluxes were mainly linked to fractions of agriculture (r^2=0.46), wetlands (r^2=0.40) and catchment areas above 600m (r^2=0.40). Algesten had in general significant higher fluxes estimates for catchment areas with higher percentage of agricultural land (approximately > 5%), whereas the headwaters model presented greater TOC fluxes values for basins significantly covered by wetlands (>10%) and for basins with high percentage of areas lying in high altitudes (>20%).

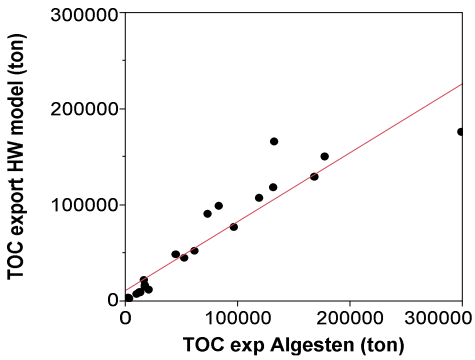

Figure 18. TOC export estimates from the headwaters model (ton) plotted against Algesten export estimates (ton; r^2=0.87).

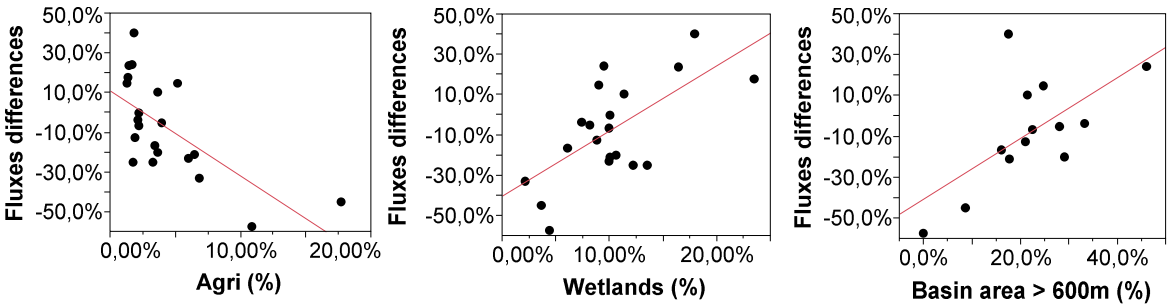

Figure 19. Differences between HW model TOC fluxes and Algesten´s plotted against agriculture (r^2=0.46), wetlands (r^2=0.40) and basin area > 600m (r^2=0.40).

Losses of TOC were also compared based on TOC observed data at the river mouth of the 21 catchments. The headwaters model rendered a loss of 45% when considering different exports to headwaters/large streams and 56% when considering equal exports from both areas against a loss of 53% for Algesten. Losses differences between both methods were found to be mostly related with the fraction of forested areas draining to small headwater streams (Figure 20). When limiting the analysis to basins where at least 58% of the total forest area is draining to these first order streams rendered a predictive relationship with a r^2=0.64.

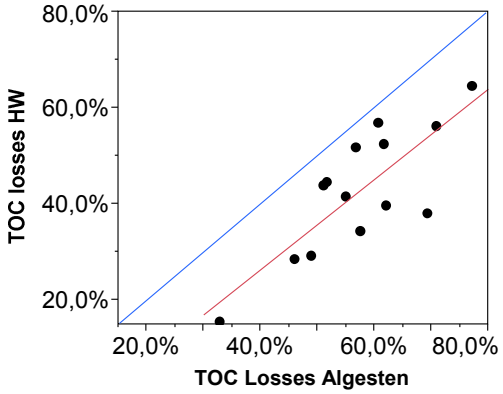

Figure 20. TOC losses from both studies by percentage forest areas draining to headwaters streams (n=14, r^2=0.64)

4.7.2. Weyhenmeyer et al. (2011)

This study looked at C concentrations for 756 lakes in Sweden and related them with C stored in the upper layers of the riparian soils. By relating TOC lake concentrations with data measurements at the river mouths, the study estimated C losses and decay rates. TOC was found to have a half-life of approximately 12 years and its degradation increased with longer residence times. The decay of C can be calculated by a first order reaction as shown in Equation 14:

$$N(t) = N_0 \cdot \exp^{(-\lambda WRT)} \qquad \textbf{(14)}$$

Where N(t) is the TOC amount at time t, N(0) TOC amount exported initially, λ is the rate of decay per year and WRT in years. Based on the estimated C decay rate was possible to calculate the export at "the initial conditions" and to compare it with TOC exports from the headwaters model. Thus, TOC at time initial time (N_0) was estimated by using the C decay rate, WRTs for 20 basins and TOC fluxes measured at the outlet of the 20 river mouths basins (N(t)). TOC estimates based on Equation 14 were compared with modelled exports in Figure 21 and total exports estimates are shown in Table 5.

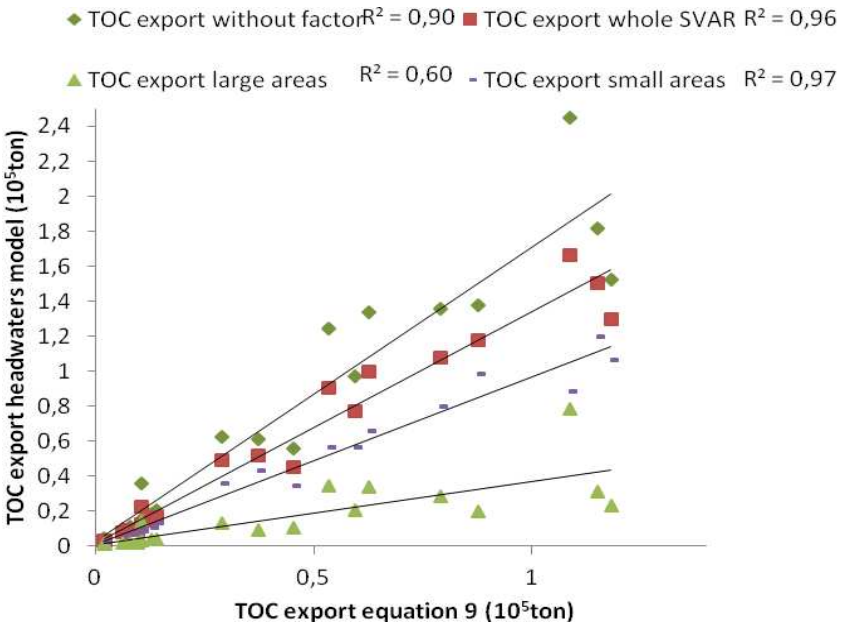

Figure 21. Comparison of TOC exports from the headwaters model with TOC exports assuming that C has a life-time of 12 years.

Table 5. Total C exports based on Equation 13 and Hwmodel estimates.

Exports	$Total_C$ export (Mt)
Eq. (13)	**0.9**
Headwaters	**0.9**
$Whole_{SVAR}$	**1.2**
$Whole_{SVAR\ w/o\ factor}$	**1.6**
Large areas	**0.3**

The figure shows that all modelled exports had good fits in relation to exports from Equation 13. Within the headwaters model exports, the export from areas draining to small streams (<3Km^2) was the most related with a r^2=0.97.

TOC long-term concentrations for all 756 lakes studied were presented for 3 years- 1995, 2000 and 2005. The average value for 1995 was 7.92 mg/l, in 2000 11.02 mg/l and 2005 10.06 mg/l. Hence there have been trends of TOC increase in surface waters over the last years and due to the fact that the year 2000 had unusual high levels of precipitation, the best year for TOC comparisons between the study and the headwaters model was 2005. The average long-term concentration found for the HW_{model} was 10.3 mg/l for the whole of Sweden, when considering that areas draining to large streams have half of the exports that areas draining to

headwaters. Assuming that areas draining to headwaters and large streams export equally rendered a mean TOC concentration of 12,8 mg/l for the headwaters model.

4.7.3. Jonsson et al. (2007) and Humborg et al. (2010)

Jonsson *et al.* (2007) examined the importance of terrestrial TOC exports to freshwater systems for the NEE of a boreal catchment (Öre river). For that carbon accumulation within the catchment was estimated, as well as exports to the water conduit and subsequent losses through sedimentation/evasion and transport to the sea were quantified. This was done based on published NEE estimates for different land-uses and by calculating CO_2 effluxes from lakes and streams, TOC sedimentation rates for lakes and TOC measured data at the river outlet. Data were gathered for 1990-2000. Half of the Öre catchment drains to small first order streams, which were also included in the study's estimates. Transport to the sea represented 55% of the TOC losses within the aquatic conduit, followed by approximately 45% of outgassing of C as CO_2 and sedimentation in lakes. Based on this and on observed TOC concentrations at the river mouth was possible to calculate the TOC export concentration for the whole catchment (17.8 mg/l). The export concentration from the headwaters model for the Öre river was 13.5 mg/l, when distinguish headwaters and larger streams, and 17.1 mg/l when considering equal exports for both areas. Losses of TOC from headwaters until the river mouth represented 27% and 43% respectively.

Humborg et al. (2010) estimated the TOC efflux for the whole of Sweden. Humborg's study hypothesized that CO_2 supersaturation in the Swedish aquatic conduit is not only due to allochthonous C aquatic respiration but has also dependence on C terrestrially respired that reaches the water conduit through groundwater withdrawn. Therefore, relationships between pCO_2/TOC and pCO_2/water chemistry variables characteristic of groundwater were compared, based on long-term water chemistry observations for lakes, streams and major river mouth basins across Sweden. The potential exchange capacity of pCO_2 from surface waters to atmosphere was assumed as the difference between the CO_2 dissolved in streams and lakes. The study found that groundwater inputs contributed as much as terrestrial C aquatic respiration for the total CO_2 efflux from water to the atmosphere. TOC in-lake respiration for all Swedish lakes was 1.29 Tg C yr^{-1}. Based on the assumption that 50% of the TOC imported from soils is mineralized on freshwater systems, the TOC influx from terrestrial soils was 2.58 Tg C yr^{-1}. Normalizing this value for total catchments area in Sweden rendered a TOC flux estimate of 5.72 g C m^{-2} yr^{-1}. To compare with these estimates, exports all SVAR catchments

from the headwaters model were summed up. The total export of TOC for the whole Sweden was 2.01 Tg C yr^{-1} when distinguishing exports to headwaters and larger streams. Considering equal export potentials for areas draining to small and large streams gave a total TOC export of 2.53 Tg C yr^{-1}. The fluxes obtained for the headwaters model when dividing both total TOC exports for the total catchment area in Sweden were 4.60 g C m^{-2} yr^{-1} and 5.80 g C m^{-2} yr^{-1}, respectively.

4.7.4. Cole et al. (2007) and Tranvik et al. (2009)

Cole *et al.* (2007) revised the concept of inland waters in the global C budget as a passive link between land and oceans compartments. They showed that the aquatic conduit is actively transforming the C received from terrestrial soils and estimated how much C must be delivered to freshwaters based on C losses estimates from different aquatic systems and quantities of C exported to the sea. Accordingly, oceans receive half of the C released by terrestrial soils and therefore, 50% of this C is lost while its transport to the sea (roughly 40% is lost by mineralization and 10% by sedimentation). Tranvik *et al*. (2009) added to these estimates emissions from streams, which were not accounted in the previous study, and reviewed the number and CO_2 emissions from lakes. This further increased the amount of OC that must be imported from inland waters and enhanced C losses to 70 % (approximately 50% lost by mineralization and 20% by sedimentation). Losses from the headwaters model from basins where wetlands and forest are predominate (>80%; Table 3) rendered an average value of 32% when distinguishing exports to headwaters areas and larger streams. Assuming that both catchment areas draining to headwaters or larger streams have an equal export potential rendered an average C loss value of 46%. Figure 22 summarizes all the estimates for the HW_{model} and literature.

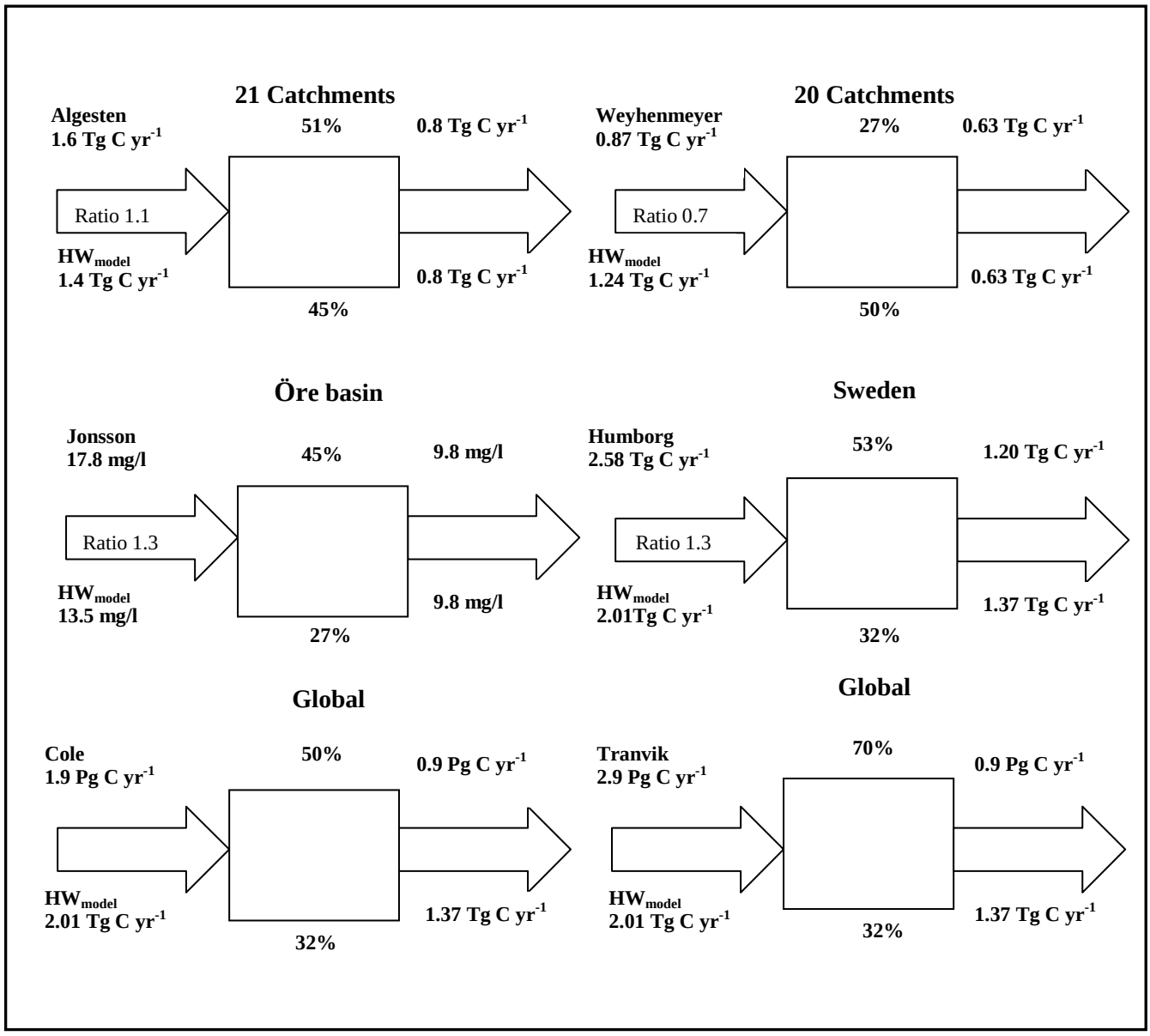

Figure 22. Exports of TOC, losses of TOC by mineralization and TOC fluxes to the sea for the HM_{model} and literature. Comparisons with Cole and Tranvik are shown in terms of proportions due to different flux magnitudes.

5. Discussion

5.1. TOC long-term concentrations in SVAR catchments

TOC long-term concentrations in headwater streams varied greatly across Sweden (1.52 to 34.6 mg/l). Close to mountain areas, where precipitation and altitude values are high, small streams had the lowest concentration values. Whereas, towards the east coast, wetland percentages increases together with decreases in altitude and precipitation levels resulted in headwater streams rich in TOC. Concentrations in larger streams were more evenly distributed (0.1 to 22.8 mg/l), with median values in most SVARs but higher in some close to the east coast. The variability between concentrations in both streams types is mainly related to the

variation of the size of catchments draining to these stream types (Temnerud *et al.*, 2010). Catchment areas draining to headwaters streams spanned a much wider range than the ones draining to large streams, thus resulting in a larger array of different concentrations for headwaters. As the concentrations of the whole SVARs are the sum of both catchment areas, these tended to follow the same trends as the concentrations in small and larger streams. Meaning that SVARs in the alpine areas had low TOC long-term concentrations, inland SVARs and SVARs on the southwest parts had median TOC concentration and surface waters on the east part appeared as TOC richer, mostly in SVARs where wetlands represent the main land use coverage. Long-term TOC concentrations could be mostly grouped by patterns of altitude, precipitation and land-use coverage that can be regionally identify across Sweden. As for instance, the very south part of Sweden where agriculture is predominant and where concentrations mostly depend on the limits applied to this type of land-use. Or mountain regions, which are expected to present lower TOC long-term concentrations due to high altitude and high precipitation values and also to low peat content soils. A similar approach was done by Ågren *et al.* (2010) who divided boreal Sweden in two regions based on significant differences in water chemistry variables and regional drivers (altitude, precipitation, runoff and temperature) to model TOC concentrations during spring flood.

5.2. TOC regional fluxes

Similarly, the division of Sweden in 7 regions showed that the highest mean TOC flux considering whole SVAR exports was found in the northeast part (6.1 g C $m^{-2}yr^{-1}$), which corresponded to the region with the highest percentage of forest and where wetlands and forested headwaters soils contributed with greater amounts of TOC per unit area (7.5 and 16.0 g C $m^{-2}yr^{-}1$, respectively). This flux was followed by TOC fluxes from region 1 and 5 (5.1 and 5.0 g C $m^{-2}yr^{-1}$). Hence region 5 contained higher percentages of wetlands and forested areas, which are the land-uses that most contribute for C exports, would be expected that the mean flux of this region largely surpassed the mean TOC flux of region 1. However, region 1 lies on much lower altitudes ($\bar{\mathbf{x}}$=113m) than region 5 ($\bar{\mathbf{x}}$=351m) which resulted in similar fluxes for both regions. In addition, region 6 was also expected to be the region with the lowest TOC values since the predominant alpine areas is characterized by shallow soils and by high precipitation and altitude levels, which are negatively correlated with TOC concentrations Ågren *et al.* (2010). Nonetheless, TOC exports are acknowledged for being mainly controlled by runoff values (Schiff *et al.*, 1998). Therefore, high runoff in these areas compensate the TOC low concentrations and resulted in significant exports that made this area having a higher

flux than could be expected. The lowest mean TOC fluxes occurred in regions 2 and 7. This was mainly due to low runoff values and also to the absence of wetland areas in both regions. Wetlands areas have been found by Jonsson *et al.* (2007) as a major TOC contributor within catchment areas despite of the small fraction that these areas usually represent.

5.3. TOC long-term concentrations in wetlands and forested areas

Figure 4 and 5 showed the potential export of headwater forested and wetlands soils for Sweden with dependence on altitude and precipitation levels. This approach analyzed how concentrations would be distributed if all the SVAR catchment area would be entirely covered by these land use types. The TOC long-term concentration followed the same trend as the distribution of TOC concentrations for headwater streams in both cases, hence these are also the main land-use types in Sweden. Concentrations varied thus mainly according with the east-west climate gradient (Ågren *et al.,* 2010). The only difference between both figures relied on the fact that wetlands present higher C export potentials (assumed as a difference of 20 mg/l between forest and wetlands). The figures further revealed that some areas that currently seem to have low TOC concentration could be large TOC contributors if forests and wetlands land-uses were predominant. As for example, the very southern part of Sweden, which is now mostly covered by agricultural land but appeared as an area that could have higher TOC concentrations if dominated by wetlands or forests.

5.4. TOC fluxes and losses in river mouth basins

TOC fluxes for 43 major Swedish river mouth basins varied from 2.1 to 7.6 g C m^{-2} yr^{-1} (when considering that areas draining to headwaters can potentially export twice as much as areas draining to large streams) with an average flux of 4.7mg/l. The highest TOC fluxes estimates (7.6 and 7.5 g C m^{-2} yr^{-1}) occurred in basins where wetland areas made up a significant fraction of the total catchment and also in basins with high fractions of areas draining to small streams regardless of land-use types. This is in accordance with published material that refers wetlands are major TOC contributors and supports headwaters as the main terrestrial TOC exporter per unit area (Ågren *et al.,* 2007). Intermediate fluxes (4 to 5 m^{-2} yr^{-1}) were linked to large basins containing some alpine areas together with areas draining mainly forested catchments that have higher DOC concentrations. Lower fluxes (2-3 g C m^{-2} $yr^{-1)}$ were found in areas where agricultural land occupied a significant fraction of the catchments and to basins with median percentages of catchment area draining to streams <3Km^2. The pattern of

variation of fluxes was in some extent supported by the variable importance analyses hence areas draining to small streams and wetland parcels were the most explanatory variables.

Losses of TOC from headwaters until river mouths varied considerable among the 43 basins. Losses tended to be more evenly distributed in basins larger than >10000 Km^2, varying within a small range (37%-57%). Whereas, losses in smaller basins spanned on considerably wider ranges (1%-64%). Some of the basin containing significant percentages of agriculture (>14%) gained C which may be related with the increase of nutrients in waters draining these soils that may lead to an increase in algae and consequently to higher C primary productions. Or this may further indicate an underestimation of TOC concentrations in this type of land-use, supported by Shih *et al.,* (2010) who found agricultural areas as a higher contributor per unit are than deciduous or coniferous forest. Nonetheless, losses of C from headwaters to the river mouths were found to be positively correlated with WRT, which is supported by many others (Algesten *et al.,* 2004; Jonsson *et al.,* 2007; Weyhenmeyer *et al.,* 2011). The most significant predictive relationship between losses and WRT resulted for basins made up of at least 58% of areas draining to headwater streams (<3Km^2) with a r^2=0.84. This thus, enforces the suitability of the model for predicting TOC concentrations from headwater streams, since the precision of predictions increase while the increase of small first order streams within catchments.

5.5. Middle basins

The comparisons between modeled and observed data in the middle of 26 basins showed C losses for 15 basins whereas the remaining gained C along the transect headwaters-monitoring site. Losses tended to be smaller for basins with high factions of agriculture areas (r^2=0.38). Nonetheless, catchment-specific characteristics could solely explain a small part of the variability of the TOC losses (Figure 14). Although losses of C until the monitoring sites could also be due to in-stream processing, this represents at the same time a minor possibility hence the WRT for these small catchments are thought to be weeks or few months (Laudon *et al.,* 2007). On the other hand, Figure 15 seemed to reveal more about the patterns of C gains/losses. It showed that differences between observed and modeled values were smaller for basins where observed TOC concentrations varied from 10-20 mg/l. Recalling the long-term concentrations used to build the model, 50% of the observations were within this interval (10-20 mg/l). This means that estimates for sites that have concentration values close to the mean value of the calibration range will, most likely, have smaller errors and thus be less different from the observed values. On the other hand, concentration estimates for sites that

are more deviate from the mean range (<10 mg/l - >20 mg/l) may introduce greater errors in the estimates, resulting in higher differences between observed and modeled values for low and high concentrations. This can be also linked with the relationship found between losses and agriculture area. Losses of C were, in some extent, smaller for basins where agriculture made up a significant part of the catchment, hence the export from agricultural soils does not account with errors that may arise from the model.

Differences between observations and modeled values are less likely when considering larger basins. Large basins, as the ones analyzed in previous section (5.4.), drain a wide range of different SVARs. When looking at the basins total loss, these are made of export estimates from low and high TOC concentration sites that tend, in the long run, to even out and to diminish the total error of the loss estimate, and to result in more reliable C losses.

5.6. Comparisons with literature

The approximation to Algesten's study revealed a very good consistency of exports estimates for major 21 Swedish catchments (r^2=0.87), although with differences in terms of magnitude. There was a clear pattern for the difference between the estimates of both studies which might be presumably related with latitude gradients. The exports for basins located in the north had in all cases higher estimates for the HW_{model}, whereas Algesten's approach had higher exports for basins in central parts. When relating differences between both exports estimates these seemed to be related with the increase of agriculture areas within the catchments together with decreases in alpine areas and wetland land-use coverage towards the south. Nonetheless, this might also be a direct consequence of the method used by Algesten which considered temperature gradients for the calculation of CO_2 solubility in water and ice-free lengths periods and that can subsequently influence the estimates of the quantity of C imported to freshwaters in north and south regions. Despite of differences on TOC exports, mean TOC losses from soils until river mouths were consistent, with a mean TOC loss of 53% for Algesten and 45% for the HW_{model}. Differences in losses were found to be mostly related with the fraction of forested areas draining to headwater streams, when these represent at least more than 58% of the total forest area. However, all these basins had lower exports for the HW_{model}. This strong relationship may thus not explain such differences, hence for basins with large percentages of headwaters streams the HW_{model} model should give higher exports than for basins with large amounts of areas draining to large streams. Therefore, this is most likely

linked to differences between both methods, since those basins were also all located in lower latitudes.

TOC exports estimates showed good correlations with estimates based on C decay rates (Weyhenmeyer *et al.* 2011). This is of great significance hence these two approaches are based on very different methods. The export from areas draining to small streams was the most related followed, in a very similar extent, by the export from the whole catchment considering different exports from areas draining to small/large streams. Exports assuming all areas exporting as headwaters rendered a weaker relationship but still very significant, whereas the "large areas" export was the less related one. This enforces, once more, the suitability of the model for headwater areas, hence the very high correlation factor obtained. It also showed that despite of large areas were attributed a random factor, the export of whole SVARs is still more reliable when including the factor than considering all areas as exporting as headwaters.

Long-term concentrations within both studies showed also good agreements. The headwaters model rendered a mean TOC concentration of 10.30 mg/l for the whole of Sweden (when applying a factor to exports from areas draining to large streams) which was higher than the comparative study (10.06 mg/l). This agrees with that fact that the model's estimate included headwater streams, whereas the comparative study only included 10% of headwater lakes. As concentrations tend to diminish downstream with groundwater withdrawn, deeper flow paths and in-stream respiration (Temnerud *et al.*, 2010), this thus justifies higher estimates from HW_{model}.

Estimates for TOC concentrations for the Öre basin were found to be higher in Jonsson *et al.*, 2007. As suggested by Weyhenmeyer, who also found lower TOC estimates, this is most likely due to different time scales and spatial boundaries used in both approaches. Hence concentrations found for short time scales and in a well-defined location are compared with long-term concentrations from models based on data from different sites. Exports and fluxes, for the whole of Sweden, were also reported as higher in Humborg *et al.*, (2010), nonetheless this study only relied in relationships between the degree of supersaturation of CO_2 in waters and velocity of gas transfer. This thus reflects a key issue in aquatic conduit that is how much C enters the conduit contrarily of focusing solely on transformations of C already within the conduit. In great spatial scales Cole *et al.*, 2007 and Tranvik *et al.*, 2009 estimated that losses

of terrestrial C to the atmosphere through gas evasion spanned on 40% to 50%. This in accordance with mean losses from HW_{model} that obtained a mean average loss of 36% for some Swedish major river mouth basins, hence their estimates are based on freshwaters worldwide that might have higher mineralization losses than cold boreal waters.

6. Conclusion

As important as quantifying the amount of C that leaves the soil pool and its fate along freshwaters, is to predict how its concentration is distributed in all small headwaters streams. This is because a great part of the landscape in Sweden drains to these small streams which play a key role for biodiversity and human health. However this is also a major challenge hence concentrations in headwaters vary widely across the country. This study showed that TOC concentrations from headwaters up to higher order streams could be fairly estimated from landscape elements. The approximation to published material and observed measurements further confirmed the model's possible application. Results' analyses suggested that model´s estimates could be refined by exploring with more precision export potentials of agricultural soils. It also suggested that the models' accuracy might be improved by dividing the model in two other models that could estimate C concentrations from SVARs with low and high concentration potentials, which were already identified by running the actual model.

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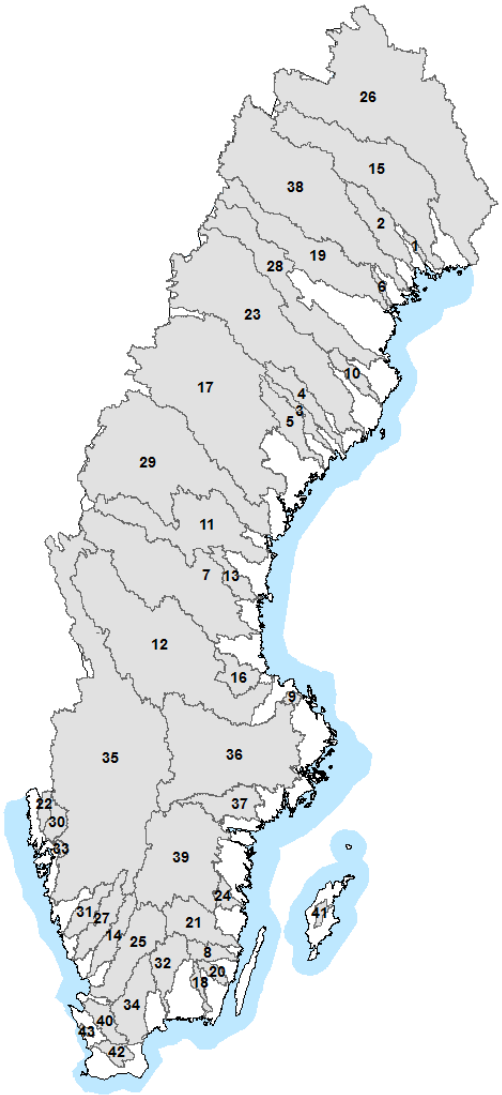
Appendices



Appendice 1. Location of the major 43 river mouth basins.