Report 1.1.5
Specific study on freshwater greenhouse gas budget

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CONTENTS

1. Description and functioning of the European waterscape

Landscape and waterscape may partially to totally retain and/or process the material that is continuously transferred by waters at the surface of continents. These processes include the particulate matter settling, the biological uptake, the bacterial transformation of organic matter and sulphur and nitrogen species leading to gaseous products (e.g. CO_2, CH_4, H_2S, NO_x, N_2). These combined processes are often regarded by biogeochemists as “retention processes” while Earth Systems modellers would rather consider these processes in terms of “filtering capacity” of surficial transfers. Since some important compounds are actually not retained but released to the atmosphere, it seems more appropriate to use “filtering capacity”. In addition to these filters, the drainage network also constitutes a biogeochemical reactor, while the matter is continuously transferred from head waters to river mouth.

Several types of filters should be considered, however, as it will be seen, they are rarely coexisting at their maximum capacity in a given river catchment/estuarine system.

Five major types of natural filters, soils, wetlands, lakes, floodplains and estuarine systems and two types of man-made filters reservoirs and irrigated land are commonly considered (Figure1.1.A&B).

The wetlands considered in this figure are mostly those occurring in headwaters (smaller stream orders): the other natural wetlands are not individually considered, they are associated with lakes, floodplains and estuaries.

In this chapter, we are first considering the European river systems and their functioning in natural conditions, then under anthropic pressures (the so-called Anthropocene era), finally we present the European river catchments and their linkage to Regional Seas.

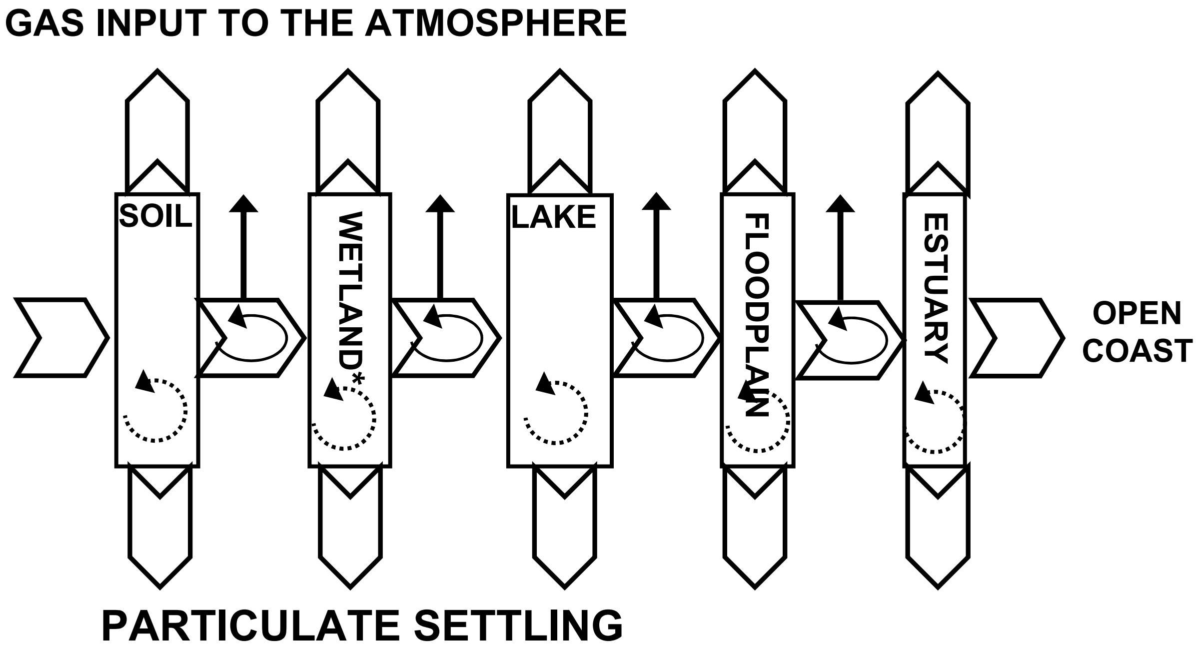


Figure 1.1.A. Schematic cascading filters within the river catchment/estuarine systems in natural conditions. * headwaters wetlands (other wetland types are included in lake, floodplain and estuary). Each filter type may store particulates, transform C, N into gaseous forms and is exposed to multiple biogeochemical cycles. Biogeochemical cycling within catchments filters. Biogeochemical cycling within river network.

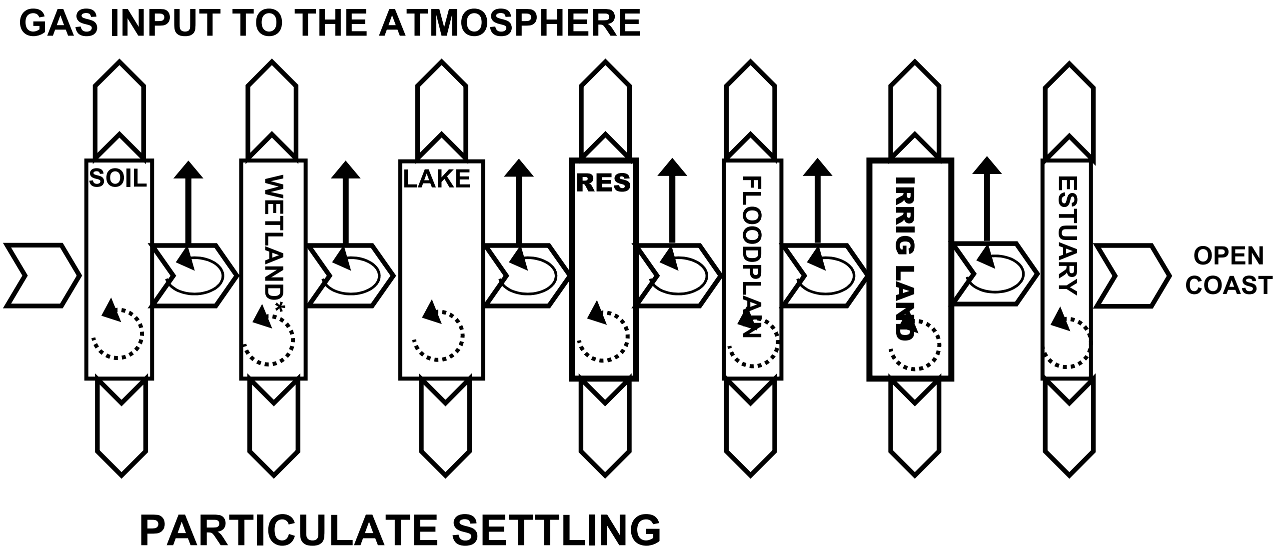


Figure 1.1.B. Schematic cascading filters within the river catchment/estuarine systems in present- day conditions, including **new filters** (Res =reservoirs, Irrig. Land = irrigated land) and **reduction of natural filters** (wetlands, floodplain). * headwater wetlands (other wetland types are included in lake, floodplain and estuary). Biogeochemical cycling within catchments filters. Biogeochemical cycling within river network.

1.1. The River system structure

1.1.1. Natural conditions at Holocene

The levels and fluxes of organic carbon in river basins and the related GHG emissions from aquatic systems depend on several sets of factors: (i) the water pathways at the very fine scale (10^{-3} - 10^{-1} km), (ii) the meso-scale and megascale spatial distribution and types (10^{0} – 10^{3} km) of water bodies and (iii) their degree of alteration by Human activities. The figure 1.1.1. is an attempt to summarize these major factors for the natural river basins (termed here "Holocene" drivers) and for impacted basins ("Anthropocene"). This distribution is now commonly made by Earth System Scientists following Crutzen (2000, 2002) to distinguish the Holocene period, when only natural drivers were forcing the biogeochemical cycles from the present-day period when many biogeochemical cycles are forced by anthropogenic drivers as CO_2 emissions and related Climate Change, Land Use Changes, direct resources uses by Humans (water, food, etc..) (Steffen *et al.*, 2004; Crossland *et al.*, 2005). This new era concept termed Anthropocene is particularly applicable to river system functioning at the Global scale (Meybeck, 2002, 2003; Meybeck and Vörösmarty, 2005) and, even more, for European waters. It has been proposed that Anthropocene era begins conventionally in 1950 (Meybeck, 2002; Steffen *et al.*, 2004) in river systems.

The levels and export rates (also termed yields: Y_{DOC} and Y_{POC} in $g.m^{-2}.y^{-1}$, equivalent to $t.km^{-2}.y^{-1}$) of dissolved and particulate organic carbon in head water streams depend on the fine-scale drainage of soils (#1_A and 1_B, figure 1.1.1. left part) (Cronan, 1990) and on the occurrence of peat deposits linked to the last glaciations (#2) that are great emitters of Green House Gases (see CarboEurope Report #8/2004/Specific Study 5). The occurrence of natural lakes whether large, deep and with long residence time (#3_A) or shallow, dissected with short residence time (#3_B) is an important sink and filter of carbon species, especially for particulate species.

The middle course of river basins is commonly characterized by (i) extended floodplains in which the carbon species are stored, exchanged and GHG are emitted (#4) (Perdue and Gjessing, 1990 ; Richey, 2004) and (ii) by slow-flowing reaches in which dissolved organic carbon can be processed (Meyer, 1990) and GHG emitted, particularly CO_2 (#5).

The lower course of rivers is the estuarine zone where freshwater and seawater mix. Estuaries can have multiple types which will be discussed in another section; most of them are also characterized by extended wetlands (#6) such as tidal flats, delta floodplains, coastal lagoons etc. in which carbon species recycling and GHG emissions are again very efficient.

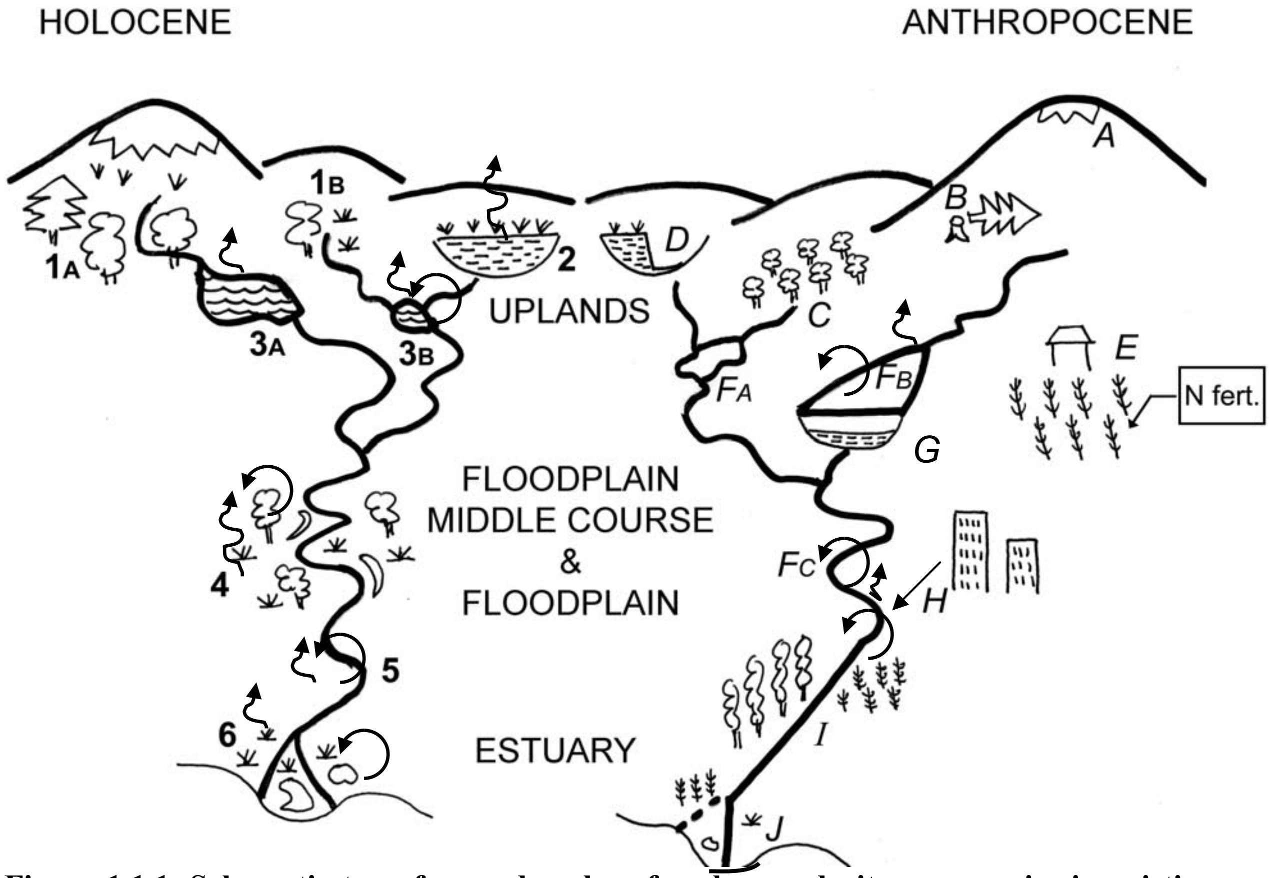


Figure 1.1.1. Schematic transfers and cycles of carbon and nitrogen species in pristine river systems (Holocene) and in impacted systems (Anthropocene). Dominant processes at the Holocene: $\mathbf{1_A}$ and **$\mathbf{1_B}$** Leaching and erosion of soil DOC and POC; **2**. Retention of POC and TOC processing in deep alpine lakes (**$\mathbf{3_A}$**) and shallow lowland lakes (**$\mathbf{3_B}$**); **4**. Storage/processing/release of C and N species and GHG in river floodplain; **5**. Processing of TOC within river channel; **6**. Storage/processing/release of C and N species and GHG in estuaries. **Dominant and/or additional processes at the Anthropocene: A**. Impact of Climate Change and Global Warming on TOC supply from soils; **B**. Deforestation; **C**. Afforestation, an other land use changes in uplands; **D**. Peat exploitation and draining; **E**. Cultivation and changes of N, P and C supply to streams from agricultural land; **$\mathbf{F_A}$**. Lake eutrophication; **$\mathbf{F_B}$.** Reservoir eutrophication; **$\mathbf{F_C}$**. River eutrophication; **G**. Storage/processing and GHG emissions in reservoirs; **H**. Organic wastes inputs from urban sources; **I**. Floodplain draining, engineering and cultivation; **J**. Delta draining, engineering and cultivation, waste inputs.

1.1.2. European rivers and their regimes

The lateral carbon transfers within river systems is pulsed by the seasonal variations of high flows and low flows, also called the river regimes. The natural hydrological regimes of European rivers are based on very long term averages over 50 years sometimes, hence the influence of reservoirs or diversions mostly built in the 1950's is minimised (Unesco, 1969). Moreover we have avoided here the stations for which there was an explicit mention of reservoir influence. The Albanian rivers are the only ones with short (5 y) data sets. The long-term monthly discharges for a selection of medium/large rivers are presented in figure 1.1.2.

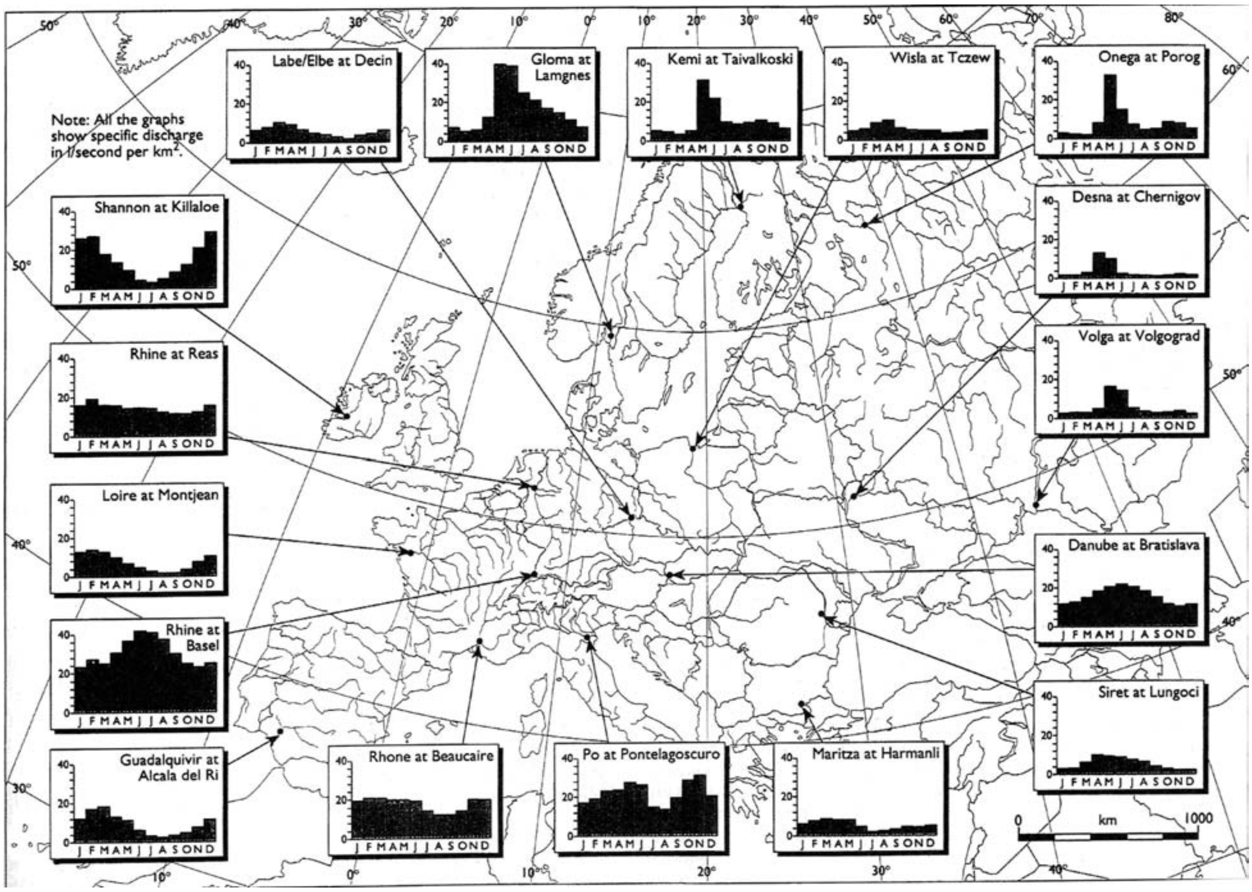


Figure 1.1.2. Mean monthly for several major river catchments in Europe (specific discharge in $l.s^{-1}.km^{-2}$)

The yearly average specific discharges (qi in $l.s^{-1}.km^{-2}$) in Europe vary from 2 to 40 $l.s^{-1}.km^{-2}$, a range which also covers the greatest part of the global distribution of runoff: only the arid and semi-arid regions ($q < l.s^{-1}.km^{-2}$) are not found in Europe.

When normalising the monthly discharges to the yearly mean the river regimes can be easily compared (figure 1.1.2.). They illustrates the variations of regimes for each regional sea (Atlantic Ocean and North Sea, including South Norway; Black Sea; Mediterranean; North Europe excluding S. Norway, Baltic and Arctic drainages).

The Atlantic rivers (Tagus, Shannon, Loire, Guadalquivir, Seine, Shannon, Rhine, and Elbe) are all characterised by pluvial-oceanic regimes with maximum flow during winter. The Gloma (Norway) and Kemi (Finland), fed by late snowmelt in May-June, is much different and characteristic of Northern Europe rivers. The Elbe and the Rhine have greater basins and are mixing rivers of different regimes including lake influences and glacial melt for the Rhine. Their complex regimes are characterised by much higher values of monthly normalised runoff in the summer months. For the Rhine the long-term seasonal variations are very smooth due to the influence of Swiss lakes and to the occurrence of multiple regimes within this basin.

The North Europe's rivers are characteristics of the nival (snow melt) to glacial (ice melt) regimes. Hence the peak discharges may occur from April (Vistula, Daugava) to August (Jökulsa in Iceland). In these regimes the minimum flows are observed at the end of the frozen period (February and March), i.e. in total opposition with the pluvial-oceanic regime.

The regimes in the Mediterranean basin are actually more variable than one would have thought. The typical pluvial-mediterranean regime with its winter high-flows and its very low summer low-flows, with complete dry-up for the smallest catchments, is not observed everywhere in the basin. The Tiber (Italy), the Ceyhan and the Buyuk Menderes in Turkey (East Aegean, the famous Meandros of Ancient Greeks) are well representative of this regime.

The Danube Po and the Rhone rivers have complex regimes mixing snowmelt, ice melt, lake influence, early autumn rainfall, winter rainfall, and even the oceanic rain influence for the Rhone. As a result these regimes are not much contrasted and are much similar to those observed on the North side of the Alps for the Rhine and Elbe. The Adige and some NE Adriatic rivers have also snow-melt regimes; the Ebro regime was also mixing mountain influences and Mediterranean influences, it is now completely regulated by a reservoir cascade.

The lake influence may be very important in some European catchments where the seasonal variations are very much smoothed by long water residence times. This influence is noted for the Rhine and the Swedish rivers; it is essential in some Finnish basins and in the Kola Peninsula. The Neva River, i.e. the Lake Ladoga outlet, is characterised by the least variable water discharge of all European rivers, probably due to the combination of natural lake effect and weir control upstream of St. Petersburg.

1.1.3. Distribution of European lakes and reservoirs

About 500,000 natural lakes larger than 1 ha were identified in Europe. The water bodies vary in size, both on a surface area -and a volume basis. The majority of the European lakes have a rather small surface area ranging from 1 ha to 1 km². Despite a very uneven distributed database it can be concluded that less than 5 % of all European lakes (in number) have a surface area larger than 1 km².

The lake distribution of Europe's is very uneven: more than 90 % of lake number and total lake area is found on the northern regions of Europe that have been formerly covered by glaciers and where hard rocks are found, i.e. from Ireland to Karelia. Most of them are found in Norway, Sweden and Finland. Another major European lake district is found at the edge of the Alps massif from France to Slovenia: it corresponds to glacial scour, as for the previous district, but these alpine lakes are much deeper than their northern counterparts, often exceeding 200 m (Leman, Constance, Maggiore, Garda, and Como). They are few major lakes of different origins as Lake Ohrid (tectonic) and Skadar (karstic dissolution) both in the Balkans or Lake Balaton in Hungary. The total natural lake area of Europe (W. Russia included) depends on the size limit of the lake, it is of the order of 10^5 km^2, i.e. about 1 % of the whole European territory but in regions of Finland and Sweden, the lake area proportion (limnic index) may reach 20 %. Largest lakes are Ladoga, Onega, Vänern and Peipus, they are not the deepest ones. In table 1.1.3., main characteristics of a few, well known and data-rich lakes representing different types were summarized.

Natural lake		Country	Area	Mean depth	Max depth
				m	m
1.	Ladoga (Ladozhskoye)	RU	17 670	51	258
2.	Onega (Onezhskoye)	RU	9 670	30	120
3.	Vänern	SE	5 670	27	106
4.	Peipus	RU, EE	3 570	23	47
5.	Vättern	SE	1 912	39	128
6.	Vygozero	RU	1 285	7	19 - 24
7.	Saimaa	FI	1 147	12	82
8.	Mälaren	SE	1 140	13	61
9.	Il'men'	RU	1 124	2.6	10
10.	Beloye	RU	1 120	4.2	20
11.	Inari	FI	1 102	14	96
12.	Päijänne	FI	1 054	17	98
13.	Topozero	RU	1 025	15	56
14.	Oulujärvi	FI	893	7.6	35
15.	Pielinen	FI	867	9.9	60
16.	Segozero	RU	781 – 910	23	97
17.	Imandra	RU	845	16	67
18.	Pyaozero	RU	660 – 754	15	49
19.	Balaton	HU	596	3	11
20.	Lac Léman	CH, FR	584	153	310
21.	Bodensee (Constance)	DE, CH, AT	540	90	252
22.	Hjälmaren	SE	478	6.1	22
23.	Umbozero	RU	422	30	115
24.	Vozhe (Charonda)	RU	420	1.4	5

Table 1.1.3. Very large European lakes and reservoirs (Henriksen and Hansen, 1995).

European lakes dynamics are very variable from North to South and from plains to alpine massifs, following the temperature patterns. Most types of thermal stratification and water mixing that have been described in the limnology literature can be found in this continent with the exception of the tropical lakes that are always very warm and stratified most of the time. Lakes can be mixed when they have equal density throughout the water column (4.0 °C for freshwaters). The most common mixing types are:

- **Cold dimictic lakes**: they mix twice a year in autumn and in spring after the melting of lake ice. They are found in Nothern and Central Europe and in mountains regions of Central and Southern Europe.
- **Monomictic lakes**: they do not freeze and mix once a year in winter.
- **Polymictic lakes**: in these shallow water bodies, the mixing may occur several times per year depending on the received wind energy. They are found in South and Central Europe.

In addition to this mixing rules, large shallow reservoirs can be mixed by wind energy and valley reservoirs can also be destratified by incoming river floods.

The trophic state of European lakes and reservoirs, i.e. the balance between the primary production that dominates place in the surface waters (euphotic zone) and the bacterial degradation of organic matter that occurs in majority in deep waters (aphotic zone), is highly variable. In natural conditions, nutrients levels ($N\text{-}NH_4^+$, $N\text{-}NO_3^-$ and $P\text{-}PO_4^{-3}$) are very low and the primary production is limited (oligotrophy). The water column is close to O_2 saturation including in deep stratified waters (hypolimnion). When nutrients levels are increasing due to Human pressures (agriculture, urbanisation), the primary production is less limited and resulting algal detritus are eventually degraded in deep waters resulting in an under saturation of O_2. In waters with excess nutrients, particularly excess phosphorus, the primary production is not anymore limited (eutrophy). Algal detritus that sink in deep waters are actively degraded and the deepest part of the hypolimnion become hypoxic ($O_2 < 2$ mg/L) and even anoxic until the seasonal or annual mixing of waters (lake overturn) is restoring the oxygen saturation throughout the whole water column. Depending on primary production and algal biomass, an hypertrophic state may develop in extreme conditions (e.g. limited hypolimnion, very high nutrient input, regeneration of nutrients from bottom sediments) and total pigments levels may reach 200 mg/m^3 or more, equivalent to about 6 mg/L concentration of very labile algal POC.

Some of the large European lakes have already shifted from their natural oligotrophic state to meso or eutrophic state as L. Vättern, Ladoga (see examples in Annexes A, table A.1.). Reservoirs are also very sensitive to eutrophication when they are built up on river basins with important agriculture and/or urbanization. The Wloclawek reservoir in Poland built in 1968 is a well-known example of hypertrophic state as well for some of the very large Volga reservoirs.

1.1.4. Floodplains

In middle and lower river courses of most European rivers, there is an important floodplain that plays a major role in river flow control, particulate matter settling and biogeochemical processes, particularly for the organic carbon and GHG production (see further, section 2.1).

The functioning of floodplains depends on the water level, i.e. on floodplain morphology and on the water discharge (figure 1.1.4.). The floodplain can be considered as a layer of river sediments from few meters to dozen of meters thick, of various grain size, porosity and organic matter contents, overlaying the river valley bedrock. At the low water stage, the base flow level (BF, figure 1.1.4.) corresponds to a very limited water mirror, most of the water is found in the hyporheic zone, i.e. in alluvial aquifers, where some bacterial degradation of organic matter may occur. At high waters (HW), typically every second year, a certain area of the floodplain is flooded and over bank sediments are deposited with their organic detritus. At very high flows (VHW) occurring every 10 or 20 years, the whole floodplain is inundated and receives river sediments. The coarser sediments have being deposited close to the river main channel.

The interface between the river and the land, the so-called riparian zone has therefore variable limits depending on flood stage. This pattern is particularly observed in natural river channels. In Europe, the construction of dykes, levees and the river channelization for navigation greatly reduces the floodplain extension.

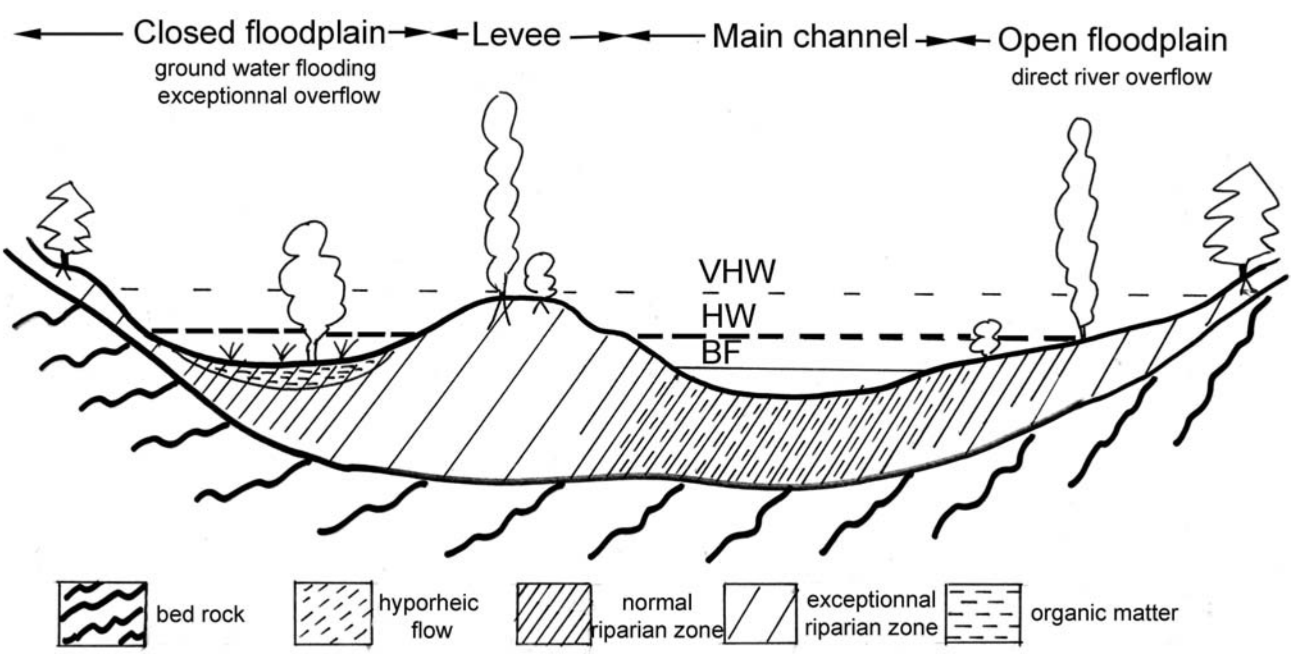


Figure1.1.4. Schematic presentation of floodplain functioning **(modified from Mulholland *et al.*, 1990). BF: base flow level; HW: normal highwater stage; VHW: exceptional flood stage**

1.1.5. River-ocean interface: European estuarine systems

The river/ocean interface is also referred to as the estuarine zone in its broader sense. It corresponds to the mixing zone of freshwaters with sea water. It has actually multiple types depending on coastal morphology, tidal energy, sediment and water supply, such as deltas, coastal lagoons, macrotidal estuaries, karstic groundwater inputs, fjords s.s. in mountains area and fjärds in lowland river mouths on hard rocks. These types are generally very dynamic depending on tidal energy, coastal currents and river discharge. They are associated, excepted in fjords and for karstic inputs with extended wetlands that can be flooded at each tide for macrotidal estuaries, during high river water stage (deltas, coastal lagoons) or during storm-surges events (deltas, coastal lagoons). The size of estuaries (depth, width, length, volume) is also very variable from one type to another and within the same estuarine type. Six main types of estuaries are here differenciated for Europe's rivers: delta, coastal lagoon, macrotidal, estuary, rias, fjords, fjärds and karstic coast.

The delta interface

Typical deltas (figure 1.1.5.a.) can be partially stratified during low and medium river flows and are fully mixed during floods. The upper estuary limit at low/medium flow is located mostly inland and the brackish plume of mixed waters is limited outside the delta. During high river flows, the plume may extend for dozens of km in the ocean and the upper estuary limit is.

The fine river detrital particles settle in the distal delta which represent the actual outer limit of the system where riverine POC can still be mineralized. The water residence time of deltas (between A and B limits) is of the order of few days. In Europe, deltas are commonly found in the Mediterranean and Black Seas (Ebro, Rhone, Po, Tiber, Axios, Danube). Undercurrents may transfer river particles to deeper areas.

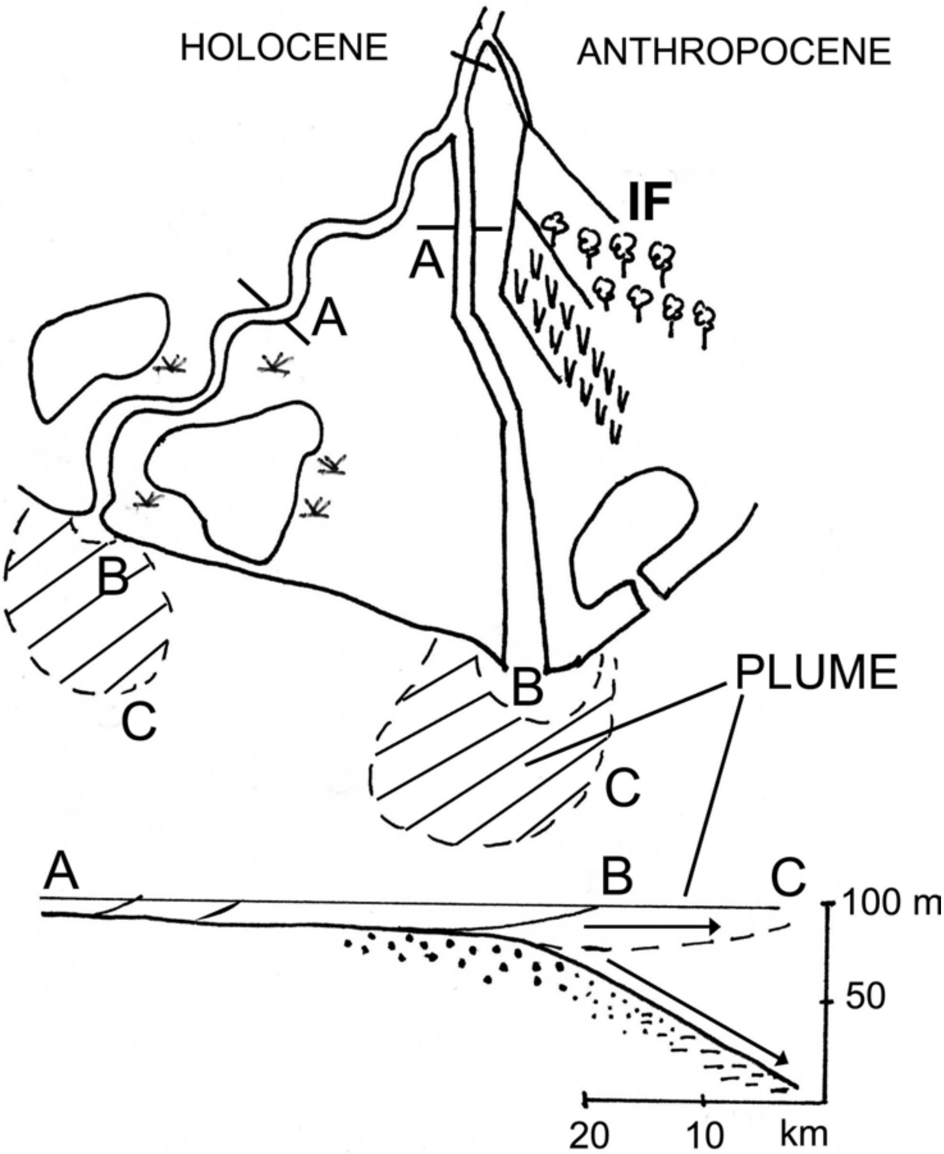


Figure 1.1.5.a. The river/ocean interface in deltas. Left: non-regulated river course; right: regulated rivers and irrigated fields (IF). A-B normal extension of brackish waters (1‰ to 90% sea water), A-C range during high water flows.

Coastal lagoons interface

Coastal lagoons are generated by sandbars closure (figure 1.1.5.b.). They are very frequent in sandy coasts as the Southern Baltic Sea (Odra, Vistula), Landes and Languedoc in France (Herault, Orb, Têt), North Adriatic (Venice lagoon) and in the western Black Sea.

The brackish areas (between 1 ‰ and 90 % sea water) is extended in coastal lagoons which are shallow water bodies with average residence time from weeks to months, depending on the river discharge. Smaller lagoons that are characteristic of many small river catchments in the Mediterranean Sea may be completely closed by sand bars during the dry period. In natural conditions, lagoons are associated with extended wetlands.

Lagoons are also very sensitive to Human pressures (filling, channelling, dredging etc.).

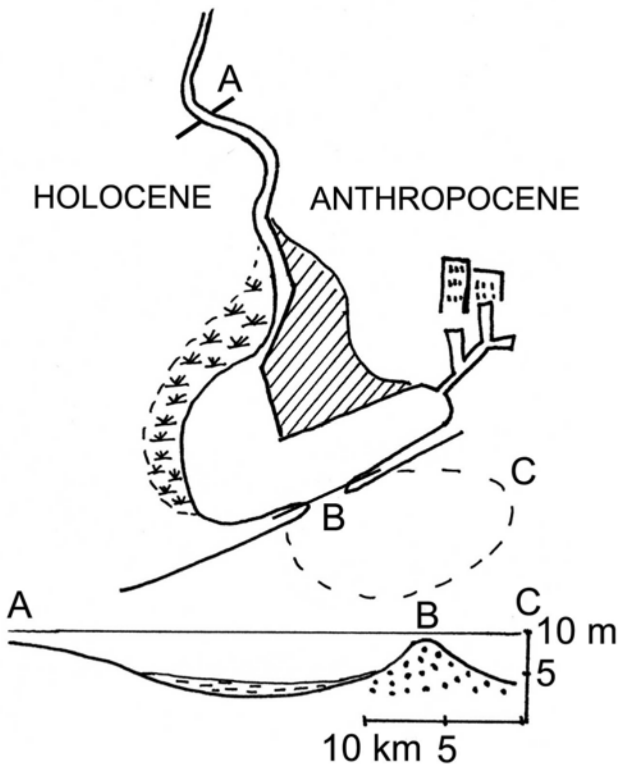


Figure 1.1.5.b. The river/ocean interface in coastal lagoons. Left: unmanaged coast; right: engineered coast (wetland filling, urbanisation, harbour, artificial coast). A-B normal extension of brackish waters (1‰ to 90% sea water), A-C range during high water flows.

The macrotidal estuary interface

Lowland macrotidal estuaries are a major feature of the North Sea river/ocean interface (Humber, Thames, Scheldt, Rhine, Weser, Elbe) and of the Atlantic Ocean (Seine, Loire, Garonne). In Brittany, Cornwall, and Nothern Spanish Coast, the rias, i.e. drowned valleys, are related estuarine systems.

Macrotidal estuaries are characterized by strong tidal currents that slow down the movement of river water. In such systems, the water residence time ranges from weeks, or less during major floods, to months during low flows despite shallow to medium depths ($z < 10$ m) in natural conditions. As a result, the total suspended matter (TSS) in the upper part of these estuaries ("inner estuary") is much higher than in both river and ocean end: in the Estuarine Turbidity Maximum (ETM, figure 1.1.5.c.), TSS exceeds 100 mg/L and may exceed 100 g/L in fluid mud layers, both characteristics of very low salinities (1 to 10 ‰). The ETM is always associated with a marked hypoxia (sag-curve of the O_2 longitudinal profile) resulting from the processing of the most labile organic matter and from the nitrification of ammonia in polluted estuaries (e.g. Seine estuary).

As for the preceding system macrotidal estuaries are regulated in many ways: damming in the upper estuary, upstream of the saline water intrusion (A, figure 1.1.5.c.) in order to limit the propagation of the dynamic tide (TL), dredging of the navigation channel and disposal of dredged material on land or in reclaimed wet-lands, channelization, construction of embankments and harbours, release of organic wastes from cities etc.

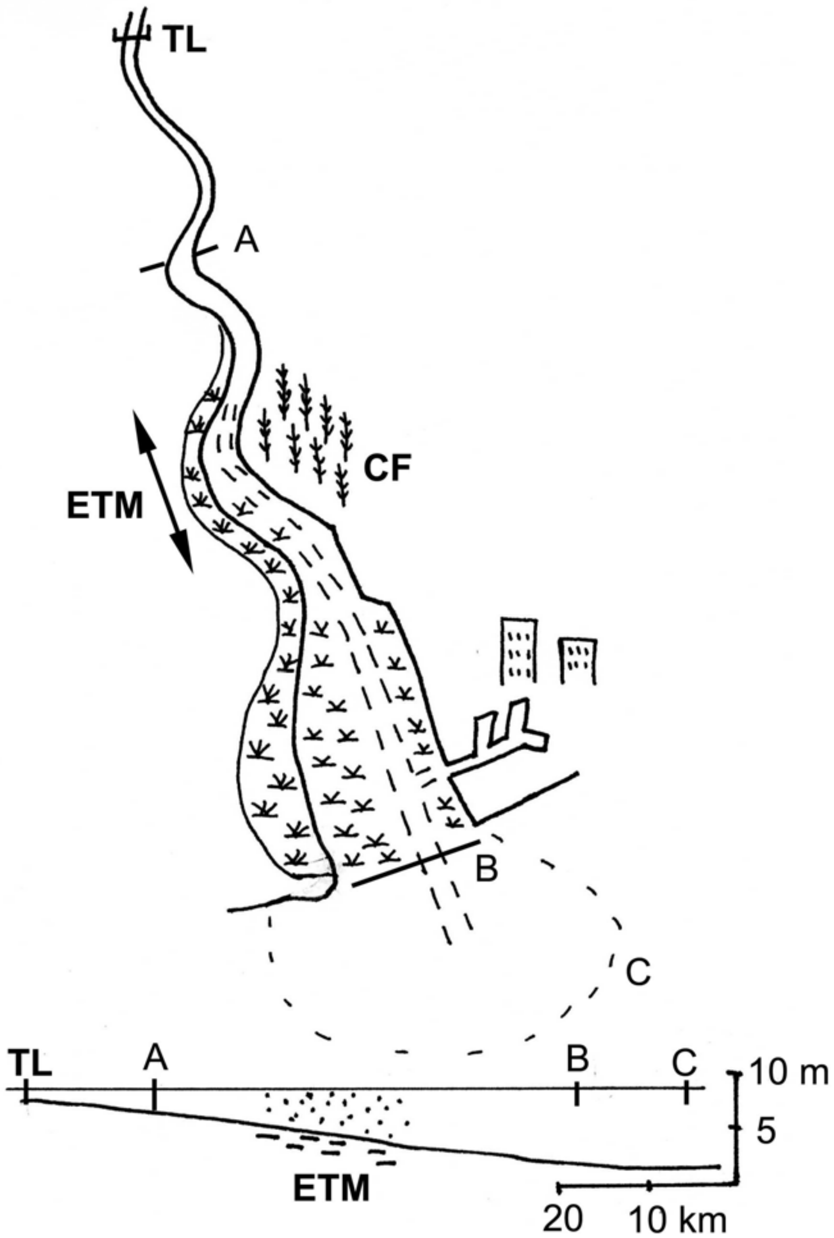


Figure 1.1.5.c. The river/ocean interface in macrotidal estuaries. The limit of tidal influence (TL) is upstream of the limit of salt intrusion (A: 0.1‰ of sea water for 99.9% of river waters). A-B normal extension of brackish waters (1‰ to 90% sea water), A-C range during high water flows. Left: non-regulated estuary, right: regulated estuary.

Fjords and fjärds

Fjords originate from glacial scouring and are characterized by their sinuous morphology, their extension (length >> 100 km for some of them), their depth (z > 100 m), and by their steep U-shaped section (figure 1.1.5.d.). For many of them under water sills trap anoxic sea water overlaid by a shallow layer of brackish clear and well oxygenated water. The river water residence in fjords is counted in years, i.e. one to three orders of magnitude difference with most other estuarine types. Fjords can be considered as perfect traps for river particulate inputs. In Europe, fjords are found in mountainous regions of Norway, Scotland and N. Iceland and N. Ireland.

Fjärds have been separated from fjords by some estuarine scientists: they result from the glacial scour on lowland hard rock and are the normal coastal feature of most Sweden, Finland, and Karelia. They lack the steep walls of fjords and are generally shallow systems in association with numerous islands and inlets (Syvitski and Shaw, 1995) (figure 1.1.5.e.). Their freshwater residence time is of the order of week to months depending on river discharge. The freshwater/sea water mixing zone (A/B) is variable and plumes of brackish water can be observed at very high flows, depending on fjärd size.

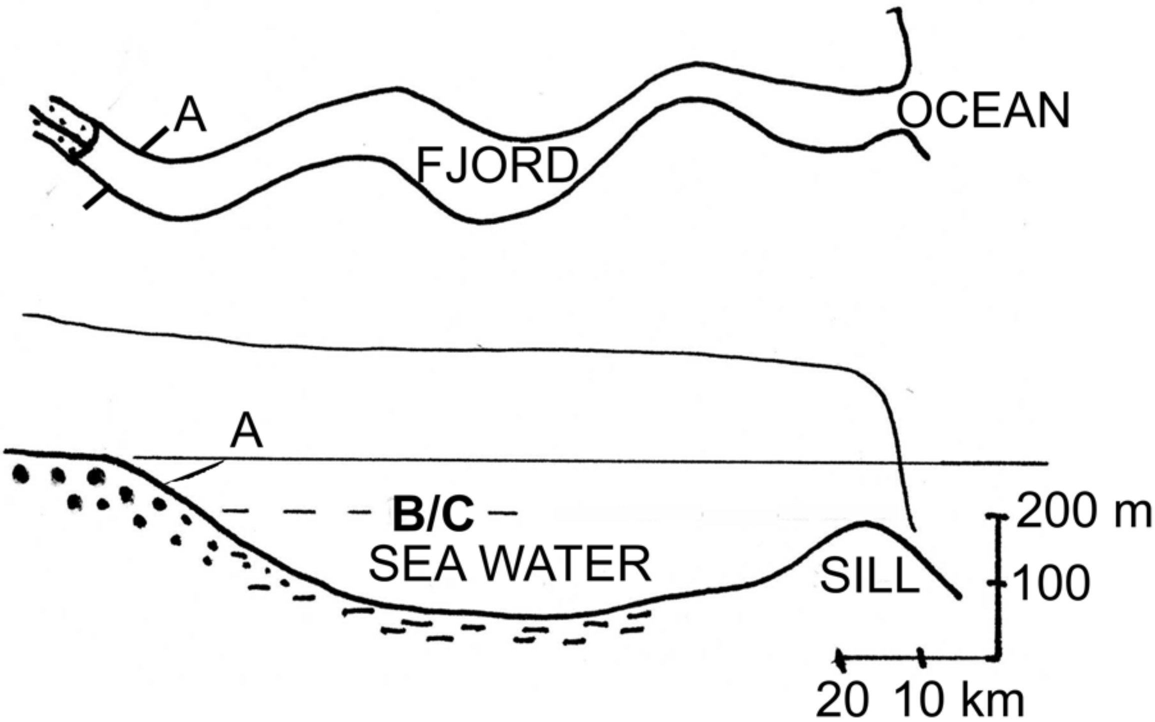


Figure 1.1.5.d. The river/ocean interface in fjords. A-B normal extension of brackish waters (1‰ to 90% sea water), A-C range during high water flows.

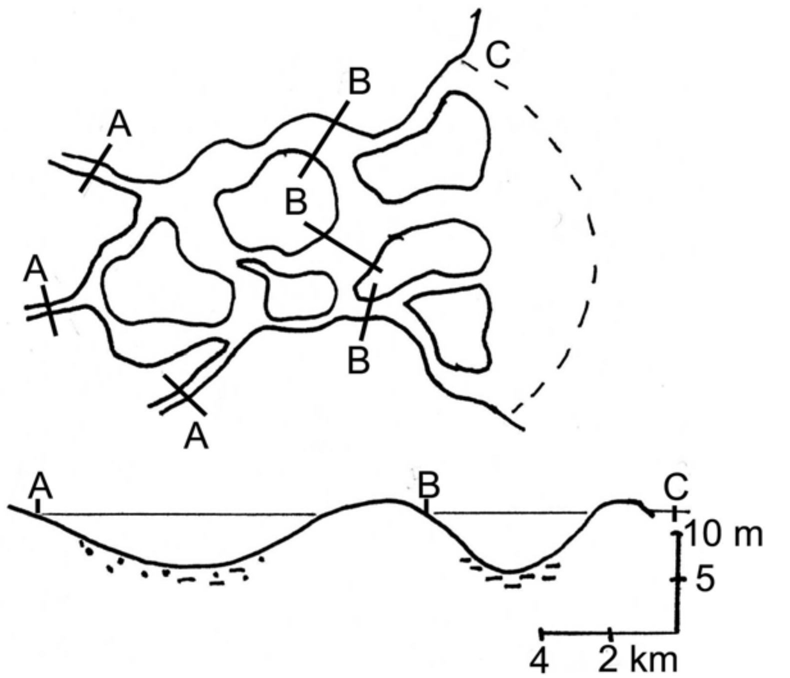


Figure 1.1.5.e. The river/ocean interface in fjärds and archipelagos. A-B normal extension of brackish waters (1‰ to 90% sea water), A-C range during high water flows.

Direct groundwater inputs in karstic regions

When extended limestone regions are bordering the seashore, the continental runoff may reach the sea through direct karstic circulations (figure 1.1.5.f.), not through river systems. These karstic springs may be located at depths reaching 100 m, i.e. the former sea level during the last glaciations. Direct karstic inputs are common in the Mediterranean coast. In Croatia, the Krka is a mixed karstic/ria estuary: the freshwater input is very much decanted and clear and overlays a sea water layer, the water mixing or interface is less than one meter.

The assessment of the distribution of European estuarine type has been based on 5 criteria: (i) lithology of coast at the 0.5 x 0.5 degree resolution; (ii) extension of Quaternary glaciation; (iii) coastline morphology at the 1/1 000 000 scale; (iv) tidal range distribution. This distribution is reported in figure 1.1.5.g.: each 0.5 x 0.5° coastal cell is linked to an upstream river catchment and is part of an European coastal segment according to the global segmentation presented by Meybeck et al. (2006). As such the drainage area runoff and all related attributes of any coastal cell, with its estuarine type, is connected to a river catchment.

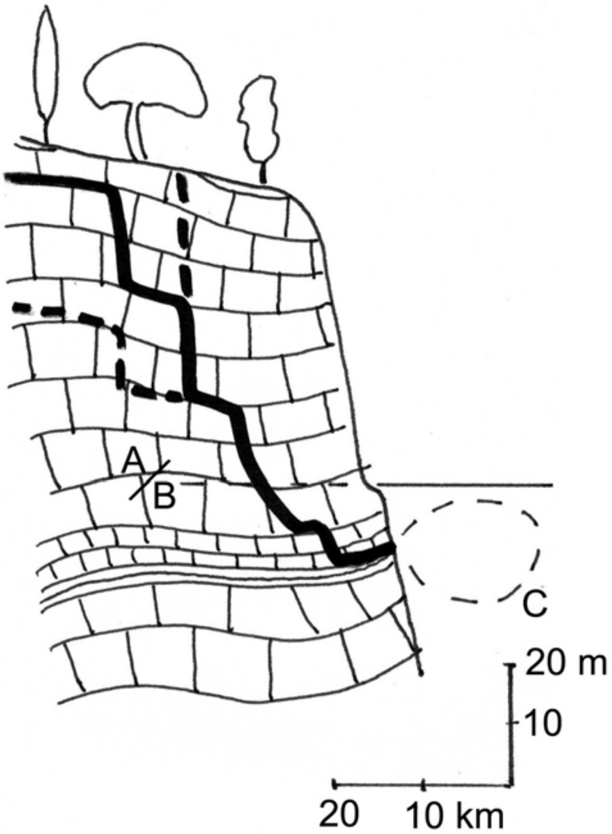


Figure 1.1.5.f. The river/ocean interface in karstic system. A-B normal extension of brackish waters (1‰ to 90% sea water), A-C range during high water flows.

Most types of estuaries are found in Europe. As a result, the dynamics, sediment pattern, oxygenation and ecology of European estuaries are very contrasted, and their related capacity to transfer river carbon and to emit Green House Gases are also very variable. As concern, the carbon cycle and the GHG emissions from estuaries types should be defined for the following characteristics: (i) settling of river particles, (ii) water residence time, (iii) light penetration and related primary production, (iv) direct inputs of organic wastes, (v) level of oxygenation. In a given type of estuary, several subdivisions with contrasted properties can be found (intra-estuarine variations) as for the macrotidal estuaries. The general features of the main types of European estuaries are here compared on the basis of seven criteria: size of water body, particularly the length of the brackish zone, water depth, ratio of inner estuary area/outer estuary area, water residence time, suspended solids concentration, oxygenation and sensitivity to river flow (table 1.1.5).

The brackish zone is here defined by the 0.1 % and 90 % of sea water. It is different from the water mixing interface width which can be very sharp (< 1 m) for some stratified estuaries. For such systems, we are taking into account the longitudinal extend of the stratified layer. Karst inputs correspond to very limited mixing zone excepted during high water periods or after major rain storms when plumes of brackish waters are extended.

All criteria show marked differences from one type to another, from size to oxygenation level. In addition to this intertype variability, some estuaries also present an important intratype temporal variability generally linked to river flow (seasonal regime, peak flows after rainstorms) (table 2.4.2.a) and, for the macrotidal estuaries, to tidal dynamics.

Fjords are probably the most stable systems mostly driven by seasonal temperature variations. Macrotidal estuaries are extremely dynamic combining river flow sensitivity and tidal sensitivity. Lagoons are very sensitive to wind action (water mixing, resuspension).

Type	**length[1] (km)**	**depth[1] (m)**	**Ratio inner/outer estuaries**	**Water residence time (y)**	**Suspended solids concentration**	**Stratification**	**Oxygenation**	**Sensivity to river flow**
delta	1 - 100	≤ 10	low to very low	$10^{-3} – 10^{-2}$	medium	limited	high O_2	high
coastal lagoon	1 – 100	< 10	very high	$10^{-2} – 10^{-1}$	low/medium	limited	variable O_2	medium
macrotidal/ria	10 – 100	≤ 10	high	$10^{-2} – 10^{-1}$	ETM[2]	none	low O_2 at ETM[2]	medium
fjord	10 > 100	> 100	very high	$10^{1} – 10^{2}$	very low	high	anoxic layer[4]	very low
fjärd	1 – 10	≥ 10	high	10^{-1}	low	medium	medium O_2	low
karst inputs	10^{-2}	N.A.	N.A.	$10^{-3} – 10^{-1}$	low	variable	high O_2	very high

Table 1.1.5. General features of principal European estuarine types (inner an outer estuaries). N.A. not applicable. [1] medium length and depth of the common brackish zone (A to B see figures 1 to 6, Appendix C). [2] estuarine turbidity maximum: TSS > 100 to 10 000 mg/L according to depth. [3] outer estuary is here the brackish zone located on the ocean side of the coastline. [4] in fjörds with sills.

1.2. Anthropisation of Europe's river system

1.2.1. Altered structure of river systems

In impacted systems that characterize the Anthropocene era (figure 1.1.1., right part), the carbon source, sinks and transfers are greatly modified. Global Change (A) includes Global warming and modifications of soil carbon cycling, and changes of water balance particularly the river runoff that is the number one driver of lateral export of carbon species (see CarboEurope Rpt). Deforestation (#B), afforestation (#C), intensive agriculture (#E) and other land use changes are also affecting the transfers of carbon. Peat land draining and exploitation (#D) may also modify the DOC export locally.

Increased nutrients levels in river systems result in eutrophication of lakes (#F_A), reservoirs (#F_B) and of slow-flowing rivers (#F_C). Reservoirs construction, from the smallest (area < 1 km^2) to the biggest (area > 1000 km^2, depth > 50 m, volume > 10^9 m^3), modifies the particulate carbon storage within river basins, the organic carbon microbial processing and increases the GHG emission.

The middle river course is also exposed to the release of organic wastes from cities, whether treated or not (#H). This lead to CO_2 emissions in receiving waters. Another very important feature is the draining and cultivation of former floodplains (#I) often completely isolated from the river course by dikes or levees, or channelled for navigation.

The estuarine part of river systems can also be much affected by channelization and dredging, cultivation, draining and filling of natural wetlands (#J). Estuaries are often privileged sites for the construction of megacities, and are also naturally chosen for harbour construction. In both cases organic wastes can still be released directly in estuarine brackish waters thus enhancing natural hypoxia that occur naturally in macrotidal estuaries.

Finally, the excess of labile organic matter originating from organic waste waters and from eutrophied rivers may be processed in the estuarine zone with subsequent release of

GHG, in addition to the slow process of degradation of resistant organic material originating from soil erosion.

In Europe, estuaries have been privileged for Human settlements since the Roman times and their natural state is often completely masked by Human pressures typical of the Anthropocene era: wetlands draining and filling for agriculture and urban settlements, construction of levees and channel dredging for navigation, construction of harbours and megacities, artificialisation of brackish wetlands for aquaculture, irrigation with diverted waters from the middle and lower river course. As a result, the water residence time of these estuaries can be accelerated by Human activities and the tidal or salt water intrusion is often progressing landwards due to river dredging and channelization. The opposite evolution may also be found in impounded river basins where the water discharge is greatly reduced by diversion and/or irrigation, as for most Mediterranean basins with the exception of the Rhône and Pô rivers.

1.2.2. Alteration of river flow regimes by Human activities

Two Human pressures alter the natural flow regimes in very significant ways. The first one is the retention of river waters in reservoirs –for any purpose as hydropower, flood control or water storage for irrigation- is distorting the natural hydrograph. This distortion is maximum when the retention is close to 6 months: at that stage the minimum natural water discharge may actually correspond to the high discharge stage. This type of distortion –from 3 to 6 months shift in seasonal regime- is often found for large hydropower reservoirs as in the Alps which store water from June to August and release it in December-January at the peak electricity demand. However such distortion does not affect much the annual transfers of dissolved carbon fluxes. Reservoirs greatly after POC and PIC transfers which are stored depending on residence times and reservoirs operation rules (bottom withdrawals are minimizing the particulates retention).

The second important pressure is the consumptive use of water through evaporation and evapotranspiration of vegetal and the water diversion from one basin to another one. These are linked to industrial uses (e.g. cooling of nuclear power plants) and, most of all, to irrigation. As a result, most Mediterranean rivers that are monitored since 1950 or before have current water discharges much lower than in the 1950's, generally between 40 and 90 % (table 1.2.2.). In such river basins, the reservoirs are numerous and they are named by geographers as "reservoirs cascades" as for all rivers of the Iberian peninsula (e.g. Ebro Tagus), of Sicily and Southern Italy, many Greek rivers and Southern French rivers (Dordogne, Lot, Durance). In reservoir cascades, the lateral transfer of carbon becomes very limited: the particulate species (POC and PIC) are settling in reservoirs. During irrigation, most river TOC is transformed into Green House Gases, mostly CO_2, while half of DIC is converted into CO_2; if calcite precipitation occurs in irrigated soils, half of it is precipitated as calcite.

	Recent (1960 ~ 2000)	Long-term (> 50 y)
Rhone (France)	NS	NS
Aude (France)	NS	
Têt (France)	NS	+ 57%
Ebro (Spain)	- 54%	- 47 %
Adige (Italy)	NS	- 36%
Po (Italy)	NS	NS
Arno (Italy)	NS	- 39%
Pescara (Italy)	- 20%	- 35%
Tiber (Italy)	- 31%	- 22%
Korka (Croatia)	- 35%	
Cetina (Croatia)	- 88%	
Shkumbi (Albania)	- 34%	
Semani (Albania)	- 29%	
Acheloos (Greece)	- 30%	
Axios/Vardar (at Skopje)(FYROM/Greece)	- 47% (1)	
Nestos	- 55%	
Medjerdah (Tunisia)	NS	- 56%
Nile (Egypt)		(- 90%)

Table 1.2.2. Rate of river flow reduction since 1960 for European rivers (Ludwig *et al.*, 2004)

1.2.3. Reservoirs

Manmade reservoirs have been built in Europe since one hundred year. They range from small reservoirs (< 0.1 km^2) for local storage of water used in agriculture to biggest multipurpose reservoirs exceeding 1000 km^2 build for irrigation (e.g. lower Volga), hydropower (most large reservoirs), flow regulation and, less frequently, recreation (see table 1.2.3.). In Nordic countries, most reservoirs are related to hydropower while in the Mediterranean river basins, irrigation is their main objective. The exact number of reservoirs is difficult to know as most small ones –the most numerous- are not registered at the national level. In countries like Spain, all major rivers are impounded with multiple reservoirs as the Ebro and Tagus. The same trend is observed in parts of Italy (e.g. Sicily), Greece (Axios, Acheloos, Aliakmon), Southern France (Dordogne, Lot, Durance). The total area of European reservoirs exceeds 50 000 km^2, i.e. it is already of the order of magnitude of natural lakes. Yet, most very large reservoirs are located in W. Russia: if these are substracted the total area of West and Central European reservoirs is probably closer to 10^4 km^2, i.e. an order of magnitude lower than natural lakes.

Reservoir depth is also very variable, from few meters to more than 150 m for the deepest alpine reservoirs (e.g. Grande Dixence, Switzerland; Almendra, Spain). But the average reservoir depth is lower than the average lake depth for a similar size class.

The residence time of water in lakes and reservoirs is a key feature for DOC photodegradation and bacterial degradation and for POC settling and storage. In lakes, it commonly ranges from few months for the smaller ones to more than 10 years for the deepest ones. Most medium-sized European lakes (area < 100 km^2) have a residence time of less than one year. Largest lakes of glacial origin are characterized by residence times exceeding 10 y (Ladoga, Onega, Vanern, Vattern, Leman, Garda, Zug, Lugano) (appendix B). Volcanic crater lakes, although of smaller size may have a very long residence time (Bracciano 137 y;

Balsena, 120 y). However, such lakes do not intercept large drainage area (1 to 10 km^2 typically), there influence on carbon transfers is therefore very limited compared to some alpine lakes that can intercept river basins 5 to 20 times their own area (i.e. 1000 to 10 000 km^2).

Many valley-reservoirs have similar or higher interception capacities (10 to 100 times their area). Their residence time is therefore somewhat shorter than lakes residence time –for similar size classes- i.e. from few days to few months. Only the very large reservoirs (e.g. Volga basin) or some of the Alpine reservoirs have residence time up to one year, or even more.

Reservoirs		**Country**	**Area**	**Mean depth**	**Max depth**
				m	m
1.	Kuybyshevskoye	RU	6 450	12.6	40
2.	Rybinskoye	RU	4 450	5.6	30
3.	Volgogradskoye	RU	3 320	10.1	41
4.	Tsimlyanskoye	RU	2 702	8.8	-
5.	Nizhnekamskoye	RU	2 650	4.9	-
6.	Cheboksarskoye	RU	2 270	6.1	-
7.	Kremenchugskoye	UA	2 250	6.0	-
8.	Kakhovskoye	UA	2 150	8.5	-
9.	Ijsselmeer	NL	2 000	-	-
10.	Kamskoye	RU	1 915	6.4	29
11.	Saratovskoye	RU	1 830	7.3	32
12.	Gor'kovskoye	RU	1 591	5.5	21
13.	Votkinskoye	RU	1 120	8.4	28
14.	Kiyevskoye	UA	922	4.0	-
15.	Ataturk	TR	815	-	-
16.	Keban	TR	675	-	-
17.	Kanevskoye	UA	582	4.3	-
18.	Lokka	FI	417	-	-
19.	Ivankovskoye	RU	327	3.4	-
20.	Dnieper	UA	320	-	60
21.	Hirfanli	TR	263	-	-
22.	Djerdap	SB, RO	253	-	92
23.	Uglich	RU	249	5.0	-
24.	Porttipahta	FI	214	-	-
25.	Narva	EE, RU	200	1.9	9

Table 1.2.3. Large european reservoirs (Henriksen and Hansen, 1995)

1.2.4. Examples of Human pressures on European river systems: the EUROCAT example

As for other criteria (hydrological regime, vegetation, lithology, relief…) that regulate carbon transfers in river systems, the Human pressures on European rivers are quite variable although this continent is probably the most impacted one together with parts of Asia (Table 1.2.4).

The population density is one of the key criteria pressures. For medium-sized and large basins (area > 10 000 km^2), it ranges between less than 1 people/km^2 for some tributaries of Botnian Bay, Barentz Sea and White Sea (e.g. Lule, Kemi, Mezen) to more than 300 p/km^2 for the whole Rhine catchment, close to the world's maximum value for such large basin (circa 220 000 km^2). For smaller watersheds as the upper Scheldt or the Maas-Meuse, the density exceeds 500 p/km^2 and reaches 1000 p/km^2 in suburban streams. For such river catchments, the organic waste inputs from urban sewage, even normally treated (treatment efficiency for BOD and COD between 80 and 90 %), represent a major contribution to the organic carbon load. Other pressures include land-use as deforestation and cultivation, some industries, particularly agro-industries as sugar factories canning, and the artificialization of river network and damming. In lowland regions, the sea level rise may already be a major coastal issue. The impacts of such pressures on the carbon budget have been mentioned before: they can either increase the organic carbon sources (industrial and urban sewage; eutrophication, active draining of wetlands), decrease these sources (filling of wetlands, cropping), modify the carbon processing during lateral transfer through channelization and reservoir construction, store particulate carbon in reservoirs. The analysis of pressures requires a detailed account at a fine resolution (10' x 10' or less) including land cover, population density, industrial sources, damming etc. This analysis is not yet realized for European rivers but is rapidly progressing as for the Elbe-Oder catchments (see section 2.2), and for selected European catchments through various EU projects.

The EUROCAT programme (www.eurocat.ulster.ac.uk/, Pirrone et al., 2005) provides an analysis for such river to coast pressures and impacts for several EU rivers with multiple impacts, the Vistula, Elbe, Rhine, Humber (U.K.), Seine, Po, Idrijca (Slovenia), Axios (Greece) and Provadijska (Bulgaria) : each catchment is different from the others (appendix D, tables D.1 to D.5), the type, magnitude and position of pressures and their impacts on river structure and functioning is very variable. The related impacts on carbon transfers and GHG emissions should therefore also be examined for each individual basin.

	Inputs from the catchment				**Coastal issues affecting GHG and carbon cycle**						**Other issues**	
	Nutrients(1)	Pollut. herit.(2)	Metals	POPs	Eutro.	Hypoxia	Int. sce	Coastal erosion	SLR	IL	HAB	Pollut. herit.
Vistula			++	++	+	++						+
Elbe	++		+	+	+							
Rhine	++		+	+	+				+?			
Humber	++	++	++	+	+	++	+	++	+++	++		++
Seine	+++		+++	+++		+++	++					
Pô	++++		+	+	++++	+++		+	+		++	
Idrijca		++++					++					++++
Axios			+?		+?	+?	++	+	?		+++	
Provadijska	++++				+++	+++	+++?				++	

Table 1.2.4.a. Scaled coastal zone issues linked to river inputs in EUROCAT entities.
(1) nutrient sources in these catchments can originate from agriculture, urbanization or from industries,
(2) from past mining activities, + to ++++ relative scale of issue for the considered coastal zone
Eutro. : eutrophication, HAB : harmfull algal bloom, Int. sce : internal sources of nutrients and metals from past contaminated sediments, Pollut.herit. : pollution heritage from past mining activities, SLR : sea level rise, IL : intertidal zone loss.

1.2.5. Human alteration of estuaries

Human activities may greatly modify the River/Ocean interface. The table 1.2.5. lists some of these modifications and related examples as described by the E.U. programme EUROCAT (www.eurocat.ulster.ac.uk and Pirrone *et al.*, 2005). Examples of Human pressures on a dozen of European river systems, including their estuaries, are presented in appendix D. Each estuarine type has its specific alterations, which are schematically presented on figures 1.1.5.a to f. Human impacts may affect estuaries in multiple ways GHG emissions from estuaries are very sensitive to wetland draining and cultivation, wetland filling. These changes also limit the storage of river POC during inundations. On the other hand, the channelization and dredging are accelerating the transfer of river particulate matter through these systems to the outer estuary. Urbanization in estuaries is often resulting in additional inputs of organic wastes even when sewage waters are treated. The impact of aquaculture on estuarine systems, particularly on rias would be a reduction of TOC concentrations through filter-feeding organisms and export of shellfish on land.

One major impact of Human activities is the reduction of river flows to the estuarine systems particularly through reservoir construction upstream of estuaries, water diversion and irrigation of riverine and estuarine flood plains. In the Mediterranean basins, this reduction of water discharge, and all related carbon inputs is commonly between 40 % (e.g. Ebro) and 90 % (e.g. Nile).

Types	**Wetland draining/cultivation**	**Channelization dredging**	**Urbanization and waste inputs**	**Reduction of water inputs[1]**	**Wetland filling**	**Aquaculture**
delta	+ to +++ (Ebro, Axios, Po)	++ to +++ (Po, Vistula)	+	+ to +++ (Axios, Ebro, Acheloos, Aliakmon)	+ to +++ (Vistula, Axios)	+ (Po)
coastal lagoon	+	+ to ++ (Odra, Venice L.)	+ to ++ (Venice L., Pregolia)	+	+ to +++	
macrotidal/ria	+ (Humber)	+ to ++ (Seine, Rhine, Provadijska)	+ to +++ (Rhine, Scheldt, elbe, Thames, Seine, Loire)	+	+ (Seine, Rhine, Humber)	+ to +++ (Spanish and Britanny rias)
fjord	none	none	limited	none	none	
fjärd	limited	limited	+ to +++ (Stocklom Archip., Helsinki Archip.)	limited	+ to ++	
karst inputs	N.A.	N.A.	+ (Krka)	+ to +++ ? (Krka)	N.A.	

Table 1.2.5. Sensitivity of estuarine types to Human pressures affecting carbon budgets and Green House Gases emissions at the River/Ocean interface with European examples from the EUROCAT project.
N.A. not applicable. [1] through upstream water consumption and/or diversion

1.3. The European river catchments and its linkage to regional seas

The lateral fluxes of river carbon from the European continent to the coastline are constrained by the structure of regional seas basins as the Baltic, the Mediterranean and the Black Sea. Regional seas are defined as semi-enclosed to enclosed portions of the world’s ocean, limited by the topography of the continental coast (e.g. capes, straights) and/or by the under ocean topography (sills, ridges, continental platforms). Regional seas may have characteristics much different than the portion of ocean to which they are related, as for salinity and average depth. The greatest part of the particulate carbon and most of the dissolved matter including DOC originating from the continents that is carried to regional seas does not reach the open ocean. The main characteristics of Europe's regonial seas are featured on table 1.3.

		North Atlantic / North Sea	Baltic	Arctic	N. Black Sea	N. Mediterranean	Europe Total [1]
Basin	M km^2	1.92	1.62	1.63	2.09	0.94	8.2
Area	%	23.4	19.7	19.9	25.5	11.5	100
Water	km^3/y	723	388	559	328	358	2356
Volume	%	**30.7**	16.5	23.7	13.9	15.2	100
Population	Mp	251	78	10.8	163	113	616
	%	**40.7**	12.7	*1.7*	26.4	18.3	100
Suspended	Mt/y	168	20.3	79	107	284	658
Sediment	%	25.5	*3.1*	12.0	16.2	**43.1**	100
Total N	Mt/y	2.74	0.64	0.475	0.90	0.95	5.7
	%	**48.0**	*11.2*	*8.3*	15.8	16.7	100
Population density	p/km^2	131	48	6.6	78	120	75.1
Runoff	mm/y	376	240	343	157	381	287
N yield	t km^{-2} y^{-1}	1.43	0.40	0.29	0.43	1.0	0.70
Total N	mg/L	3.8	1.65	0.85	2.74	2.65	2.42

Table 1.3. Relative weights of European Regional Seas basins (Meybeck and Dürr in preparation). Bold : proportions much higher than the area weight ; *Italics* : proportions much lower than the area weight.

[1] Caspian drainage excluded

1.3.1. Main characteristics of Europe's Regional Seas catchments: runoff.

The highest relief area in Europe is characterized by high runoff. Another control factor of runoff is the proximity to the Atlantic coast and to the N and E Adriatic coast. The water budget for each coastal segment and regional seas is based on Fekete *et al.* (1999, 2001). This data set includes all European basins and adjacent continents linked to European regional seas.

The limits of Europe's regional seas and their catchments characteristics have been recently considered (Meybeck *et al.*, 2006). Details are found in appendix E. The drainage area is nearly equally distributed between four catchments, the European part of the Mediterranean Sea catchment is somewhat smaller. The water volume is preferentially discharged by the North Atlantic / North Sea basin, then by the Arctic. It is unexpected to find that the Mediterranean water flux proportion (15.2 % of Europe's total) is higher than the area proportion (11.5 %), while the Black Sea contribution is relatively lower (13.9 % of water flux for 25.5 % of area). This means that wet mountainous regions of the Mediterranean of Europe fed from the Pyrenees, Alps and Dinarides have a much greater influence on the water budget, hence on all fluxes, than the dryer regions in S. Spain, Italian Peninsula and islands and Greece.

1.3.2. Europe's Regional Seas Catchments: population pressure.

Pressures on river basins are also much differentiated. The population is essentially found in the North Atlantic / North Sea drainage (40.7 %, 131 p/km^2) while the Arctic drainage represents only 1.7 % of the population (d=6.6 p/km^2). The total nitrogen flux originates from the North Atlantic / North Sea for 48 %, nearly as much as the combined fluxes for the rest of Europe (76.6 % of Europe's drainage basin). Most of this modelled excess total N is linked to the use of industrial fertilizers in North Atlantic / North Sea rivers. These European regional seas combine some of the highest figures at the global scale for human population density (131 p/km^2) and the total N yield (1.43 t km^{-2} y^{-1}), respectively 20 and 5 times more than the Arctic drainage figures (see table 1.3).

1.3.3. Suspended sediment distribution in Europe's coastal catchments

The database on global scale sediment yield for pre-dammed catchments has been elaborated by Ludwig and Probst (1998). In the Ludwig/Probst model, the lowest yields are expected for the Baltic Sea (Ys = 12.5 t.km^{-2}.y^{-1}) and the highest for the North Mediterranean Sea (Ys = 300 t.km^{-2}.y^{-1}) :

N. Medit. Sea. >	Atlantic >	N. Black =	Arctic	> North Sea >	Baltic
(Ys = 300 t.km^{-2}.y^{-1})	(131)	(48)	(48)	(36)	(12.5)

The sediment fluxes are very much contrasted: 43 % of Europe's fluxes originate from 11.5 % of its area, i.e. the Mediterranean catchment (pre-damming estimates) and only 3.1 % originate from 19.7 % of Europe, i.e. the Baltic catchment.

The river damming, very important in the N. Mediterranean basin greatly modifies the sediment transfer across the river catchment, i.e. the net sediment inputs to regional seas may be actually much lower. The theoretical weighted average Total Suspended Sediments concentrations have also been computed from the ratio between total sediment fluxes and water fluxes for each coastal basin. These average TSS range from a minimum of 35 mg/L for the Botnian Bay and the Gulf of Finland, to values exceeding 1000 mg/L around the Mediterranean or in the South Black Sea (i.e. Turkish rivers). Such 30 times range is possible although the TSS levels in the N and E Baltic may be even lower due to the very high lake retention which may have been underestimated by Ludwig and Probst (1998). The very high TSS for South Black Sea Rivers (prior damming) is possible although values from 500 to 1000 mg/L seem more likely, as for the Mediterranean Basin Rivers.

1.3.4. Distribution of estuarine types in Europe

Ten major types of land/ocean interface, i.e. of estuaries in its broader definition, are considered here: (1) deltas ss with high sediment inputs, (2) karstic coastlines (that may include some small deltas), (3) deltas with low sediment inputs and lagoon formation, (4) lagoons and deltas, (5) ria coast, (6) fjord coast, (7) fjärd coast, (8) macrotidal estuaries, (9) glacierised sedimentary coast and (10) arheic (i.e. absence of river input to the coast, even occasional only found in S. Mediterranean coast). As the categories #3 and 4 are actually very close, and sensitive to human action that may regulate the connectivity between lagoons and open sea; they have been grouped in this first analysis. It has been sometimes quite difficult to classify some catchments. The Po Delta has been considered in the Deltas and lagoons types due to the numerous lagoons that are found in this system which is also receiving sediments from other Alpine rivers (Adige, Brenta) and Apennine rivers. Yet the artificialisation of this system, particularly its canalisation for navigation, the construction of levees etc. is accelerating the riverine fluxes to the coastal zone and decreasing the filtering capacity of the system, a characteristic of deltas.

The analysis presented here is a first attempt made especially within the CarboEurope project to link the whole European drainage to the ocean -from Iceland to the Pechora basin in N. Russia and from Portugal to Azov Sea- to the estuarine typology (Meybeck and Dürr, in preparation). With such approach, the characteristics of European river catchments can be aggregated by estuarine types and/or the European coastal segments can be decomposed into the different estuarine types (see figure 1.3.4). The total European area considered is thus 8.2 Mkm^2; mapping is also realized for the whole Mediterranean and Black Sea catchments.

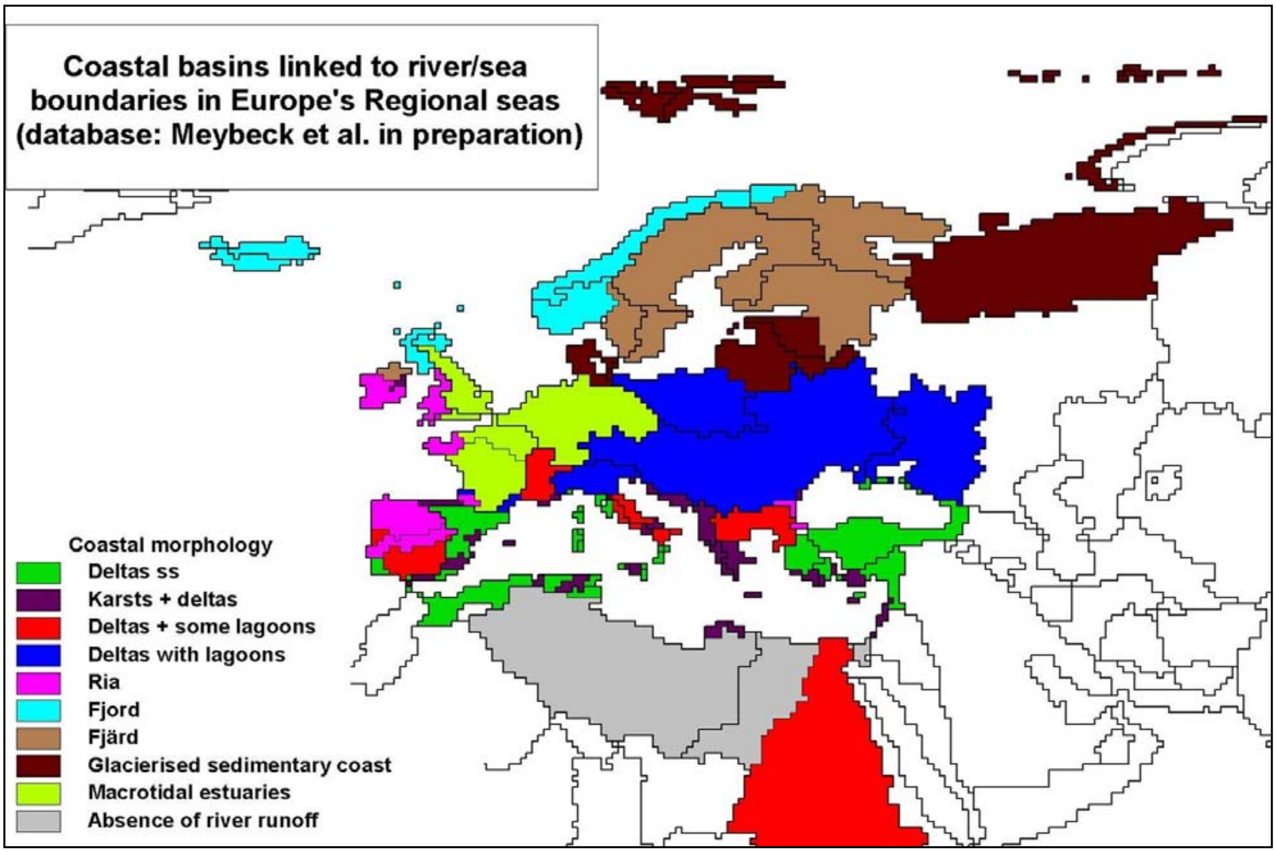


Figure 1.3.4. Coastal basins linked to 10 major types of land/ocean interface in Europe's regional seas (Meybeck and Dürr, in preparation).

We are conscious of the simplifications of this analysis: for instance some rias may be associated with macrotides, however their first order characteristic is genetic. The macrotidal systems should be renamed 'non-ria macrotidal systems' etc..

The estuarine types are not randomly distributed in European coast. This is not a surprise for Fjords and Fjärds, nor for macrotidal estuaries which can only be found in part of the Atlantic Ocean and in the North Sea. 'Deltas ss' and 'deltas and lagoons' are more spread throughout Europe at least in 3 or 4 regional seas. The arheic type is only found in the South

Mediterranean Seas (Ionian, SE Mediterranean). It is difficult to give any river examples to the karstic basins: by definition these inputs are subterranean; the Krka estuary in Croatia has been extensively studied in the early 90's as an example of a mixed karst/ria type.

For each of the coastal segments the accounting of each estuarine type has thus been realised, then the corresponding upstream river network has been delineated and characterised as for the previous analysis (runoff, population, sediment input etc.). The average characteristics or total fluxes of all European river catchments linked to a specific estuarine type are then determined, together with the distribution of these river catchments for each coastal segments.

1.3.5. Distribution of European river catchments per estuarine types

Drainage area

The most important type of river / coast linkage in Europe, in terms of drainage area, is the 'deltas and lagoons' type (37 % of Europe's drainage area) (Appendix G). This estuarine type is mostly found in the NW Black Sea (Danube, Dniestr, Dnepr) and the Azov (Don), in the South Baltic (Oder, Vistula) and in North Adriatic (Po delta and Venice lagoon). The sediment grain size of such deltas is usually finer than the delta type ss.

The second type is the formerly glacierised sedimentary regions found in Barents Sea and the Southern Gulf of Finland (18.4 %). The importance of glaciations in land / coastal zone linkage is illustrated as such: 40,3 % of Europe river basins is presently linked to a coast that has been formerly glacierised and shaped by this process (5.9 % for fjords, 16.4 % for fjärds, and 18.4 % for sedimentary coastline). The glacierised sedimentary rocky coasts are found in the Botnian Bay, the Southern Gulf of Finland, and in the Barents Sea catchment.

The macrotidal estuaries are connected to about 11.2 % of Europe area (Gironde, Loire, Seine, Thames, Humber, Rhine / Maas, Weser, Ems, Elbe). This relatively low ranking is a surprise since this type of estuaries has attracted the attention of scientists over decades, particularly for geochemistry and sedimentology, due to the occurrence of the turbidity maximum in these systems, their long water residence time, and the vicinity of major research institutes.

Pure deltas with high coarse sediment supply are spectacular but they do not correspond to extended drainage (3.0 %). According to this analysis they are generally associated with mountains ranges close to the coastline: Caucasus (NE Black Sea), Alps and Pyrenees (Rhone and Ebro in Balearic basin). This type also occurs in small catchments around the Mediterranean and the Southern and NE Black Sea.

Pure karsts are very difficult to delineate at the 30' resolution and are generally associated with small deltas (3.4 % of Europe basin area). They are essentially found in the Mediterranean coastal segments.

Rias are found in Cornwall, Brittany, Galicia and part of Portugal (The Tagus estuary has been put into this category) (5.1 % of Europe's basin area).

None of Europe coastline is arheic: these types are only found in the South Ionian Sea (from Tunisia to Libya) and in the East Mediterranean Basin, outside of the Nile Delta.

Continental runoff

The water balance, on which the computation of continental runoff is based, includes both surficial runoff (river inputs) and groundwater inputs (karts and alluvial aquifers mostly) (see table C.2. in Annex C).

Most of the water discharged from Europe reaches the coastal through the deltas and lagoons types (25.7 %), then through the formerly glacierized sedimentary coast (18.8 %). The macrotidal estuaries receive only 11.4 % of Europe's waters, less than fjords (14.7 %) and fjärds coasts (14.5 %).

However it must be remembered that Europe's limits are placed at the Ural mountain range and include therefore the Barents Sea drainage : the weight of Nordic sea catchment is therefore greater than in many European Union statistics that barely consider Northern Russia as discharging into Europe's Seas.

The average river runoff for each type of estuary is also presented in table C.2. It ranges from about 200 mm/y for deltas with lagoons to more than 700 mm/y for fjords. It was a relative surprise to find that karstic coasts have actually a higher runoff than Europe's average (445 mm/y vs. 287 mm/y): in this survey they occur mostly in the East Adriatic (Albania coast) and Bay of Biscay, both very wet, thus compensating the dryer karstic coast of Greece and Mediterranean islands.

European population

Due to their relatively high drainage area deltas and lagoons types are under the pressure of 269 M people, i.e. 43.6 % of Europe's population connected to the world's ocean (Caspian basin excluded). The macrotidal estuaries type is second with 180 M people, i.e. 29.2 % of the population.

Nordic types with former glacierised coastline correspond all together to only 10.8 % of the population. Only 11.1 M people are connected to fjords sensu stricto.

When combining the filtering capacities of these river estuarine systems it is found that the highest filtering capacities i.e. macrotidal estuaries (pristine conditions) and fjärds are intercepting 208 M people (34 % of Europe), while the lowest filtering capacities i.e. deltas ss + karstic coasts correspond to 59 M people (9.5 % of the population). The rest of Europe's population is intercepted by river/estuarine types with intermediate filtering capacities.

The highest population density is found on catchments connected to macrotidal estuaries (d=196 p/km2), the lowest ones are observed for the Nordic types (23.1 p/km2 for fjords, 21.2 p/km2 for fjärds and 18.3 p/km2 for formerly glacierised sedimentary coasts).

2. Carbon transport in river systems

2.1. River carbon species

River carbon origins and ages are detailed on table 2.1 in two broad categories: (i): old particulate carbon resulting from the mechanical erosion of carbonate rocks, this carbon is mostly as PIC but there is a growing evidence of old recycled sedimentary POC and old dissolved inorganic carbon (DIC) resulting from the dissolution of carbonate rocks by acids during weathering reactions, (ii) recent carbon: organic carbon originating from erosion and leaching of soils (DOC and POC) and atmospheric CO2 implied in most weathering reactions :

Reaction 1: non-carbonated minerals + CO2 + H2O →HCO3- + cations + weathered minerals + dissolved silica

Reaction 2: (Ca, Mg)CO3 + CO2 + H2O → 2 HCO3- + Ca2+ and Mg2+

In reaction 1, all riverine DIC originates from atmospheric CO2 and/or from soil organic acids, in reaction 2 only half of it originates from CO2.

Other natural origins of riverine carbon are autochtonous POC resulting from recent debris of algae and macrophytes, particularly in eutrophied rivers. Another autochtonous source of PIC is calcite precipitation when pH exceeds 8,2 which is the commonly case for eutrophied rivers in carbonated basins. Anthropogenic sources of organic carbon are mostly found in organic wastes from agro-industries and cities. The riverine carbon ages counted since the original atmospheric CO2 fixation range from hundred millions years (carbonated rocks) to few days (autochthonous POC and PIC).

	Sources	Age (y)	Flux # 10^{12} g $C.y^{-1}$	Sensitivity to global change A	B	C	D	E	F
PIC	Geologic	10^4-10^8	170	●					●
DIC	Geologic	10^4-10^8	140		●	●			●
	Atmospheric	0-10^2	245		●	●			●
DOC	Soils	10^0-10^3	200			●			●
	Pollution	10^{-2}-10^{-1}	(15 ?)					●	
CO_2	Atmospheric	0	(20 to 80)			●	●		
POC	Soil	10^0-10^3	(100)	●					●
	Algal	10^{-2}	(< 10)				●		●
	Pollution	10^{-2}-10^0	(15)					●	
	Geologic	10^4-10^8	(80)						●

Table 2.1. Origins and ages – since original atmospheric CO2 fixation – of carbon species in rivers. A : land erosion, B : chemical weathering, C : global warming and UV changes, D : eutrophication, E : organic pollution, F : basin management damming).

The riverine carbon concentration is classically reported in mg C/L. Particulate forms of river carbon can be expressed in mg C/L, yet they are also reported in % C of total suspended solids (TSS), termed here PIC % and POC %. The sum of river carbon species originating from recent CO2 is termed total atmospheric carbon (Meybeck, 1993a):

TAC = DOC + non-fossil POC + 100% silicate weathering DIC + 50% carbonate weathering DIC

2.2. Organic pollution and carbonaceous pollution

The input of organic matter from domestic and industrial waste water to rivers is generally known as «organic pollution» but the term carbonaceous pollution can be used preferred to avoid confusion with organic toxic substances. Such impact has been monitored and modelled through biological oxygen demand BOD_5 and chemical oxygen demand COD since the 1940's, now these indicators are gradually replaced by direct TOC measurements.

The impact of a megacity as Paris impact (10 million people altogether) on the Seine River is a good example of carbonaceous pollution. The DOC increases markedly downstream of the release of treated domestic sewage from the gigantic Seine-Aval plant (8 million equivalent people) despite a satisfactory efficiency of this plant (80%) for the TOC removal (Servais et *al.*, 1998). Then most of the remaining excess DOC is degraded into CO_2 within one week before reaching the estuary (figure 2.2.a).

In the more industrialized countries as Western Europe and North America, industrial TOC sources were common until the seventies in some industrials sectors as pulp and paper, agro-industries and others. These industrial wastes have generally been decreased in these regions by at least an order of magnitude, principally between 1960 and 1980.

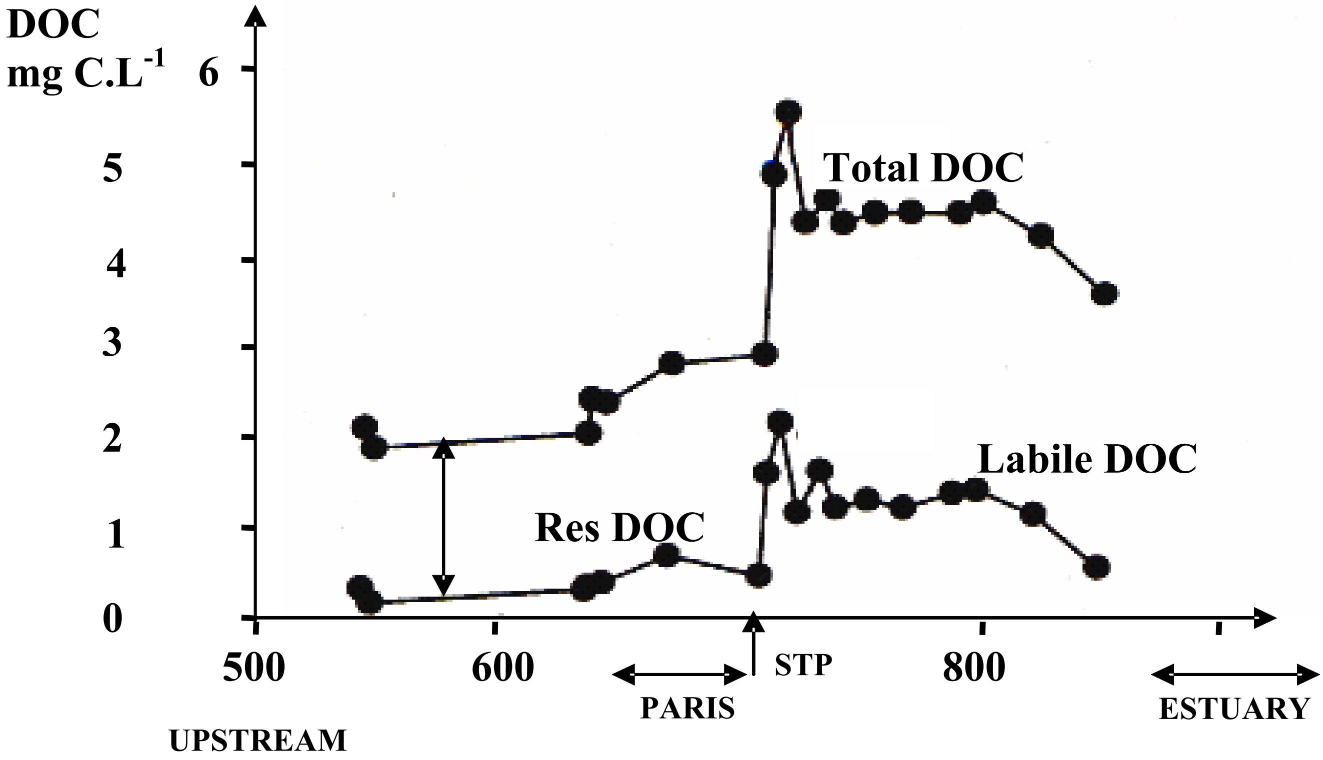


Figure 2.2.a. Longitudinal profiles of total dissolved organic carbon, easily degradable (lab. DOC) and resistant (res. DOC) in the Seine River across Paris megacity. Most treated sewage (8 M equivalent people) is injected at KP 700 (STP) (from Servais *et al.*, 1998)

DOC and POC trends in impacted rivers depend on population density, domestic sewage collection and sewage treatment (both urban and industrial). In most European rivers, there is a marked improvement of oxygenation, i.e. a gradual decrease of TOC, since the 1970's due to increasing collection and treatment rates as observed for the Thames and Rhine and, later, for the Seine and the Danube.

The Elbe River is one of the best example documented (Behrendt, *et al.*, in preparation) (figure 2.2.b). From 1982 to 2003, DOC has been decreased by half (10.7 mg/L in 1985-89 to 5.7 mg/L in 1999-03). This DOC decrease is probably due to (i) the closure of some industries discharging organic wastes, (ii) the improvement of municipal waste water treatment. In the Rhine and Weser Rivers, the DOC decrease was less marked (about 30 % for the same period), probably due to the second type of response (Behrendt *et al.*, in preparation). Parallelly, POC has slightly increased from 2.4 to 2.9 mg/L. This increase can partially be accounted for by the chlorophyll increase from 55 to 77 mg.m^{-3} (+ 39 %). This algal biomass may be responsible for part of the total suspended solids increase (+ 15 %) during the same period. A final example of trend of river carbon sources is also provided by the Elbe (figure 2.2.c). Before the reunification of Germany, the sewage collection and treatment was limited in GDR and DOC was therefore diluted by river discharge (Q), a pattern typical of point sources. The recent DOC vs. Q pattern does not show any more dilution but a slight increase with discharge, typical of soil DOC leaching (see also CarboEurope report 8).

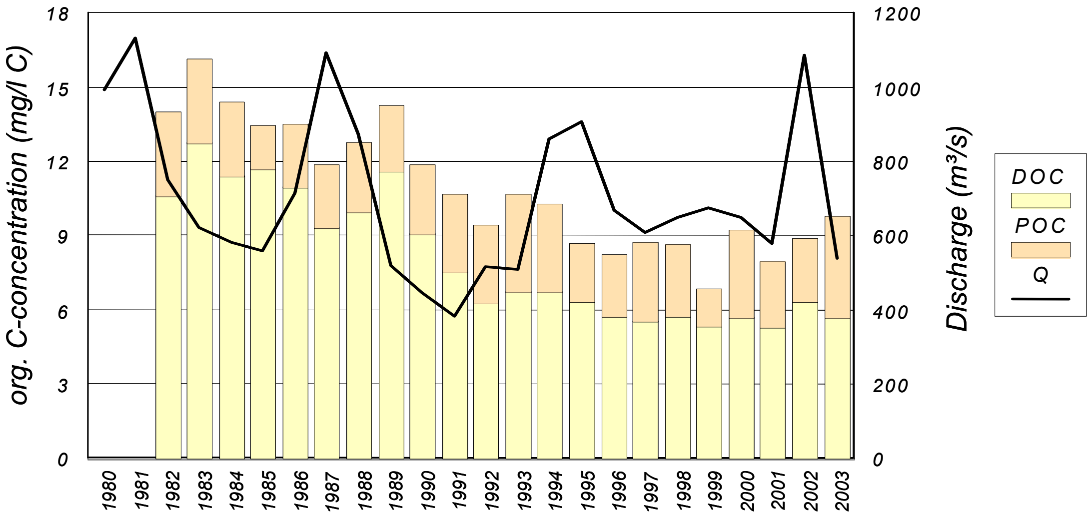


Figure 2.2.b. Change of DOC and POC concentration in the Elbe at Zollenspieker in the time period 1982 to 2003 (Behrendt, in preparation).

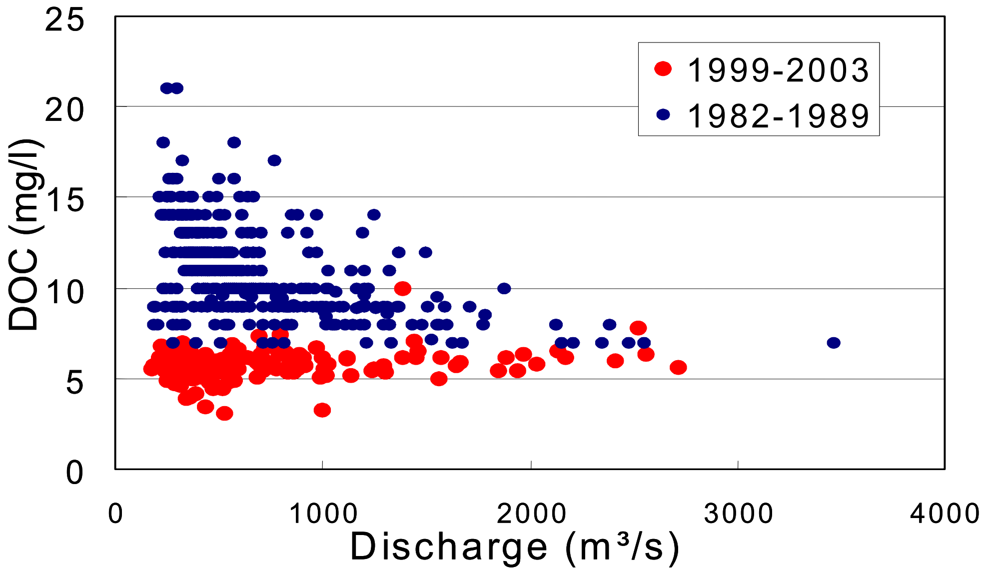


Figure 2.2.c. DOC concentration vs. river discharge for the Elbe River (1982-1989 and 1999-2003) (Behrendt, in preparation).

DIC trends in rivers

DIC trends in rivers under anthropogenic pressure, based on bicarbonate levels (HCO_3^-), are generally much more stable than trends of other major ions (Cl^-, SO_4^{2-}) or nutrients (NO_3^-). The Kura River trend in European Russia is a good example of such stability while sulphate was increasing due to irrigation, industrialisation and mining (Tsirkunov and Nikanorov, 1984). In such systems, if the water is concentrated through evaporation, the calcite saturation level is easily reached, therefore regulating the DIC level.

2.3. Eutrophied rivers and autochtonous fluvial carbon

Two types of autochtonous fluvial carbon can be observed during the summer period: algal POC and precipitated calcite. When summer chlorophyll A exceeds 100 µg/L, as the Rhine, Seine and Loire in Western Europe, the ratio POC/total pigments (in g/g) observed in rivers reaches a limit around 35 ± 5 during algal peaks (figure 2.3.a). Such ratio is similar to the one describing algal blooms in lakes and was described by Dessery *et al.* (1984) on the Oise, a tributary of the Seine, then confirmed in the Seine and Loire basins (Meybeck *et al.*, 1988; Garnier *et al.*, 1998). This ratio can be used to express the algal POC from total pigments levels (as the chlorophyll A + phaeopigment measurements by the Lorenzen method). Most of the algal POC is a highly labile POC species (Servais *et al.*, 1998) easily degradable in few days where the production/respiration ratio is well below 1, as for instance in turbid estuaries receiving eutrophic river waters (Garnier *et al.*, 1998).

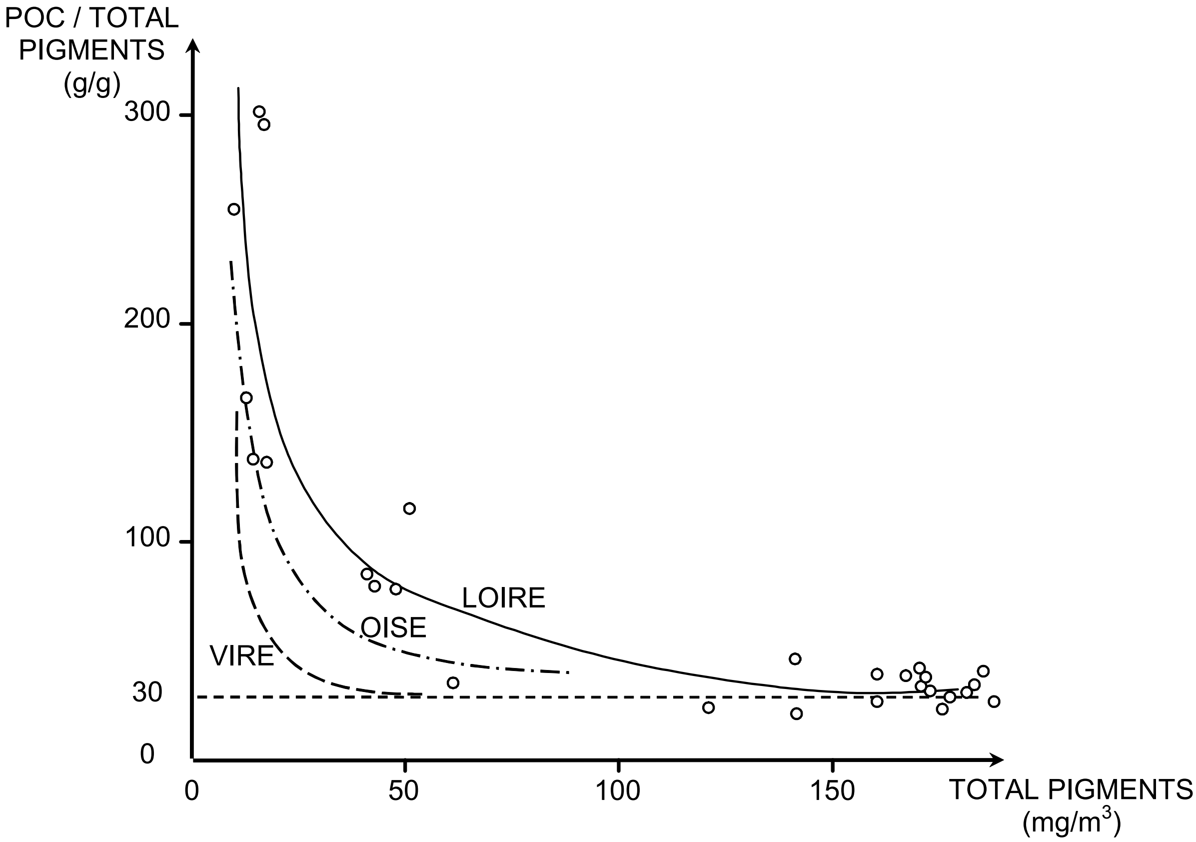


Figure 2.3.a. Relation between the POC / total pigments ratio (g/g) vs. total pigments in the Loire River compared to two other eutrophied french rivers : Oise (Seine tributary) and Vire (Normandy) (data from Dessery *et al.*, 1984 and Meybeck *et al.*, 1988).

Precipitated calcite is commonly observed in rivers and lakes draining carbonated basins (DIC > 35 mg/L), when pH values increase above 8.2 during algal blooms. The eutrophic lower Loire river (France), which drains carbonated rocks and has high DIC levels is a good illustration of seasonal variations of autochthonous POC and PIC (figure 2.3.b). In this basin the winter algal POC is around 0,8 mg C/L - a value attributed to the erosion of benthic diatoms and macrophytes during the high flow period - and the non-algal POC (detrital plus anthropogenic) is much higher (2,5 mg C/L). In summer algal POC reaches 5 mg C/L and dominates non-algal POC (0,5 mg C/L), while the autochthonous PIC reaches 3,6 mg C/L, i.e. precipitated calcite ($CaCO_3$) reaches 30 mg/L (Meybeck *et al.*, 1988). In summer, the sum of autochthonous species (autochthonous PIC and algal POC) dominates the sum of detrital and soil-derived species (detrital PIC + detrital POC+ DOC), however the corresponding fluxes are limited. Summer algal POC is totally degraded in the turbid Loire estuary resulting in severe dissolved oxygen depletion (Meybeck *et al.*, 1988). The precipitation of 2 moles of PIC generates an emission of 1 mole CO_2.

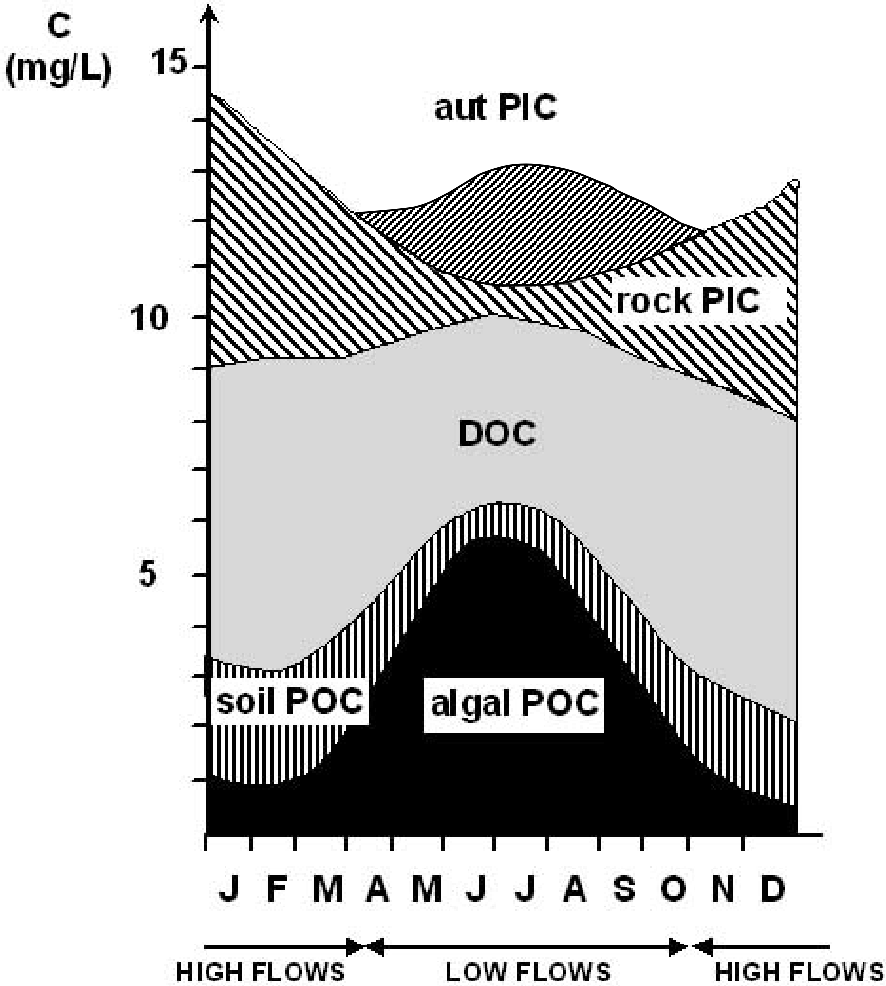


Figure 2.3.b. Seasonal evolution of carbon species in the eutrophied Loire River at mouth. Aut. PIC = summer precipitated calcite, det. PIC = detrital carbonate minerals (data from Meybeck et al., 1988). Autochthonous carbon species are dominating in summer low flows (autochthonous PIC and algal POC) (corrected from Meybeck *et al.*,1988 and Meybeck, 1993b). (The dominant C species, DIC around 24 mg/l, is omitted here).

The labile nature of algal biomass is also well demonstrated in the Elbe case study. Chlorophyll peaks (1999-03) may now exceed 200 µg/L, while they did not reach this level in 1986-89. These phytoplankton peaks are now mostly degraded between the first and third week, i.e. they are correlated with the difference between BOD_{21} and BOD_7, which was not the case in 1986/89.

The attention on eutrophication has been given first on lakes and reservoirs; it is now a major issue in river channels as well: peak chlorophyll values exceed 150 µg/L in many european rivers as the Loire, Seine, Rhine and the Elbe. In most cases, phosphorous has been identified as a limiting nutrient and is now one order of magnitude, and plus, higher than the natural background in these systems. Biogeochemical models indicate that total phosphorous should be reduced to 10 to 20 % of its present level in order to significantly constrain the algal growth (Billen et al. 2005; Garnier et al. 2001; Behrendt et al. 2003).

2.4. Organic carbon distribution and trend: the British example

The export of carbon species at a medium-coarse resolution (10 000 km^2) can also be very heterogenous. For DIC, the control factors are (i) lithology and (ii) water runoff (see also CarboEurope Report). For DOC, control factors are (i) runoff, (ii) soil carbon content. For a relatively homogenous runoff range as for British rivers, the soil organic matter is clearly the dominant factor (Hope *et al.*, 1997) as shown on figure 2.4.a, where specific fluxes (g DOC.m^{-2}.y^{-1}) vary over an order of magnitude with maximum fluxes in N. Scotland, due to the higher occurrence of wetland as peatbogs originating from the last deglaciation.

Estimates of DOC and POC export suggest that in Britain 0.68 ± 0.07 and 0.20 Mt of organic carbon respectively were transported in rivers to tidal waters in the 1993 hydrological year (Hope et al. 1997). The estimates for DOC were based on (i) routine monitoring and (ii) a predictive model linking catchment soil C storage to DOC fluxes; this was used in regions were there was no DOC data available. DOC fluxes will clearly vary from year-to-year due to differences in runoff.

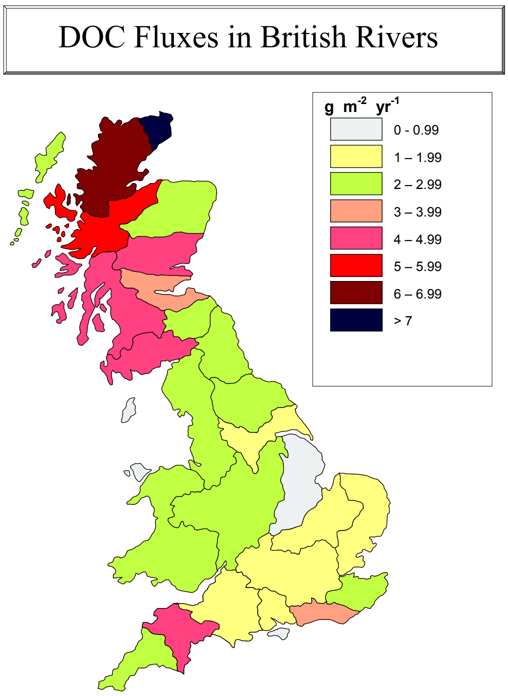


Figure 2.4.a. Regional variation in DOC specific fluxes in British rivers (after Hope *et al.*, 1997). The area weighted average is 3 g.m^{-2}.y^{-1}.

There has been a lot of recent interest in the UK on the rise in DOC concentrations in upland streams and lakes, with much discussion on the possible causes. Freeman et al. (2001b) observed a significant increase over the period 1988-2000 in DOC concentrations in 20 out of 22 sites in the UK Acid Waters Monitoring Network (Figure 2.4.b). Annual increases, which averaged 5.4%, were linked to changes in enzyme activity within organic peat-dominated soils, associated with climate warming (Freeman et al. 2001a). In a larger study of long-term (8-42 year) DOC records from 198 rivers and lakes in the UK, Worrall *et al.* (2004) found that 77% of the sites showed a significant increase in DOC concentrations. Possible drivers for this increase include (i) changes in discharge, (ii) increased N deposition and/or recovery from acidification, (iii) climate warming including the frequency of severe droughts, and (iv) land-use/land management change.

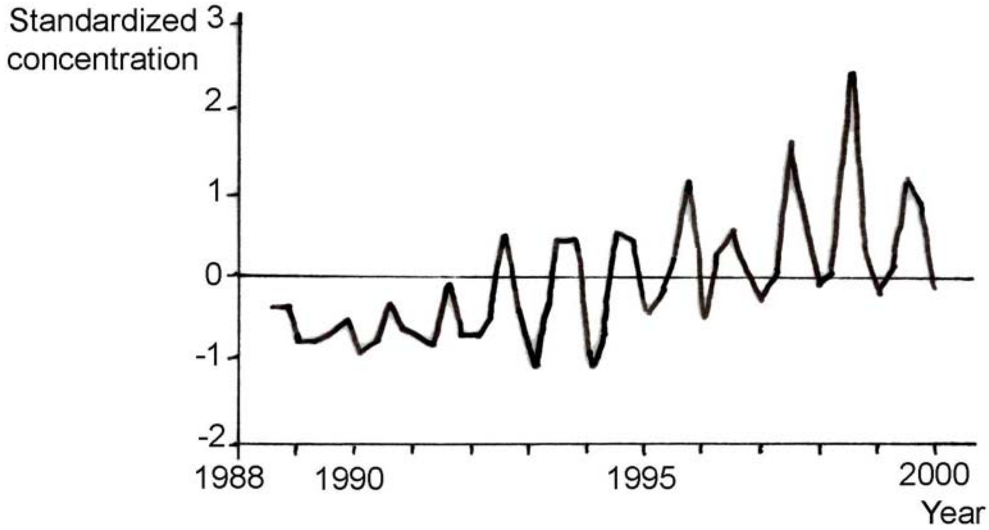


Figure2.4.b. Increase in median standardised DOC concentrations in 11 UK lakes between 1988-2000. A set of 11 UK streams showed a similar temporal trend (after Freeman *et al*., 2001).

2.5. Carbon levels in European rivers

Carbon species data (DOC, POC and HCO_3^-) on European rivers have been collected from multiple sources and published by Meybeck and Ragu (1996). The atmosphere DIC has been estimated from the bicarbonate contents on the basis of Europe's lithology map (Dürr *et al*., 2005): in the Scandinavian shield 100 % of DIC is of atmospheric origin, while in many parts of France, Spain, Adriatic and Aegean coasts, the abundance of limestone is such that only half of the DIC is of atmospheric origin. The total atmospheric carbon has then been computed as TAC = DOC + POC + atm DIC.

Yields of carbon, i.e. carbon exports per unit catchment area, are first linked to the river runoff, as expected (Meybeck, 2005), then, for TAC, to the catchment lithology (figure 2.5).

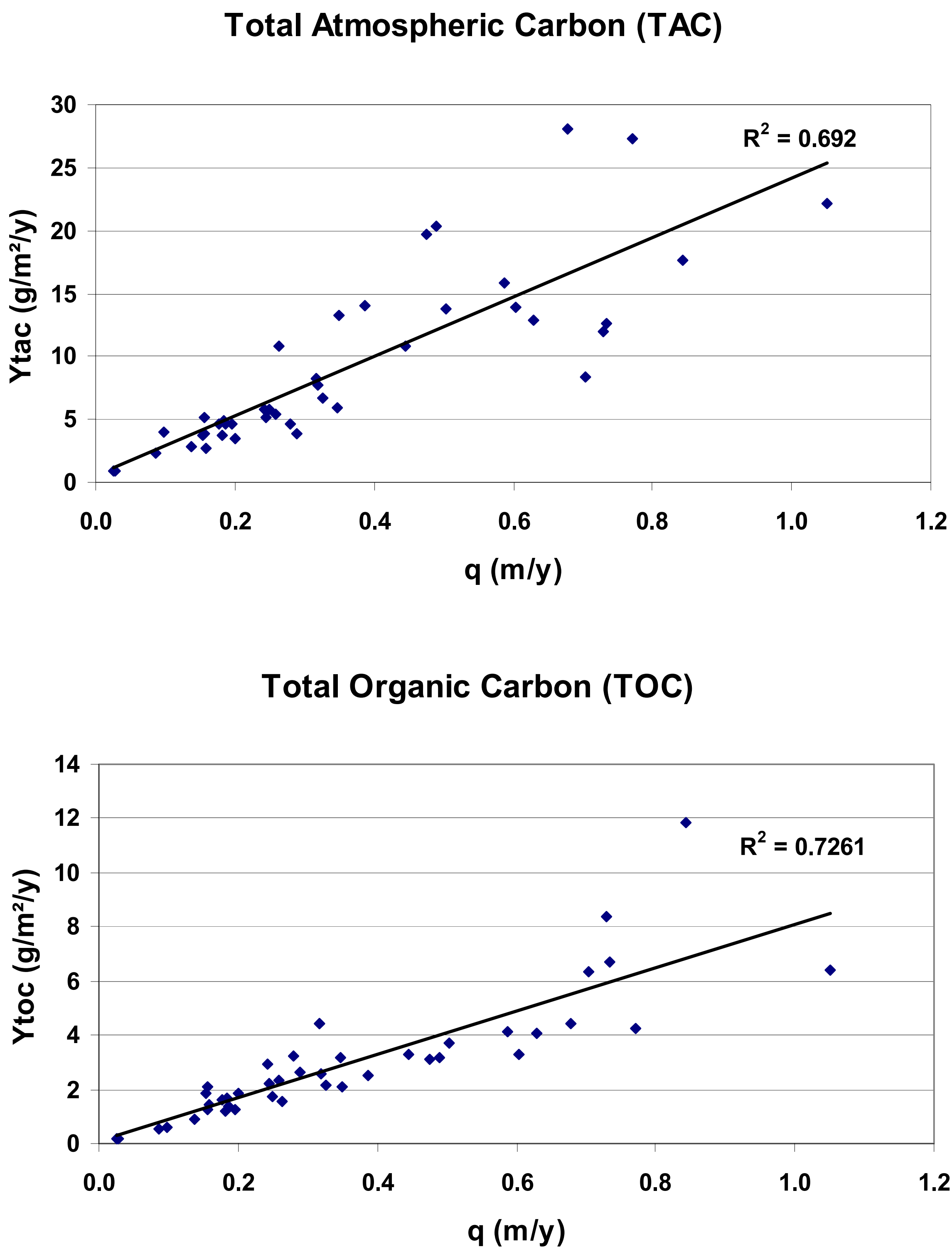


Figure 2.5. Relationship between carbon yields Y_{TOC} and Y_{TAC} (gC exported per m² of river catchment per year) and catchment runoff q (meter per year) for the 43 European coastal types of the CarboEurope Model.

3. Carbon cycling within river systems and GHG origins and pathways

3.1. Mineralisation of organic carbon in aquatic systems

3.1.1. Importance of water residence time

Abiotic processes as adsorption/co-precipitation, flocculation involving transformation and degradation of DOC are relatively limited in aquatic systems relatively to microbial processes (Mulholland *et al.*, 1990). Photochemical degradation can be more important in lakes and reservoirs with long residence time, low turbidity and high DOC, although it is somewhat difficult to separate it from microbial degradation.

In aquatic systems, degradation for a given class of labile DOC, depends on the magnitude of water residence time (figure 3.3.1.a.b.). DOC compounds with short turnover times (i.e. highly labile) relative to hydraulic residence times will be maintained at low and relatively constant concentrations. DOC compounds with long residence times (i.e. highly refractory) relative to water residence times will remain largely unaltered in the aquatic system and their equilibrium concentrations will reflect only the supply rate (Mulholland *et al.*, 1990) excepted if the water residence time is very high as for some very large lakes (up to 10 years and more, see table A.3. in Annex A) or for large fjords.

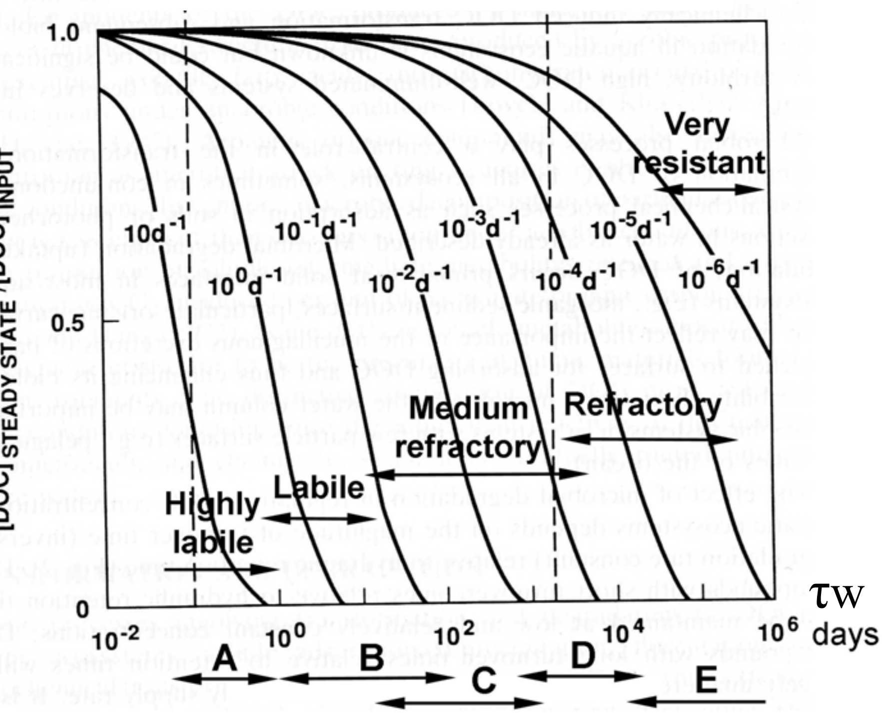


Figure 3.1.1.a. Conceptual relationship between the water residence time (τw) in days and the ratio of DOC concentrations at steady state over DOC concentrations in input to aquatic system for DOC compounds of different degradation rates (in days^{-1}). For a given residence time (τw_i), only compounds with degradation rates similar or greater than τw_i will be present in appreciable amounts (relative to inputs) at steady state. Ranges of residence

times in aquatic systems: A = deltas; B = river channels; C = shallow lakes and reservoirs; D = large lakes and reservoirs; E = stratified fjords (Mulholland *et al.*, 1990).

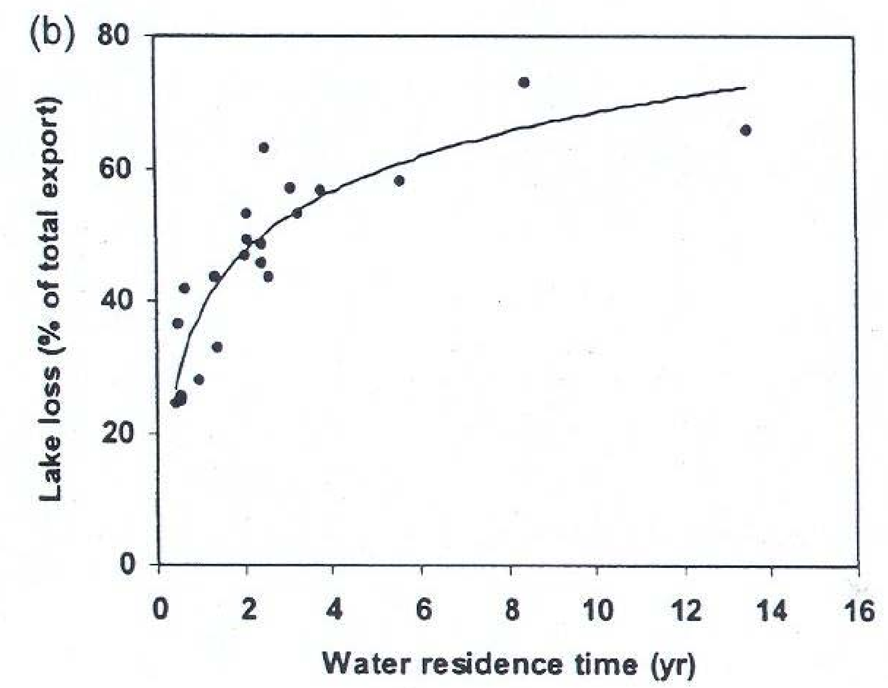


Figure 3.1.1.b Loss of organic carbon (mineralization plus sedimentation) in lakes, as a function of mean water residence time in the catchments (*$r^2 = 0.81$, $P < 0.0005$, $y = 38.03 + 13.16 \ln(x)$*. Calculations are based on 79 536 lakes in 21 catchments in boreal Sweden. Loss of organic carbon in lakes) (Algesten *et al.*, 2003).

3.1.2. The riverine organic carbon transfers

- **Headwaters**

In headwaters streams, the potential sources and sinks of DOC and POC for aquatic systems are quite complex (figure 3.1.2.). DOC sources include primarily organic-rich soil horizon of terrestrial ecosystems, detrital accumulations with aquatic systems and terrestrial-aquatic interfaces such as floodplains wetlands (Mulholland *et al.*, 1990).

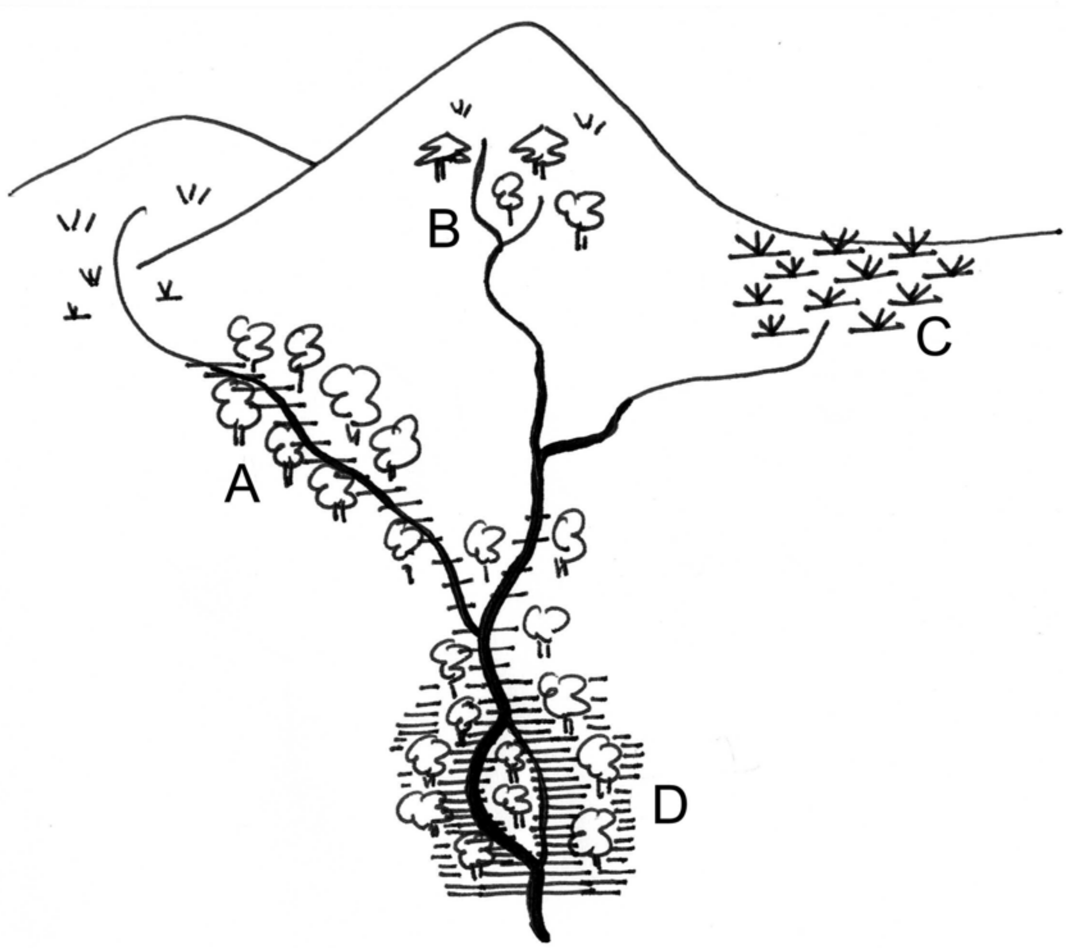


Figure 3.1.2. Schematic position of DOC sources and POC sinks in headwaters. A = lowland riparian soils; B = upland well-drained soils; C = upland wetland; D = floodplain. POC_{net} sinks: A and D; POC_{net} sources: B; DOC_{net} sources: A, B, C; DOC_{net} sink: main channel and open waters (not represented).

Therefore, the DOC and POC exports are highly dependant on water pathways (Mulholland *et al*., 1990). In well-drained soils encountered in headwaters, the groundwater table is generally located well below the surficial soil horizons O/A and B which are the richest in DOC. During the low water stages streams are mostly fed by these organic-poor groundwaters. During storm periods, overland flow and hyporheic flows remobilize and leach POC and DOC which increase in these streams. In upland wetlands, particularly those containing peat layers the groundwater table is always away in contact with organic-rich layers even during drier periods. In lowland riparian soils, the organic-rich soil layers are drained by groundwaters and even by floodplain surficial drains during the high water stages and are rich in DOC while during low flows, the water table may be located at the limit of such horizons.

- **Flooded area of middle and lower river courses**

In floodplains, the organic carbon levels and lateral transport is highly dependant on the water level (Mulholland *et al*., 1990). During low water stages, the DOC originates from a restricted part of the main river channel associated with the hyporheic flow and the normal riparian zone. At medium-high water periods, the open floodplain extends and includes new organic sources and some closed area of the flood plain may be inundated by the groundwater rise (see figure 1.1.4, left part). These portions of floodplain soils are naturally much richer in organic matter. At the very high flows even natural levees and islands are inundated by river overflow. As such natural floodplain is highly dynamic and spatially variable.

The processing of organic carbon in wetlands and riparian areas is always associated with the emissions of Green Houses Gases (CO_2, CH_4, N_2O) that depend on the extend of wetlands, the primary sources of DOC in natural river systems, the oxic/anoxic conditions of these aquatic systems and their hydraulic residence time (Mulholland *et al*., 1990). It is therefore essential to delineate for each river system, the exact proportions and location of these wetlands and their variations in time. For the smaller stream orders, the flooding may last few hours to few days while for bigger rivers, it may last few months. Interannual variations may also be important particularly under Mediterranean climate.

3.1.3. Particulate organic carbon degradation in estuaries

In most types of estuaries, the riverine organic material is processed thus resulting in GHG emissions of CO_2, CH_4 and NO_x (figure 3.1.3.a). The discharge of organic wastes from coastal cities to estuaries may enhance these GHG emissions. Estuarine limits are fluctuating with riverine hydrology, tides and currents. We consider here the mixing of 1‰ sea water and 90% sea water with freshwaters as the upper and lower limits of estuaries (respectively A, B and C for very high river flows in figures 1.1.5.a to f). When the water residence time is high ($> 10^{-1}$ y), the organic carbon at steady state correspond to less labile and more refractory species. The bacterial activity is enhanced in more turbid waters that characterize the macrotidal estuaries. As a result, the oxygen levels in such systems are often below 2 mg/L when TOC river inputs originate from algal production or organic wastes. In deep stratified fjords, deep waters are permanently anoxic.

The accumulation of POC-rich fine particles occurs at different locations in estuarine systems (see figures 1.1.5.a to f). In macrotidal estuaries, there can be bottom layer of fluid mud (TSS > 10 g/L) and fine particles may accumulate in tidal flats. In deltas, this accumulation is observed in the outer estuary (termed prodelta by sedimentologists), in coastal lagoons and fjärds, it is found in the least dynamic zones of the inner estuary. Fjords are trapping all river particulates even the finest material. Karst inputs of suspended matter are limited and they are generally dispersed by coastal currents.

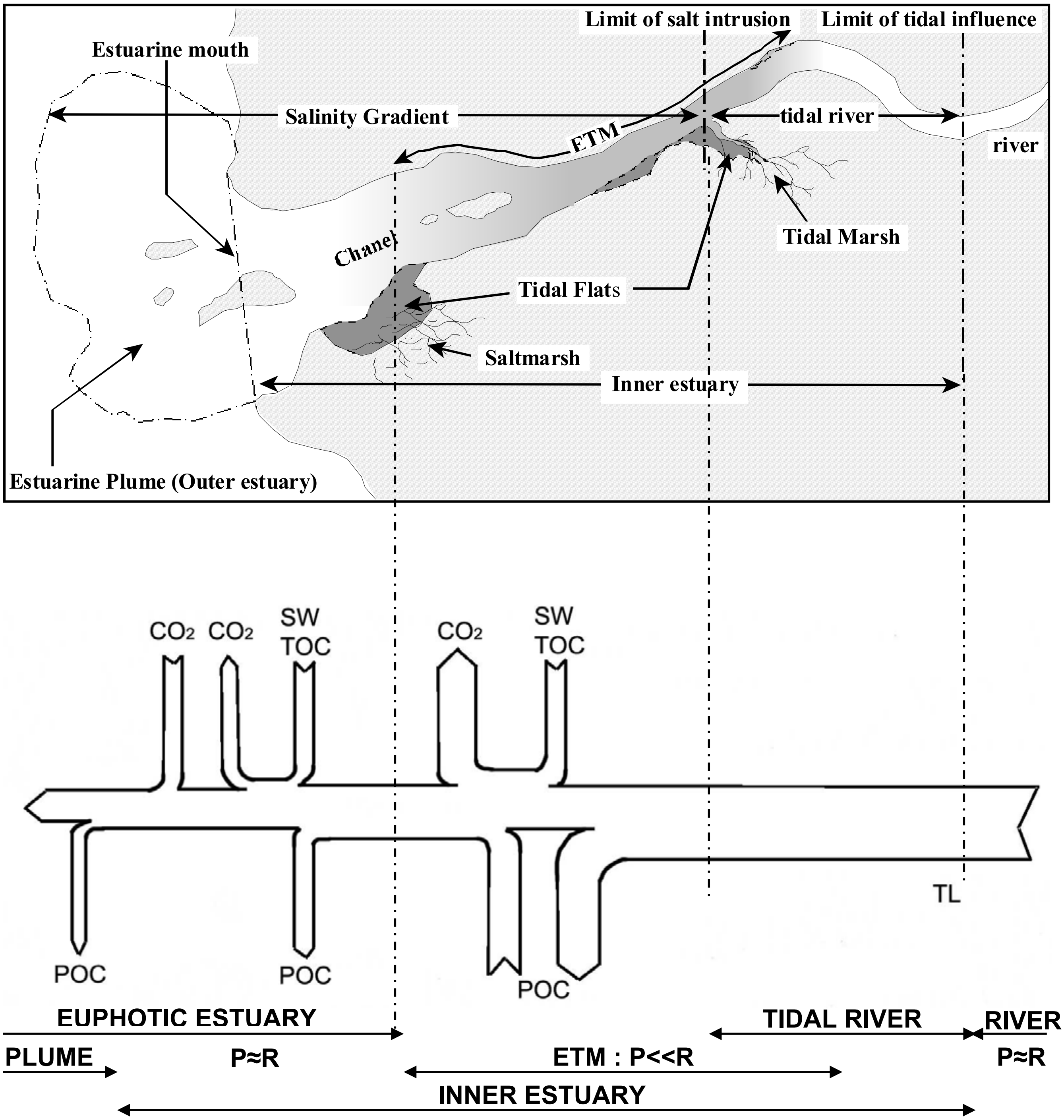


Figure 3.1.3.a. Schematic representation of an idealized tidal estuary with estuarine turbidity maximum (ETM) and sewage waste waters inputs (modified from Abril and Borges, 2004).

Estuaries are known as net heterotrophic (Gattuso *et al*., 1998), particularly those on macrotidal coastlines (Atlantic, North Sea) which have long residence times and high turbidities. The figure3.1.3.a. is a schematic representation of main carbon cycling processes for a turbid macrotidal estuaries, the most studied type of estuary in western Europe for normal river flows. In the turbid estuary (TSS > 100 mg/L), the respiration is largely dominant over the primary production and the residence time of waters may reach several months. Most of these estuaries also receive large amount of sewage waters from coastal settlements. In the lower eutrophic estuary photosynthesis becomes possible and production and respiration are close to equilibrium and there is a net POC sedimentation.

During very high flow events, freshwaters are forced downstream the estuarine system and a brackish plume is observed far on the shelf on top of sea water. The retention of POC is shifted from the lower estuary to the outer estuary. The transfer of POC from river to coast takes much longer than the DOC transfer and can be pulsed. The average reference time of particulate in such systems ranges from 0.5 to 5 y.

The organic carbon mineralized in estuaries is mostly POC that originates from soils, freshwater phytoplankton and sewage. DOC is both consumed by bacteria and released from POC and sediments. Besides some exceptions, DOC sources and sinks are often balanced or insignificant compared to the river input (Abril *et al.*, 2002). Two major variables control the percentage of POC mineralized in tidal estuaries: (1) the origin and resulting lability of the riverine POC, algal and sewage POC being much more bioavailable than soil POC; as a consequence, estuarine POC mineralization increase with the POC river concentration, when the contribution of sewage POC increase (case of the Scheldt in Belgium); (2) the residence time of water and particles in estuaries (figure 3.1.3.b).

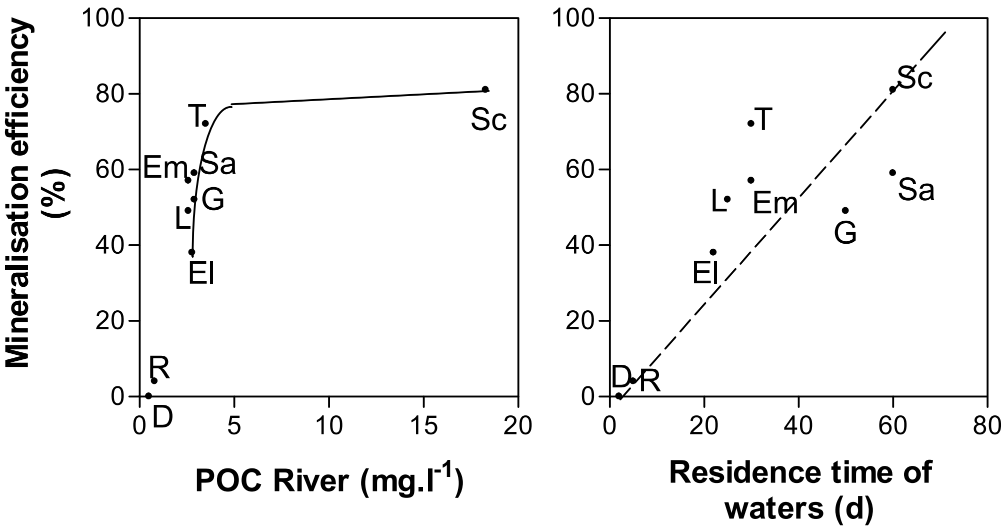


Figure 3.1.3.b. Percentage of riverine POC mineralized in some European tidal estuaries as functions of POC concentration in rivers and residence time of waters in estuaries. D=Douro (Portugal); R=Rhine (NL); El=Elbe (Germany); L=Loire (France); G=Gironde (F); Em=Ems (NL/Germany); Sa=Sado (P); T=Thames (UK); Sc=Scheldt (Belgium) (Abril *et al,.* 2002).

3.2. Gaseous transfer of CO_2 and CH_4 in aquatic systems

3.2.1. Gas exchange processes and their control

Eddy covariance techniques and CO_2 exchange

Eddy covariance techniques used for monitoring energy and mass exchange between atmosphere and surfaces has been of limited use between freshwater systems and the atmosphere. Most research has been conducted in the interface between i.e. wetlands/ peatlands and only a few on lakes. Only two studies have been published concerning the exchange of CO2 between lakes and the atmosphere utilizing eddy covariance technique (Anderson *et al.*, 1999 and Eugster *et al*., 2003). Andersson *et al.* (1999) presents data from Williams Lake, (USA) and Eugster *et al*. (2003) presents from Toolik Lake (U.S.A.; Alaska) and Soppensee (Switzerland). Both papers have only discontinuous data (few days). Groups in Finland (Ojala *et al*.) and Sweden (Jonsson *et al*.) have continuous monitoring during the ice free season in boreal and sub-arctic lakes. Applications of these techniques to reservoirs, rivers and estuaries are not known to us, except at tropical, non-European sites (Guérin et al. 2007).

Gas transfer at the air-water interface

The flux of a gas across the air-water interface (F) can be computed according to:

$$F = k\Delta \mathrm{C} \qquad (1)$$

where ΔC is the air-water gradient of the gas and *k* is the gas transfer velocity (also referred to as piston velocity).

It is well established that k depends on a variety of variables but the most important one is turbulence at the air-water interface (in the case of sparingly soluble gases such as CO_2, CH_4, N_2O and O_2 the critical variable is turbulence in the liquid phase). In open oceanic waters, the gas transfer velocity of CO2 is usually parameterized as a function of wind speed because wind stress is the main generator of turbulence in these systems.

The gas transfer velocity can be studied along the river-estuary continuum using tracer mass balance approaches or by the simultaneous determination of F and ΔC. The latter approach seems more adequate along the river-estuary continuum since it provides estimates at the time-scale characteristic of the processes controlling k (minute to hour), while tracer mass balance approaches provide values at longer time scales (day to week). Floating chamber and micro-meteorological approaches can be used to measure F directly at the required time scales characteristic of the processes controlling k. Floating chamber methods are easy and relatively cheap to apply, while micro-meteorological approaches disrupt less turbulence at the air-water interface, although being more difficult to deploy in the field and more expensive than chamber methods.

Along the river-estuary continuum, various processes besides wind stress contribute to water turbulence (figure 3.2.1.a and table 3.2.1), hence, k plotted against wind speed shows a large range of values (figure 3.2.1.b).

In rivers and streams, k mainly depends on turbulence generated by water current shear that is variable from one system to another and also modulated by depth (table 4.2.1). In these systems, the contribution of wind stress is usually low to nil due weak wind speeds and strong fetches limitation (table 3.3.1). This explains the large range of k values encountered at wind speeds below 2 m s-1 (figure 3.2.1.b).

In estuaries, the lowest k values for a given speed are found in small and micro-tidal estuaries due to a strong fetch limitation and a negligible contribution of tidal currents to water turbulence (table 3.3.1 and figure 3.2.1.b). The highest k values for a given wind speed are encountered in large and macro-tidal estuaries where the contribution of tidal currents to water turbulence is highly significant and where fetch limitation is low (table 3.2.1).

Lakes seem to show the less scatter and variability in the k-wind relationships, along the river-estuary continuum (figure 3.2.1.b). Wind speed in these systems seems to be the main generator of water turbulence (table 3.2.1). The k-wind relationships in lakes are further modulated by fetch-limitation and convective cooling. The latter process has not been documented in the other systems and can be probably neglected in highly turbulent systems such as streams and macro-tidal estuaries.

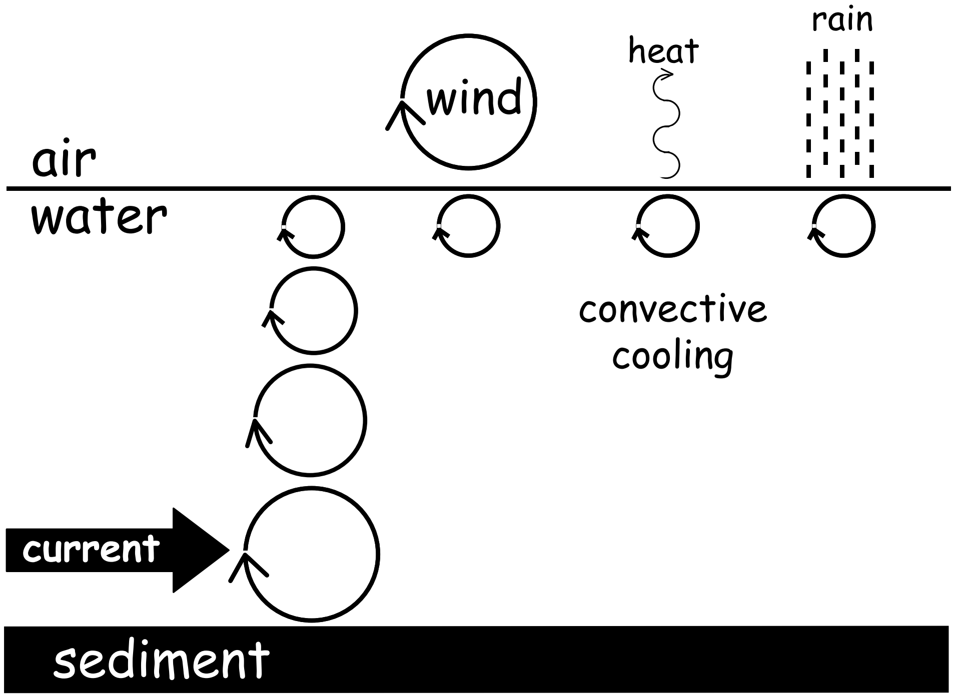


Figure 3.2.1.a. Conceptual scheme of the main processes controlling turbulence at the air-water interface in fresh-water and estuarine environments (Borges).

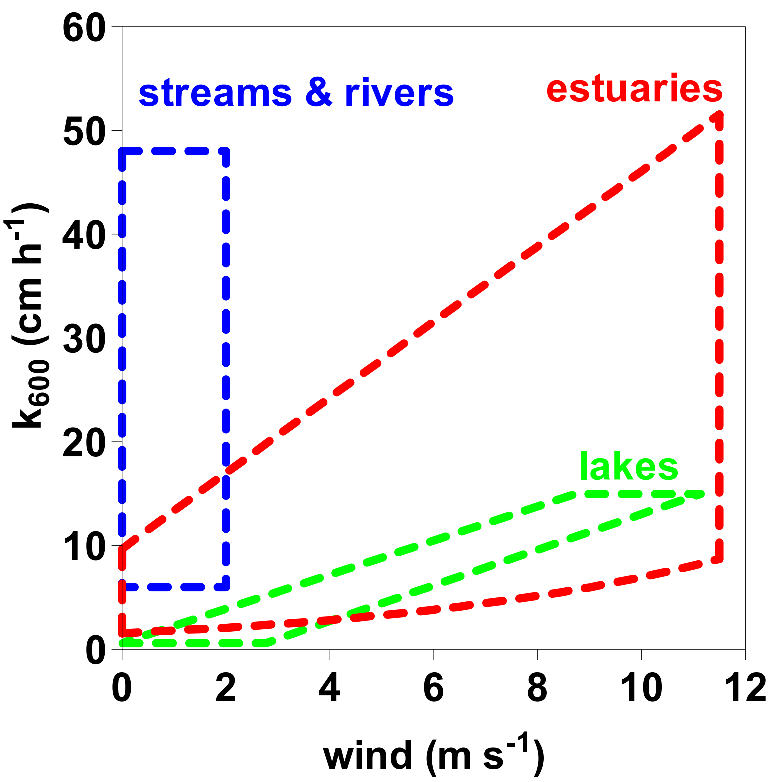


Figure 3.2.1.b. Distribution of the gas transfer velocity (k_{600}) in fresh-water and estuarine environments as a function of wind speed. The polygons enclose the maximum and minimal values of k_{600} in streams and rivers (based on Wanninkhof et al. 1990), lakes (based on Frost & Upstill-Goddard 2002) and estuaries (based on Kremer et al. 2003 and Borges et al. 2004a,b)

	Streams	Rivers	Lakes	Inner estuaries	Outer estuaries
k_{600} intensity	+++	+	++	++++	+++
Wind stress	0	+	++	+++	++++
Water current	+ to ++++	+	0	0 to ++++	+
Convective cooling	0	0	++	0	0
Rain	+	+	+	+	+
Fetch limitation	++++	+++	++	+ to +++	0

Table 3.2.1. Relative variation of the gas transfer velocity (k_{600}) and of the contribution of various processes to k_{600}, in various systems in freshwater and estuarine environments. ++++ corresponds to very high and 0 to nil.

3.2.2. Measurement techniques of CO_2 and CH_4 transfers

Bog-pool system

The bog-pool system in regions without permafrost is presented on figure 3.2.2.a. Emissions of CO_2 and CH_4 can be measured by floating chambers. Direct transport of DOC, CH_4 and CO_2 from peat to overlaying pool waters is difficult to measure at such scale.

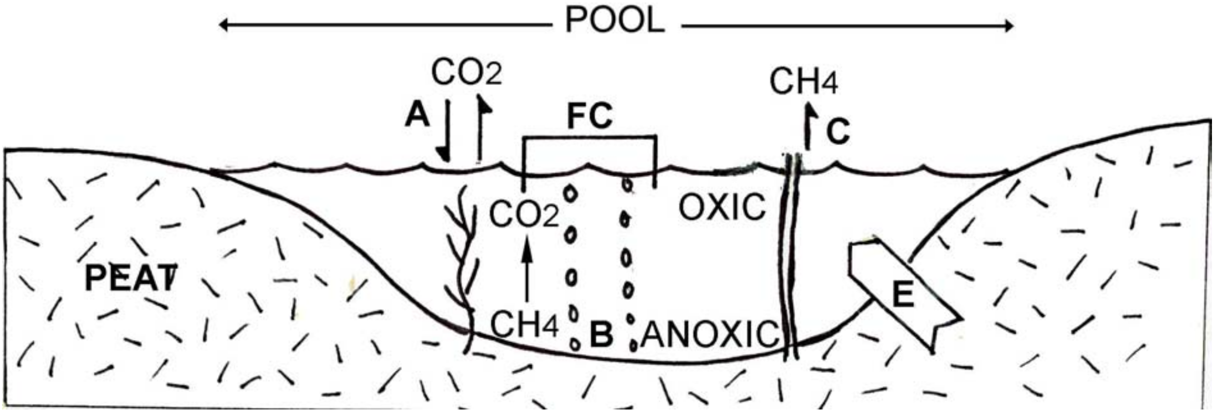


Figure 3.2.2.a. Wetland bog-pool system: main processes that control C and GHG fluxes. A = photosynthesis/respiration; B = CH_4 ebullition and its evasion, measured in floating chamber (FC); C = CH_4 production associated with macrophytes; E = transport of DOC, CH_4 and CO_2 from peat.

Peat land stream channels

Many peatlands contain a large number of 1st order streams (i.e. without tributaries) which progressively increase in size (two first order streams meet to form a second order stream etc.) and complexity into drainage systems in which a wide range of processes affect GHG concentrations and emissions. In peatland systems stream water surface area typically make up between 0.2-0.6 % of the total catchment area. These streams are acidic and organic-rich and vary in character between deep, slow flowing channels to fast flowing, shallow and rocky sections, where rapid degassing of GHG's occurs (particularly CO_2) (figure 3.2.2.b). Many of these stream systems are extremely "flashy", i.e. they show strong temporal variability with high flow being characterised by low pH and high DOC concentrations. Fluxes of DOC are therefore associated with storm events. Field measurements include (i) floating chambers and (ii) upstream/downstream budgets of all carbon species.

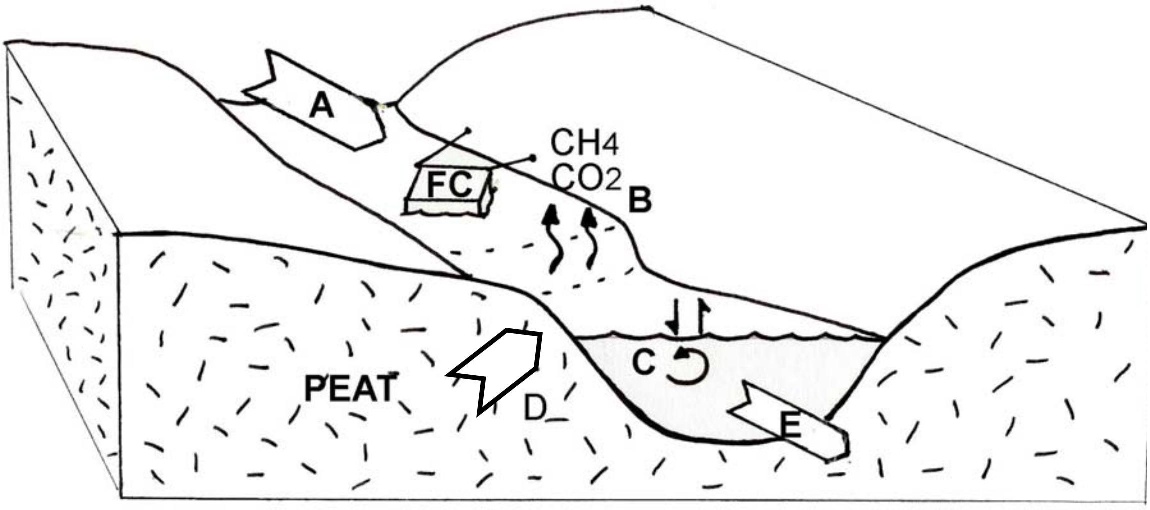


Figure 3.2.2.b. Peatland stream channels: main processes that control carbon and GHG fluxes. A = Upstream inputs (DOC/DIC/POC/CO_2/CH_4); B = CO_2 evasion (major) and CH_4 evasion (minor) due to flow turbulence; C = CO_2 in-stream processes (minor); D = lateral inputs from peat; E = downstream outputs; FC = floating chamber.

CO_2 evasion in headwaters

There is a limited amount of evidence that suggests that the source of CO_2 lost by degassing from water surfaces in peatlands is allochthonous. For example, in a study of CO_2 concentrations in peatland soils and an adjacent stream, Hope *et al.* (2004) found that the CO_2 concentrations in shallow peats and riparian soils varied in a similar way to the stream. It is also known that vertical diffusive transport of CO_2 in waterlogged peat is a slow process (Clymo and Pearce, 1995) and that because of differences in hydraulic conductivity, lateral water movement in peat appears to be more important than vertical transport (Chason and Siegel, 1986). It is therefore likely that CO_2 produced by decomposition of soil organic matter (SOM) is transported laterally by mass flow to the drainage system where it is lost to the atmosphere. In many peatlands there is clearly a strong hydrological connectivity between the drainage system and the soil CO_2 reservoir.

As for other water bodies, the emission rates of gaseous forms of carbon stream surfaces are primarily controlled by (1) the difference in gas concentration between water and the atmosphere, and (2) by the degree of turbulence. Stream turbulence in natural systems is caused by the roughness of the stream bed, gradient, channel constrictions and flow rate. Many peatland streams occur in incised gullies with narrow (5-10m) flood plains resulting in them being relatively sheltered from the wind, in contrast, to extended surface waters such as lakes, pools, reservoirs, estuaries strongly influenced by wind shear and wave action, which have a major control on gas transfer. There has also been considerable importance attached to the role that diffusion and bubble transport play in gas transfer at the stream-atmosphere interface. This is relevant to streams where bubble formation is extremely common under many flow conditions and will result in rapid vertical gas transfer compared to diffusive loss. This causes problems with some of the methods and assumptions that are made in calculating gas transfer coefficients for stream surfaces (but less so for lakes).

A number of barriers exist to the routine measurements of gaseous carbon emissions in surface waters in peatland landscapes and upscaling the values to the whole catchment. Firstly a range of quite different methods exist for estimating vertical gas transfer, some of which have been imported from oceanography and are more applicable to lakes rather than streams. In addition, the strong spatial variability in $epCO_2$ and $epCH_4$ makes upscaling to catchment scales difficult and many methods are also unsuitable for use in the remote parts of the catchment, where vertical emission rates are typically highest.

Several direct and indirect methods exist for measuring the loss of gaseous C (evasion) from water surfaces; for a comprehensive review see MacIntyre *et al*. (1995). Many of the methods originate from studies at the ocean-atmosphere interface. They include (i) modelling approaches such as the surface renewal and stagnant film models, (ii) the use of free floating chambers and enclosures and (iii) the injection of deliberate gas tracers such as propane and SF_6.

In fast flowing small streams changes in the ratio of a volatile and non-volatile tracer in the study reach can be used to measure k, the gas diffusion coefficient (Hope et al., 2001). The non-volatile tracer is used to quantify any additional groundwater input over the study reach. Tracer gases must satisfy a number of criteria; in particular they should be biologically and chemically inert and have comparable solubility to the gas of interest.

Free floating chambers have been widely used to measure gas fluxes from lakes and large river estuaries (McMahon & Dennehy 1999). Gas fluxes are calculated by measuring the change in gas concentration over time, although the use of chambers has been criticised because they exclude wind shear and therefore modify surface conditions. However, in upland streams the deployment of free-floating chambers is an attractive method, because they are robust, light and transportable. Affects on surface flow can be minimised by orientating the chamber into the current and wind shear is less of a problem in the sheltered environment of a typical stream channel. Turbulence in peatland streams is largely produced by the roughness of the streambed suggesting that the impact of the chamber will be less important than in open waters.

Carbon budgets and CO_2 and CH_4 evasion in lakes and reservoirs

Several methods should be combined to assess carbon and GHG budgets in lakes and reservoirs; they concern measurements in the water column, in sediment pore waters and at the air-water and sediment-water interfaces (figure 3.2.2.c). Dissolved CO_2 and CH_4 profiles are obtained from the water column (W1 to W3). River inputs of carbon species should be controlled (e.g. at a monthly time step or less) at river inlets (RI) and lake outlet (RO). Carbon evolution in sediments (POC and PIC) from long core analysis (C) can be very informative on the long term evolution (100 yr) of the lake and/or on the evolution of the reservoir since impounding. Surficial cores preserving the water-sediment interface are now commonly used to measure CH_4 profiles in pore waters.

Various types of chambers are now used: dark and transparent floating chambers (FC_1 and FC_2), gas bubble traps installed at the sediment-water interface (IC), at the oxic-anoxic interface –when existing (GC_1)- and at the air-water interface in both littoral (GC_1) and pelagic zones (GC_2). The combination of all approaches remains exceptional.

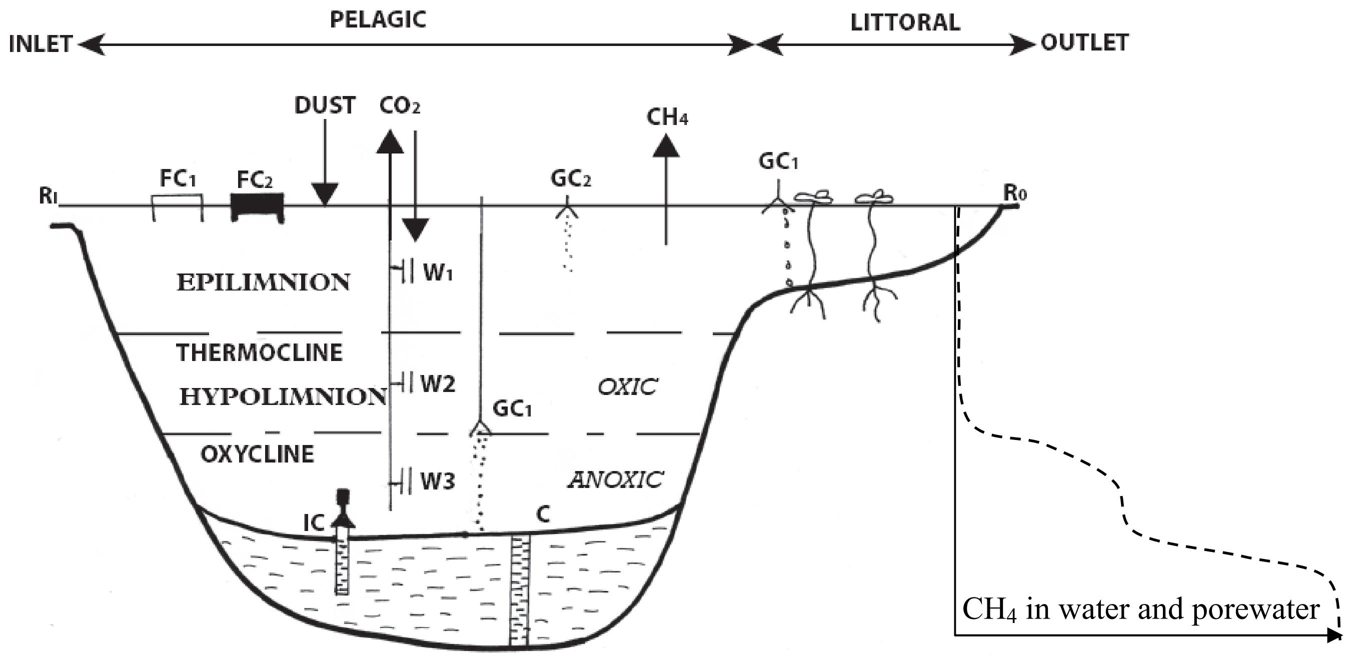


Figure 3.2.2.c. Methods for carbon and GHG budgets in lakes and reservoirs. $FC_{1,2}$: transparent and dark floating chambers. $GC_{1,2,3}$: gas collectors. IC: interface core, C: long core. R_I, R_O: river input/output (DOC, POC, DIC, CO_2). $W_{1,2,3}$: water samples at various depth.

3.2.3. Gas transfer velocity in estuaries

As for rivers and lakes, the flux of CO_2 across the air-water interface in estuaries can be computed according to:

$$F = \alpha\, k\Delta pCO_2 \qquad (2)$$

where α is the solubility coefficient of CO_2, ΔpCO2 is the air-water gradient of pCO_2, *k* is the gas transfer velocity of CO_2 (also referred to as piston velocity) (see appendix F).

Very recently, Borges *et al.* (2004a) established a linear relationship between *k* and wind speed at 10 m height (U_{10}) in three European estuaries (Randers Fjord, Sheldt and Thames) with contrasting physical characteristics, based on CO_2 floating dome measurements (figure 3.2.3.a.). Although the floating method has been dismissed by several workers (e.g. Liss and Merlivat 1986; Raymond and Cole 2001), Kremer et al. (2003b) and Borges et al. (2004b) provide convincing evidence that if the floating chamber does not disrupt too much the underlying water turbulence, then the corresponding gas transfer measurements should be reasonable estimates of those from the undisturbed surface. Also, the floating chamber technique provides gas transfer velocity estimates at short time scales (minute), compared to the tracer mass balance approaches (hour to day), and, thus, at the characteristic time scale of the processes controlling *k* in estuaries. Thus, the work of Borges et al. (2004a) constitutes the first ever investigation of *k* in different estuaries using a consistent and comparable method.

Figure 3.2.3.a. shows a distinct increasing trend of *k* values with wind speed in the three estuaries, in addition *k* values for macrotidal estuaries are higher (Thames) and lower in the microtidal “Randers Fjord”. Furthermore, the slopes of the linear regression functions are

similar in the Scheldt and the Thames, and, significantly higher than the one in the Randers Fjord. The y-intercept of the linear regression function in the Thames is higher than those of the Randers Fjord and the Scheldt.

In figure 3.2.3.b., the slopes of the regression functions of the 3 estuaries studied by Borges et al. (2003a) plus those investigated by Kremer et al. (2003a) are plotted on a semi-logarithmic scale against their respective estuarine surface area. This clearly shows a significant effect of fetch-limitation on *k* that induces a decrease of the slope of the *k* versus wind speed regression functions with increasing fetch-limitation. The non-linearity of the relationship suggests that the effect of fetch limitation is disproportional stronger in small estuaries (< 30 km^2). However, this figure should be interpreted with caution since besides the estuarine surface area, fetch-limitation is expected to depend on the shape of the estuary (funnel, oval, narrow or wide linear channel, ...) and on the relation between the direction of prevailing winds and the direction of main axis of the estuary (parallel or across).

In conclusion, the different y-intercepts and slopes of the linear regressions of k can be explained as function of wind speed in estuarine environments: the higher contribution of tidal currents to water turbulence in macro-tidal estuaries compared to micro-tidal ones increases the y-intercept; the higher fetch-limitation in small estuaries compared to larger ones decreases the slope. The net CO_2 budget of estuarine plumes remains to be studied. The documented estuaries provide contrasting results. In the Scheldt, which is highly eutrophic and which receives organic wastes, the plume is a net CO_2 emitter, while the Amazon plume is a net of CO_2.

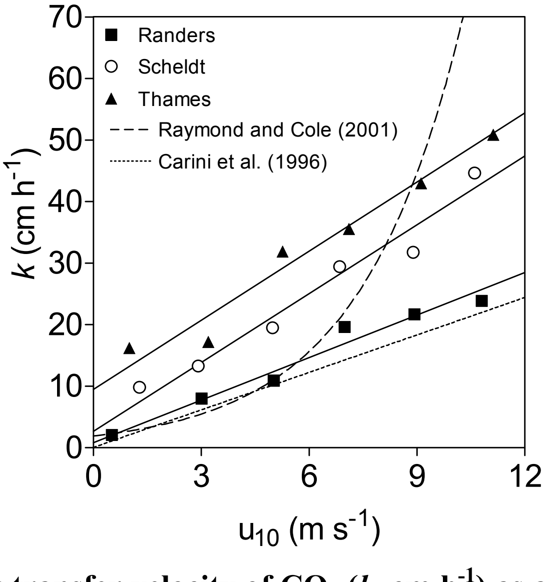


Figure 3.2.3.a. The gas transfer velocity of CO_2 (*k*, cm h^{-1}) as a function of wind speed at 10 m height (u_{10}, m s^{-1}) in three studied estuaries. The data were averaged over wind speed bins of 2 m s^{-1}. The long-dashed line corresponds to the Raymond and Cole (2001) relationship and the short-dashed line corresponds to the Carini *et al*. (1996) relationship (see appendix K, figure K.2 for details).

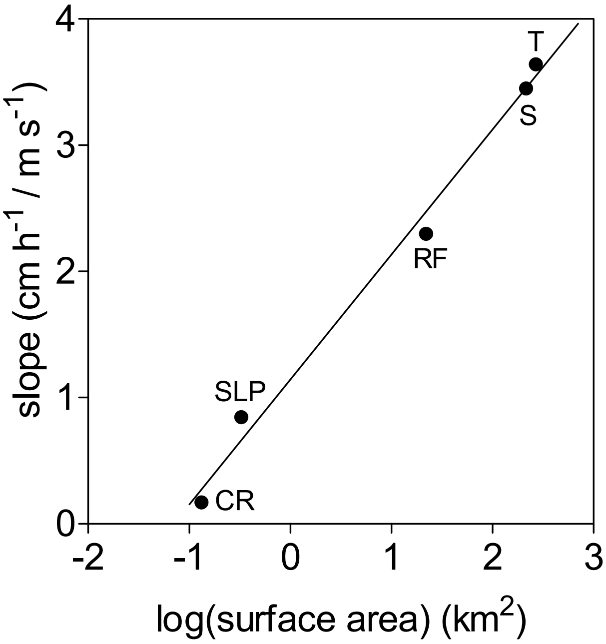


Figure 3.2.3.b Influence of wind-fecht. Slope of the Model I regression functions of *k* versus wind speed from the Thames (T), Scheldt (S), Randers Fjord (RF), Childs River (CR) and Sage Lot Pond (SLP) versus the logarithm of the estuarine surface area (new data on Sinnamary and Gironde are confirming this relation).

3.3. Green House Gas emissions in natural and man-made water bodies

Carbon flows through rivers to estuaries has been intensively studied in terms of lateral fluxes from the continents to the oceans (CarboEurope Report 8/2004/Specific Study 5). At the global scale, the order of magnitude of these organic and inorganic carbon fluxes is close to 1 $PgC.y^{-1}$. The CO_2 emissions from rivers and estuaries is a more recent topic of interest (Richey et al. 1982; Frankignoulle *et al.*, 1998; Cole and Caraco, 2001; Richey *et al.*, 2002) and the CH_4 emissions in rivers and estuaries is also recent (Bange, 1994; Middelburg *et al.,* 2002). CO_2 and CH_4 emissions in lakes and reservoirs are more commonly studied (Cole et al. 1994; Bastviken et al. 2004?), although the corresponding regional or global fluxes are less addressed. The denitrification (transformation of nitrate into gaseous N_2 and N_2O) that occurs in aquatic systems (Seitzinger, 1990; Garnier et al. 1998) is also a provider of GHG.

Most rivers, lakes reservoirs, and estuaries are indeed supersaturated in CO_2, CH_4 and N_2O with respect to the atmospheric equilibrium and are therefore net sources of GHG gases to the atmosphere. These concentrations and fluxes result from multiple factors (i) the waterscape and the relative occurrence of wetlands, floodplains; river mainstem, lakes, reservoirs, extension of land/ocean interface, (ii) the different types of these subsystems (e.g. lake trophic types, estuarine dynamics, stream order), (iii) the net production/respiration (P/R ratio) balance in each theses aquatic subsystem, (iv) the anthropic impacts on these. It is not yet possible to present a complete account of these multiple interactions: each river system is actually unique. The general picture is presented into 3 main sections: (i) the headwater processes, (ii) the river main stream and estuary GHG, (iii) the lake and reservoirs. A tentative integration of all these components is then presented.

During its travel from headwaters to the coastal zone, the river carbon is intensively recycled by biological and chemical processes, in a different way in each natural or man-made filter the water passes through (see chapter 1). In addition, gas exchange of CO_2 and CH_4 with the atmosphere occurs all along this continuum with an intensity that may vary by several orders of magnitude between the different filters. As a first consequence, **sites of high GHG degassing are not necessarily sites of intense GHG production, but can also be located just downstream of a site of production on land or in the aquatic system itself.** A second consequence is that high GHG concentrations in waters do not necessary reflect in situ aquatic production (if production occurs upstream) and do not necessary imply high GHG degassing (if gas exchange is physically limited). Also, gas concentrations in a given system can be relatively low, when for instance production and degassing are simultaneously high. This can be the case when degassing is enhanced by physical processes, and results to short residence time of gases in the water. The dynamics of GHG in aquatic systems must then be apprehended as the results of a complex interaction between sources, lateral transport, residence time and degassing intensity.

3.3.1. CO_2 and CH_4 emissions from headwaters and peatland streams

General functioning

Peat soils cover vast areas of the northern boreal and temperate regions of the world primarily as relatively flat lying or undulating interconnected bog-pool systems (e.g. Finland and Estonia) or, as in countries like the UK, blanket peat which typically occurs in the headwater regions of upland river catchments. It is estimated that approximately 40% of global terrestrial carbon is stored in peatlands (Gorham 1991; 1995) and the stability of this C pool has significant consequences for atmospheric concentrations of CO_2. A detailed account of European peatlands can be found in the CARBOEUROPE discussion paper "EU Peatlands: Current Carbon Stocks and Trace Gas Fluxes".

Temporal Variability of GHG emissions

Since relatively few measurements have been made on gaseous C emissions from peatland streams **we currently know very little about temporal variability**. However, it is known that $epCO_2$ concentrations vary seasonally with the highest concentrations in summer and lowest in winter (Dawson et al. 2002). Initial data from the Moor House catchment in N England indicates that evasion rates are directly related to stream flow. This suggests that vertical fluxes from the stream surface will be highest during major discharge events at the end of dry summer periods.

Spatial (intra-site) Variability of GHG emissions

Streams draining peatlands are supersaturated with respect to CO_2 and CH_4 as demonstrated for U.K. (Dawson *et al*., 1995, 2002, 2004; Hope *et al*., 2001, 2004). Figure 3.3.1.a, left shows that $epCO_2$ values are typically highest in the upper peat-dominated parts of the catchment (often close to the source area) and decrease downstream as the relative importance of peat soils decrease and mineral soils increase. These relationships have also been found at larger spatial scales. The variation in $epCO_2$ (and $epCH_4$; data not shown) from the Trout Beck catchment in N England (figure 3.3.1.a, right) shows that many of the highest values occur close to the stream source or in small tributaries. Peats, which contain soil atmosphere CO_2 concentrations up to 3-4% (Hope et al. 2004), therefore act as significant CO_2 reservoirs and when connected to the drainage system produce "hotspots" of vertical CO_2 and CH_4 evasion to the atmosphere.

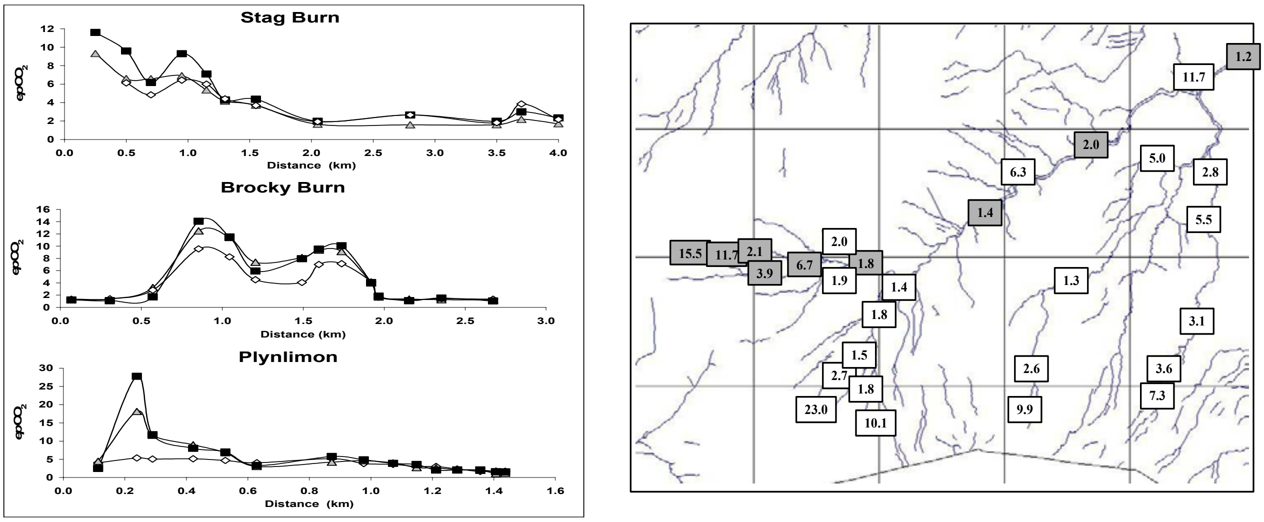


Figure 3.3.1.a. Spatial structure of $epCO_2$ in UK peatland streams. Left: longitudinal changes in $epCO_2$ downstream from the source of 3 peatland streams sampled on 3 separate occasions (after Dawson *et al*., 1995, 2002); right: spatial variation in $epCO_2$ values in the Trout Beck catchment (N. England 16/17.10.03; each square represents 1 km^2; unshaded values represent tributaries).

Significant spatial changes in CO_2 evasion have also been measured within catchments, with streams often showing evasion rates increasing upstream, with the highest values at or near the peatland source area (figure 3.3.1.b).

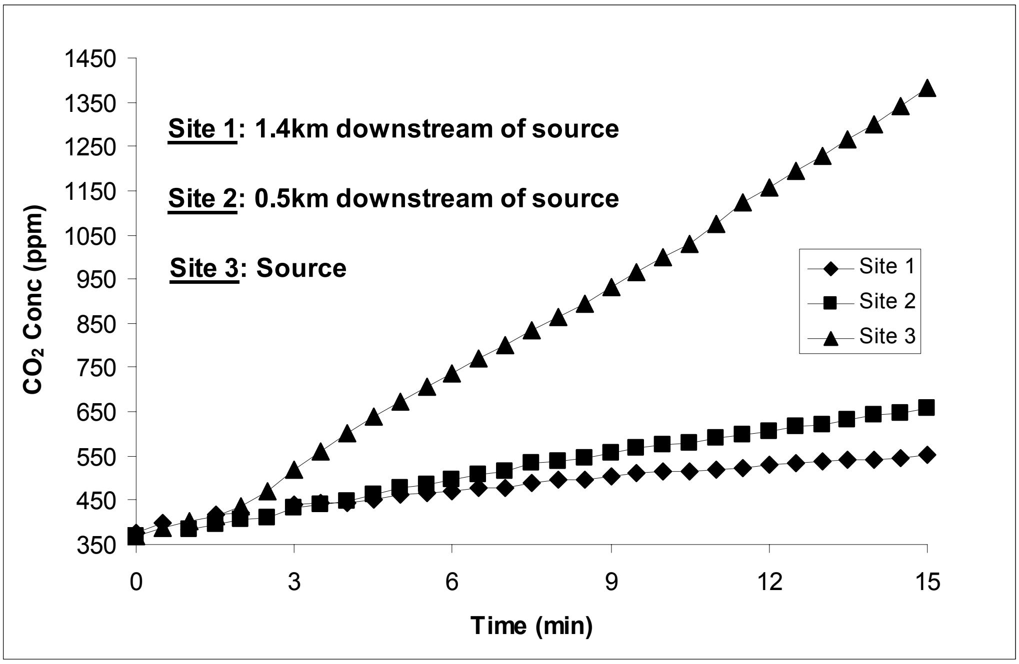


Figure 3.3.1.b. Spatial changes in CO_2 emission rates into floating chambers in the source region of the River Severn, mid-Wales (data collected on 16.11.04; Billett unpublished).

Spatial (inter-site) Variability of GHG emissions

Table 3.3.1a shows some first data from to quantify the vertical emissions of CO_2 and CH_4 measured using floating chambers.

The initial results suggest that instantaneous evasion rates for CO_2 (per unit area of stream surface) are comparable to those measured by Hope et al. (2001) in NE Scotland, suggesting that they are an important flux term in the peatland carbon cycle.

Catchment	Date	Instantaneous CO_2 Evasion Rate ($\mu g\ C\ m^{-2}\ s^{-1}$)
Cottage Hill Sike (N. England)	19/20 Aug 04	337-960
Rough Sike (N. England)	19/20 Aug 04	108-284
Black Burn (C. Scotland)	07 Sept 04	129-320
Loch More Tributary (N. Scotland)	04 Nov 04	42-152
Afon Hafren (Mid Wales)	16 Nov 04	47-268

Table 3.3.1.a. Instantaneous CO_2 emission rates measured using floating chambers in UK peatland streams (Billett unpublished). Rate are calculated for the stream water mirror.

Lateral and Vertical Fluxes of GHG

The presence in peatlands of streamwater supersaturated in CO_2 and CH_4 suggests that gaseous C is lost by degassing from stream surfaces to the atmosphere. Although, there are few published whole catchment values (summarised in table 3.3.1.b) of evasion from peatland surface waters. This CO_2 evasion would be significant and in many cases comparable to other flux terms in the peatland C cycle. For example, lateral fluxes of DOC in peatland drainage systems are of the order of 20 g m^{-2} yr^{-1}, rated to drainage area (Gorham, 1995; Billett *et al.*, 2004). **Vertical loss of CO_2 by surface degassing is typically 1-2 orders of magnitude greater than downstream lateral losses of free CO_2** (Hope *et al.*, 2001). Degassing and downstream losses of CH_4 appear to be relatively unimportant in terms of C transport (table 5.1.2), although it has more importance in terms of radiative forcing.

Location	Evasion Flux (g C m^{-2} yr^{-1})	Reference
Black Burn (C Scotland)	CO_2 – 4.6 CH_4 – 0.004	Billett et al. (2004)
Brocky Burn (NE Scotland)	CO_2 – 14.1 CH_4 – 0.01	Hope et al. (2001)
North Slope of Alaska (25 lakes; 4 rivers)	CO_2 – 11.8 CH_4 – 0.25	Kling et al. (1991; 1992)

Table 3.3.1.b. Published gaseous C evasion rates from peatland surface waters calculated on a catchment area basis for comparison lateral flux terms such as DOC.

3.3.2. Temporal variations of GHG in lakes

Seasonal variations of pCO_2 in temperate dimictic lakes may reach a factor of three as observed for the Mirror Lake (New Hamsphire) by Cole *et al.* (1994). In such lakes, two CO_2 peak are observed in autumn, before the winter freezing of lakes and in April/May during the snow melt period and the spring lake overturn. Yet, the CO_2 increase may start in the water column one month before, while the lake is still ice-covered (figure 3.3.2.a).

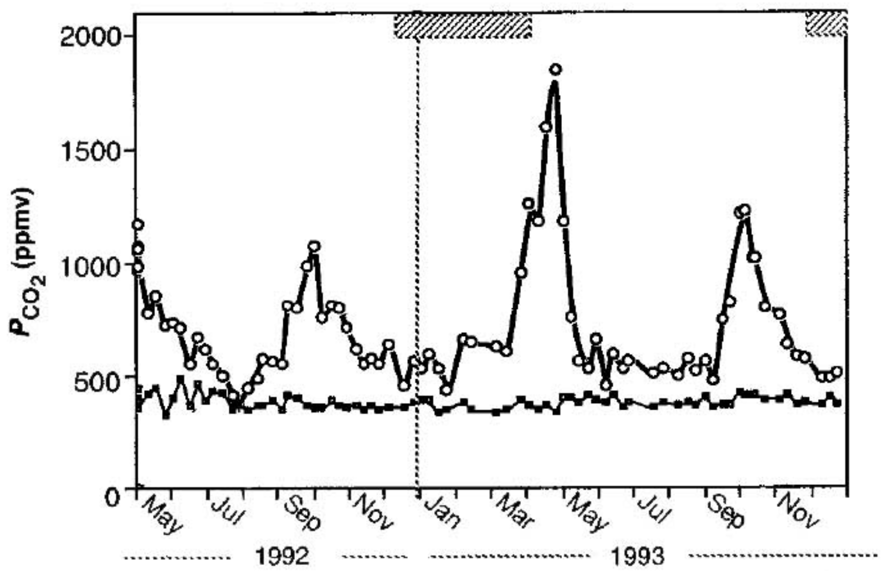


Figure 3.3.2.a. Seasonal cycle of direct measurements of the P_{CO2} in the surface water of Mirror Lake (circles) and in overlying air (squares), showing persistent supersaturation. Mirror Lake is as soft water lake in New Hamsphire; ppmv, parts per million by volume. The hatched areas represent ice cover (Cole *et al*., 1994).

CH_4 fluxes from lakes occurs through three different pathways: (1) diffusion at the water-air interface; (2) ebullition of gas bubbles formed in anoxic sediments and (3) temporal storage in stratified lakes followed by rapid degassing after the seasonal overturn (Bastviken et al. 2004). In general, these three types of methane fluxes are the same order of magnitude in lakes and are higher in small systems (figure 3.3.2.b).

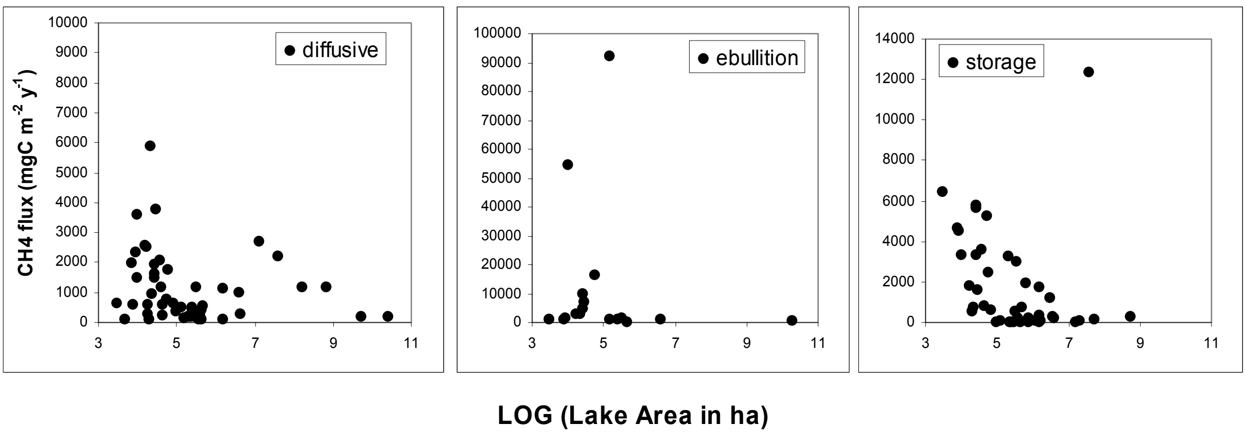


Figure 3.3.2.b. Methane fluxes in world lakes, according to the lake size (data from Bastviken et al. 2004)

3.3.3. Carbon cycling and CO_2 and CH_4 emissions in lower rivers and estuaries

The lateral transfer of dissolved organic and inorganic carbon in rivers is fully developed in a companion report (CarboEurope 8/2004/Specific Study 5). We are focusing here on GHG emissions.

CO_2 distribution

Both rivers and estuaries are supersaturated in CO_2 (Kempe 1982; Frankignoulle *et al.*, 1998; Cole and Caraco 2001). However, these two kinds of ecosystems differ in terms of carbon cycling and in the origin of this CO_2. In river waters, the median pCO_2 value is around 2 700 µatm, i.e. 7 times the atmospheric equilibrium (figure 3.3.3.a and Appendix H). This super-saturation is caused by both CO_2 inputs from soils and groundwaters and by internal CO2 generation in waters by respiration of DOC and POC.

Rivers courses are often characterized by a succession of net autotrophic and net heterotrophic sections. In temperate European rivers, a positive relationship is found between pCO_2 and DOC (Figure 3.3.3.b), which is the result of two processes: either CO_2 and DOC originate from the same soil source and/or CO_2 is produced by internal respiration on DOC within the river waters. The second process is likely dominant when sewage-derived DOC is important like in some UK rivers and Belgian small rivers (Neal *et al.*, 1998; Abril *et al.,* 2000).

In autotrophic river sections some atmospheric CO_2 is converted to organic carbon which is transported laterally and fuels respiration downstream in heterotrophic river sections or in estuaries. Undersaturations of river waters with respect to the atmosphere have been reported in some eutrophic rivers (Neal *et al.*, 1998). This is however relatively uncommon because, in order to create a net CO_2 influx to the water, net autotrophy must be intense enough to first consume the dissolved CO_2 advected from soils and groundwaters and, second, create CO_2 under-saturation in the water.

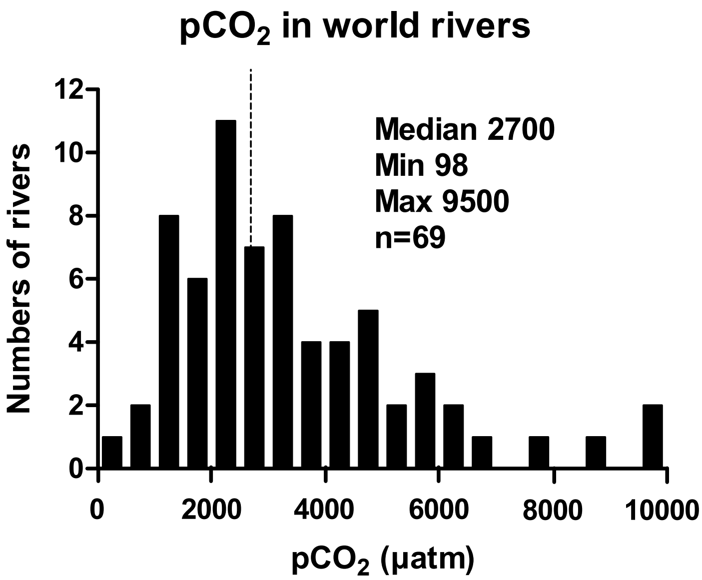


Figure 3.3.3.a. Frequency distribution of pCO_2 in world rivers (Data from Appendix J_1)

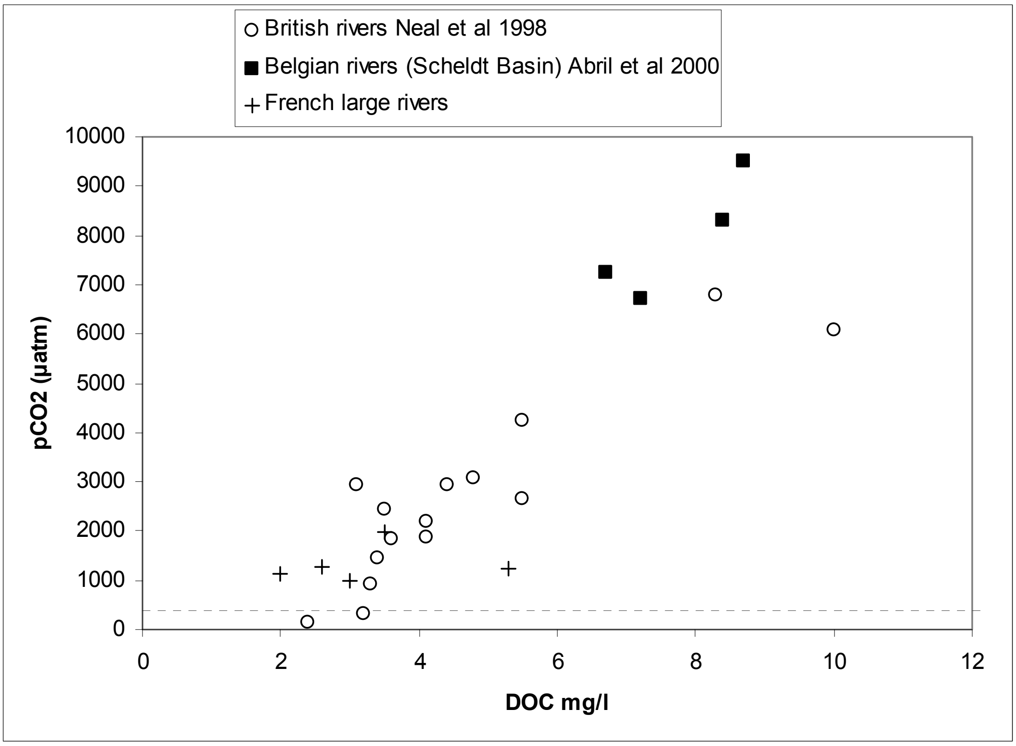


Figure 3.3.3.b. Relationship between the yearly average pCO2 and DOC in some temperate (non-peat) European rivers (Abril et al. in prep).

CH4 distributions in rivers and estuaries

Methane concentrations in freshwaters main channels are almost always higher than the atmospheric equilibrium. Median Saturation ratio for reported data so far are about 5 800% in rivers (0.145 µmol.l^{-1}, figure 3.3.3.c and Appendix H) and 2 500% in European estuaries (Middelburg *et al.*, 2002). Spatial and temporal variability is extremely high, over two to three orders of magnitude. This high variability is due to the fact that most of this methane is not produced in the rivers and estuaries themselves, but rather advected from surrounding areas. This was described in detail by the pioneer work of Richey *et al.* (1988), for the Amazon system, where methane found in the river main stem is due to lateral transport from large floodplains. Similarly, high methane concentrations in streams are attributed to soils and groundwaters inputs (Jones and Mulholland, 1998; Hope *et al.*, 2001, see previous section). Methane emissions to the atmosphere are moderate in estuaries (0.02-0.5 mmol.m^{-2}.d^{-1}, see Appendix H), except in vegetated tidal flats and marshes, particularly those at freshwater sites, where sediments may be CH_4-saturated (Appendix H). Finally, aerobic methane oxidation in rivers constitutes a significant methane sink in river waters.

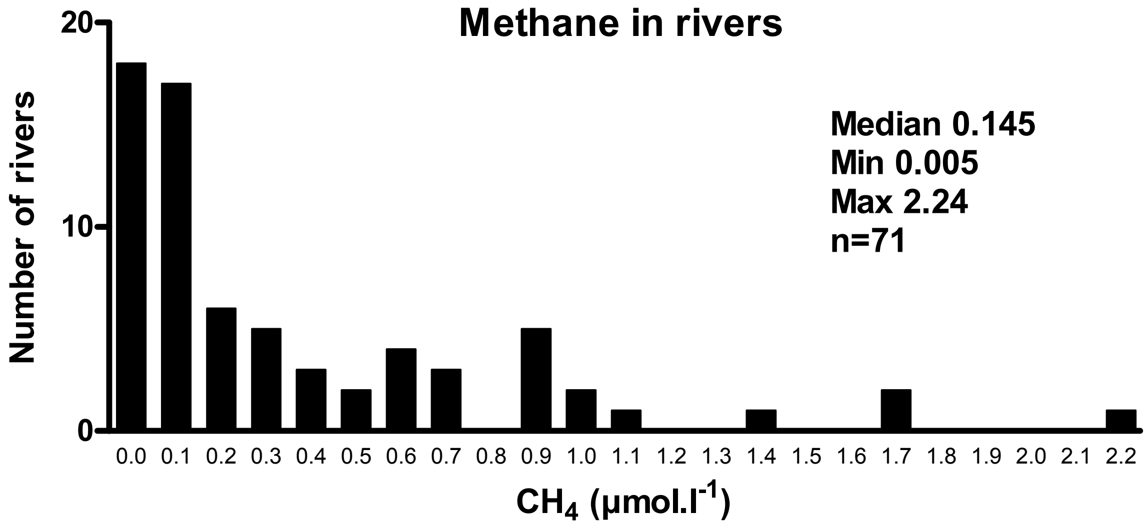


Figure 3.3.3.c. Frequency distribution of the CH_4 concentrations reported so far in rivers. The median concentration of 0.145µmol.l^{-1} corresponds to saturation ratio of 5 800% with respect to the atmosphere (data from appendix H).

CO_2 in eutrophic rivers

The highly eutrophic Loire constitutes an ideal large river-estuary continuum for studying the links between lateral and vertical carbon and internal autotrophic and heterotrophic processes. Eutrophication of the river waters leads to the development of phytoplankton blooms in the river, summer Chl a exceeding 100 µg.l-1. As a result, in summer, more than 80% of the POC transported laterally to the estuary is algal POC (Meybeck et al. 1988; Figure 3.3.3.d).

Beside this intense carbon fixation by phytoplankton, the under saturations in CO2 in the Loire river are very restricted in time (4 months per years, figure 3.3.3.d) with a summer CO2 influx one order of magnitude lower than the winter out flux. **On average over the year the eutrophic Loire River is still a net CO_2 source**, although probably a net autotrophic system that receives large amounts of soil CO_2.

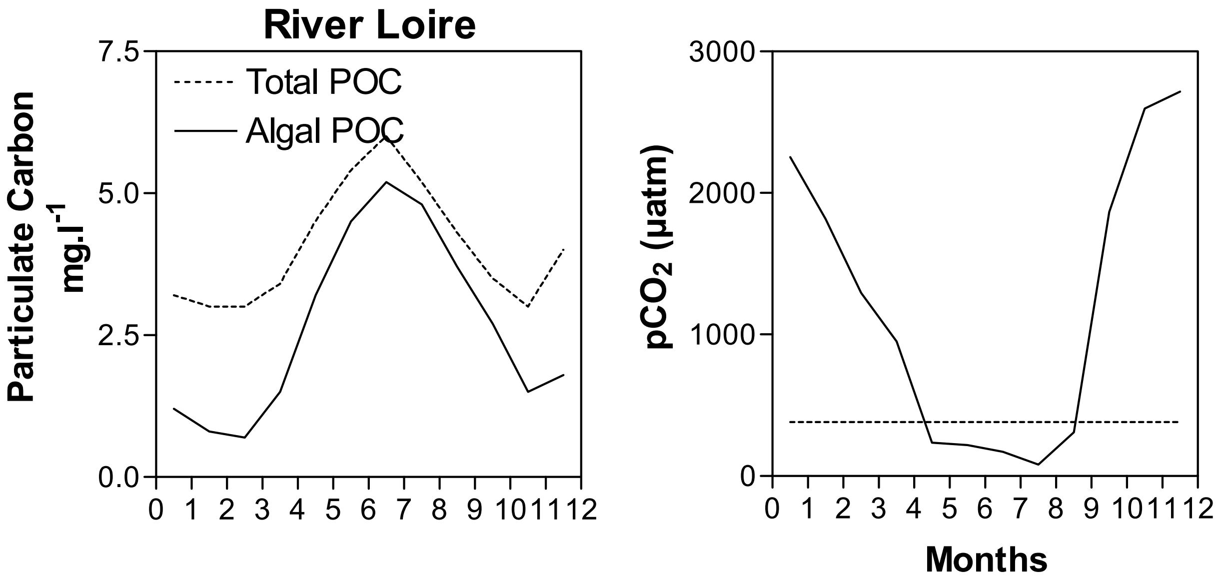


Figure 3.3.3.d. Case of the eutrophic Loire River. Left panel from Meybeck *et al.* (1988), Right panel calculated using pH and temperature from Moatar et al (1999), and total alkalinity from Grosbois *et al.* (2000); Abril et al., in prep.

3.3.4. CO_2 and CH_4 transfers in estuaries

The macrotidal estuaries are by far those for which the GHG transfers have been the most studied, in particular during the Biogest project (Scheldt, Rhine, Loire, Gironde etc.)

Longitudinal profiles

In the turbid Loire estuary, all the algal POC produced upstream is mineralized which results to extremely high pCO_2 and problems of hypoxia particularly in summer (figure 3.3.4.a). Most of the CO_2 emissions from the estuary to the atmosphere can be quantatively explained by the algal POC carried by the river and lost in the estuary. When considering the overall Loire system, the total CO_2 emissions (river main stem plus estuary) is 8 times lower than the lateral C flux. The CO_2 emissions/ POC export ratio of the Loire is is 0.5, a low value compared to 10 for the Amazon were floodplains are very extended (Richey *et al.*, 2002).

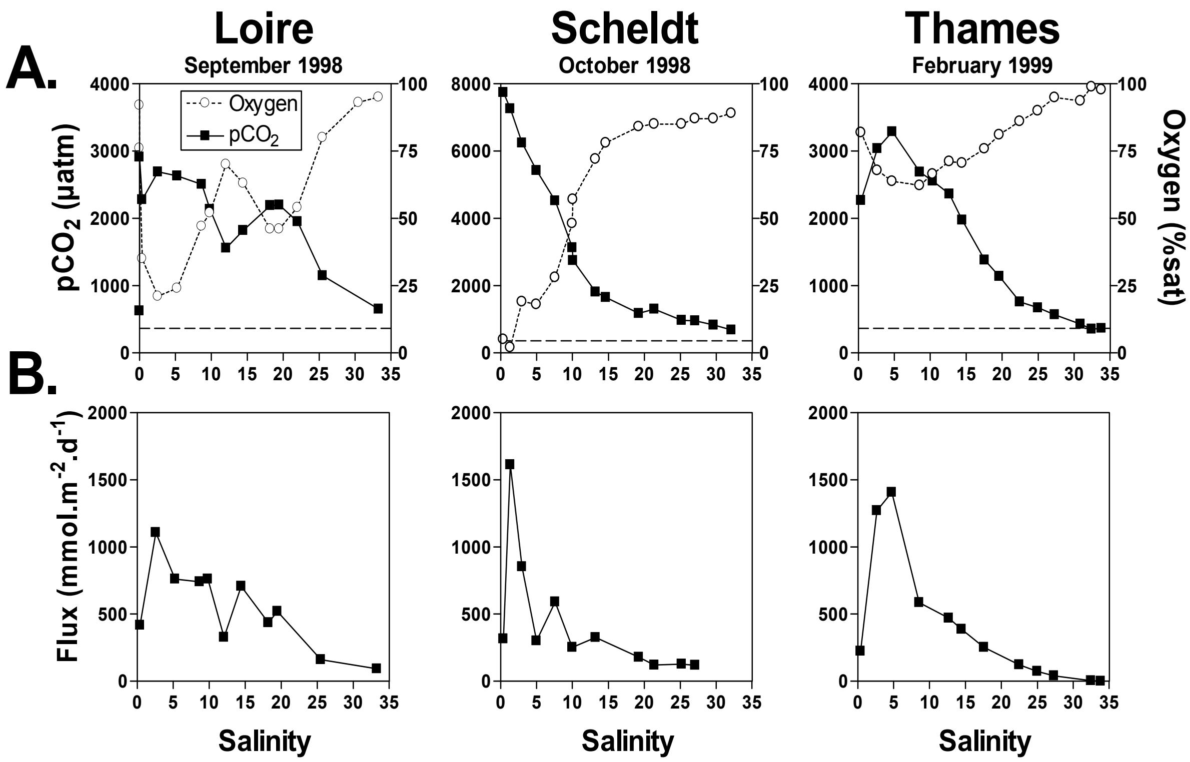


Figure 3.3.4.a. Typical distributions versus salinity of: A. pCO_2 (black scares in µatm) and Oxygen (open squares %Saturation) in surface waters, showing the net anti-parallelism between the two parameters. B. water-air CO_2 fluxes (floating chamber method) measured in three European estuaries studied during the BIOGEST project (Frankignoulle *et al.,* 1998; Abril *et al*., 2003). Doted lines are the atmospheric pCO_2 value of 365 µatm. Note the different scale for the Scheldt estuary.

CH_4 emissions from subtidal estuarine waters result in majority of river and lateral inputs from river and marshes followed by physical ventilation (Upstill-Goddard *et al.,* 2000; Abril and Iversen 2002; figure 3.3.4.b), rather than intense in-situ production in the sediments, where oxic and suboxic conditions dominate (Abril and Borges, 2004). Aerobic methane oxidation in estuarine waters and surface sediments is also a significant methane sink, particularly in the estuarine tubidity where methanotropic activity is enhanced (Abril et al. 2007).

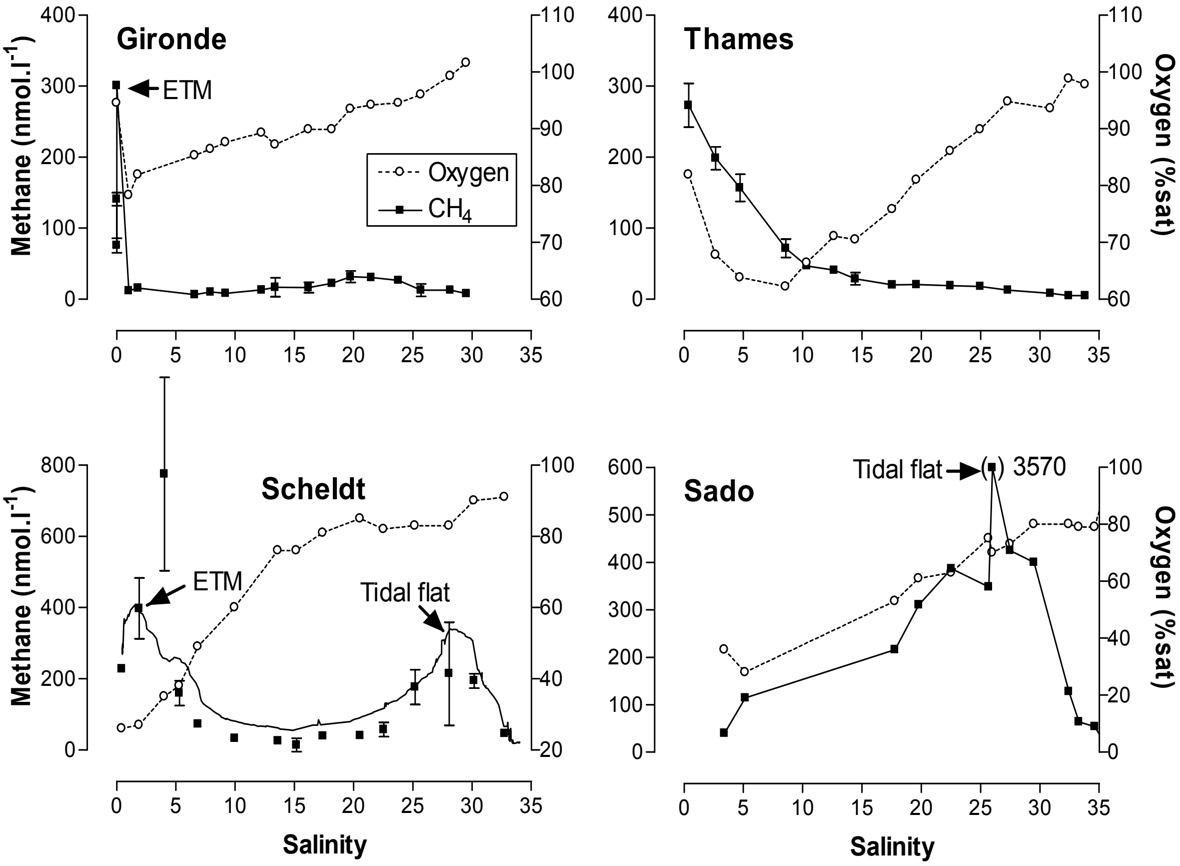


Figure 3.3.4.b. Some examples of non-conservative methane (black squares) and oxygen (open circles) distributions versus salinity measured in European estuaries studied during the BIOGEST project (Middelburg et al. 2002). Gironde (France) October 1996; Thames (UK) February 1999; Scheldt (Belgium/the Netherlands) December 1996, the line is from continuous measurements with an equilibrator; Sado (Portugal) September 1997.

Seasonal variability

pCO_2 seasonal variability in estuaries can be important. It depends on the river hydrology, and on the balance between the bacterial respiration and the phytoplankton production. Very contrasted profiles can be observed as for the Loire (figure 3.3.4.c). At winter high flows, the water residence time and the estuarine respiration are limited and the pCO_2 is nearly controlled by the river inputs and decreases with salinity. During summer, the river low flows favour in the low salinity zone an important estuarine turbidity maximum (ETM) in which the respiration is maximum, nearly four times the level observed in the river. It is interesting to note that summer pCO_2 in the river is lower than winter pCO_2, despite much higher temperature, due to the important riverine phytoplankton production.

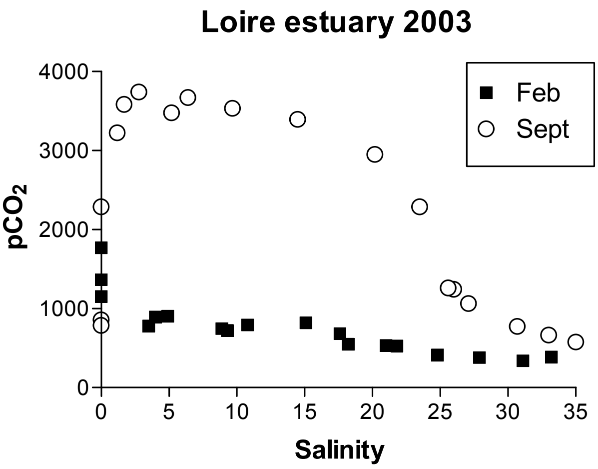


Figure 3.3.4.c. pCO_2 distributions versus salinity in the Loire estuary, showing a maximum at the intermediate salinity region which corresponds to the turbidity maximum. Note in particular the increase in pCO_2 at the river – turbidity maximum transition (very low (<1) salinity region in summer. (Abril et al. 2004 and Abril and Maro, unpublished)

3.3.5. NO_x produced by denitrification in river systems

NO_x emissions from river systems are relatively limited since the greatest part of nitrate is denitrified as N_2. However when the green House potential of NO_x is considered this process should be taken into account. So far the direct measurements of NO_x in rivers are very limited: most nitrogen budgets are considering denitrification as a whole on the basis of the nitrate budgets.

The nitrogen cycling trend in the impacted Seine and Scheldt river systems has been recently modelled by Billen *et al*. (2005) for the period 1950/2000 (figure 3.3.6) using the River Strahler model (Billen *et al*., 1994, 1999, 2005; Garnier *et al*., 1995, 2001). The Seine river system (present population density about 185 inhab/km²) and the Scheldt river system (near 415 inhab/km²) offer two striking examples of multiple anthropogenic perturbations in Western Europe. Land use, agricultural practices and urban activities in these catchments have been documented over the last 50 years: they have deeply changed, modifying in turn the water quality of the drainage network and the fluxes of nutrient transferred from land based sources to the estuarine and marine coastal zones.

For both basins, the annual nitrogen loading from the watershed (from either groundwater or surface runoff), and its “retention” (i.e. mostly denitrification) within the riparian wetlands and the drainage network and the nitrogen delivery to the estuarine zone have been simulated for the 50 last years (figure3.3.5). Surprisingly, compared with the Seine, the Scheldt basin does not deliver much larger amounts of nitrogen with respect to its watershed area, in spite of its higher population density. Specific delivery of nitrogen by the Scheldt is presently around 2000 kgN/km²/yr, compared with 1800-2000 kgN/km²/yr for the Seine basin. During the 1970’ies, these figures were 2200 kgN/km²/yr and 180 kgP/km²/yr for the Scheldt basin and 1500 kgN/km²/ for the Seine basin. This result is due to a greater effectiveness of “nitrogen retention” processes in the Scheldt than in the Seine drainage network. Indeed, specific point sources of nitrogen, mostly urban sewage, are at least 50% larger in the Scheldt than in the Seine basin, while non-point sources of nitrogen are similar. In-stream denitrification is much larger in the Scheldt basin which explains a similar net delivery. Continuing improvement of the oxygen status of surface waters in the drainage network of the Scheldt in the future could well lead to a further decrease of in-stream denitrification.

In both systems, the “nitrogen retention”, i.e. essentially the denitrification (lower parts of the figure 3.3.5) is gradually increasing. Although the emission of N_2O at the basin scale has not been yet estimated, it is believed that it corresponds to few percent of the denitrification. Assuming a constant proportion between N_2O emission and denitrification, the emission increase during the 1950-2000 would be between 5 and 10 times.

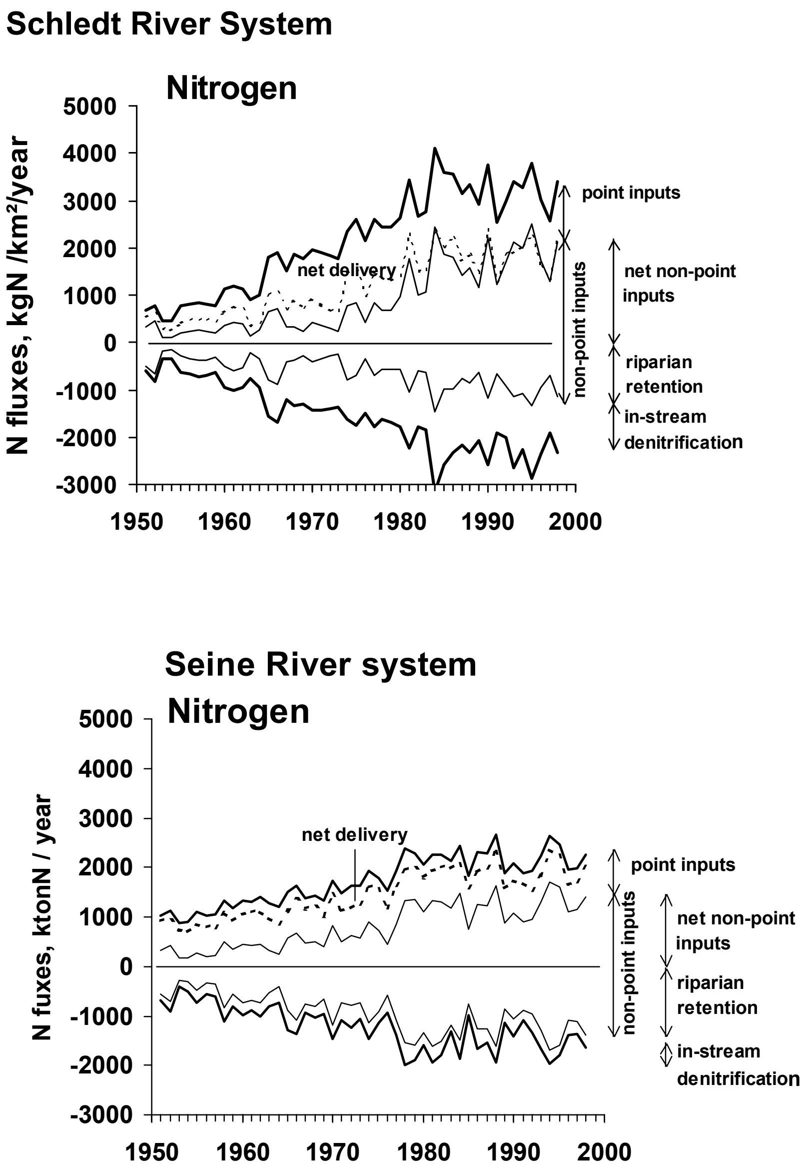


Figure 3.3.5. Reconstruction of the major terms of the nitrogen budget of the Scheldt and Seine river systems during the last 50 years (Billen *et al.*, 2005).

3.4. Carbon storage within river systems

3.4.1. Carbon storage in lakes and reservoirs

Carbon storage processes

Processes controlling the carbon burial in lake sediments are complex and not fully understood. Important parameters are characteristics of the watershed, lake morphometry, climate and hydrology. The catchment characteristics control the input of carbon and nutrients to the lake. The inflow of inorganic carbon (bicarbonate) is related to the weathering of carbonate and silicate rocks. Organic carbon is entering the lake generally in dissolved form (Wetzel, 2001) and originates from surrounding soils, especially peatlands (Molot & Dillon, 1996). In addition inorganic and organic carbon can reach the lake as particulate detritus from the catchment (see CarboEurope Rpt 8/2004/Specific Study 5).

A large scale lake study (Pajunnen, 2004) for example reports an average POC content of 8.6% for Finnish lakes, while the proportion of PIC is negligible in this type of watershed, where carbonate rocks are absent. Several investigations from lakes in other regions support the assumption that organic matter usually exceeds carbonate in many European lakes with the possible exception of Jura lakes and subalpine lakes, where carbonate rocks are dominant. Furthermore the mineralization of organic carbon in the sediment decreases the pore water pH and thereby enhances dissolution of carbonate minerals when present (Dean, 1999).

C/N ratios in the sediments of many boreal and temperate lakes suggest that organic matter is a mixing of organic debris originating from lake primary production with watershed, allochthonous material. Their proportion depends on the trophic state of the lake and on the relative importance of lake catchment area over lake area

Particulate organic matter which escapes mineralization within the watershed can be deposited at the lake bottom. In the upper sediment bacterial decomposition is proceeding. This decomposition is highest under oxic conditions, thus the preservation of organic matter in lakes with anoxic hypolimnon is usually better. Incomplete mixing or a permanent stratification of the water column (termed meromixis, a rare situation) promotes these conditions. Even with oxic bottom water, depletion of oxygen normally occurs below the uppermost millimetres of the sediment due to benthic oxygen consumption. This water-sediment interface can be disturbed by bioturbation, mixing and sediment resuspension.

Intralake variations

The lake bottom can be divided into areas of erosion, transportation and accumulation. Proportions of these areas are depending on lake morphometry, particularly on the slope (Hakanson & Janson, 1983). The effect of “sediment focusing” leads to higher sedimentation rates in deeper part of the lakes with marginal thinning of the sediment layers. Because most cores are taken from the deepest part of the lake, their use to estimate whole lake sedimentation rate can lead to important overestimations if no further information (e.g. acoustic sounding profiles) is available.

Interlake variations of carbon storage rates

When the carbon accumulation rates is high as many small lakes catchment/lake area ratio are generally higher than in large ones (Dean & Gorham, 1998; Kortelainen et al., 2004). Particularly small shallow lakes can bury high amounts of organic carbon (Einsele et al., 2001). Excluded from this trend are very small lakes (<0.1km^2), which often have catchments free of open streams and therefore a limited influx (Pajunnen, 2004). Anyway, the accumulation rates in lakes with similar size can vary significantly due to watershed characteristics.

For the boreal zone, which contains most European lakes, Dean & Gorham (1998) calculated carbon mass accumulation rates of 72 gC/m^2/y for small and medium lakes (lake area <5000 km^2) and 5 gC/m^2/y for very large lakes, respectively. Finnish data suggest, that particularly the rate for small lakes could be strongly overestimated: average long term carbon accumulation calculated for the whole European lake area would be closer to 4 gC/m^2/y.

For several closed and open modern lake basins calculations were made by Einsele *et al.* (2001). The results are summarized in appendix B. Values for small lakes and artificial reservoirs were taken from the literature. Einsele *et al* (2001) made a comprehensive review of atmospheric carbon trapping in large lakes including organic carbon (OC) originating from soils erosion and lake production, and the part of atmospheric CO_2 that is used in weathering reactions: on silicate rocks, 100% of dissolved inorganic carbon DIC originate from atmospheric CO_2, on carbonate rocks only 50%. Large to medium-sized lake basins show high to very total high atmospheric carbon ($TC_{(AT)}$) burial rates ranging from 4 to 25 g/m^2/a. Small and shallow lakes have very high accumulation rates of atmospheric carbon. High total mass accumulation rates, high influx of plant debris or anoxic conditions can cause high burial rates of atmospheric carbon even in large lakes. The common contribution of carbonate is very limited. It solely reaches considerable amounts in closed to semi-closed lakes, where evaporation is high and silicate rocks strongly dominate the drainage area. Large, open oligotrophic lakes have typical low carbon burial rates (<5 g/m^2/a).

The carbon burial rates are influenced by climatic conditions and are generally enhanced by a warmer and wetter climate. Anthropogenic influence usually increases the storage of carbon in lake sediments. Anthropogenic land use can raise the sedimentation rates leading to a higher preservation of organic carbon. Increased nutrient input causes a higher primary production and therefore a higher OC content in lake sediments. [Appendix B].

3.4.2. Long-term carbon accumulation

Rates of net carbon accumulation are determined from core data. To calculate carbon mass accumulation rates (MARs) measurements of carbon content, dry bulk density, water content and a good sediment chronology is needed. Investigations providing all these data are rare and covering different time scales (e.g. last 50 y, 200 y, 2000 y..) depending on core length and sedimentation rate.

Paleorecords of carbon and nitrogen levels from sedimentary archives

Analyses of carbon and nitrogen species in aquatic sediments of river systems (lakes, reservoirs, floodplain and ox-bow lakes, estuaries) is not yet commonly realized as for micropollutants. Yet the information retrieved in well-chosen core can be essential for the reconstruction of past carbon levels and fluxes in river systems from Holocene variations to more recent Anthropocene impacts.

Sediment accumulation rates and organic carbon content of small shallow Lake Candia in Northern Italy is an example of long term carbon burial and anthropogenic influence (figure 3.4.2). C/N ratios about 10 throughout the whole core suggest primary production as the main source of organic carbon. Carbonate content is negligible. In natural conditions, terrestrial and lacustrine productivities were coupled to climate: warmer periods (e.g. Little Optimum of the Medieval Warm Epoch) lead to higher organic matter content in the sediment while lower carbon content indicates cooler climate (e.g. Little Ice Age). Since ca. 1830 carbon accumulation and climate have been decoupled due to a sharp eutrophication. The gradual increase in older sediment may be misleading, because the calculation of mass sedimentation rates is based on ^{210}Pb (for ca. the last 150 years) and ^{14}C (only 2 values). Anyway, a marked increase of carbon accumulation as reported from many other European Lakes exposed to eutrophication is observed.

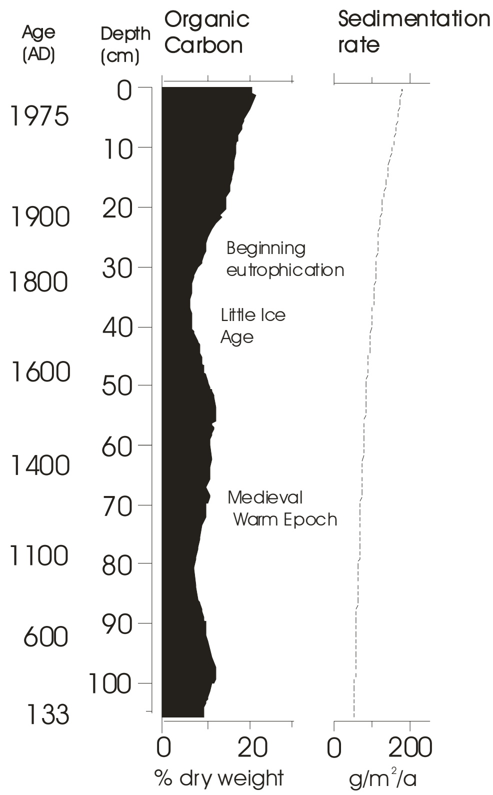


Figure 3.4.2. Long term evolution of organic carbon content and sedimentation rate in Lake Candia (Italy) (modified from Lami *et al.*, 2000).

These long term data are averaged for the entire lifetime of the lake that is mostly about 10.000 years due to the glacial origin. Recent, anthropogenic changes have been taken into account. Other studies concerning the last two centuries, are suggesting a very strong anthropogenic influence on lake sedimentation (eg. Neumann *et al.*, 2002; Miguel *et al*, 2000). Land use changes in the catchment are leading to increased erosion and therefore to higher sedimentation rates of detrital inorganic material which promote the potential preservation of organic carbon. This trend is often associated with a higher nutrient inflow resulting in enhanced lake primary production. Direct release of organic wastes in lakes may also increase the sedimentation of POC.

To which degree this recent POC increase will be preserved within the sediment is difficult to quantify. In the youngest sediments, influenced by major anthropogenic changes, the mineralization of organic matter is still very strong. Anyway, in most lakes the direct Human pressures of the lake watershed seem to eclipse the effect of natural environmental changes (e.g. climate variations) on lake sedimentation.

4. Carbon and GHG budgets of river systems at the European scale

4.1. River carbon budget

4.1.1. Methodology used for the CarboEurope River Carbon Model

Limits of Europe and description of Europe's Regional Seas catchments

When considering river budgets to oceans and regional seas, the boundaries of the European territory must include the catchments of the White Sea and Barents Sea, Baltic Sea, North Sea, Mediterranean Sea and Black Sea in addition to the direct catchment of the North Atlantic Ocean: the total area of the exorheic parts (i.e. flowing to the ocean) of the European continent is 8.2 Mkm^2, this excludes the drainage area of the endorheic Caspian Sea – principally the Volga River catchment. These boundaries are presented on figure E1 at Annexe E, and their related area and discharge river are presented in Annex G (tables G.1. and G.2.). The delineation of Europe's Regional Seas and the characteristics of their catchment is based on several data bases, which are presented in details at Annex E.

River carbon concentrations

At such scale, there is no European river water quality database. We have therefore used multiple sources of data, which have already been collected by Meybeck and Ragu (1996), for the world's major rivers, by Gordeev (1998) for the rivers of the Former Soviet Union (from Pechora to Don and Danube), and by Abril *et al*. (2002) in their study of macrotidal estuaries. The list of rivers for which an estimate of DOC, POC or DIC has been available is presented in Appendix E (table E1). Meybeck *et al.* (2006) have decomposed the world's coastline into a set of 140 segments that are linked to a continental river catchment, and define the COSCAT dataset. We have determined the DOC, POC, atmospheric DIC (i.e. originating from the CO_2 and/or organic acids involved in weathering reactions) and the total atmospheric carbon, TAC = DOC + POC + DICatm, for each of the 15 European COSCAT (Table J2).

River carbon input to estuaries

The construction of a dataset of river carbon species (DOC, POC, DICatmospheric and TAC) has been realized for the 15 coastal catchments (COSCAT) of European seas (Caspian Sea excluded) and per major estuarine types as follows:

Step 1: All basic information is collected per COSCAT catchment (e.g. the Thames, Rhine, Weser, Elbe, Scheldt are in the North Sea COSCAT; The Pö, Adige, Neretva, Vijose are in the Adriatic COSCAT)

Step 2: DIC levels are estimated, when not directly measured, from the catchment lithology from the Dürr *et al*. (2005) database at 30' x 30'.

Step 3: The POC levels, when missing, are estimated on the basis of the average total suspended solids (TSS) and the relationship between their POC contents (POC %) and the TSS (this is fully see detailed in another CarboEurope report). The average TSS in natural conditions – i.e. without river damming – is derived from the global model of Ludwig and Probst (1998).

Step 4: When direct measurement of TOC (TOC = DOC + POC)) are available, they are used to confirm the DOC and POC estimates or to infer DOC from TOC and POC.

Step 5: The atmospheric DIC is estimated from the general relationship between DICatm and total DIC: the minimum proportion of DICatm is 50 % of DICtotal, when weathered rocks are calcareous (see details in CarboEurope report); the maximum DICatm reaches 100 % for non-calcareous rocks as the Scandinavian shield. The results of average carbon species concentrations for DOC, POC, DIC atmospheric and TAC are presented in Appendix J for each coastal segment (table J2).

Step 6: The documented DOC, POC and DICatm levels have also been clustered according to their estuarine types: deltas, deltas plus lagoons, rias, karst, macrotidal estuaries, fjords, fjärds and formely glacierized sedimentary coast. These types also correspond to the major drivers of carbon levels and fluxes in river catchments. For instance, in fjords and fjärds river catchments, draining plutonic and metamorphic rocks, DIC is estimated to be 100% of atmospheric origin, POC is very low (fjärd coast) or medium (fjord coast) due to the occurrence of wetlands and peats. In karstic coast, riverine POC is limited, DOC is very low, DICtot is very high and DICatm/DICtot = 0.5.

Step 7: A matrix linking 15 COSCATs (the Nansen Basin, COSCAT #409, which corresponds to parts of the Spitzberg drainage and other Artic islands and the NE Black Sea have been omitted) and 8 estuarine types have been constructed resulting in 43 European river aggregations. Many of the matrix intersection remain void (e.g. most karstic coast is found in the Mediterranean Sea; fjords and fjärds are found only in Northern Europe i.e. in Baltic drainage, White Sea, Norwegian Sea, North Sea and very limited in the Hutton-Rock all basin, in Iceland and Ireland). About half of Europe's river drainage to the ocean has been documented for river carbon concentration; the other half has been simply extrapolated on the basis of similarities between catchments types).

An example of the CarboEurope River Model database is presented on Appendix J (table J4) for TAC for each COSCAT entity and per estuarine type.

Step 8: The drainage area and river flow volumes, for each of the 43 European river aggregation (or coastal types) are determined from GIS analysis of the 30' x 30' global river network.

Step 9: The river fluxes to the upper estuarine limit are calculated as the products of average river concentrations and total water volumes for each of the 43 river aggregations, thus allowing for the determination of total fluxes, average concentrations and average yields (Cexport per unit area per year) for each entity (Appendix J, Tables J3 and J4).

4.1.2. Estuarine filters and net river fluxes to the oceans

Estuaries can be very efficient biogeochemical reactors and/or particle traps. As a result, estuaries can be net sources or sinks of carbon species. These properties are generally checked through concentrations vs. salinity diagrammes (figure 4.1.2) realized at a fixed period through out the whole range of salinity from the river end member (upstream of the tidal limit) to the outer estuary (generally more than 95 % sea water). The shape of these curves can be very different. In order to allow for the comparison of all chemical compounds, the concentrations are here normalized to the river end-member (C_{in}).

We are defining here a **estuarine filter coefficient (α)**, which defines the behavior of carbon species in the estuarine environments: $\alpha > 1.0$ for net estuarine source, $\alpha < 1.0$ for net sinks and $\alpha = 1.0$ for conservative behavior. α_1, α_2, α_3, α_4 refer to DOC, POC, SPM and DIC, respectively (table 4.1.2).

River and ocean end members: for many nutrients (NO_3^-, PO_4^{3-}, SiO_2) and DOC, the river concentration are much higher than for ocean end members. For DIC, it can be either higher or lower, depending on the catchment lithology and regional sea salinity.

Dissolved Organic Carbon (DOC) behavior (figure 4.1.2.a): generally, river DOC is conservative in most estuaries ($\alpha_1 = 1.0$) except when sewage is a major C source ($\alpha_4 < 0.5$) and/or when extended tidal flats occurs and release DOC ($\alpha_4 > 2$) (Abril *et al.*, 2002) When river DOC is originating from sewage inputs or from phytoplankton, it can be easily degraded in estuaries ($\alpha_1 = 0.5$). On the contrary, in coastal lagoons, DOC can be produced by algal blooms and the estuary is a net source of DOC ($\alpha_1 = 3.0$). Similar, behaviors for dissolved nutrients have been noted, particularly for dissolved silica.

Dissolved Inorganic Carbon (DIC) behavior (figure 4.1.2.b): in most documented case studies, DIC is most of the time conservative ($\alpha_4 = 1.0$). Depending on the relative levels of DIC in river and marine end members, DIC can either decrease, increase or be stable with increasing salinity since the river DIC levels range above and with increasing the ocean average DIC.

Organic Carbon Content in suspended particles (**macrotidal**) (figure 4.1.2.c): the content (POC %) is expressed in % of suspended particulate matter and presented as a longitudinal profile. The river end-member at the tidal-limit (TL) presents marked seasonal variations with maximum during summer low flows when river algal POC is high and minimum for the soil POC export during floods. POC in the estuarine turbidity maximum (ETM) is nearly constant and lower than the average river POC (% of SPM) weighted by the TSS fluxes, due to bacterial degradation proportional to particles residence time in ETM. In the estuarine's plume, POC ranges from those of the ETM, which are expelled during major river floods and those typical of coastal algal blooms (spring/summer neap tides). The ratio between the net flux of SPM to ocean and the river SPM input to the estuary depends on these complex hydrodynamics and on the particulate matter residence time.

In deep and large fjords, no SPM escape the estuarine system, while in karstic springs and deltas, 100 % of river SPM reaches the coastline limit.

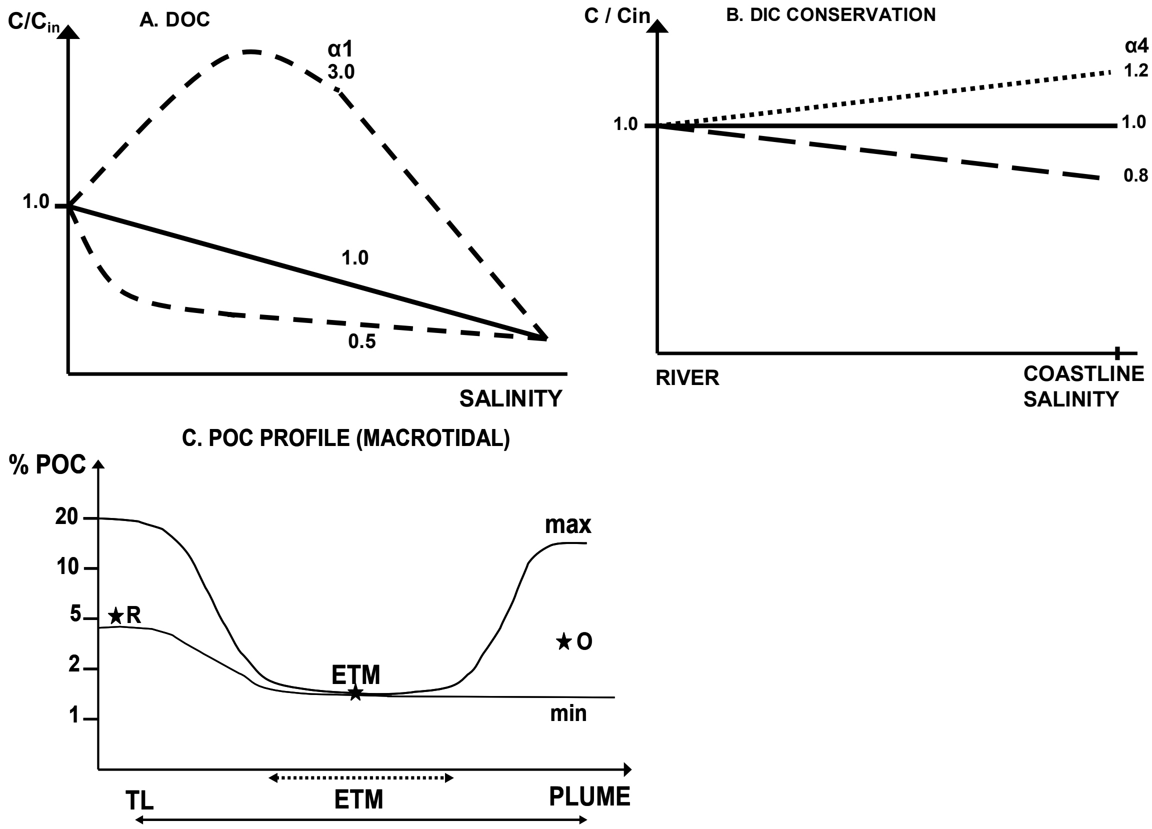


Figure 4.1.2. Estuarine filter coefficients: schematic evolution of carbon species from rivers to the coastline boundary. A and B. theoretical dilution line normalized to river end-member (the river DIC can either be lower or greater than sea water DIC): α_1 is the ratio of the theoretical river-end member as extrapolated from the straight part of the dilution line. DIC is assumed to be conservative in the estuarine filter ($\alpha_4 = 1.0$). C. profile of POC content (in % of suspended particulate matter) in a macrotidal estuary, from river end-member at the Tidal Limit (TL) to the outer estuary plume. R, ETM and O: long-term averages weighted per suspended matter fluxes for river, estuarine turbidity maximum and outer estuary. Min and max: range of POC % according to season, river discharge and tidal dynamics. Minimum ETM level is specific in each estuary.

The net river fluxes are calculated after step 9 using a set of estuarine filter coefficients specific for each carbon species and each estuary on the basis of the analysis of their fate in estuarine systems (see sections 1.1.5. and 3.1.3). These coefficients are presented on table 4.1.2.

	Process			
Type	DOC degradation α1	POC degradation α2	DIC conservation α4	SPM retention α3
macrotidal(1)	1.0 ± 0.15	0.2 to 0.95 (mean 0.5)	1.0(11)	1.0
fjord(2)	< 0.5(2)	0.9	1.0	0.0
fjärd(3)	1.0 ± 0.3	0.8	1.0	0.5
karst(4)	1.0	1.0	1.0	1.0
delta(5)	1.0 ± 0.1	1.0 ± 0.1	1.0	1.0
delta + lagoon(6)(10)	1.0 ± 0.1	1.5	1.0	0.5
Ria(9)	1.0	0.8	1.0	0.6
Polluted macrotidal(7)	0.3	0.2	1.0	1.0
Tidal flat macrotidal(8)	3.0	2.0	1.0	0.8

Table 4.1.2. Estuarine filter coefficients (α) used in European river flux model. (1)POC degradation depending on POC sources and seasons; no net SPM retention. (2)DOC degradation for very long residence time $\tau_W > 10$ y; some POC production sedimentation of all POC. (3)Production/degradation of DOC; POC degradation is partially compensated by production, POC deposition in inner estuary. (4)Flow-through system. (5)Near flow-through system; POC is only deposited in outer delta. (6)Important production in lagoon; important sedimentation of POC. (7)Polluted river inputs (DOC and POC) are degraded within the estuary (e.g. Scheldt). (8)Extended tidal flat generate high internal inputs of DOC and POC; some net retention of SPM in tidal flats. (9)POC degradation is partially compensated by production; net retention of 40% of SPM. (10)Also used for “sedimentary glaciated” type of estuaries. (11)may seasonally range from 0.7 (Scheldt) to 1.5 (Loire), less documented for other estuarine types.

Step 10: The filtering functions of estuaries with regards to river carbon inputs of DOC, POC and DIC are established for each major type of estuaries (table 4.1.2.).

Step 11: The river carbon fluxes are multiplied by the estuarine filter coefficients to end up with the net fluxes to the coast, i.e. to outer estuaries.

4.1.3. River carbon levels and fluxes per estuarine types for Europe

Coastal types (n = 43) are here defined as the aggregation of river basins linked to the ocean or regional seas by an identical estuarine type and belonging to single Coastal Catchment. For example, the Krka and Vijose, both in Adriatic, belong to the Adriatic/Karst coastal type and the Pô, Brenta and Adige to the Adriatic/deltas with lagoons type.

The average concentrations, fluxes and yields can be calculated by estuarine types, regional seas of their combinations (tables 4.1.3.a, b, c). The model shows a five fold range of DOC and POC and a 14 fold range for DIC concentrations due to much contrasted lithologies. In the Scandinavian shield, the atmospheric carbon is essentially carried as DOC while in carbonated basins (e.g. North Ionian, Tyrrhenian), DIC makes more than 80 % of total atmospheric carbon. As a result, the TAC is not much variable with 2-fold range only.

The budget of river atmosphere carbon to European seas, upstream of the estuarine zone is estimated to 52.75 10^6 $tC.y^{-1}$ of which 28.6 % is carried as DOC, 14.0 % as POC and 57.4 % as atmospheric DIC, i.e. the CO_2 that is directly transferred from the atmosphere, or derived from soil respiration, during soil weathering reactions. The ratio of TOC over TAC ranges from less than 0.20 for the North Ionian, Tyrrhenian and Adriatic to more than 0.75 for the Norwegian basin and reaches 0.87 for the Botnian Bay. POC proportions are quite variable in these European catchments: POC matches DOC for the Atlantic catchment (Hutton-Rockall) but is less than 20 % of TOC in the Gulf of Finland.

The river budget to estuaries is also computed per estuarine types. Delta with lagoons is the estuarine type which receives the greatest amount of total atmospheric carbon (29.5 %) ahead of the “sedimentary glacierized type”. This is due to the extension of the related catchments (Danube, Oder, Vistule, Dniepr, Don for the first type, Northern Dvina and Pechora for the second) and to their relatively carbonated nature, which generates important proportions of DICatm. The macrotidal estuaries, which is the best studied types, receives only 12.1 % of the carbon inputs.

COSCAT		401	402	403	404	405	406	407	408	411	412	414	415	416	417	418	Total EUROPE (per carbon type) (%)
DOC	(a)	18.0	26.7	29.6	30.9	66.7	59.7	41.4	47.0	13.2	18.9	8.7	7.6	7.6	9.1	12.8	28.65
POC	(a)	11.4	24.0	15.0	8.9	20.0	8.0	36.9	8.7	11.3	15.0	14.9	11.5	12.1	10.3	13.0	14.02
DICatm	(a)	70.5	49.3	55.4	60.3	13.3	32.3	21.7	44.3	75.5	66.1	76.4	80.9	80.3	80.6	74.1	57.33
TAC Fluxes	(e	5095.4	3343.6	6494.8	3141.8	1869.0	2085.8	2353.8	9457.9	1309.1	7324.8	1156.2	1020.5	4738.9	776.8	2589.9	100.00
TOC/TAC	(f)	0.29	0.51	0.45	0.40	0.87	0.68	0.78	0.56	0.25	0.34	0.24	0.19	0.20	0.19	0.26	0.43

Table 4.1.3.a. Total river atmospheric carbon fluxes (TAC) to estuaries (e): in 10^3 tC/y; a: proportion of carbon species per coastal catchments; (f): TOC/TAC per coastal catchments).

Estuarine types		Deltas ss		Karsts + Deltas %		Deltas with lagoons		Ria		Fjord		Sedimentary glacierised		Macrotidal estuaries		Fjärd		Total EUROPE (per carbon type) %	10^3 tC/y
DOC	(a)	9.4		4.9		17.4		22.0		39.6		43.9		19.6		63.8		28.65	
	(b)		0.95		1.52		17.91		4.94		13.84		32.12		8.31		20.40		15115.3
POC	(a)	14.6		10.5		13.4		9.8		34.8		8.0		12.6		15.3		14.02	
	(b)		2.98		6.65		28.15		4.49		24.86		11.97		10.90		10.00		7397.9
DICatm	(a)	76.0		84.6		69.2		68.3		25.5		48.1		67.8		20.9		57.33	
	(b)		3.81		13.07		35.67		7.69		4.46		17.59		14.39		3.33		30244.9
TAC Fluxes	(e	1514.2		4674.6		15579.1		3405.1		5279.7		11059.5		6415.6		4830.3			
	(b)		2.9		8.9		29.5		6.5		10.0		21.0		12.1		9.1	100.0	52758.1
TOC/TAC	(f)	0.24		0.15		0.31		0.32		0.74		0.52		0.32		0.79		0.43	

Table 4.1.3.b. Total river atmospheric carbon fluxes (TAC) to estuaries per estuarine types (e: in 10^3 tC/y; a: proportion of carbon species per coastal catchments; (b): proportion of each coastal catchments; (f) TOC/TAC per estuarine types).

4.1.4. Net river carbon budgets to coastline zone after their estuarine filters for Europe

The net river budgets to the coastal zone are generated by the products of river inputs to the upper estuaries with the estuarine filter coefficients.

Estuarine retention

With the hypothesis of the CarboEurope model, the estuarine retention is variable: 46 % of the river POC fluxes would not reach the coastal zone (outer estuaries), they would be degraded and/or sedimented. On the contrary, the DOC "retention", i.e. degradation in long-residence time estuaries would be less than ten percent. Of the 52.7 10^6 tC atmospheric transported by rivers about 4.4 10^6 tC would be retained and/or transferred to the atmospheric at the land-ocean interface.

Net budgets to regional seas and coastal catchments

They are presented in three ways (i) per regional seas (coastal catchments); (ii) per estuarine types and regional seas. These budgets are presented in tables 4.1.4.a, b, c.

4.1.5. Net river carbon fluxes to three European mega regions

In addition to the 18 coastal segments that defines here the European coastline, we have re-clustered the river carbon fluxes for 3 mega-regions that will also be used for the GHG emission model that is presently not known for the 18 segments. These mega-regions have been defined from the combination of several criteria: (I) climate, (ii) lithology (carbonate rocks), (iii) relief and water drainage. These mega regions are reassembled from the coastal catchment (COSAT) puzzle as such:

Northern Europe = Botnian Bay (# 405) + Gulf of Finland (# 406) + Norwegian basin (# 407) + Barents Sea (# 408)

Middle Europe = Iberian-Biscay (# 401) + Hutton-Rockall (# 402) + North Sea (# 403) + South Baltic Sea (# 404) + Azov Sea (# 411) + North Bmack Sea (# 412)

Southern Europe = West Aegean (# 414) + North Ionian (# 415) + Adriatic (# 416) + Tyrrhenian (# 417) + Balearic (# 418)

- Northern Europe has been mostly glacierized and hard crystalline rocks are dominant. Human pressures are limited.
- Middle Europe corresponds to temperate and continental climate with high to very high human pressures. Glaciation has been very limited.
- Southern Europe drains to the Mediterranean to the Mediterranean Sea. River flow can be very much altered and reduced by damming and irrigation.

The conclusions made for the river budgets to estuaries are mostly valid for the net river budget to the coastline. The mega regions budgets are more contrasted and show important features (table 4.1.5.a).

Most of DOC (52.8 %) is originating from the Northern Europe rivers, which represent only 31 % of the drainage area and 34 % of the water flow.

POC is essentially carried (55.4 %) by Middle Europe rivers (57.6 % of Europe's area; 50.5 % of its river flow), as for the atmospheric DIC (54.8 %).

Southern Europe, which represents only 11.5 % of Europe's ocean catchment (Caspian Sea excluded) and 15.3 % of its water flow, contributes for 21 % of the Total Atmospheric Carbon inputs, thanks to the highly carbonated nature of its rocks.

COSCAT		401	402	403	404	405	406	407	408	411	412	414	415	416	417	418	Total EUROPE (per carbon type) (10^3 tC/y)
Net DOC	(b)	6.5	4.7	11.4	6.9	8.9	8.9	3.6	31.5	1.2	9.8	0.7	0.5	2.6	0.5	2.4	14069.53
Net POC	(b)	8.8	2.3	7.9	5.0	3.7	1.8	0.1	9.6	3.7	27.5	4.3	2.4	14.3	1.5	6.8	3992.56
Net DICatm	(b)	11.9	5.4	11.9	6.3	0.8	2.2	1.7	13.9	3.3	16.0	2.9	2.7	12.6	2.1	6.3	30244.87
Net TAC	(b)	10.1	5.0	11.4	6.3	3.4	4.1	2.1	18.6	2.7	15.2	2.4	2.1	9.8	1.6	5.2	48306.96

Table 4.1.4.a. Net River Carbon Fluxes to coastline (e: 10^3 tC/y; b: proportion of each coastal catchments).

COSCAT		401	402	403	404	405	406	407	408	411	412	414	415	416	417	418	Total EUROPE (per carbon type) (%)
Net DOC	(a)	18.9	27.5	29.0	31.7	75.8	62.6	49.5	49.2	13.2	18.9	8.7	7.7	7.6	9.3	13.2	28.65
Net POC	(a)	7.3	3.9	5.7	6.5	9.1	3.6	0.3	4.3	11.3	15.0	14.9	9.8	12.1	8.1	10.8	14.02
Net DICatm	(a)	73.9	68.6	65.3	61.8	15.2	33.8	50.2	46.6	75.5	66.1	76.4	82.5	80.3	82.5	76.1	57.33
Net TAC Fluxes	(e)	4866.1	2399.9	5512.5	3063.2	1644.7	1989.9	1018.4	9005.3	1309.1	7321.5	1156.2	1000.7	4736.7	758.4	2524.5	100.00
NET TOC/TAC	(f)	0.26	0.31	0.35	0.38	0.85	0.66	0.50	0.53	0.25	0.34	0.24	0.18	0.20	0.17	0.24	0.43

Table 4.1.4.b. Net river carbon fluxes to coastline (e: in 10^3 tC/y; a: proportion of carbon species per coastal catchments).

Estuarine types		Deltas ss		Karsts + Deltas		Deltas with lagoons		Ria		Fjord		Sedimentary glacierised		Macrotidal estuaries		Fjärd		Total EUROPE (per carbon type)	
																		%	10^3 tC/y
Net DOC	(a)	10.2		4.9		17.4		23.1		43.7		45.7		20.9		70.3		28.65	
	(b)		1.02		1.64		19.25		5.31		7.43		34.51		8.93		21.91		15115.33
Net POC	(a)	7.8		10.5		13.4		5.1		0.0		4.2		6.7		6.7		14.02	
	(b)		2.76		12.31		52.17		4.16		0.00		11.09		10.10		7.41		7397.94
Net DICatm	(a)	82.0		84.6		69.2		71.8		56.3		50.1		72.4		23.0		57.33	
	(b)		3.81		13.07		35.67		7.69		4.46		17.59		14.39		3.33		30244.87
Net TAC Fluxes	(e	1404.0		4674.6		15579.1		3239.0		2394.6		10616.7		6012.6		4386.4		100.00	
			7.58		27.02		107.08		17.16		11.89		63.18		33.42		32.66		52758.14
NET TOC/TAC	(f)	0.18		0.15		0.31		0.28		0.44		0.50		0.28		0.77		0.43	

Table 4.1.4.c. Net river atmospheric carbon fluxes (TAC) to coastline per estuarine types (e: in 10^3 tC/y; a: proportion of carbon species per coastal catchments; (b): proportion of each coastal catchments; (f) TOC/TAC per estuarine types).

4.2. Europe budget of GHG emissions from continental waters

4.2.1. Methodology and distributions of water type

The GHG budget is depending on two factors: (i) the rate of GHG per unit area of water mirror for the different types of water bodies and (ii) the distribution of the water mirror area for each of the mirror types. Both need precise field surveys and must take into account possible temporal variations of both rates and mirror extension. Field results obtained by scientists and individual lake, wetland, peat bog or river reach will have to be extrapolated to other water bodies of similar functioning. A fine scale typology of water bodies oriented towards GHG emissions is therefore needed as well. Finally, the spatial distribution of water types should be realized, combining remote sensing techniques and field truth.

As a first estimate of the order of magnitude of GHG emissions from Europe's water bodies (the "CarboEurope River Model"), we are considering first the average GHG emission rate from three typical European landscapes: the Northern Europe, the Middle Europe and the Southern Europe. Each of them is characterized by a given distribution of water bodies, i.e. of water mirror types.

The distribution of waterscape mirror is then combined to an estimate of GHG emission rate for each type of water body to calculate the total GHG emitted by water bodies. As this stage of knowledge, there is not enough field data on GHG emissions rates to differenciate the variability between similar water bodies (e.g. Nordic lakes vs. temperate lakes): all water bodies are characterized by an identical emission rate throughout Europe. This assumption is based on the fact that (i) emissions rates for a given GHG are more variable from one type of water mirror to the other than within a given type (ii) distribution of water mirrors, in % of land are also very much variable.

Europe's distribution of water bodies in model

The relative proportions of water mirrors chosen in the model are very different for the three European regions (figure 4.2.1.a): Northern Europe is here characterized by an extreme proportion of water mirror, 13 % (identical to some regions of Canada), of which about 2/3 can be considered as lakes (i.e. deeper, possibly stratified and ¼ can be considered as very shallow open waters associated to wetlands (of which 1/5 is here assumed to be peat bogs). Middle Europe has much less lakes and wetland and the reservoir area matches the lake area. In Southern Europe, most wetlands have been drained, there are even less natural lakes (0.8 % of land area in this configuration) than for Middle Europe but the proportion of reservoirs is higher (1.7 % of land area) which makes them the dominant type of water bodies.

The separation of Europe into three regions has been made on the basis of catchment boundaries to regional seas as defined by Meybeck *et al.* (2005). These coastal catchments ("COSCATs") are relatively homogeneous in terms of past Earth System history (glaciation), orography, climate and human impacts. The Northern regions (2.53 Mkm^2) range from the Norwegian fjords to the Pechora drainage but the Southern Baltic COSCAT is included in the Middle Europe since the Odra and Wisla catchments are much extended. Similarly the South Norwegian fjords are part of the North Sea COSCAT, which is considered in the Middle Europe regions with the Elbe and Rhine catchments. The Middle Europe catchments (4.7 Mkm^2) represent more than a half of Europe catchment, due to the enormous weight of Black Sea tributaries (Danube, Dniepr, Dniestr, Don). The Southern Europe catchments (0.94 Mkm^2) actually correspond to the Mediterranean drainage of Europe's territory.

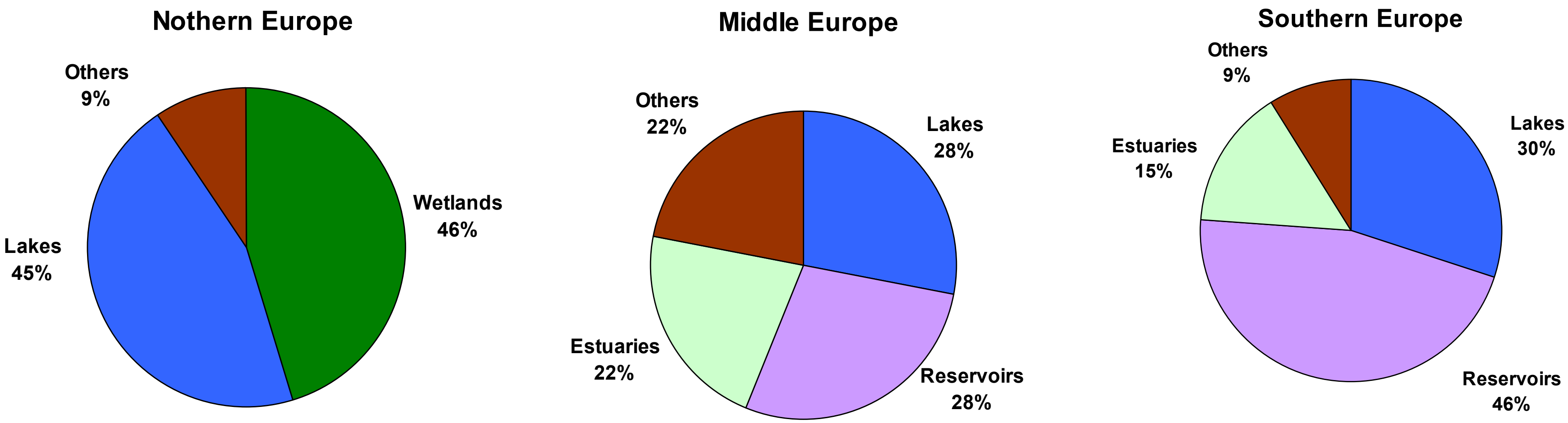


Figure 4.2.1. Relative proportions of water mirrors in Nothern Europe (2.54 Mkm²), Middle Europe (4.7 Mkm²) and Southern Europe (0.94 Mkm²).

Global significance of CO_2 and CH_4 emissions from rivers and estuaries

The significance of CO_2 and CH_4 emissions from rivers and estuaries can be theoretically estimated by multiplying an average flux density of each gas by the surface area of rivers and estuaries. Flux densities from estuaries were compiled by Middelburg *et al.* (2002), Abril and Borges (2004) and Borges (2004). The gas transfer velocity (k_{600}) is highly variable in estuaries with wind, current and water depth. An average gas exchange rate k_{600} of 15 $cm.h^{-1}$ is appropriate for estuaries. This value is high compared to lakes or ocean because of the contribution of tidal currents to surface turbulence. In rivers, k_{600} is also highly variable with water depth, current velocity and to a lesser extend, windspeed. Few experiments have been conducted so far to determine k_{600} in stream and rivers, using either gas tracers (propane or SF6) injections, floating chambers or eddy covariance techniques. k_{600} varied from 2.6-9.7 $cm.s^{-1}$ in a peatland small stream (calculated from Hope et al. 2001), to 20-60 $cm.s^{-1}$ in the large but shallow Loire River (Abril and Maro, unpublished). Similarly to the work of Borges et al. (2004) in estuaries, there is a need for a better characterization of k_{600} and controlling factors in rivers.

In table 4.2.1, the order of magnitudes of CO_2 and CH_4 emissions by rivers and estuaries have been calculated. Owing to the large spatial and temporal variability, these numbers must be considered as tentative estimates only. Nevertheless, they illustrate the importance of gas emissions on the carbon budget of rivers and estuaries. The CO_2 emission is the same order of magnitude as the global riverine carbon transport to the ocean. As recently discussed by Borges (2004), the CO_2 emission from world inner estuaries appears significant at the global scale. However, a rigorous up-scaling of air-water CO_2 fluxes in the Coastal Ocean is hampered by the poorly constrained estimate of the surface area of inner estuaries. By contrast, the CH_4 emissions from rivers and estuaries are a very negligible component (<1%) of the global CH_4 emissions (about 500 $TgC.yr^{-1}$).

		Surface area 1000 km2	Gas flux[d] mmol/m2/d	Total flux TgC.yr-1
CH_4	Rivers	360[a]	0.3 - 0.9	0.5 - 1.5
	Estuaries	600[c]-1400[b]	0.02 - 0.5	0.06 - 3
CO_2	Rivers	360[a]	40 - 200	70 - 340
	Estuaries	600[c]-1400[b]	100	290 -613

Table 4.2.1. A tentative global estimate of CO2 and CH4 fluxes from world rivers and estuaries. [a] from Lehner and Doll (2004); [b] from Woodwell 1978; [c] assuming the Woodwell's surface area is overestimated at 60%; [d] range or average value, depending on the number of data available (From Abril and Borges, 2004; Borges 2004 and Abril and Borges, in prep).

4.2.2. GHG emissions rates

In this model, we are considering separately the CO_2 and CH_4 emissions and their combination as Global Warming Potential (GWP) assuming CH_4/CO_2 = 23 mole/mole in warming potential. As water mirror in wetlands, particularly in peat lands, have much higher rates than for lakes and reservoirs, they have been considered separately (table 4.2.2.a).

	CO_2 flux	CH4	CH4 GWP	
	mol/m^2/y	mol/m^2/y	mol CO_2/m^2/y	10^3 t C-CO_2 / km²
Non peat wetland water	200	2	46	2.95
Peat wetland water	410	5.5	126.5	6.43
Peat drains	410	5.5	126.5	6.43
Non peat drains	100	2	46	1.75
Lakes	7	0.2	4.6	0.139
Reservoirs	7	0.2	4.6	0.139
Large rivers (main stems)	20	0.3	6.9	0.323
lower floodplain	100	1	23	1.48
inner estuaries (channels)	40	0.04	0.92	0.49

Table 4.2.2.a. Mean emissions rates of GHG used in model.

The water mirror distribution in this model is established tentatively for the three European sub-regions: Northern, Middle and Southern, which are characterized by different Earth System history (glaciations on Northern Europe have generated multiple lakes), different climates (Southern Europe is generally drier, excepted for limited hot spots of rainfall in Albania and Slovenia), different Human impacts (much more reservoirs found in Southern Europe) and different land/ocean interface (more deltas and karst in Southern Europe). The relative proportions of the different water mirrors chosen in this model are reflecting these variations, although they have not been checked by land cover analysis for two reasons: (i) we are extending Europe to its geographic boundaries, i.e. to Ural, in order to fully consider the European regional seas catchments: White/Barrents and Black Sea, and land cover data is not available for Eastern Europe (ii) the land cover information should be obtained at a very fine resolution in order to obtain the water mirror related to wetlands.

4.2.3. GHG emissions from Europe's water mirrors

According to the average emission rates that have been chosen, the methane GWP is negligible in estuarine waters with regards to CO_2 (2 % of GWP) but is between 19 % and 40 % in all other water bodies: about 1/5 in wetlands and 40 % in lakes and reservoirs. For the three European regions, the methane contribution to the GWP (N_2O excluded) is about 23 %.

The GHG emission budget, expressed in CO_2 equivalent, is obtained by the product of emission rates and mirror areas (table 4.2.3.a, b). In this model, the decomposition per water mirror types and per European regions allows for the following remarks:

- Northern Europe (31 % of Europe's territory) is emitting 87 % of GHG due to the high occurrence of water mirror, principally wetlands, and peat bogs. Middle Europe (57 % of territory) would only be related to 12 % of emissions and Southern Europe's emissions would be negligible (1.2 %) although it represents 11.5 % of the territory.

This budget is extremely sensitive to the proportions of wetlands water mirror (58 % of GHG emissions) and of peat bogs (25 % of GWP emissions), the distribution of which is actually the least well known of all water bodies

- Lakes and reservoirs emissions would only contribute to a mirror proportion (5.6 %) of GHG emissions.

- The sensitivity of GHG budget to wetlands water mirror and peat bogs can be addressed as follows: the GHG emissions budget is recalculated without these two water mirrors (table 4.2.3.b), assuming their emissions have be fully accounted for in the CarboEurope Wetland project. As such, the emissions in CO_2 equivalent would be reduced from 670 Tg/y to 118 Tg/y. Small first and second order streams could contribute to a significant proportion of this reduced emissions (15.3 %), lakes and reservoirs to 32 % and floodplains and inner estuaries to 22 % each.

Such analysis is demonstrating the great sensitivity of the GHG budget to the definition of the waterscape that should be made at a very fine resolution. The temporal variations of the waterscape itself adds another degree of complexity.

-

Water mirrors	GWP emission rates	Nothern Europe Mkm² 2.53 Mirror area	GWP Fluxes	Middle Europe Mkm² 4.7 Mirror area	GWP Fluxes	Southern Europe Mkm² 0.94 Mirror area	GWP Fluxes	Total Europe Mkm² 8.17 Mirror area	GWP Fluxes	GWP
	10^3 t C-CO_2 / km²	km²	10^6 t C-CO_2	km²	10^6 t C-CO_2	km²	10^6 t C-CO_2	km²	10^6 t C-CO_2	%
Non peat wetland water	2.95	126500	373175	4700	13865	94	277	131294	387317	57.7
Peat wetland water	6.43	25300	162679	470	3022	0	0	25770	165701	24.7
Peat drains	6.43	152	977	0	0	0	0	152	977	0.1
Non peat drains	1.75	759	1328	9400	16450	188	329	10347	18107	2.7
Lakes	0.139	126600	17597	47000	6533	9400	1307	183000	25437	3.8
Reservoirs	0.139	25300	3517	47000	6533	14100	1960	86400	12010	1.8
Large rivers (main stems)	0.323	10120	3269	14100	4554	1410	455	25630	8278	1.2
Lower floodplain	1.48	7590	11233	9400	13912	940	1391	17930	26536	4.0
Inner estuaries (channels)	0.49	12650	6199	37600	18424	4700	2303	54950	26926	4.0
Total		334971	579974	169670	83293	30832	8022	535473	671290	100.0
% Mirror area		62.6		31.7		5.8		100.0		
% GWP			86.4		12.4		1.2		100.0	

Table 4.2.3.a. Tentative GHG Budget for CO_2 and CH_4 emissions from all water mirrors, including wetlands.

		Nothern Europe		Middle Europe		Southern Europe		Total Europe		0
		Mkm²		Mkm²		Mkm²		Mkm²		0
		2.53		4.7		0.94		8.17		0
Water mirrors	**GWP emission rates**	**Mirror area**	**GWP Fluxes**	**Mirror area**	**GWP Fluxes**	**Mirror area**	**GWP Fluxes**	**Mirror area**	**GWP Fluxes**	**GWP**
	103 t C-CO2 / km²	km²	106 t C-CO2	km²	106 t C-CO2	km²	106 t C-CO2	km²	106 t C-CO2	%
Peat drains	6.43	152	977	0	0	0	0	152	977	0.8
Non peat drains	1.75	759	1328	9400	16450	188	329	10347	18107	15.3
Lakes	0.139	126600	17597	47000	6533	9400	1307	183000	25437	21.5
Reservoirs	0.139	25300	3517	47000	6533	14100	1960	86400	12010	10.2
Large rivers (main stems)	0.323	10120	3269	14100	4554	1410	455	25630	8278	7.0
lower floodplain	1.48	7590	11233	9400	13912	940	1391	17930	26536	22.4
inner estuaries (channels)	0.49	12650	6199	37600	18424	4700	2303	54950	26926	22.8
Total		183171	44120	164500	66406	30738	7745	378409	118272	100.0
% Mirror area		48.4		43.5		8.1		100.0		
% GWP			37.3		56.1		6.5		100.0	

Table 4.2.3.b. Tentative GHG Budget for CO_2 and CH_4 emissions from water mirrors, excluding wetlands.

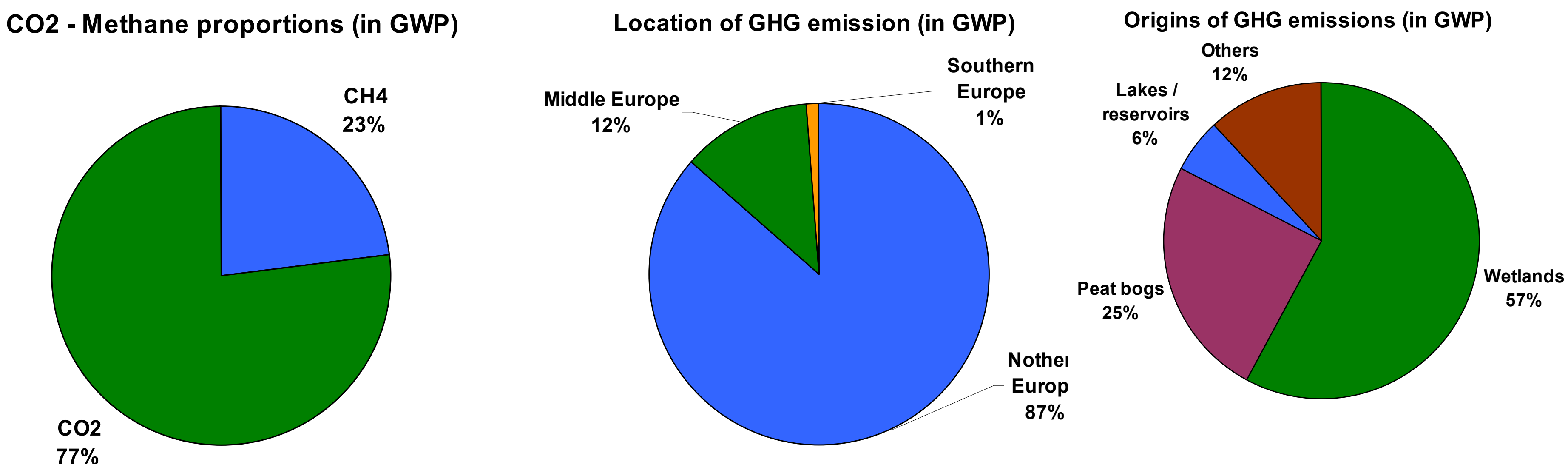
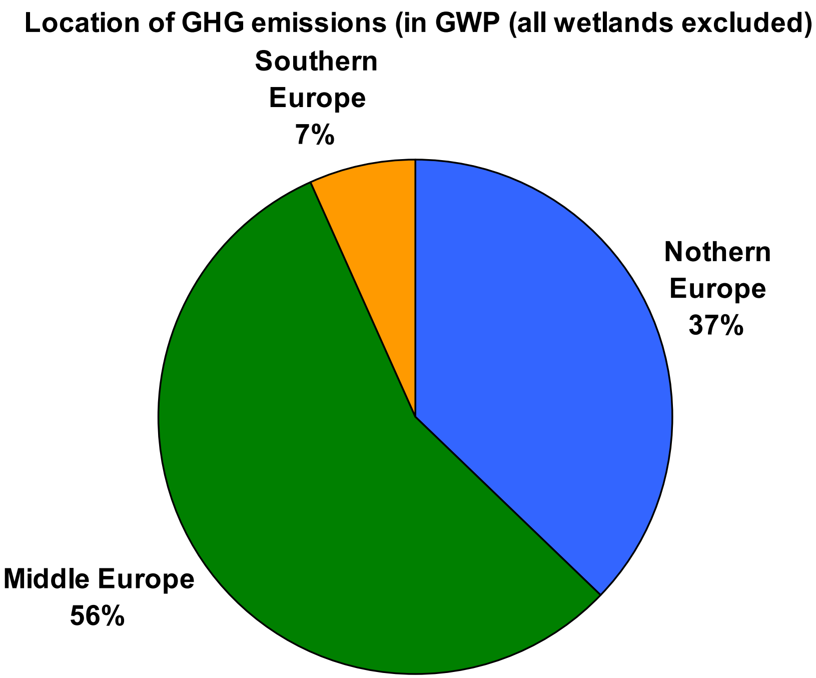


Figure 4.2.3.a. Relative proportions of CH_4 and CO_2 emissions expressed as GWP, from Europe's continental waters (all water mirrors including wetlands) (CarboEurope River Model).



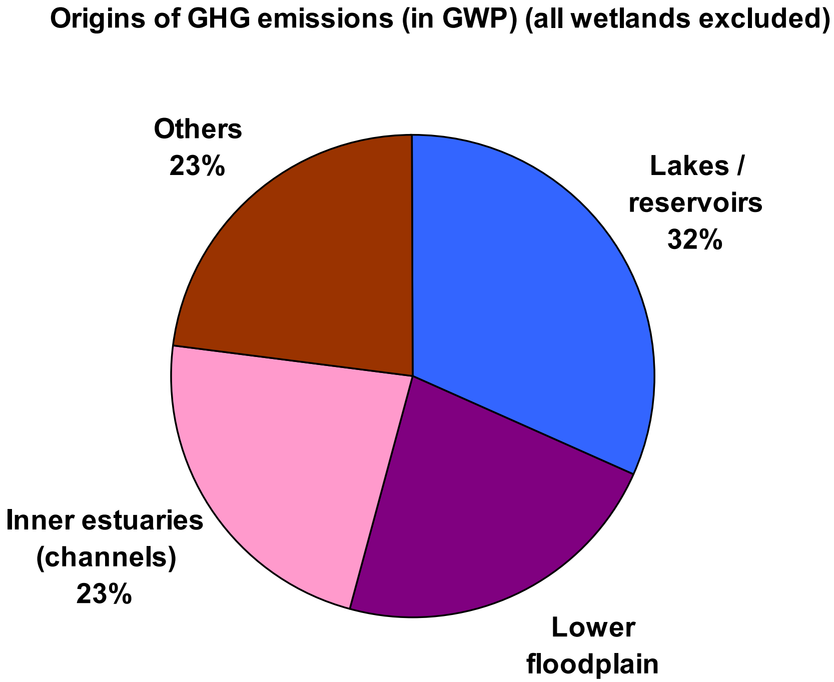


Figure 4.2.3.b. Relative proportions of CH_4 and CO_2 emissions expressed as GWP, from Europe's continental waters (water mirrors without wetlands) (CarboEurope River Model).

5. Limits of present budgets and recommendations

5.1. Spatial resolution issues

Northern wetlands and their related GHG emissions are actually very fine landscapes mosaics, particularly as concerns the water mirror and its temporal variations. Both remote sensing imageries by satellite as Landsat TM and by aerial photography are used. The Stordalen mire in Northern Sweden has been used for a companion of both data sets (figure 5.1).

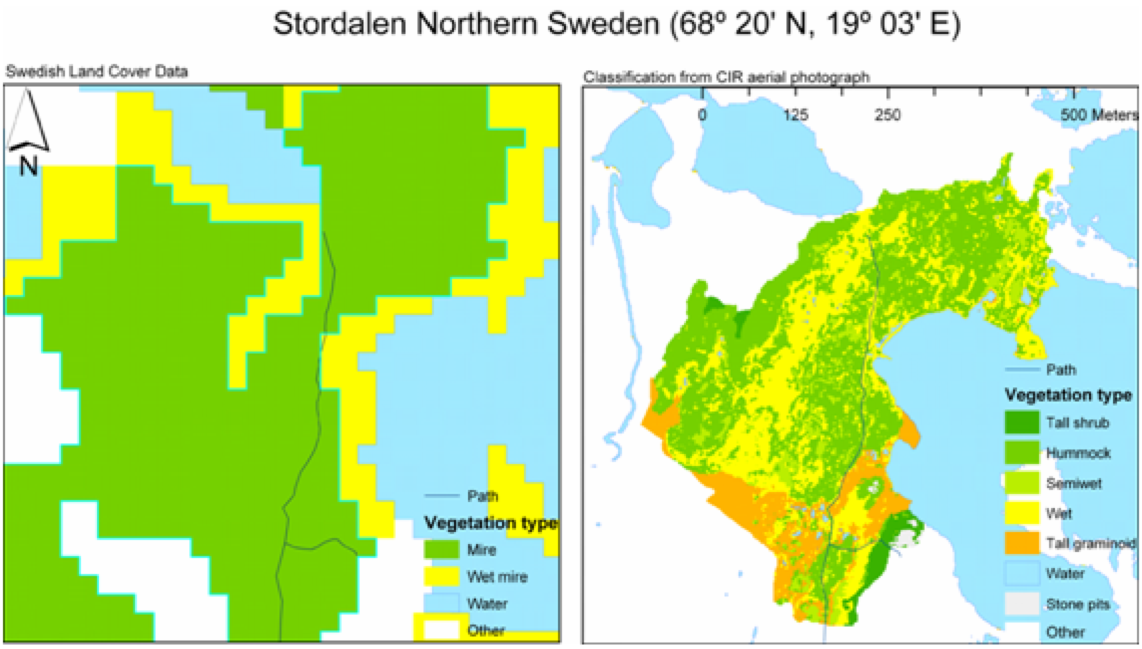


Figure 5.1. Maps over Stordalen mire northern Sweden using SMD (Landsat TM) and an aerial photograph based map (right) from 2000 visualizing the map precision/ spatial resolution dependency. The hummock class in the aerial photograph based map has a user accuracy of >83 %. (Malmer *et al.*, submitted)

It becomes evident when comparing the maps (figure 5.1.) made from images with different spatial resolution (30 and 1 meters) that the small-scale heterogeneity of the specific peatland gets lost using the Swedish land cover database (SMD) produced with a moderate spatial resolution input data i.e. Landsat TM. Not only the precision is low in the SMD map, but the accuracy is also low in comparison with the aerial photograph derived map. Any detector will frequently integrate intercepted radiance within the field of view (FOV) from more than one class, this becomes more apparent for coarse spatial resolution images over highly heterogenous landscapes.

With the small-scale heterogeneity of northern peatlands comes that the vegetation assembly and water table are largely variable and change at a scale of meters. At the fringe between the dry and wet mire change for example the CH4 -flux from a small sink-neutral-small source (dry ombrotrophic) to a large source (wet minerotrophic).

There is a high level of generalization in SMD and even more in the CORINE Land Cover (CLC2000), where only areas larger than 1 ha (25) is presented, together with mixed pixels. Such questionable accuracy greatly reduce the usefulness of the SMD's (CLC 2000) water and wetland classes for scaling GHGs to European scale.

Such comparison needs to be realized on other sites and countries. Until then the resolution (precision) and the accuracy of CLC 2000will remain questionnable for all types of water and peatland classes in Europe.

The delivery of a good estimate of GHG emissions for EU water bodies (standing and flowing) is currently hindered by a lack of emission data for certain types of water bodies and accurate information about surface area (e.g. water mirror area of peatland surface waters). The latter is particularly important because a relatively small difference in surface area will make a significant impact on the overall vertical flux. In addition, many water bodies exhibit strong seasonal (temporal) variability in surface area – this need to be taken into account in the context of the EU GHG emission budget.

5.2. Hypotheses on future evolution of riverine carbon fluxes at the Anthropocene

The anthropogenic forcing of the earth surface system (e.g. climate, land cover) is now equivalent and even greater than the natural one. The term Anthropocene is now recently reused by Crutzen (Crutzen, 2002, Crutzen and Störmer 2000) to qualify this situation. The Anthropocene concept can perfectly be applied to river systems and a conventional date at 1950 has been proposed as a starting point (Meybeck 2002, 2003 a). Several hypotheses on the future evolution of river carbon transport are proposed (figures 5.2.a to f; Meybeck, 2005): they show very different patterns including stepwise increase or decrease, non linear responses, and thresholds typical of Earth System functioning (Steffen *et al.*, 2003).

One of the most spectacular evolution of river systems is the gradual stepwise decrease of rivers flows due to irrigation in dry and semi-arid regions at is has been observed for the Colorado, Nile, Amu Darya and, to a lesser extend, for the Orange, Indus or Huang He, and in Southern Europe (e.g. Axios, Ebro). When these river systems are less connected to the oceans (neo-arheism), there is a gradual reduction of all river carbon fluxes, wether dissolved or particulate (figure 5.2.a), which may lead to a total reduction of fluxes.

Land cover change due to human pressures has many impacts on river carbon exports. It is here hypothetized (figure 5.2.b) that forest clearing and particularly clearcutting are dramatically increasing soil erosion in a first phase thus exporting more soil POC. If the soil layer is completely lost as in semi-arid regions and some Mediterranean basins (case a) the parent rock may be exposed and if it is erodible, a new long-term equilibrium can be observed with high erosion rates yet with much lower soil POC export. In most temperate regions (case b), a gradual recovery after forest cutting is likely: a phase of lower soil POC export by rivers during which organic carbon is gradually accumulating in the soil (carbon sequestriation, CS) could be observed before a new equilibrium is reached. Such patterns are difficult to put in evidence on the basis of direct river measurements since they must have been performed on long periods, decades, and with no other human impact on the basin.

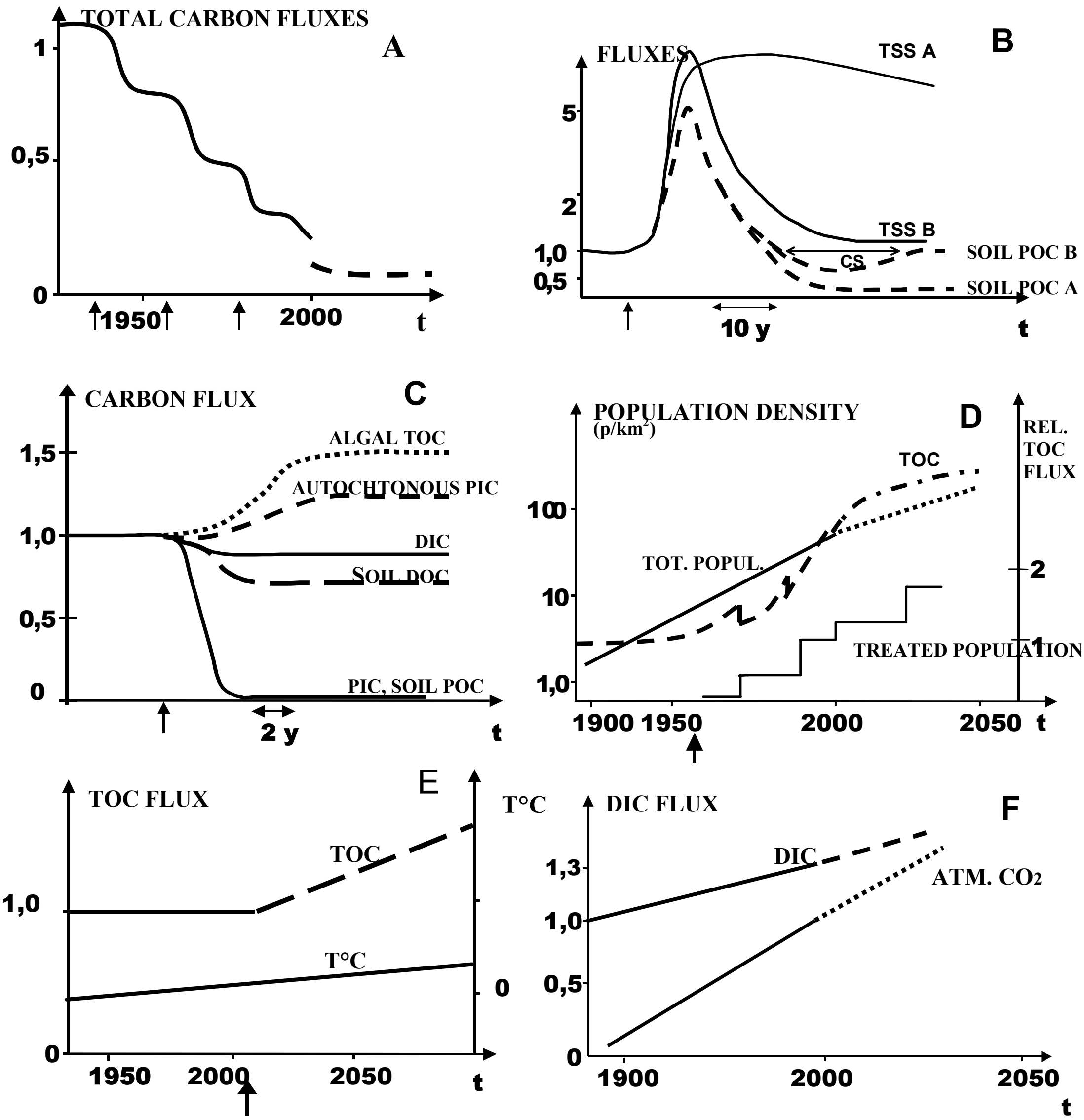


Figure 5.2. Working hypotheses for the contrasted future of carbon fluxes at the Anthropocene. (All fluxes are normalized to pristine average conditions.) A. Stepwise reduction of fluxes in neoarheic rivers with water consumptum periods. B. Stepwise evolution of TSS and soil POC, without proper soil conservation practises (a) and with soil recovery (b); (CS = soil organic carbon sequestration). C. Contrasted trends after damming (settling vs.. autochthonous carbon production). D. Non-linear response of river TOC flux downstream of fast-growing megacity with marked time-lag between population growth and urban sewage collection. E. Threshold TOC increase due to permafrost melt in arctic basins. F. Gradual DIC increase in forested area due to CO_2 elevation, (arrows indicate start of pressure).

The impact of river damming is presented on figure 5.2.c: the construction of large reservoirs also leads to the reduction of TSS fluxes, hence of soil POC fluxes, reaching 90% for reservoirs exceeding 6 months of water residence time. At the global scale, reservoir trapping could exceed 30% of the large river sediment fluxes (Vorosmarty et al., 2003). In large reservoirs soil DOC can be degraded by UV, but there is also a production of autochthonous TOC from algal development and sometimes a precipitation of calcite, which is partially exported in the river outlet during whitening events. Most detrital carbon inputs (as POC and PIC) and part of DIC inputs are retained in lakes or reservoirs.

River courses downstream megacities are extremely impacted particularly from untreated urban organic wastes (carbonaceous pollution). The figure 5.2.d is an attempt to describe the evolution of the TOC fluxes or levels downstream of a fast-growing city for which the exponential population growth rate is faster than the sewage collection and treatment rate, an evolution so far encountered in many European cities until the 1980's and in most developing nations. Above a certain population density threshold which correspond to the self-assimilating capacity of the river system (i.e. proportional to the ratio waste inputs/river discharge), there is a general increase of TOC with possible stepwise improvement phases related to the installation of waste waters treatment plants. Since the collection/treatment rate is lagging behind population development, the organic carbon excess (i.e. labile TOC) gradually increases until anoxic conditions are met, either in the river itself or in ultimate receiving waters (e.g. estuaries). Due to partial waste treatment and biogeochemical processing of labile TOC in the river, the TOC increase is not proportional to population development.

In addition to these human pressures and impacts which are now widely distributed as the global scale, yet with an heterogeneous distribution, two global impacts may eventually influence river carbon fluxes: (i) temperature changes and (ii) CO2 increase. In the arctic regions characterized by the dominance of permafrost and frozen wetlands as peatbogs (figure 5.2.e), a temperature increase (T-T0) above the melting point threshold of permafrost, would lead to a major extrasource of TOC in rivers, mostly as DOC. Another impact of temperature increase on DOC export by peatsoils has been envisaged by Reynolds and Frenner (2001): the activation of phenol oxidase enzyme. This point has been questioned by Evans et al. (2002) who invoke hydrological changes as the key control.

The long term observation of peat catchments in Northern England since 1962 shows various DOC trends, stationary for most catchments and positive for one, with marked interannual variations possibly linked to pH, river flows and land use change in addition to enzymatic latch mechanisms (Worral et al., 2003). Such debate emphasizes the complexity of the organic carbon-export processes.

We have previously postulated that DIC levels were very stable in world rivers, at least compared to other species: Cl-, SO42-, Na+ and K+ which are increasing by factors 2 to 10 in all impacted basins. However this may not be true on the long term. A recent CO2 doubling experiment at a 1/1 scale in the Duke forest, U.S.A. (Andrews and Schlesinger, 2001) has demonstrated that groundwaters were enriched in DIC during the experiment. The authors suggested that such carbon-enriched waters would act as a potential carbon sequestering site, postulating a long residence time for groundwaters (>> 10 y). It is however more likely that these DIC-enriched surficial ground waters will mostly feed the local river system at low flows, thus increasing DIC fluxes. The confirmation of such trend can only be achieved on carefully selected long term river surveys: the increase of DIC flux in the Mississippi is much more due to increased rainfall on the basin than to DIC level increase between 1953 and 2001 (Raymond and Cole, 2003). Finally it must be noted that the process of river acidification which resulted in decreased DIC fluxes, once very pronounced in Scandinavia and NE USA and Canada, has now been gradually decreased.

Due to the combination of enhanced and decreased carbon fluxes under human impacts it is not yet possible to predict the direction of these contrasted river carbon evolutions at the global scale: these multiple impacts will have to be addressed at the local to regional scale for each carbon species, taking into account, some new carbon sources and filters, and the modifications of existing ones within the Anthropocene.

5.3. For an European network of river carbon and GHG

The GHG emissions from continental aquatic systems, from headwaters to estuaries involves a dozen of specific subsystems (figure 5.3.) which process the carbon species and emit GHG. The CH4/CO2 ratio is different from one subsystem to another. In addition, large variabilities are also observed between water bodies of the same types (i.e. lakes, estuaries…) and for one given water body, marked seasonal variations, sometimes spiky (eg at lake overturn) are noted. The growing artificialisation and regulation of water bodies and the construction of new types (reservoirs, irrigated fields, wastewater treatment plants –WWTP) is adding a degree of complexity since its spatio-temporal evolution is very little known at the European scale (eg maps of existing reservoirs every decade, irrigated area maps). The floodplain control which has been established in Europe for the last 150y is still progressing in some regions while few contries are already “re-naturalizing” some floodplain areas, as along the Rhine River. Facing this enormous variability, the existing networks on continental aquatic systems that could be used to assess and predict carbon and GHG fluxes are very limited:

- Organic carbon species (DOC, POC) in rivers is not a priority water quality survey in Europe: Biological and Chemical Oxygen Demands (BOD and COD) are still widely used to state the organic pollution level. Only DIC is properly surveyed.
- pCO_2 estimates in rivers need adapted of pH and Total Alkalinity taking into account diurnal variations.
- Currently, there is no EU network on small streams (headwaters) where much of the GHG emissions is taking place.
- Lakes and reservoirs are not adequately surveyed across EU climate and biogeochemical gradients. The reservoir age is also an important control factor of GHG emissions that should be addressed.
- The land-ocean interface is critical for: (i) direct emission of GHG and (ii) net fluxes of carbon species to the coastal zone. As for the other types of water bodies, there is no network of estuarine surveys dedicated to this questions from fjords to karstic coasts. Most of the few academic studies have been carried out so far on macrotidal estuaries linked to the North Sea and Atlantic Ocean, from the Elbe to the Sado estuaries.

Our estimate of river carbon fluxes and GHG emissions, the "CarboEurope Model", is therefore our best attempt to use very dispersed data and we are aware that it represents a very first estimation. In order to improve these budgets, there should be a major European effort and a specific attention to the "river carbon" question should be given. Unfortunately, this is not the case in the new EU Water Framework Directive, targeted to the good ecological state in which water quality issues are dominant, while the role of aquatic systems in geochemical cycles is minored. In order to fill these gaps, we propose few directions of surveys and studies:

- Carbon storage in lakes

The lakes should be divided into main regional classes concerning their origin (glacial, periglacial, fluvial and others) and their geographic situation (high mountains, low land etc.). Lakes in glacially affected regions enclose over 80% of the European lake surface, mostly situated in Scandinavia and northwest Russia. In a next step lakes are classified according to parameters affecting the carbon sequestration and evasion, including lake size, rock types, soil cover, vegetation and climate. Factors controlling the carbon budget will be determined on a restricted set of well-investigated case studies, along a N-S transect across Europe and include different geomorphologic regions.

From the World register of dams (2003) we have calculated an area of ~48×10^3 km^2 covered by reservoirs in Europe, which is a strong underestimate because only large dams are mentioned and some data are missing. Combing this figure with the carbon burial rate estimates from Dean and Gorham (1998), the organic carbon burial for European reservoirs may be around 19×10^6 t/a, exceeding the value for lakes by a factor of 2. The uncertainties for both lakes and reservoirs C storage is still very high but they certainly have the same order of magnitude. Reservoir retention is excepted to retention in Southern Europe and lake retention in Northern Europe.

- Peat streams and GHG escape

Currently we are some way from producing reliable estimates of CO_2 and CH_4 emission rates from peatland surface waters. What data there are suggests that the flux term for CO_2 may be significant, particularly in the source areas of peatland drainage systems. Estimates for CH_4 are likely to be much smaller although some bog pool systems are known to be large sources of CH_4 (e.g. MacDonald *et al.,* 1998). Upscaling emission rates to produce catchment scale values will have to incorporate the high degree of spatial and temporal variability that exists in peatland drainage systems.

In addition to streams, which are a feature of many UK peatlands, bog/wetland areas particularly in countries like Canada, Finland and Estonia, are characterised by large numbers of lakes or pools, which present a considerable surface area to the atmosphere. It is not uncommon to find areas where > 50% of the land surface comprises bog-pool systems, whereas stream networks generally comprise between 0.2 - 0.6% of the surface area of a well drained catchment (Cole and Caraco, 2001; Hope *et al.,* 2001; Algesten *et al*., 2003). Both types of water surface are physically different and offer considerable potential for gas exchange with the atmosphere.

- Lower rivers, floodplains and estuaries

Currently, the few data available suggest that river systems, with their floodplains and estuaries, emit more carbon to the atmosphere as CO_2 and CH_4, than they transport to the coastal zone as organic and inorganic carbon. However, this degassing/export ratio is highly variable from one river to another, depending on the nature and occupation of the watershed, the biological processes occurring in the aquatic system, the extend of floodplains and the typology of the estuaries. In addition, data also show that the CH_4/CO_2 emission ratio is very different in each sub-system and higher in floodplains than in main stem rivers and estuaries. Monitoring stations of GHG concentrations should be installed in all European large rivers and combined to more detailed process-based field studies in typical sub-systems. In addition, studies carried within the framework of CarboEurope should be performed at the scale of river watersheds and should include river export and GHG degassing from aquatic surfaces, together with terrestrial-atmosphere carbon exchange.

Finally, the surface area of the water mirror and its seasonal variations is poorly constrained, which precludes an accurate up-scaling of GHG fluxes from European river systems. Significant effort based on satellite observations, hydrological modelling and GIS developments and adapted to aquatic GHG exchanges is needed to fill these gaps.

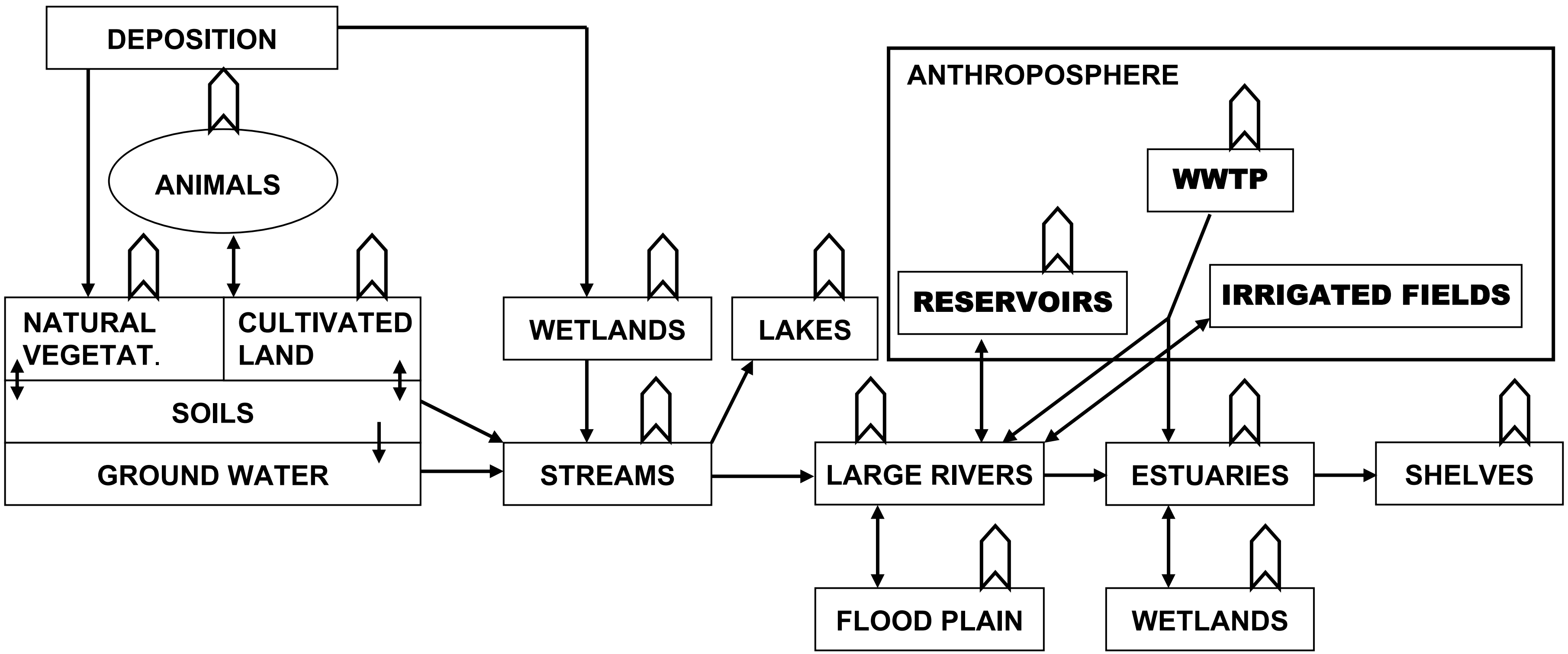


Figure 5.3. Schematic decomposition of continental aquatic systems for the modelling of GHG gas emission (and lateral carbon transfers (⟶) from headwaters to oceans. **In bold**: managed components. WWTP: Waste Water Treatment Plants. Each box corresponds to a specific model, which is constrained by the outputs.