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Excess atmospheric carbon dioxide transported by rivers into the Scheldt estuary

Gwenaël Abril[a,b]*, Henri Etcheber[b], Alberto V. Borges[a], Michel Frankignoulle[a]

[a] « Mécanique des fluides géophysiques », unité d'océanographie chimique, Institut de physique (B5), université de Liège, B-4000 Sart Tilman, Belgique
[b] Département de géologie et océanographie, CNRS–UMR EPOC 5805, université Bordeaux-1, avenue des Facultés, 33405 Talence, France

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Abstract – The transport of excess atmospheric CO_2 (defined as the fraction of dissolved inorganic carbon (DIC) that can escape as CO_2 to the atmosphere due to water-air equilibration), by the five rivers entering the Scheldt estuary is investigated. Excess CO_2 originates from both respiration in the soil and the river and represents 10 % of the DIC and 6 % of the total carbon input into the estuary. The ventilation of this CO_2 in the estuary is however a minor contribution (10 %) to the total estuarine emission to the atmosphere, compared to heterotrophic activity and acidification due to nitrification within the estuarine zone. © 2000 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

carbon dioxide / respiration / soils / rivers / ventilation / estuaries

Résumé – Excès de gaz carbonique atmosphérique apporté par les fleuves à l'estuaire de l'Escaut. L'apport d'excès de CO_2 (défini comme la fraction du carbone inorganique dissous (CID) qui peut s'échapper vers l'atmosphère par équilibration entre l'eau et l'air), par les cinq rivières alimentant l'estuaire de l'Escaut est étudié. L'excès de CO_2, produit par la respiration dans les sols et les rivières, représente 10 % du CID et 6 % des apports totaux de carbone à l'estuaire. La ventilation de ce CO_2 dans l'estuaire ne représente cependant qu'une faible part (10 %) de l'émission totale de CO_2 vers l'atmosphère par l'estuaire, en comparaison avec l'activité hétérotrophe et avec l'acidification due à la nitrification. © 2000 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

gaz carbonique / respiration / sols / rivières / ventilation / estuaires

Version abrégée

1. Introduction

Les études du transport de carbone par les fleuves font généralement la distinction entre les formes organiques et inorganiques et les origines atmosphériques et lithologiques [4, 18, 20]. Cependant, les fleuves sont aussi largement sursaturés en CO_2 vis-à-vis de l'atmosphère et transportent donc un excès de CO_2 atmosphérique, qui résulte de la respiration dans les sols et le milieu aquatique et peut représenter une fraction significative du carbone inorganique dissous (CID). Cet excès de CO_2 est en partie transporté longitudinalement par les eaux de surface et en partie transféré vers l'atmosphère, dans des proportions qui dépendent du débit, de la différence de pression partielle en CO_2 (pCO_2) et du coefficient d'échange gazeux eau–air *K* [1, 11, 22]. Dans les fleuves et les estuaires, les valeurs de *K* sont supérieures à celles de l'océan, pour une même vitesse de vent, car la turbulence créée par les courants favorise aussi la ventilation des gaz [1, 6, 10–13, 17, 21]. Il a

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* Correspondence and reprints: i5gw@civil.auc.dk
Present address: Aalborg university, Department of Civil Engineering, Environmental Engineering Laboratory, Sohngaardsholmsvej, 57, 9000 Aalborg, Denmark

été récemment montré que les estuaires européens macrotidaux constituent une source significative de CO_2 pour l'atmosphère [13]. La majorité de ce CO_2 est produit dans les estuaires par l'activité hétérotrophe, qui minéralise une partie du carbone organique apporté par les fleuves et par l'acidification due à la nitrification [12, 13]. Il semble cependant qu'une partie provienne aussi d'un apport fluvial de CO_2 qui, lorsqu'il est soumis aux courants de marée et au vent dans les estuaires, est ventilé vers l'atmosphère. L'objectif de ce papier est d'évaluer l'importance de ce phénomène à l'échelle de l'estuaire de l'Escaut.

2. Méthodes et site d'étude

Afin d'appréhender l'importance du transfert de CO_2 entre fleuve, estuaire et atmosphère, nous utilisons ici une série de données de carbone organique particulaire et dissous (COP, COD), oxygène, pH et alcalinité acquise pendant un an (mai 1997–mai 1998) dans les cinq rivières alimentant l'estuaire de l'Escaut (Belgique, Pays-Bas ; *figure 1*). Il s'agit d'un bassin versant à dominante urbaine et agricole très fortement pollué, notamment la rivière Zenne, qui reçoit les eaux usées de la ville de Bruxelles [31, 32] (*tableau I*). Des déficits en oxygène marqués s'étendent depuis les différents affluents en amont des points de prélèvements, jusqu'en aval de la ville d'Anvers (Antwerp, *figure 1*). La pression partielle en CO_2 et la spéciation du CID sont calculées à l'aide des constantes de dissociation de l'acide carbonique de Mehrbach et al. [19] et du coefficient de solubilité de Weiss [30]. L'excès de CO_2 est défini comme la quantité de CID qui rejoint l'atmosphère sous forme de CO_2 après équilibration complète entre l'eau et l'air. On le calcule par différence entre le CID observé et le CID calculé avec la pCO_2 atmosphérique et l'alcalinité mesurée. Cette définition rend compte de manière quantitative des phénomènes de respiration et d'échanges eau–air, et permet une comparaison avec le déficit en oxygène [7]. Les flux de carbone transportés par les rivières sont calculés à partir de moyennes mensuelles pour les éléments dissous (DOC, DIC et excès de CO_2), en s'appuyant sur les estimations de flux de matières en suspension de Wollast et Marijns [32] pour le carbone particulaire organique et inorganique.

3. Résultats et discussion

Les concentrations en carbone organique témoignent d'une forte pollution de ces rivières, qui se traduit par des déficits marqués en oxygène (*tableau II*). Les eaux sont largement sursaturées en CO_2, dont une partie est due à la respiration en milieu aquatique. La *figure 2* montre l'évolution saisonnière de l'excès de CO_2 et du déficit en oxygène dans les cinq rivières. Bien qu'ils ne soient pas directement corrélés, on observe des évolutions temporelles relativement parallèles de ces deux paramètres, notamment dans l'Escaut supérieur, la Dendre et la Nete, où les valeurs augmentent en automne et en hiver. Ceci peut être attribué en partie à un lessivage des sols lors d'événements de crue [17] et, également en partie, à une diminution de la production phytoplanctonique en hiver [21], notamment dans l'Escaut supérieur et la Dendre, qui sont très eutrophisées et où les concentrations en chlorophylle-*a* atteignent 100 $\mu g{\cdot}L^{-1}$ au printemps et en été [1].

Comme cela a déjà été constaté dans d'autres études [15], l'excès de CO_2 est toujours supérieur au déficit en oxygène. Une seule exception est observée lors d'une crue dans la rivière Zenne, dont le bassin versant est très urbanisé : les deux paramètres étaient alors égaux. Des corrélations obtenues en comparant les valeurs moyennes de chaque rivière (*figure 3*) permettent de distinguer deux origines de ce CO_2. La *figure 3a* montre que le déficit en oxygène est positivement corrélé au carbone organique total ; les eaux des rivières Dendre et Dijle sont significativement plus pauvres en matière organique et mieux oxygénées que celles de l'Escaut supérieur et de la Nete. Ceci suggère que la respiration dans le milieu aquatique détermine en grande partie la fraction de l'excès de CO_2, qui se traduit par un déficit en oxygène. La *figure 3b* montre que l'excès de CO_2, qui n'est pas imputable à un déficit en oxygène, est anti-corrélé à la valeur du drainage du bassin versant. Pour les rivières à bassin versant agricole, modérément polluées et oxiques (Escaut supérieur, Dendre, Nete, Dijle), ce CO_2 est dû en majorité à la respiration des racines dans les sols. Dans la Zenne, le fait que, lors de la crue d'automne 1997 (jours 280, *figure 2*), l'excès de CO_2 et le déficit en oxygène soient égaux suggère que l'apport des sols est faible dans ce bassin versant majoritairement urbain. L'excès de CO_2 non imputable à un déficit en oxygène est alors dû aux processus anaérobiques. Cependant, nous discutons le fait que la majorité des processus anaérobiques (dénitrification, réduction du fer, du manganèse et des sulfates) produisent des ions bicarbonates, plutôt que du CO_2 [3]. Une réoxydation des composés réduits (manganèse, fer et sulfures dissous) est nécessaire pour produire finalement du CO_2 [28]. Or, elle s'accompagne d'une consommation en oxygène ; ce CO_2 est donc inclus dans le déficit en oxygène, tout comme celui produit par la respiration aéobie. Dans le cas de la rivière Zenne, qui est très fortement réduite, il est probable que la méthanogenèse produise du CO_2, sans consommer d'oxygène.

Les calculs de flux de carbone organique et inorganique transporté par les cinq rivières (*tableau III*) indiquent que l'excès de CO_2 correspond en moyenne à 10 % du CID, avec un maximum de 13 % dans la Nete et un minimum de 7 % dans la Zenne. Un budget de CO_2 de l'estuaire de l'Escaut relativement bien équilibré est obtenu (*tableau IV*). Dans ce budget, l'apport de CO_2 par les rivières contribue pour seulement 10 % de l'émission estuarienne, l'activité hétérotrophe et la nitrification dans l'estuaire étant les deux sources majeures de CO_2. Les flux longitudinaux, entre les rivières et l'estuaire et entre l'embouchure de l'estuaire et la mer du Nord, sont inférieurs d'un ordre de grandeur aux flux verticaux entre l'estuaire et l'atmosphère. L'apport par les fleuves est trois fois supérieur à l'exportation vers la mer du Nord, ce qui indique une ventilation nette du CO_2 apporté par les eaux douces.

4. Conclusion

L'utilisation de l'excès de CO_2 et sa comparaison avec le déficit en oxygène s'avère être une démarche efficace en milieu fluvial et complémentaire des mesures classiques de pCO_2. Elle a permis notamment de différencier les sources pédologiques et aquatiques du CO_2. Dans le cas de l'estuaire de l'Escaut, l'apport de CO_2 par les fleuves est une composante minoritaire de l'émission estuarienne vers l'atmosphère. Cependant, la quantification de cet apport reste nécessaire, car elle semble être plus importante dans d'autres estuaires, notamment dans celui de la Gironde [13].

1. Introduction

The transport of carbon by rivers is now a well-documented component of the global carbon cycle [4, 18, 20]. Distinction is generally made between the organic and inorganic species that both originate partly from the atmosphere and partly from surficial rocks (e.g. [20]). Rivers and estuaries also show significant supersaturation of CO_2 with respect to the atmosphere [5, 11, 13, 15–17, 21, 22]. Consequently, a fraction of the dissolved inorganic carbon (DIC) in rivers is present as 'excess CO_2', and can escape to the atmosphere due to physical water–air equilibration. This excess CO_2 results from: (1) input from surrounding areas, including soils [5, 17], wetlands [15], intertidal marshes [9], and urban areas [16]; (2) production by heterotrophic organisms and assimilation by phytoplankton and periphyton [5, 11, 13, 21]; and (3) evasion to the atmosphere that is determined by both the pCO_2 difference between the water and the atmosphere and the gas exchange coefficient K. Many different empirical relationships are used, giving the value of K as a function of either the river discharge [17, 21], the current speed and water column depth [6], the wind speed [10] or the wind and current speeds. However, these studies all show that because of the turbulence of the water, gas exchange coefficients are higher in rivers and estuaries than in the ocean for the same wind speed. Moreover, spatial and temporal variabilities are high because of the hydrodynamical and geomorphological complexity of these environments [1, 10–13, 21, 23].

Estuaries have been recently recognised as a significant source of CO_2 to the atmosphere [13]. This CO_2 is produced in majority in the estuarine zone that is known to be heterotrophic ecosystem, where organic carbon carried by rivers is partly mineralized [14, 29]. However, mass balance calculations show that in some sites, estuarine net heterotrophy accounts for only a part of the total emission to the atmosphere [1, 13]. In addition to organic carbon, rivers also transport significant amount of excess CO_2. Moreover, gas exchange coefficients are higher in estuaries than in rivers [1], so that physical ventilation of the CO_2 input by rivers occurs in the estuaries [13]. Although it sometimes represents a significant fraction of the DIC, very few studies quantify the transport of excess CO_2 by rivers [11, 22]. In this paper, we use a one-year data set of oxygen, pH, alkalinity and organic carbon in the five rivers entering a highly polluted European estuary, the Scheldt (Belgium, the Netherlands). We first describe the seasonal variation of excess CO_2 and discuss its origin. We then calculate the fluxes of excess CO_2 transported by the rivers and we compare it with other carbon species. Finally, we assess the contribution of excess CO_2 input by rivers, to the total CO_2 emission to the atmosphere from the estuary.

2. Material and methods

2.1. Study site and sampling

The characteristics of the five rivers that enter the Scheldt estuary (Belgium and the Netherlands; *figure 1*) are summarised in *table I*. On the one hand, high population density, agricultural and industrial activities and the lack of sewage treatments lead to high organic and nutrient loads [31]; on the other hand, low discharges limit the dilution of pollutants. This is reflected in *table I* by the ratio between number of inhabitants and river discharge, particularly high for the Zenne River that receives the wastewater from the city of Brussels. The transport of solids is also strongly affected by pollution, about 70 % of the suspended particulate matter (SPM) being from anthropogenic origin [32]. As a consequence of this pollution, intense heterotrophic activity and nitrification occur in the rivers and upper estuary and a permanent hypoxic zone develops from upstream in the different tributaries to downstream of the city of Antwerp (*figure 1*) [31]. In this area, pCO_2 often reaches 10 000 µatm and fluxes to the atmosphere sometimes exceed 500 $\text{mmol·m}^{-2}\text{·d}^{-1}$ [12, 13]. In order to evaluate carbon inputs from the five rivers into the estuarine zone, sampling stations were selected close to the limit of the tidal influence (*figure 1*). Stations were visited every 4–5 weeks from May 1997 to May 1998. Subsurface water was sampled with a 1.5-L Niskin bottle [1].

2.2. Chemical analysis and calculations

Just after sampling, pH and temperature were measured and oxygen was fixed with Winkler reagents. For

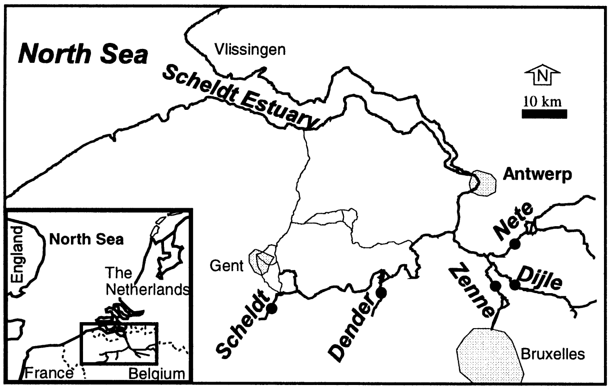

Figure 1. Map of the Scheldt estuary, showing the sampling stations on the five rivers: Scheldt, Dender, Zenne, Dijle and Nete.
Figure 1. Carte de l'estuaire de l'Escaut, montrant les stations de prélèvement sur les cinq rivières : Escaut supérieur, Dendre, Zenne, Dijle et Nete.

pH measurements, a Ross combination glass electrode was calibrated against NBS standards. Samples were then filtered through pre-combusted Whatman GF/F filters (porosity 0.7 μM). The filter was dried and stored for particulate organic carbon (POC) and the filtrate was stored partly in 250 mL polyethylene bottles for total alkalinity (TAlk) and partly in 10 mL pre-combusted vials and acidified for dissolved organic carbon (DOC). Within 24 h, TAlk was obtained from Gran titration and oxygen by the Winkler technique. POC and DOC were measured respectively with a LECO CS analyser and a Shimadzu TOC 5000 analyser; filters for POC were acidified with 2 N HCl. Particulate Inorganic Carbon (PIC) was also measured, but only once at each season and only in samples from the estuarine mixing zone. It was obtained by difference between total and organic carbon on two distinct filters.

pCO_2 and dissolved inorganic carbon (DIC) were calculated from pH and TAlk measurements, with the dissociation constants of carbonic acid from Mehrbach et al. [19] and the CO_2 solubility coefficient from Weiss [30]. Excess CO_2 (expressed in $\mu mol \cdot L^{-1}$) is defined as the quantity of DIC that is transferred as CO_2 to the atmosphere after complete water–air equilibration. It was calculated as the difference between the in-situ DIC and a theoretical DIC at atmospheric equilibrium. The latter was obtained by resolving the inorganic carbon system with the observed alkalinity and the atmospheric pCO_2 of 370 μatm. Because of high carbonate alkalinities that increase the buffer capacity of the inorganic carbon system, excess CO_2 was higher than dissolved CO_2. We compare excess CO_2 in the rivers with oxygen depletion, defined as the difference between the concentration at atmospheric equilibrium [7] and the measured concentration.

Fluxes of dissolved carbon species (DOC, DIC and excess CO_2) transported by the rivers were estimated using monthly concentrations and average discharges; for particulate species, we used the SPM fluxes calculated by Wollast and Marijns [32], based on inhabitant equivalents. For POC, SPM fluxes from each river were multiplied by the average POC content of the suspended matter. For PIC, only measurements in the estuarine mixing zone were available but the value was rather constant (1.5 % of the SPM), which allowed an estimation of the flux for the whole basin.

3. Results and discussion

3.1. Organic carbon, oxygen depletion and excess CO_2 in the five rivers

The high total organic carbon (TOC) and low oxygen concentrations observed in the five rivers (*table II*) reflect the levels of pollution, exceptionally high in the Zenne river. The observed pCO_2 are typical for populated areas in industrial countries [21]. Surprisingly, the most polluted Zenne river had the lower pCO_2 and a moderated excess CO_2 compared to the Scheldt and Dender rivers (*table II*).

Excess CO_2 and oxygen depletion time-series are presented in *figure 2*. In all rivers, excess CO_2 was higher than oxygen depletion. A relative parallelism was observed between the two parameters in the Scheldt and Dender rivers, with higher values in autumn and winter. There was however no significant relationship between the river discharge and excess CO_2 or oxygen depletion at the scale of individual rivers. In the Scheldt, Dender

Table I. General characteristics of the five rivers in the Scheldt basin [32].
Tableau I. Caractéristiques générales des cinq rivières du bassin versant de l'Escaut [32].

	Surface km^2	Discharge $(m^3 \cdot s^{-1})$	Drainage $(L \cdot s^{-1} \cdot km^{-2})$	Solid transport $(10^3\ t \cdot yr^{-1})$	Specific yield $(t \cdot km^{-2} \cdot yr^{-1})$	Population density $(inhab \cdot km^{-2})$	Inhabitants/ discharge $(inhab \cdot m^{-3} \cdot s)$
Scheldt	10 505	30	3	208	20	115	47 870
Dender	1 381	9	6	65	47	319	59 620
Zenne	1 150	11	9	91	79	1 177	182 810
Dijle	3 420	24	7	95	27	259	46 780
Nete	1 605	16	10	48	29	243	49 080
Total	18 160	90	5	507	27	242	48 840

Table II. Observed organic and inorganic carbon and oxygen levels in the five rivers entering the Scheldt estuary; average (minimum–maximum).

Tableau II. Concentrations en carbone organique et inorganique et oxygène observées dans les cinq rivières alimentant l'estuaire de l'Escaut ; valeur moyenne (minimum–maximum)

	POC (mg·L^{-1})	DOC (mg·L^{-1})	Oxygen (%sat)	TAlk (meq·L^{-1})	DIC (mmol·L^{-1})	Excess CO$_2$ (µmol·L^{-1})	pCO$_2$ (µatm)
Scheldt	4.6	8.7	28	6.0	6.4	655	9 500
	(2.2–9.1)	(6.4–13.6)	(0–55)	(5.2–6.9)	(5.5–7.5)	(440–980)	(7 030–16 300)
Dender	2.9	8.4	46	6.2	6.7	615	8 300
	(0.9–7.1)	(6.5–10.2)	(2–80)	(5.1–7.4)	(5.3–7.8)	(415–885)	(4 100–11 600)
Zenne	20.4	19.5	4	6.4	6.4	525	5 700
	(11.6–40.1)	(8.7–29.7)	(0–30)	(2.7–8.3)	(2.8–8.6)	(215–653)	(2 800–9 300)
Dijle	3.9	6.7	38	4.0	4.4	445	7 252
	(1.5–11.2)	(5.4–9.9)	(14–65)	(3.0–4.7)	(3.2–5.5)	(300–600)	(2 800–10 900)
Nete	6.2	7.2	31	2.4	2.9	355	6 700
	(2.2–13.1)	(5.7–9.6)	(3–60)	(1.8–3.1)	(2.1–4.3)	(290–450)	(5 400–7 900)

and Nete, flood events sometimes lead to a rise of both parameters, probably due to an input of carbon from soils, but sometimes did not (*figure 2*). On the contrary, in the highly polluted Zenne River, the flood in early October (day 280) led to a decrease of excess CO$_2$ and oxygen depletion and this was the only sample where the two parameters were equal. Excess CO$_2$, pCO$_2$ and DIC distributions in rivers are a complex combination of rock, soil and riverine processes and exchanges. Because of this complexity, the relationship between pCO$_2$ and the discharge is often not evident, as reported for example by Neal et al. [21] in densely populated basins in the UK. By contrast, in the Garonne basin, Semhi [25] reported higher pCO$_2$ at high river discharges, due to the predominance of input from soils with surface runoff.

Hamilton et al. [15] discussed that the excess CO$_2$ that cannot be accounted for by the oxygen depletion can either originate from root respiration of superior plants in soils or anaerobic bacterial metabolism in waters, sediments and soils. However, except methanogenesis from acetate that produce CO$_2$ together with CH$_4$, anaerobic processes (denitrification, iron, manganese and sulfate reductions) consume protons and, in a first step, produce in majority bicarbonates together with reduced species (dissolved iron, manganese and sulfides). In a second step, when these compounds are reoxidized, protons are produced and bicarbonate ions are stoichiometrically titrated into CO$_2$ [28]. This oxidation is done most of the time by oxygen. In a similar way, nitrification produces protons and transforms an amount of bicarbonates into CO$_2$ equivalent to the quantity of oxygen it consumes [3, 12, 23]. For these reasons, oxygen consumption and CO$_2$ production in the aquatic system, by both aerobic and anaerobic processes, are close to each other, except if methanogenesis is important. If some reduced compounds escape oxidation, bicarbonates are produced [3]. We can therefore consider that, except in anoxic and highly reduced waters (like the Zenne river), the oxygen depletion is close to the fraction of excess CO$_2$ produced by heterotrophic organisms in soils and waters, and the fraction that cannot be accounted for by the oxygen depletion originates in majority from root respiration in soils.

The relative contribution of river versus soil respiration to CO$_2$ in rivers is poorly documented. In pristine basins, soil respiration sometimes dominates [17] and sometimes not [11]. In polluted rivers, the contribution of aquatic respiration increases [16, 21]. In our study site, oxygen depletion represented on average 30 % of the excess CO$_2$ in the Dender and 60 % in the Nete. From one river to the other, we found a significant relationship between average oxygen depletion and total organic carbon (TOC): even excluding the highly polluted Zenne river, the Dender and Dijle rivers were significantly less polluted in organic matter and better oxygenated than the Scheldt and Nete rivers (*figure 3a*). In addition, because nutrient loads are also high, the Scheldt and Dender rivers are also eutrophysed ecosystems, where chlorophyll-*a* concentrations reach 100 µg·L^{-1} in spring and summer [1]. Consequently, photosynthesis also influences oxygen and CO$_2$, and is possibly responsible for the seasonal signal observed in these two rivers (*figure 2*), similar to the one reported by Neal et al. [21] in UK rivers.

In each river, the fraction of excess CO$_2$ that cannot be accounted for by the oxygen depletion and that originates mostly from root respiration in soils was negatively correlated with the drainage of the basin (*figure 3b*). This can be explain by the facts that the Scheldt basin has a low slope but a relatively high rainfall and soils are often flooded or saturated and in direct contact with the river. In that particular case, the negative relationship with the drainage suggests that when retention times of waters in soils are high, water becomes more enriched in CO$_2$. As reported by Jarvie et al. [16], this soil source of CO$_2$ is probably enhanced by the intense agricultural land-use. By contrast, in the Garonne basin, Sehmi [25] reported that during low drainage periods, pCO$_2$ was lower because groundwaters were the major source of water to the river. However, the link between hydrology and excess CO$_2$ is still incompletely understood and our sampling frequency is insufficient to understand precisely the phenomena at the scale of individual rivers.

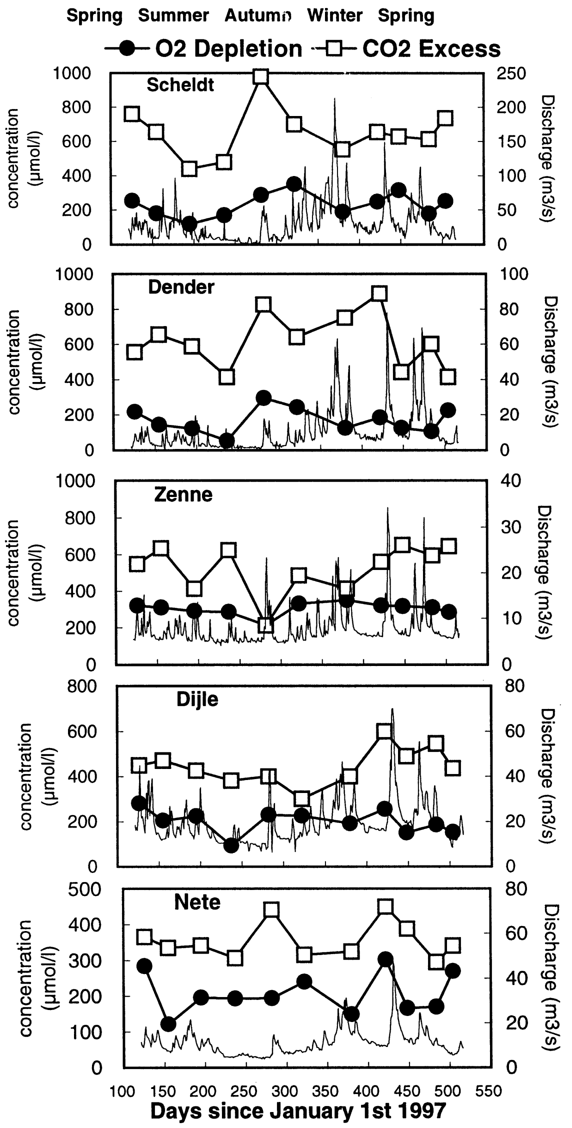

Figure 2. Seasonal variations of excess CO_2 (open squares), oxygen depletion (full circles) observed during the study period (May 1997–May 1998). Day zero is 01/01/1997. River discharge are reported on the right axis.

Figure 2. Variations saisonnières de l'excès en CO_2 (carrés ouverts) et du déficit en oxygène (cercles pleins) observés pendant l'étude (mai 1997–mai 1998). Le jour zéro est le 01/01/1997. Les débits sont reportés sur l'axe de droite.

In the Zenne River, when we sampled the flood event at day 280, both excess CO_2 and oxygen depletion were lower than during dry periods. Exceptionally, waters were oxic, because of dilution of domestic effluents with rainwater. Excess CO_2 was equal to oxygen depletion, which suggests that inputs from root respiration in soils are very limited in this urban basin. The excess CO_2 that cannot be accounted for by the oxygen depletion observed during dry periods is thus rather produced by anaerobic processes in the highly reduced waters. Sulfate reduction, methanogenesis and methane oxidation by sulfates may produce significant amounts of CO_2 without consuming oxygen. However, anaerobic processes produce in majority bicarbonates [3] and this is why the Zenne is also the river where excess CO_2 represent the lower fraction of DIC (7 % compared to more that 10 % in the four other rivers).

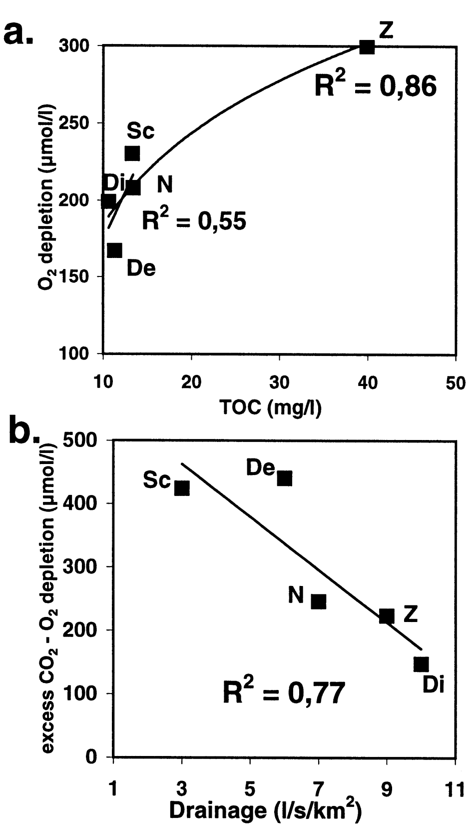

Figure 3. Relationship between (**a**) oxygen depletion and total organic carbon (TOC) and (**b**) the difference between excess CO_2 and oxygen depletion and the drainage (average values); Sc = Scheldt, De = Dender, Z = Zenne, Di = Dijle and N = Nete.

Figure 3. Relation entre (**a**) déficit en oxygène et carbone organique total (COT) et (**b**) la différence entre l'excès de CO_2 et le déficit en oxygène et le drainage (valeurs moyennes) ; Sc = Escaut supérieur, De = Dendre, Z = Zenne, Di = Dijle and N = Nete.

3.2. Carbon fluxes between the rivers, the estuary and the atmosphere

The results of flux calculations are given in *table III*. The total organic carbon input (dissolved and particulate: $83 \cdot 10^3$ $TC \cdot yr^{-1}$ for an average total river discharge of 70 $m^3 \cdot s^{-1}$) is consistent with previous estimates that give values around $100 \cdot 10^3$ $TC \cdot yr^{-1}$ for an average discharge of 90 $m^3 \cdot s^{-1}$ [27, 31]. Excess CO_2 represented 7 % of the DIC in the Zenne, 13 % in the Nete and 10 % in the Scheldt, Dender and Dijle. It accounts for 6 % of the total carbon input and is of the same order of magnitude as the DOC input (9 %). For an average river flow of 90 $m^3 \cdot s^{-1}$, the total input of excess CO_2 from rivers into the estuary is estimated to $18 \cdot 10^3$ $TC \cdot yr^{-1}$.

Table III. Inputs of organic and inorganic carbon into the Scheldt estuary (in TC·yr^{-1}).
Tableau III. Apports de carbone organique et inorganique dans l'estuaire de l'Escaut (en TC·an^{-1}).

	ORGANIC CARBON		INORGANIC CARBON		
	DOC	POC	DIC		PIC
			At equilibrium	Excess CO_2	
Scheldt	6 930	22 900	54 300	6 300	–
Dender	1 920	8 500	16 900	1 900	–
Zenne	4 480	20 060	17 800	1 400	–
Dijle	3 850	7 580	28 000	3 200	–
Nete	2 220	4 300	10 000	1 400	–
TOTAL	19 400	63 340	127 000	14 200	7 500
Percentage	9 %	27 %	55 %	6 %	3 %

The flows of carbon through the Scheldt estuary are now well documented, both by field and model approaches [8, 12, 13, 23, 24, 27, 31]. In contrast to highly turbid French estuaries (Gironde and Loire [1, 2]), there is no evidence for carbonate dissolution or precipitation in the Scheldt estuary [23]. Heterotrophic activity, that mineralizes a large fraction of the organic carbon carried by the rivers, and acidification, due to nitrification, are the major processes that produce CO_2. Although there is still some uncertainty in the numbers presented in *table IV*, the CO_2 budget is relatively satisfactory, compared to the one proposed for the Hudson estuary [22]. Heterotrophic activity and nitrification produce similar amounts of CO_2. The input of excess CO_2 from rivers represents only 10 % of the estuarine emission to the atmosphere. Advective flux of CO_2, from the river to the estuary and from the estuarine mouth to the North Sea are one order of magnitude lower than water–air exchange in the estuarine zone. Moreover, input from river is higher than export to the North Sea, which confirms the existence of a net ventilation phenomenon, but being rather low. Frankignoulle et al. [12] found that in the estuarine area at salinities 1 and 11 (a few kilometres up- and down-stream the city of Antwerp), oxygen depletion and excess CO_2 were close to each other. This supports the idea that the excess CO_2 transported by the rivers rapidly reaches the atmosphere in the very low salinity region of the estuary, and that downstream in the estuary, a steady state exists between respiration and evasion to the atmosphere.

4. Conclusion

Excess CO_2 has revealed a useful parameter to assess the dynamic of CO_2 in river systems. Although pCO_2 describes the intensity of exchanges at the water-air interface, it is strongly dependent on the buffer capacities of the waters and thus the lithological composition of the basins. Excess CO_2 is mainly affected by respiration and can be quantitatively compared to oxygen concentrations. However, sampling frequency for measuring these two parameters must be increased, particularly during flood events, to better understand the origin and transport of CO_2 between soils, rivers and the atmosphere. Excess CO_2 transport by rivers followed by ventilation in the estuary did not represent an important fraction of the CO_2 emission from the Scheldt estuary to the atmosphere. However, in other estuaries this component may be more important. For example, in the Gironde estuary, nitrification and heterotrophic activity account for only one half of the CO_2 emission to the atmosphere [13].

Table IV. A CO_2 budget for the Scheldt estuary (in 1 000 TC·yr^{-1}). When two references are given, the estimations are consistent at ± 10 %.
Table IV. Budget de CO_2 pour l'estuaire de l'Escaut (en 1 000 TC.an^{-1}). Lorsque deux références sont indiquées, elles sont cohérentes à ± 10 %.

	Input	Output	References
River input of excess CO_2^{a}	18		This study
Net heterotrophic activity (respiration–primary production)	100		[26, 31]
Acidification by nitrification ^{b}	90		[24, 27]
Emission to the atmosphere ^{c}		170	[13]
Transport to the North Sea		11	Borges, unpublished
TOTAL	210	181	

^{a}: normalised to the average river flow;
^{b}: calculated according to the reaction: $NH_4^+ + 2\ O_2 \rightarrow NO_3^- + 2\ H^+ + H_2O$;
^{c}: average of 12 cruises at all seasons.

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References

[1] Abril G., Dynamique du carbone dans les estuaires européens : processus de minéralisation et transfert continent–océan–atmosphère, thèse, université Bordeaux-1, 1999, 294 p.

[2] Abril G., Etcheber H., Le Hir P., Bassoullet P., Boutier B., Frankignoulle M., Oxic/anoxic oscillations and organic carbon mineralization in an estuarine maximum turbidity zone (The Gironde, France), Limnol. Oceanogr. 44 (1999) 1304–1315.

[3] Abril G., Frankignoulle M., Nitrogen-alkalinity interactions in the highly polluted Scheldt basin (Belgium), Water Res. (submitted).

[4] Amiotte Suchet P., Probst J.L., A global model for present-day atmospheric/soil CO_2 consumption by chemical erosion of continental rocks (GEM-CO_2), Tellus 47B 2 (1995) 273–280.

[5] Barth J.A.C., Veizer J., Carbon cycle in St Lawrence aquatic ecosystems at Cornall (Ontario), Canada: seasonal and spatial variations, Chem. Geol. 159 (1999) 107–128.

[6] Bennet J.P., Rathbun F., Reaeration in open-channel flow, US Geol. Surv. Prof. Pap. 737, 1972.

[7] Benson B.B., Krause D., The concentration and isotopic fractionation of oxygen dissolved in freshwater and seawater in equilibrium with the atmosphere, Limnol. Oceanogr. 29 (1984) 620–632.

[8] Borges A.V., Frankignoulle M., Daily and seasonal variations of the partial pressure of CO_2 in the surface seawater along the Belgian and southern Dutch coastal areas, J. Mar. Sys. 19 (1999) 251–266.

[9] Cai W.J., Pomeroy L.R., Moran M.A., Wang Y., Oxygen and carbon dioxide mass balance for estuarine-intertidal marsh complex of five rivers in the southeastern US, Limnol. Oceanogr. 44 (1999) 639–649.

[10] Clark J.F., Wanninkhof R., Schlosser P., Simpson H.J., Gas exchange rates in the tidal Hudson River using a dual tracer technique, Tellus 46B (1994) 274–285.

[11] Devol A.H., Richey J.E., Quay P., Martinelli L., The role of gas exchange in the inorganic carbon, oxygen and ^{222}Rn budgets of the Amazon River, Limnol. Oceanogr. 32 (1987) 235–248.

[12] Frankignoulle M., Bourge I., Wollast R., Atmospheric CO_2 fluxes in a highly polluted estuary (The Scheldt), Limnol. Oceanogr. 41 (1996) 365–369.

[13] Frankignoulle M., Abril G., Borges A., Bourge I., Canon C., Delille B., Libert E., Théate J.M., Carbon dioxide emission from European estuaries, Science 282 (1998) 434–436.

[14] Gattuso J.P., Frankignoulle M., Wollast R., Carbon and carbonate metabolism in coastal aquatic ecosystems, Annu. Rev. Ecol. Syst. 29 (1998) 405–434.

[15] Hamilton S.K., Sippel S.J., Melack J.M., Oxygen depletion and carbon dioxide and methane production in waters of the Pantanal wetland of Brazil, Biogeochemistry 30 (1995) 115–141.

[16] Jarvie H.P., Neal C., Leach D.V., Ryland G.P., House W.A., Robson A.J., Major ion concentrations and the inorganic carbon chemistry of the Humer rivers, Sci. Tot. Environ. 194–195 (1997) 285–302.

[17] Jones J.B., Mulholland P.J., Carbon dioxide variation in a hardwood forest stream: an integrative measure of whole catchment soil respiration, Ecosystems 1 (1998) 183–196.

[18] Ludwig W., Probst J.L., Kempe S., Predicting the oceanic input of organic carbon by continental erosion, Global Biogeochem. Cycles 10 (1996) 23–41.

[19] Mehrbach C., Culberson C., Hawley J.E., Pytkowich R.M., Measurements of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure, Limnol. Oceanogr. 18 (1973) 897–907.

[20] Meybeck M., Riverine transport of atmospheric carbon: sources, global typology and budget, Water Air Soil Poll. 70 (1993) 443–463.

[21] Neal C., House W.A., Jarvie H.P., Eatherall A., The significance of dissolved carbon dioxide in major lowland rivers entering the North Sea, Sci. Tot. Environ. 210–211 (1998) 187–203.

[22] Raymond P.A., Caraco N.F., Cole J.J., Carbon dioxide concentration and atmospheric flux in the Hudson river, Estuaries 20 (1997) 381–390.

[23] Regnier P., Wollast R., Steefel C.I., Long-term fluxes of reactive species in macrotidal estuaries: estimates from a fully transient, multicomponent reaction-transport model, Mar. Chem. 58 (1997) 127–145.

[24] Regnier P., Steefel C.I., A high resolution estimate of the inorganic nitrogen flux from the Scheldt estuary to the coastal North Sea during a nitrogen-limited algal bloom, spring 1995, Geochim. Cosmochim. Acta. 63 (1999) 1359–1374.

[25] Sehmi K., Érosion et transfert de matière sur le bassin versant de la Garonne. Influence de la sécheresse, thèse, université Louis-Pasteur, Strasbourg, 1996, 203 p., en dépôt à la Soc. géol. France.

[26] Soetaert K., Herman P.M.J., Carbon flows in the Westernscheldt estuary (The Netherlands) estimated by means of a global ecosystem model (MOSES), Hydrobiol. 311 (1995) 247–266.

[27] Soetaert K., Herman P.M.J., Nitrogen dynamics in the Westerschelde estuary (SW Netherlands) estimated by means of the ecosystem model MOSES, Hydrobiol. 311 (1995) 225–246.

[28] Stumm W., Morgan J.J., Aquatic chemistry, 2nd Ed., John Wiley and Sons, New York, 1981.

[29] Veyssy E., Colas C., Etcheber H., Maneux E., Probst J.L., Transports fluviaux de carbone organique par la Garonne à l'entrée de la Gironde, Sci. Géol. Bull. Strasbourg 49 (1996) 127–153.

[30] Weiss R.F., Carbon dioxide in water and seawater: the solubility of a non-ideal gas, Mar. Chem. 2 (1974) 203–215.

[31] Wollast R., The Scheldt Estuary, in: Salomon W., Bayne B.L., Duursma E.K., Förstner U. (Eds.), Pollution of the North Sea, an assessment, Springer-Verlag, 1988, pp. 183–193.

[32] Wollast M., Marijns R., Évaluation des contributions de différentes sources de matières en suspension à l'envasement de l'Escaut. Final report to the Ministry of Public Health and Environment (Belgium), 1981, 152 p.