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RESEARCH NOTE

NITROGEN–ALKALINITY INTERACTIONS IN THE HIGHLY POLLUTED SCHELDT BASIN (BELGIUM)

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Abstract—We present results of one year observations in highly heterotrophic and oxygen-depleted rivers of the polluted Scheldt basin. Monthly measurements revealed a high variability for dissolved inorganic carbon and nitrogen, with the following strong parallelism: highest alkalinity and NH_4^+ were associated with lowest NO_3^- and oxygen and *vice-versa*. In river water incubations, nitrification lowered the alkalinity whereas denitrification raised it; in an anoxic, NO_3^- -free incubation an increase of alkalinity was observed, partially due to ammonification. A stoichiometric analysis, taking into account the amount of protons produced or consumed by each process involving nitrogen, revealed that monthly variations of NO_3^- and NH_4^+ with ammonification, nitrification and denitrification could explain the 28 and 62% alkalinity variations at all stations, except one. The remaining part of the alkalinity variations was attributed to other anaerobic processes (Mn-, Fe- and SO_4 -reductions). This trend seems to be the result of the whole catchment metabolism (riverine waters and sediments, sewage networks and agricultural soils). The observed HCO_3^- concentrations in the Scheldt basin were 2–10 times higher than the representative concentrations reported in pristine basins and used in chemical weathering models. This suggests the existence of an anthropogenic source, originating from organic matter decomposition. We conclude that in highly polluted basins, nitrogen transformations strongly influence the acid–base properties of water.
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Key words—alkalinity, ammonification, nitrification, denitrification, polluted rivers

INTRODUCTION

Dissolved inorganic carbon (DIC) in rivers exists in majority in the dissolved gaseous forms of carbon dioxide (CO_2), and in the anionic forms of bicarbonates (HCO_3^-) and carbonates (CO_3^{2-}). At usual pH values, HCO_3^- represents more than 80% of the DIC and is considered to result from chemical weathering of rocks on drainage basins (Meybeck, 1987; Amiotte Suchet and Probst, 1993). Other processes also affect the DIC in rivers: photosynthesis, respiration and exchange with the atmosphere, occurring in soils and in rivers, directly affect the CO_2 fraction (Kempe, 1984; Richey *et al.*, 1991; Frankignoulle *et al.*, 1998). However, they generally modify the anionic forms to a much smaller extent, because of the buffering capacity of the system (Frankignoulle, 1994) and total alkalinity is considered as a rather conservative property of natural waters (Kempe, 1990).

In aquatic ecosystems that receive large amounts of organic matter and nutrients, the assumption of

the conservative property of alkalinity may become largely erroneous (Kempe, 1990) because the transfer of electrons involved in oxidation and reduction reactions is coupled with the transfer of protons (Stumm and Morgan, 1996; see Table 1). Frankignoulle *et al.* (1996) have observed a significant decrease of alkalinity with nitrification in the water column of the upper Scheldt estuary. Important alkalinity production due to ammonification, denitrification, Mn(IV)-, Fe(III)- or SO_4 -reductions have been reported in lakes (Cook *et al.*, 1986), in an anoxic fjord (Yao and Millero, 1995) and in the Black sea (Goyet *et al.*, 1991).

The Scheldt basin (Belgium) has to support a high organic and nutrient load, owing to the large number of inhabitants, the development of agricultural and industrial activities and the lack of sewage treatments (Wollast, 1988). Moreover, the influence of tides increases the residence time of waters and favours the aquatic processes versus the dispersion of pollutants. As a consequence, a permanent hypoxic zone is found upstream the city of Antwerp (Fig. 1) where heterotrophic activity and biological transformations of nitrogen are intense (Billen *et al.*, 1985; Wollast, 1988; Abril *et al.*, 2000).

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MATERIALS AND METHODS

The study site was the hypoxic area of the polluted Scheldt basin (Fig. 1). During one year, we have sampled the five major tributaries of the Scheldt estuary, at the upstream limit of the tidal influence (Stations A–E) and in the Scheldt tidal river, where the waters flowing from the five rivers get mixed by the tides (Station F). Residence time of waters in this area are between 10 and 30 days (Wollast, 1998). Stations were visited every 4–5 weeks during one year. Subsurface water was sampled with a 1.5 l Niskin bottle, oxygen was immediately fixed with Winkler reagents and samples were directly filtered through Whatman GF/F filters. The filtrate was partly stored in 250 ml plastic bottles for total alkalinity (TALK) and partly frozen in 10 ml propylene vials for inorganic nitrogen. The day after, TALK was obtained from the Gran titration and oxygen by the Winkler technique. Inorganic nitrogen species were determined with a Technicon Autoanalyser within 3 months.

Incubations, conducted in April 1998 with samples from stations A–C and F, consisted in following the evolution of oxygen, TALK and inorganic nitrogen over 15 days, without contact with the atmosphere and in the dark. For each station, 32 BOD bottles (300 ml) were filled with the water collected with a 5 l Niskin bottle and incubated at *in situ* temperature. Every 1 or 2 days, oxygen was measured in two bottles and TALK and inorganic nitrogen in two others.

RESULTS

Field data

A high temporal variability was observed, with a strong parallelism between TALK and NH_4^+ on the

one hand, and oxygen and NO_3^- on the other (Fig. 2). Highest TALK and NH_4^+ were associated with lowest NO_3^- and oxygen, whereas lowest TALK and NH_4^+ and highest NO_3^- were observed when waters were more oxygenated. Anoxic conditions, as observed in Autumn in the Scheldt and Dender rivers and most of the time in the Zenne river, were associated with an absence of NO_3^- as a result of water column denitrification (Billen *et al.*, 1985). Most of the time, at all these stations, nitrite represented less than 10% of total dissolved inorganic nitrogen.

Incubations

In the incubations, different conditions observed *in situ* were reproduced (Fig. 3). Incubations 1 and 4 started in oxic conditions. A significant decrease of TALK was observed during the first 50-h, with nitrification (rates: 0.3 and $1.7 \mu\text{eq kg}^{-1} \text{h}^{-1}$ for incubations 1 and 4, respectively). After a period of relative stability at low oxygen concentrations, denitrification raised the TALK at the rates of 0.5 and $3.5 \mu\text{eq kg}^{-1} \text{h}^{-1}$ for incubations 1 and 4, respectively; these rates are comparable to those measured by Billen *et al.* (1985) with the same technique. The variations of alkalinity and nitrogen were consistent (within the limits of both incubation and analytical techniques) with the stoichiometry of

Table 1. Stoichiometry of reactions that significantly affect the TALK in the environment^a

| | |
|---|--|
| Ammonification | $\text{R-NH}_2 + \text{H}^+ + \text{H}_2\text{O} \rightarrow \text{R-OH} + \text{NH}_4^+$ |
| Nitrification | $\text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + 2\text{H}^+ + \text{H}_2\text{O}$ |
| Denitrification | $5\text{CH}_2\text{O} + 4\text{NO}_3^- + 4\text{H}^+ \rightarrow 5\text{CO}_2 + 7\text{H}_2\text{O} + 2\text{N}_2$ |
| Manganese(IV) reduction | $\text{CH}_2\text{O} + 2\text{MnO}_2 + 4\text{H}^+ \rightarrow \text{CO}_2 + 3\text{H}_2\text{O} + 2\text{Mn}^{2+}$ |
| Iron(III) reduction | $\text{CH}_2\text{O} + 2\text{Fe}_2\text{O}_3 + 8\text{H}^+ \rightarrow \text{CO}_2 + 5\text{H}_2\text{O} + 4\text{Fe}^{2+}$ |
| Sulphate reduction | $2\text{CH}_2\text{O} + \text{SO}_4^{2-} + 2\text{H}^+ \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} + \text{H}_2\text{S}$ |
| Calcification and carbonate dissolution | $\text{CaCO}_3 \leftrightarrow 2\text{CO}_3^{2-} + 2\text{Ca}^{2+}$ |

^a R-NH₂ and CH₂O represent the nitrogen and carbon reactive parts of organic matter.

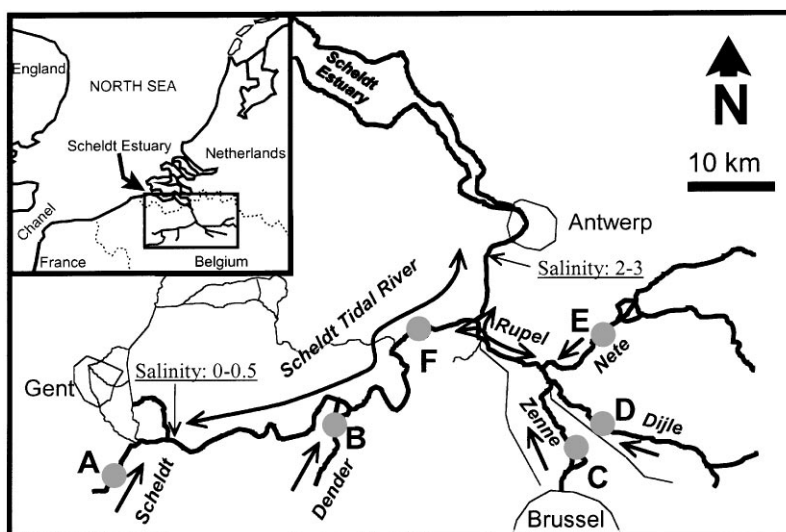


Fig. 1. Map of the study site showing the sampling stations in the five rivers (A–E) and in the Scheldt tidal river (F).

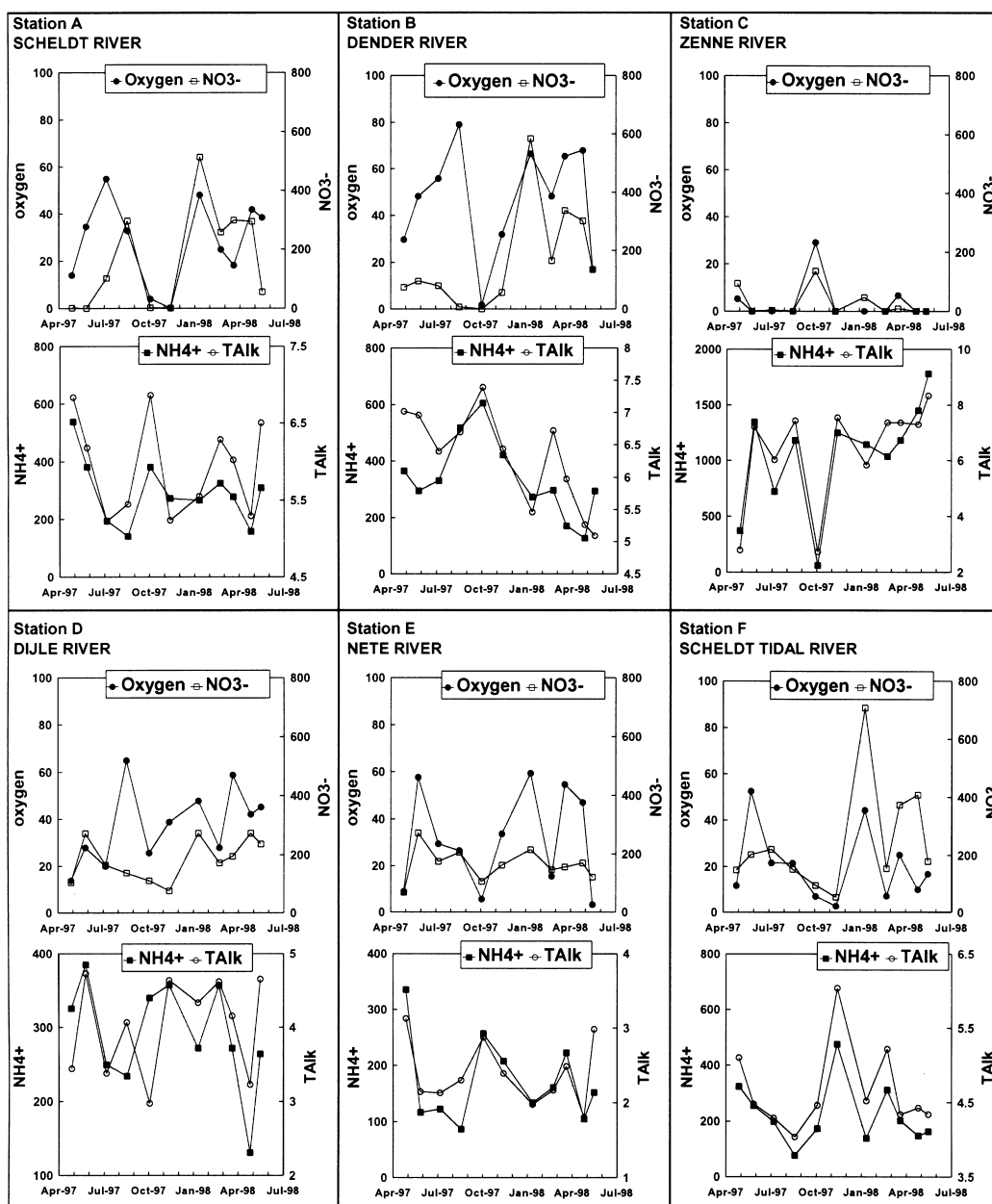


Fig. 2. Seasonal variations of oxygen (in percents of saturation), nitrate (NO_3^- in $\mu\text{mol.kg}^{-1}$), ammonium (NH_4^+ in $\mu\text{mol.kg}^{-1}$) and total alkalinity (TAlk in meq.kg^{-1}) in the Scheldt basin from April 1997 to May 1998.

nitrification and denitrification (Table 1) except at the end of incubation 4 (between hours 325 and 373), where the decrease of NO_3^- was $260 \mu\text{mol.kg}^{-1}$ and the increase in TAlk was $160 \mu\text{eq.kg}^{-1}$; the reason is that denitrification was not complete and NO_2^- increased by $95 \mu\text{mol.kg}^{-1}$.

Incubation 2 remained oxic and TAlk behaved conservatively, the variations of N-species being small.

Incubation 3 of water from the highly polluted Zenne river started and remained anoxic and NO_3^- -free; TAlk increased at a rate of $2.3 \mu\text{eq.kg}^{-1} \text{h}^{-1}$; during the first 100 h of incubation, NH_4^+ was produced by ammonification at a rate of

$1.6 \mu\text{mol.kg}^{-1} \text{h}^{-1}$ and could consequently explain 70% of the TAlk increase; after that, another process should induce the TAlk production.

DISCUSSION

Stoichiometric relationship between alkalinity and nitrogen in the Scheldt basin

Our field observations and the incubations suggest that the bacterial processes of ammonification, nitrification and denitrification rapidly and strongly affect the alkalinity in rivers. In addition, we

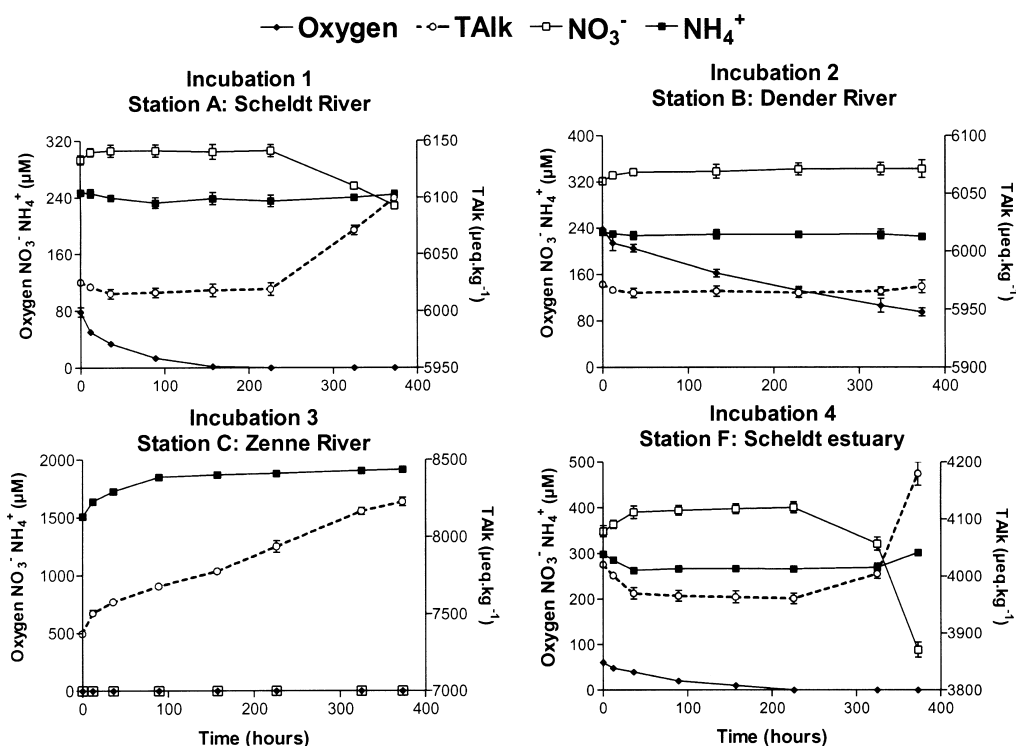


Fig. 3. Evolution of oxygen, nitrate (NO_3^-), ammonium (NH_4^+) and total alkalinity (TAlk) in incubations of waters from stations A, B, C and F. All units in $\mu\text{mol kg}^{-1}$ except TAlk in $\mu\text{eq kg}^{-1}$.

observed Chlorophyll-*a* concentrations up to $150 \mu\text{g l}^{-1}$ at some stations (Abril, 1999). Assuming a N/Chl-*a* weight ratio of 10 in biomass, phytoplankton is able to take up to $50\text{--}100 \mu\text{mol kg}^{-1}$ of nitrogen during spring and summer. NH_4^+ -uptake lowers the alkalinity, whereas NO_3^- -uptake raises it (Brewer and Goldman, 1976). In the upper Scheldt estuary, the latter is about 10 times lower than the former (Middelburg and Nieuwenhuize, 2000), and the effect of phytoplanktonic activity on alkalinity is consequently inverse of the ammonification effect.

The interaction between nitrogen and alkalinity can be interpreted in terms of production and consumption of protons, according to the stoichiometry described in Table 1:

$$\Delta\text{TAlk} = \Delta\text{TAlk}_{\text{ammonification}} + \Delta\text{TAlk}_{\text{nitrification}} + \Delta\text{TAlk}_{\text{denitrification}}$$

with

$$\Delta\text{TAlk}_{\text{ammonification}} = +1. \Delta\text{NH}_4^+_{\text{ammonification}}$$

$$\begin{aligned} \Delta\text{TAlk}_{\text{nitrification}} &= +2. \Delta\text{NH}_4^+_{\text{nitrification}} \\ &= -2. \Delta\text{NO}_3^-_{\text{nitrification}} \end{aligned}$$

$$\Delta\text{TAlk}_{\text{denitrification}} = -1. \Delta\text{NO}_3^-_{\text{denitrification}}$$

In oxic conditions, ammonification produces NH_4^+ and nitrification consumes NH_4^+ to produce NO_3^- . In the absence of denitrification, the NO_3^- variations

are induced in majority by the nitrification process:

$$\Delta\text{NH}_4^+_{\text{oxic}} = \Delta\text{NH}_4^+_{\text{ammonification}} - \Delta\text{NH}_4^+_{\text{nitrification}}$$

$$\Delta\text{NH}_4^+_{\text{nitrification}} = -\Delta\text{NO}_3^-_{\text{nitrification}} = -\Delta\text{NO}_3^-_{\text{oxic}}$$

The subtraction of these two relations results in

$$\Delta\text{NH}_4^+_{\text{ammonification}} = \Delta\text{NH}_4^+_{\text{oxic}} + \Delta\text{NO}_3^-_{\text{oxic}}$$

The variations of alkalinity in oxic conditions can thus be written as

$$\begin{aligned} \Delta\text{TAlk}_{\text{oxic}} &= \Delta\text{TAlk}_{\text{ammonification}} + \Delta\text{TAlk}_{\text{nitrification}} \\ &= (\Delta\text{NH}_4^+_{\text{oxic}} + \Delta\text{NO}_3^-_{\text{oxic}}) - (2\Delta\text{NO}_3^-_{\text{oxic}}) \\ &= \Delta\text{NH}_4^+_{\text{oxic}} - \Delta\text{NO}_3^-_{\text{oxic}} \end{aligned}$$

In anoxic conditions, ammonification produces NH_4^+ and denitrification consumes NO_3^- . In the absence of nitrification there is no transfer between these two species.

$$\Delta\text{NH}_4^+_{\text{ammonification}} = \Delta\text{NH}_4^+_{\text{anoxic}}$$

$$\Delta\text{NO}_3^-_{\text{denitrification}} = \Delta\text{NO}_3^-_{\text{anoxic}}$$

The impact of ammonification and denitrification can consequently be written as

$$\begin{aligned} \Delta\text{TAlk}_{\text{anoxic}} &= \Delta\text{TAlk}_{\text{ammonification}} + \Delta\text{TAlk}_{\text{denitrification}} \\ &= \Delta\text{NH}_4^+_{\text{anoxic}} - \Delta\text{NO}_3^-_{\text{anoxic}} \end{aligned}$$

Both in oxic and anoxic conditions, the term $\Delta\text{NH}_4^+ - \Delta\text{NO}_3^-$ describes the theoretical impact of

nitrogen transformations on alkalinity. We have compared this model with the observed monthly variations at the six studied stations (Table 2).

The relationship between variation of the observed alkalinity and those predicted by the stoichiometric model were significant ($P < 0.05$) at all stations except one (station D; Dijle river). Intercepts were never significantly different from zero. The slope of the relationship was always significantly higher than one. Slopes of 3.55 and 1.60 at stations C and F, respectively, indicate that the variations of nitrogen species explain only 28 and 62% of the alkalinity variations. This fact suggests that other anaerobic processes than denitrification also induce alkalinity variations: when anoxic conditions set up, nitrate become rapidly depleted and Mn(IV)-, Fe(III)- and SO_4 -reductions may occur, contributing to the alkalinity increase; when the water is reoxygenated these processes are stopped and the alkalinity decreases to its natural level. Moreover, Mn^{2+} and Fe^{2+} and a part of H_2S are reoxidised decreasing alkalinity together with nitrification.

The case of the Zenne (Station C) must be considered apart because this river receives the waste water from the city of Brussels without treatment (Abril *et al.*, 2000). During low river discharge, the sewage flow represent about one-half of the total flow. A part of the high slope of the regression must be attributed to dilution of waste waters with river waters during high river discharge. However, this river is most of the time anoxic and NO_3^- -free and behaves as an efficient reactor that produces alkalinity (see incubation 3). Sulphate concentrations are $660 \mu\text{mol kg}^{-1}$ in the waste water of the city of Brussels (Verbanck *et al.*, 1994) which gives an important potential for sulphate reduction in the anoxic river.

Rivers are highly dynamic systems and the concentrations of ions vary in time with the processes that occur in the rivers waters and sediments, but also with the variations of the sources. For that reason, the concentrations in rivers is probably an integrative measure of the whole catchment metabolism. In urban sewage networks, the same bacterial processes occur. In agricultural soils, vegetable growth lowers the alkalinity; on the contrary returning the material into the soil leads to ammonification that raises alkalinity, followed by nitrification that lowers it (Yan *et al.*, 1996). Application of organic fertilisers (cattle wastes), as it is the case on the Scheldt basin (Billen *et al.*, 1985) should induce ammonification and nitrification in soils. Moreover, denitrification in soils is enhanced by the use of both organic and inorganic fertilisers (Mulvaney *et al.*, 1997) and is intense in this area (Billen *et al.*, 1985). It is however worth to note that, in soils, interactions with mineral phase, as well as adsorption and desorption processes may complicate the nitrogen-alkalinity relationship.

Table 2. Linear regression analysis of ΔTALK versus $\Delta\text{NH}_4^+ - \Delta\text{NO}_3^-$ at the studied stations, with Δ difference between two following months

| Station | Slope ^a | R^2 | P |
|-------------------------|--------------------|-------|---------|
| Rivers | | | |
| Scheldt (A) | 1.89 ± 0.80 | 0.409 | 0.0465 |
| Dender (B) | 1.71 ± 0.52 | 0.579 | 0.0106 |
| Zenne (C) | 3.55 ± 0.42 | 0.897 | <0.0001 |
| Dijle (D) | 2.18 ± 2.32 | 0.099 | 0.3743 |
| Nete (E) | 2.74 ± 0.70 | 0.659 | 0.0043 |
| Tidal River Scheldt (F) | 1.60 ± 0.34 | 0.714 | 0.0021 |

^aWith 95% confidence intervals.

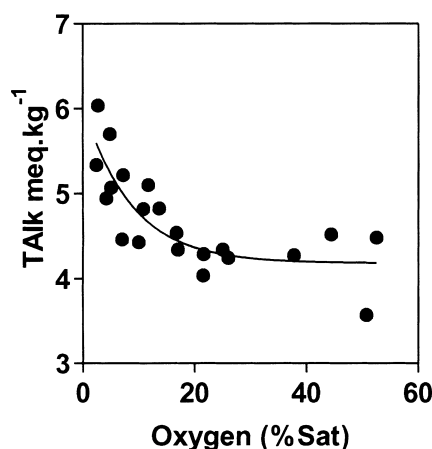


Fig. 4. Relationship between total alkalinity (meq kg^{-1}) and oxygen (percents of saturation) at station F.

High alkalinity in the Scheldt basin: an anthropogenic origin?

Alkalinity variations in the polluted Scheldt basin are linked to oxygenation conditions and underlying aerobic and anaerobic processes. Figure 4 shows that, at station F, alkalinity is significantly higher when oxygen is lower than 20% of saturation. This alkalinity excess is the result of anthropogenic organic matter decomposition under anaerobic conditions. In addition, the comparison with representative HCO_3^- concentrations established in pristine monolithologic basins that are used in chemical weathering models (Meybeck, 1987; Amiotte Suchet and Probst, 1994) suggests that a part of the background alkalinity is also anthropogenic: for carbonate rocks, the representative concentration is $3.17\text{--}3.19 \text{ meq kg}^{-1}$, that is two times lower than the average concentrations observed in the carbonated Scheldt and Dender basins; for sandstones, it is $0.12\text{--}0.15 \text{ meq kg}^{-1}$, that is more than one order of magnitude lower than our observations in the Dijle and Nete sandy basins. For the highly polluted Zenne

river, if one subtracts the alkalinity originating from wastewater (Verbanck *et al.*, 1994), which represent half of the river flow during dry periods, one gets an alkalinity of 2.7 meq kg^{-1} , still high for a basin dominated by sands.

Direct domestic input evaluated with the per capita loading (Verbanck *et al.*, 1994) and the population of the basin (Wollast, 1998) only represents 8% of the total HCO_3^- flux entering the estuary.

Alkalinity production results in an atmospheric CO_2 storage. However, this theoretical "alkalinity pump" (Kempe, 1990) can be efficient only if the reduced inorganic species produced are not further reoxidised, or if the reoxidation occurs in chemical pathways that do not release protons. This happens for example, when H_2S escapes to the atmosphere (Yao and Millero, 1995), when iron sulphides are produced (Cook *et al.*, 1986; Goyet *et al.*, 1991; Yao and Millero, 1995), when sulphides are reoxidised by oxygen into elemental sulphur (Goyet *et al.*, 1991) or when Fe^{++} precipitate with phosphates (Anschutz *et al.*, 1998). We have no data to provide evidence for such reactions in the Scheldt basin, except the fact that suspended particulate matter in this hypoxic zone is enriched in iron sulphides (Verlan *et al.*, 1998). The long-term effect of nitrogen loads on alkalinity is difficult to assess because it depends on the chemical form introduced in the environment: NH_4^+ inputs should decrease the alkalinity by nitrification, whereas NO_3^- inputs should increase it by denitrification.

CONCLUSION

The influence of human activity on organic carbon and nutrients concentrations in rivers is known for a long time. Our study reveals that, when nitrogen loads exceed HCO_3^- natural levels, HCO_3^- also becomes strongly affected by pollution:

- (1) alkalinity is always significantly higher in anoxic waters;
- (2) a major part of the alkalinity variations can be attributed to ammonification, nitrification and denitrification; the remaining part is probably due to other anaerobic processes;
- (3) HCO_3^- concentrations are 2–10 times higher than in pristine basin and chemical weathering becomes a minor contributor to the DIC input to the sea.

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