Impact of nitrogen fertilizers on the natural weathering-erosion processes and fluvial transport in the Garonne basin

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Abstract

Knowledge of the impact of N-fertilizers on the weathering-erosion processes of soils in intensively cultivated regions is of prime importance. Nitrification of NH_4^- fertilizers produces HNO_3 in the basin of the Garonne river, enhancing soil degradation. Their influence on the weathering rates was determined by calculating the consumption rate of atmospheric/soil CO_2 by soil weathering and erosion, and its contribution to the total dissolved riverine HCO_3^-. This contribution was found to be less than 50% which corresponds normally to a complete carbonate dissolution by carbonic acid, suggesting that part of the alkalinity in the river waters is due to carbonate dissolution by an acid other than carbonic acid, probably HNO_3.

1. Introduction

In recent years, pollution by NO_3 leaching from agricultural land has become an important concern (Gray et al., 1978; Etchanchu and Probst, 1988; Postma and Boesen, 1991; Goolsby and Battaglin, 1993), because of potential pollutions of surface and ground waters (Korom, 1992; Lacroix, 1993; Battaglin et al., 1994). This pollution includes spreading of N-fertilizers, mismanagement of irrigated crops, disposal of livestock waste (Hallberg, 1989) and cultivation of virgin land (Ronen et al., 1988). Many studies examined specifically the relationships between land use in drainage basins and N export by river waters and the origin of N (Behnke, 1975; Mariotti et al., 1975; Mariotti and Létolle 1977; Caussade et al., 1984; Collin et al., 1984; Probst, 1985; Blaison et al., 1985; Mariotti, 1986). Positive correlations were reported between (1) N loadings in river waters and demographic indices of various countries (Meybeck, 1982; Peierls et al., 1991), (2) N loss from agricultural land areas and N increase in surface waters (Omernik, 1976; Vagstad et al., 1997) and (3) application of fertilizers and N levels in stream waters (Smith, 1977). Hoyas et al. (1997) showed that approximately 85% of the total supply of N to a catchment area relates to agricultural activities, of which application of mineral fertilizers alone contributes 65–70%.

Nitrate can be produced from NH_4 in the presence of O_2 (is nitrification by autotrophic bacteria), or can be reduced to N_2O or N_2 in the absence of O_2 (is deni-

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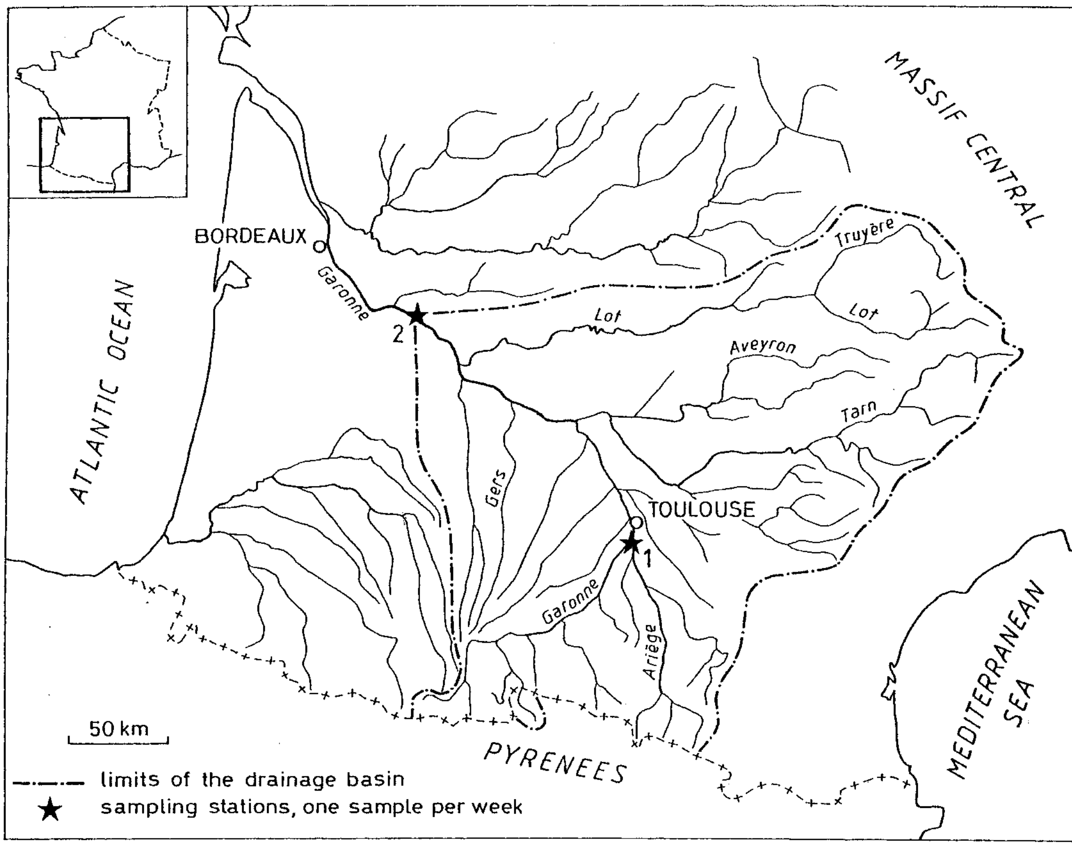


Fig. 1. Geographical sketch of the Garonne drainage basin with location of the two sampling stations.

trification). These two processes can take place simultaneously within a soil profile depending on the local O_2 fugacity (Reddy et al., 1976), nitrification releasing protons which may contribute to carbonate dissolution. Khdyer and Cho (1983) noted that the production rate of NO_3^- decreases with soil depth, as the microbial activity, organic matter content and partial pressure of O_2 decrease.

The study of the chemical composition of the Garonne river water from 1971 to 1984 by Etchanchu and Probst (1988) showed that the evolution of Ca^{2+}, Mg^{2+} and HCO_3^- cannot be related to a readjustment of the calcite equilibrium since the coefficient of calcite saturation for the water fluctuates around equilibrium. This can be explained by protons released during carbonate dissolution (Faurie, 1977; Durand and Dutil, 1972; Yanagita, 1990) from nitrification of N-fertilizers. The main objective of this study is to determine the effect of N-fertilizers on weathering-erosion processes, more specifically on the carbonate dissolution in the Garonne basin. The new aspects addressed here are (1) a regular measurement of the dissolved NO_3 concentrations in the Garonne waters over a 3-a period (one sample a week), and (2) a study of the relationship between the NO_3 concentrations and the proportion of weathering-related CO_2 consumption as reflected in the dissolved HCO_3 concentration.

2. Physical and hydrological setting of the Garonne basin

The city of La Réole located about 100 km to the south of Bordeaux in southwestern France, marks the outlet of the Garonne-river drainage basin. The drained area of 52,000 km^2 includes most of the Aquitaine basin which is bounded by the highlands of the Massif Central to the north-east, the Pyrénées mountains to the south and the Atlantic ocean to the west (Fig. 1). The Massif Central consists mainly of carbonate-rich marine sediments mostly of Jurassic age, as well as of Tertiary and Quaternary volcanics. The pre-Jurassic schists, gneisses and granites of the Pyrénées mountains were thrust under Mesozoic marine limestone about 40 Ma ago during the Alpine orogeny. The crystalline core of the Pyrénées mountains also includes Precambrian granites. The floor of the Aquitaine basin was flooded several times during the Oligo-Miocene by the westerly ocean. Each retreat of the marine waters was followed by lacustrine–fluviatile deposits of limestones and of molasses above carbonates in transitional continental environments (Bourgeat et al., 1984).

During the study period (1989–1992), the yearly discharge of the Garonne river ranged between 52 and 4790 $m^3 s^{-1}$, averaging 403 $m^3 s^{-1}$ at La Réole (station 2 on Fig. 1). The upstream Garonne river and the Ariège tributary together supply about 32% of the total Garonne discharge at the basin outlet, whereas tributaries draining the Massif Central contribute 62%, and small rivers draining the Molasse in the center of the basin contribute the remaining 5–6%. The study period is recognized to be a drought period: when compared to the interannual discharge from 1910 to 1992, the average discharge of the study period shows a deficit of 25% in the upper drainage basin, and of 34% in the whole Garonne basin. The most important hydrological deficit was observed in 1989.

3. Methodology

3.1. Sampling and analytical methods

The Garonne river was sampled weekly at two stations during the 1989–1992 period, one of which is located upstream (at Portet, station 1 on Fig. 1) that is influenced by drainage from the Pyrénées mountains and the other is located downstream (at La Réole, station 2 on Fig. 1) being influenced by the whole basin (Fig. 1). The measured discharges were made available by the 'Service Hydrologique Centralisateur' (Toulouse) by the speed exploration method and by jaugeage. The speed exploration method consists in measurements of runoff volumes at a given section in the basin along a vertical and by integrating the volumes along the section between the bottom and surface of the stream, allowing determination of an average discharge in $m^3 s^{-1}$. The jaugeage method is based on the tarage curve. The samplings were made in order to follow the interannual variations of the major dissolved elements (Semhi, 1996), and to quantify the amounts of atmospheric/soil CO_2 consumed by rock weathering. The water samples collected in polyethylene bottles, were pressure filtered through a Millipore HAWP 047-00 filter of 0.45 μm pore size, consisting in an ester of cellulose (nitrate + acetate) filter. The major cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) were analyzed by atomic absorption on a Z 8200 spectrometer with an air–C_2H_2 gaseous mixture. La was added (0.5%) to the sample for Ca^{2+} and Mg^{2+} analyses. These measurements were made with an accuracy of 1 μmol L^{-1}. The major anion (NO_3^-, Cl^- and SO_4^-) concentrations were determined by liquid-ion chromatography on a Dionex chromatograph 4000I equipped with columns AG11 and AS11 and NaOH as eluant. The detection limit was 1 μmol L^{-1}. The HCO_3^- concentrations were measured by alkalimetric titration with H_2SO_4. The total analytical precision varies between 1 and 2%.

Table 1
Ratios (in eq eq^{-1}) between dissolved elements and Cl^- in atmospheric precipitation (Meybeck, 1986)

C_i	Na^+	K^+	Mg^{2+}	Ca^{2+}	HCO_3^-	SO_4^{2-}
C_i/Cl^-	0.850	0.018	0.190	0.037	0.004	0.100

3.2. Calculations of the Garonne river fluxes

The fluxes were calculated on the basis of following equation:

$$\mathrm{Fa} = \sum_{i=1}^{n} C_{\mathrm{im}} \times Q_{\mathrm{im}},$$

where Fa is the annual flux (in kmol), n the number of measurement periods (in weeks), Q_{im} the weekly discharge (in $m^3 s^{-1}$), and C_{im} the weekly discharge-weighted mean of the concentration (in mmol L^{-1}) calculated as follows:

$$C_{\mathrm{im}} = \frac{C_1 Q_1 + C_2 Q_2}{Q_1 + Q_2}$$

where C_1 and C_2 are the instantaneous concentrations (in mmol L^{-1}) of the first and last sample, respectively, during each measurement period, and Q_1 and Q_2 are the corresponding discharges (in $m^3 s^{-1}$).

3.3. Corrections for atmospheric inputs

The contribution of the atmospheric input to the amounts of the major dissolved elements was estimated on the basis of the ratio between the concentrations of the dissolved elements C_i(p) and the chlorides Cl(p) in precipitation (Meybeck 1986; Table 1). The mean Cl^- concentration in the atmospheric precipitation over the Garonne basin was estimated by using the decrease of Cl^- concentrations measured in precipitation at several stations in France (Ulrich et al., 1994), relative to the distance of the sampling location (d) to the ocean (Fig. 2). The corrected concentrations from atmospheric input $C_{\mathrm{i(f)cor}}$ can be estimated as follows:

$$QC_{\mathrm{i(f)cor}} = QC_{\mathrm{i(f)}} - PC_{\mathrm{i(p)}}$$

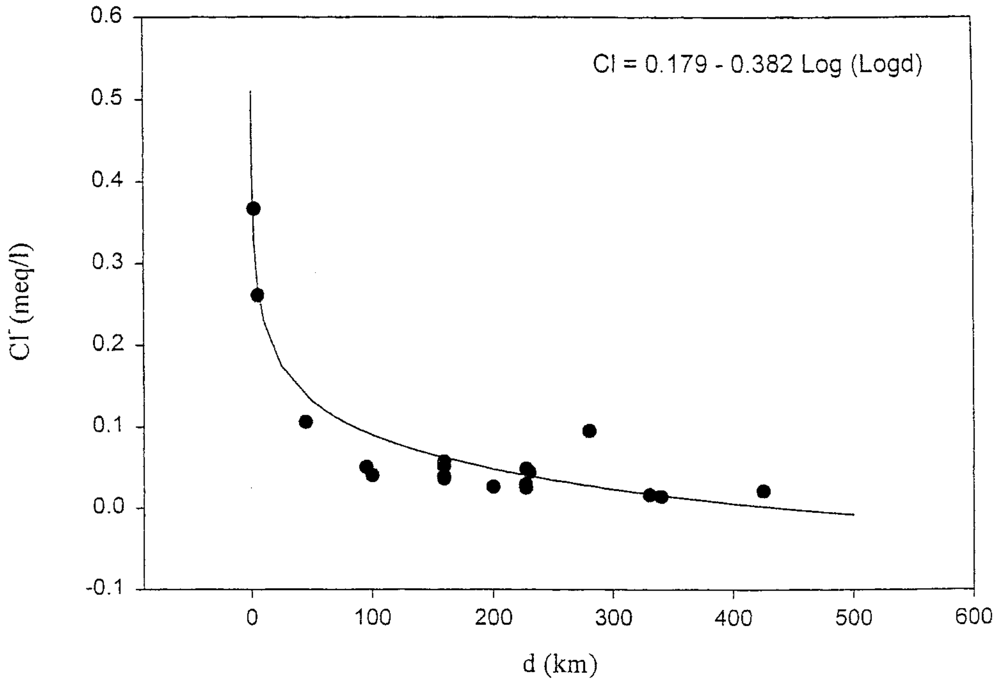


Fig. 2. Relationship between Cl^- concentrations (in meq L^{-1}) in precipitation and distance (in km) to the Atlantic coast.

$$C_{i(f)cor} = C_{i(f)} - \frac{P}{Q} C_{i(p)},$$

where $C_{i(f)}$ is the observed concentration of the dissolved elements, $C_{i(p)}$ the concentration of the same elements dissolved in precipitation P calculated on the basis of the above mentioned ($C_{i(p)}/C_{l(p)}$) ratio, Q (in L km^{-2} s^{-1}) the annual mean discharge and P (in L km^{-2} s^{-1}) the annual mean precipitation. The precipitation P were estimated by using the regression between the mean annual discharge Qs (in L km^{-2} s^{-1}) and the annual precipitation P (in cm) in the Garonne basin, on the basis of following regression:

$$Qs = 0.034\,P - 19.5.$$

3.4. CO_2 flux consumed by chemical weathering: the code MEGA

The amount of atmospheric/soil CO_2 consumed by chemical weathering was estimated from HCO_3^- ion fluxes measured in the waters and from major dissolved elements, by using the geochemical code MEGA (Amiotte Suchet, 1995; Amiotte Suchet and Probst, 1996) to calculate the contribution of the atmospheric CO_2 to the total exported HCO_3 flux. The modeling procedure decomposes the major-element fluxes and it uses the stoichiometric dissolution or hydrolysis of the different minerals susceptible to react. It allows, after correction of the atmospheric input of cations and anions, determination of the mineralogical origin of the major elements dissolved in the river waters. In the code, Na is supposed to be released by dissolution of halite (Eq. (1)) and Na-silicates (for example Eqs. (7) and (8)), Cl by dissolution of halite and sylvite (Eqs. (1) and (2)), K by dissolution of sylvite and orthose (Eqs. (2) and (6)), SO_4 by dissolution of gypsum (Eq. (3)), Ca by dissolution of gypsum (Eq. (3)), calcite (Eq. (4)) and Ca-silicates (Eq. (9)), Mg by dissolution of dolomite (Eq. (5)) and Mg-silicates (for example Eq. (10)). An illustration of the concept is given in Fig. 3. The different reactions involved are:

- halite dissolution

$$NaCl \rightarrow Na^+ + Cl^- \quad (1)$$

- sylvite dissolution

$$KCl \rightarrow K^+ + Cl^- \quad (2)$$

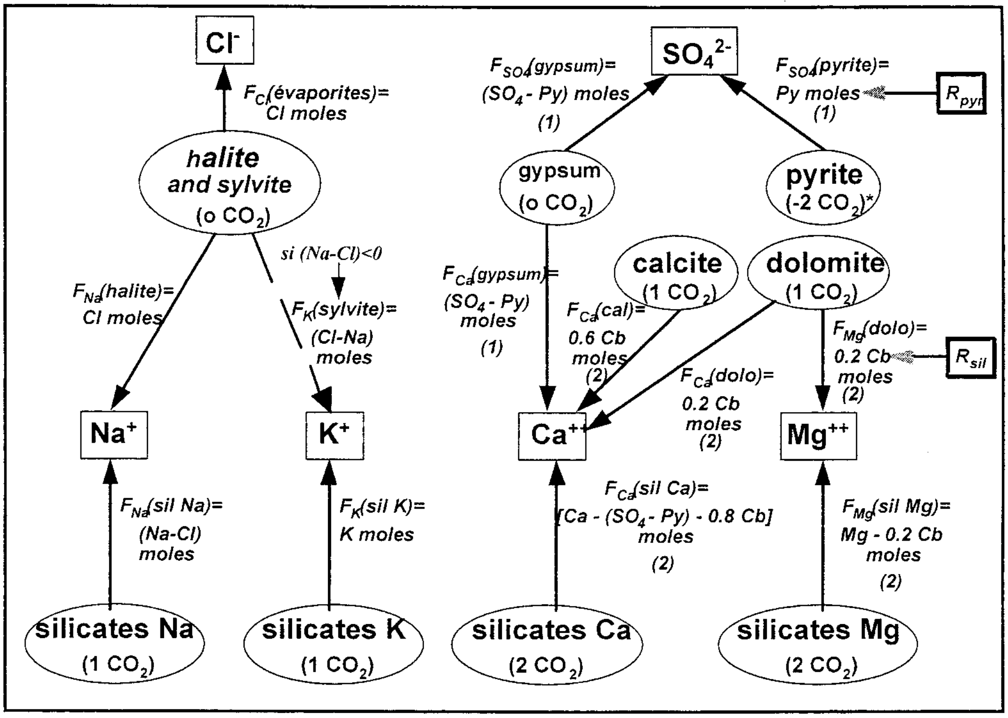
- gypsum dissolution

$$CaSO_4 \rightarrow Ca^{2+} + SO_4^{2-} \quad (3)$$

- calcite dissolution

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3 \quad (4)$$

- dolomite dissolution



(1) Py= molar flux of SO_4 procuded by pyrite oxydation, Py=Rpyr(Na+K-Cl)(1/Rsil+1)
Rpyr = SO_4/(Na+K+Ca+Mg) and Rsil = (Na+K)/(Ca+Mg) is measured in waters draining silicate rocks
(2) Cb = molar flux of Ca and Mg derived from carbonate weathering;
Cb = Ca+Mg-(SO_4-Py)-1/Rsil(Na+K+Cl), Rsil = (Na+K)/(Ca+Mg) is measured in waters draining silicate rocks

Fig. 3. Schematic concept of the MEGA code for the origins of the major dissolved elements relative to weathering of silicate, evaporitic and carbonate rocks (Amiotte Suchet and Probst, 1996).

$$MgCaCO_3 + CO_2 + H_2O \rightarrow Mg^{2+} + Ca^{2+} + 2HCO_3 \quad (5)$$

- hydrolysis of orthoclase to montmorillonite

$$2KAlSi_3O_8 + 2CO_2 + 4H_2O \rightarrow Al_2Si_4O_{10}(OH)_2 + 2K^+ + 2HCO_3^- + 2SiO_2 \quad (6)$$

- hydrolysis of albite to kaolinite

$$2NaAlSi_3O_8 + 2CO_2 + 3H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 2HCO_3^- + 4SiO_2 \quad (7)$$

- hydrolysis of albite to montmorillonite

$$2NaAlSi_3O_8 + 2CO_2 + 4H_2O \rightarrow Al_2Si_4O_{10}(OH)_2 + 2Na^+ + 2HCO_3^- + 2SiO_2 \quad (8)$$

- hydrolysis of anorthite to kaolinite

$$CaAl_2Si_2O_8 + 2CO_2 + 2H_2O \rightarrow Al_2Si_2O_5(OH)_4 + Ca^{2+} + 2HCO_3^- \quad (9)$$

- hydrolysis of chlorite to kaolinite

$$Mg_5Al_2Si_3O_{10}(OH)_8 + 10CO_2 + 5H_2O \rightarrow Al_2Si_2O_5 + 5Mg^{2+} + 10HCO_3 + H_4SiO_4 \quad (10)$$

The flux of HCO_3^- contributed by carbonate dissolution ($F_{carb}HCO_3$) was calculated as follows:

$$F_{carb}HCO_3 = F_{Ca\ carb} + F_{Mg\ carb}$$

where $F_{Ca\ carb}$ is the amount of Ca released by dissolution of calcite, and $F_{Mg\ carb}$ the amount of Mg released by dissolution of dolomite. The flux of CO_2 (FCO_2) is the difference between the total HCO_3 (F_tHCO_3) measured in the waters of the Garonne river and $F_{carb}HCO_3$, as follows:

Table 2
Mean chemical compositions of the Garonne waters during the 1989–1992 period (in mmol L^{-1})[a]

Elements	Upstream (Portet)		Downstream (La Réole)	
	This study	P&B[a]	This study	E&P[a]
Na^+	0.192	0.174	0.348	0.304
K^+	0.032	0.026	0.051	0.051
Mg^{2+}	0.134	0.206	0.247	0.247
Ca^{2+}	0.982	0.848	1.047	1.197
NO_3^{2-}	0.082	0.048	0.161	0.097
SO_4^{2-}	0.164	0.125	0.187	0.198
SiO_2	0.071	0.083	0.075	0.116
HCO_3^-	1.826	1.738	2.131	2.344
Cl –	0.179	0.141	0.366	0.310

[a] P&B stands for data by Probst and Bazerbachi (1986) during the 1980–1981 period, E&P for data by Etchanchu and Probst (1988) during the 1971–1983 period.

$$FCO_2 = F_t HCO_3 - F_{carb} HCO_3$$

4. Fluvial transport of nitrates

Under normal physico-chemical conditions encountered near the earth's surface, N compounds generally occur as NH_4^+, NO_2^-, NO_3^-, dissolved organic N or particulate organic N in natural waters. Natural levels of dissolved N in rivers are very low, equivalent to 8.6 μmol L^{-1} on average, of which only 15% are present as NH_3 and 1% as NO_2^- (Meybeck, 1982). Inorganic N dissolved in natural waters ($N\text{-}NO_3 + N\text{-}NO_2 + N\text{-}NH_4$) is estimated to be equivalent to 12.9 μmol L^{-1} in the temperate zone, 6.5 μmol L^{-1} in the tropical zone, 10 μmol L^{-1} in the taiga and 2.2 μmol L^{-1} in the tundra (Meybeck, 1982). The percentage of $N\text{-}NH_4$ ranges from a few percent to as much as 80%. Nitrite-N is never abundant in rivers, accounting for no more than 7% of the total dissolved inorganic N (Meybeck, 1982). The most important N species of surface waters are nitrates and organic N (Hutchinson, 1957). In the waters of the Seine river (central France), NO_3^- concentrations could be as high as 483 μmol L^{-1} during winter and 241 μmol L^{-1} during summer time (Greiner, 1997). Williams et al. (1995) noted NO_3^- concentrations of about 20 μmol L^{-1} for the Emerald lake waters (southern Sierra Nevada, CA). Nitrates are soluble in water, but not significantly adsorbed by clay-rich soils. They may be picked up by plants or reduced into nitrites within the root zones in soils.

One of the most detailed study of the N budget in river waters was that of Bennekom and Salomons (1981) who noted that man's activity has increased the N load by a factor of three to four. Probst (1985) compared the amounts of nitrates exported by the Garonne river to the total amount of N-fertilizers and concluded that river exportations depend on both fertilizer inputs, and intensity of soil leaching which relates to the river discharge. In this study, the authors examined the global seasonal variations of NO_3^- fluxes without distinction between natural and anthropogenic origin.

Table 3
Annual fluxes of dissolved elements exported by the Garonne river during the 1989–1992 period (kmol km^{-2} a^{-1})[a]

Elements	Upstream (Portet)		Downstream (La Réole)	
	This study	P&B[a]	This study	E&P[a]
Na^+	80.43	126.52	83.91	121.74
K^+	12.53	16.11	14.32	15.35
Mg^{2+}	56.79	135.80	62.14	107.00
Ca^{2+}	401.25	587.03	267.33	496.26
NO_3^{2-}	31.29	27.42	36.61	41.94
SO_4^{2-}	68.47	82.31	46.10	83.25
SiO_2	29.45	53.08	18.14	46.59
HCO_3^-	752.95	1189.34	537.05	967.21
Cl^-	86.48	93.80	90.99	132.39
TDS	1519.65	2311.42	1156.59	2011.72
Q (m^3/s)	134	217	403	684

[a] P&B stands for data by Probst and Bazerbachi (1986) during the 1980–1981 period, E&P for data by Etchanchu and Probst (1988) during the 1971–1983 period.

4.1. Mean concentrations and annual fluxes of major dissolved elements

The mean annual concentrations and fluxes of the Garonne waters were estimated by Semhi (1996). During the 1989–1992 period, the concentrations of the major elements in the waters are within the range of concentrations of the elements in most surface waters. Like waters in many rivers, those in the Garonne river have Ca^{2+} as the major cation and HCO_3^- as the major anion (Table 2). The average NO_3^- concentrations were 82 and 161 μmol L^{-1} NO_3^- at Portet and La Réole, respectively. Compared to results obtained during more humid cycles (+15 and +33% relative to the mean interannual discharge, for the upstream and downstream stations, respectively), the river transport of the soluble elements is less important for all elements during the study period than during the humid ones, except for the nitrates at Portet (Table 3).

4.2. Seasonal variations of NO_3^- concentrations

The seasonal variations of the NO_3^- concentrations

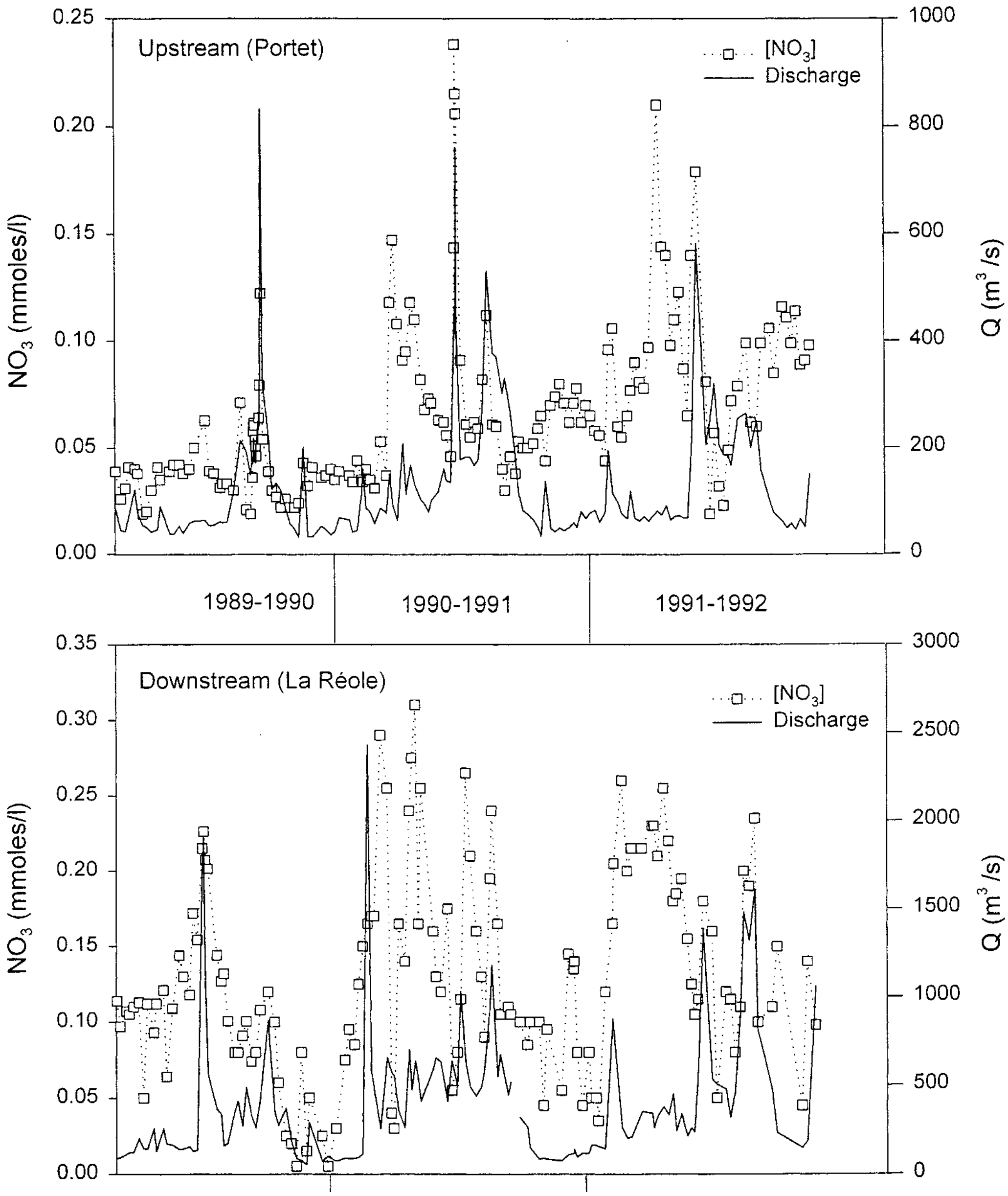


Fig. 4. Seasonal variations of daily discharge (dotted lines) and NO_3 concentrations (crosses and straight lines) in the waters of the Garonne river during the 1989–1992 period.

is marked by high concentrations during high-water periods (Fig. 4). This suggests that NO_3^- concentrations in the waters relate to removal of NO_3^- from soils, since fertilizers represent the main source of NO_3^- in this extensively farmed region. Seasonal distinctions emerge in the winter and spring periods during which NO_3^- concentrations increase most with increased discharge (Fig. 5). The NO_3^- concentrations vary widely during the summer for small discharge variations, suggesting that (1) the discharge does not significantly influence the NO_3^- contents during this period of the year and (2) other factors, such as biological processes, affect them more significantly. Among these biological inputs, one may suggest that raising different types of crops around the year induces different N-uptakes and consequently different types of N-residuals in the soils. In addition, large variations in NO_3^- concentrations during summer could be induced by mineralization and nitrification processes increasing the NO_3^- contents in soils and subsequently enhancing NO_3^- removal by

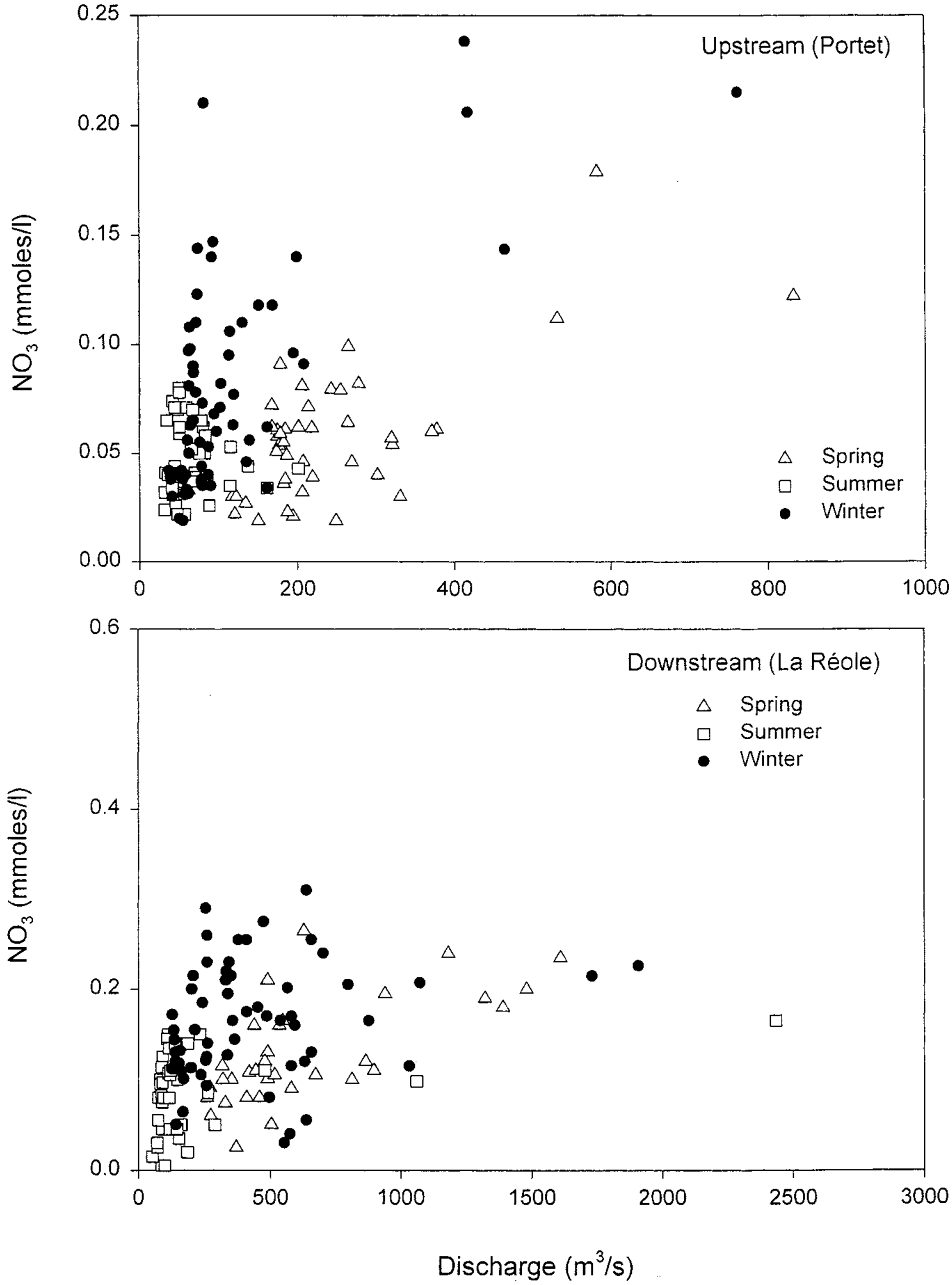


Fig. 5. Relationship between NO_3 concentrations (in mmol L^{-1}) in waters and discharge (m^3 s^{-1}) measured during the 1989–1992 period.

running waters after rainfalls. Similar seasonal variabilities reported by Elder (1985) in the Apalachicola river (in northwestern Florida), were explained by variable rates of uptake and N-metabolism by microbiota activity during summer. Determine and Lamberts (1987) considered that nitrification of NH_4^- is a major source of NO_3^- flux in the Belgian part of the Meuse river during low discharge periods, especially in the waters having important NH_4 loads.

When the discharge is very high, the NO_3^- removed from soils is diluted by surface runoff waters that are less concentrated in nitrates. This observation reported by Foster (1981) can explain the small variations of the NO_3^- concentrations for large discharge variations during winter and spring. During summer, however, ground waters become dominant suppliers to rivers. Ground waters transport dissolved nitrates, that are derived in varying amounts from decaying plants and agricultural fertilizers, and delivered to the river waters during summer.

4.3. Nitrate fluxes, concentrations and export rates

The NO_3^- budget in the Garonne waters during the 1989–1992 period was estimated to be 31.3 kmol km^{-2} a^{-1} upstream and 36.6 kmol km^{-2} a^{-1} downstream. As already mentioned, the NO_3^- load increases, while most other elemental loads decrease during the dry period. Calculation of the NO_3^- fluxes from the Pyrénées mountains and Massif Central + Molasse region indicates that 4–59% of the measured nitrate flux at La Réole originates in the Pyrénées mountains. The highest contributions of the Pyrénées region occurred during spring and summer, which are also the periods of high discharge (Semhi, 1996). Best correlations between these two variables were also obtained during winter time.

Cooke and Williams (1970) reported that most agricultural soils contain from 107 to 429 kmol ha^{-1} of organically bound N in their upper 150 mm. During this study, the NO_3^- concentrations measured in the Garonne waters at Portet and La Réole, increased relatively to those measured by Probst (1985). The NO_3^- concentrations increased by 78% at La Réole during the 1971–1984 period (Etchanchu and Probst, 1988), which was attributed to increased use of N-fertilizers, spreading having nearly doubled during the last 20 a in the Aquitaine basin (Probst, 1985).

5. Weathering and consumed atmospheric/soil CO_2

The amount of atmospheric/soil CO_2 consumed by chemical weathering in a drainage basin can be estimated from HCO_3^--ion flux measured at the outlet of the basin. The contribution of atmospheric/soil CO_2 to the total river alkalinity reaches 100% in the case of silicate hydrolysis, according to the hydrolysis reaction of albite (Eqs. (7) and (8)). On the other hand, the contribution of atmospheric/soil CO_2 to the total river alkalinity may not exceed 50% in a drainage basin such as that of the Garonne river where carbonate outcrops are abundant, according to the stoichiometric coefficients of the calcite-dissolution reaction (Eq. (4)).

The transformation of inorganic or organic N to a more oxidized state releases protons (Eq. (11)) which may contribute to carbonate dissolution (Eqs. (12) and (13); Faurie, 1977; Yanagita, 1990). The equations of these two reactions are the following:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \quad (11)$$

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \quad (12)$$

$$Mg_{0.5}Ca_{0.5}CO_3 + H^+ \rightarrow 1/2Mg^{2+} + 1/2Ca^{2+} + HCO_3^- \quad (13)$$

and the global equation becomes:

$$NH_4^+ + 2O_2 + 2CaCO_3 \rightarrow NO_3^- + 2Ca^{2+} + 2HCO_3^- + H_2O \quad (14)$$

or

Table 4
Annual fluxes of dissolved HCO_3, Ca + Mg and atmospheric CO_2 consumed by weathering[a]

		Upstream (Portet)	Downstream (La Réole)		
		this study (1989–1992)	this study (1989–1992)	AS[a] (1971–1991)	E&P[a] (1971–1984)
HCO_3 (kmol km^{-2} a^{-1})	silicate	19	52	47	–
	carbonate	775	504	798	–
	total	794	556	845	802
Ca + Mg (kmol km^{-2} a^{-1})	silicate	136	57	30	–
	carbonate	369	258	434	–
	total	505	315	505	600
atmospheric CO_2 (kmol km^{-2} a^{-1})	silicate	19	41	47	–
	carbonate	356	355	364	–
	total	375	269	411	441
Q	(m^3 s^{-1})	217	403	620	684

[a] AS stands for data by Amiotte Suchet (1995) and E&P for data by Etchanchu and Probst (1988).

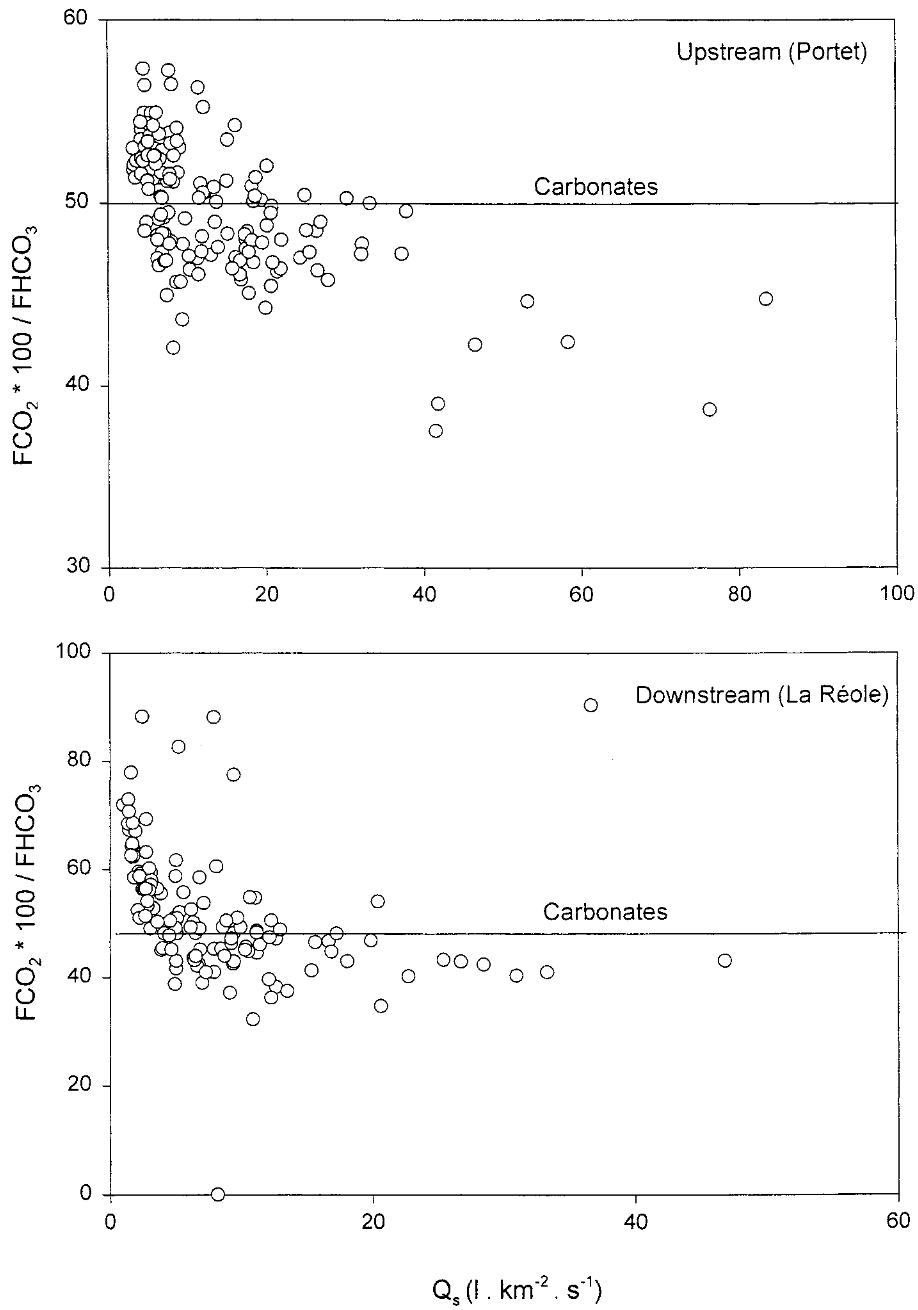


Fig. 6. Relationship between the contribution of atmospheric/soil CO_2 to the total river alkalinity and the Garonne river discharge (in L km^{-2} s^{-1}).

$$NH_4^+ + 2O_2 + 2MgCaCO_3 \rightarrow NO_3^- + 2Ca^{2+} + 2Mg + 2HCO_3^- + H_2O \quad (15)$$

The observed flux in Ca + Mg during the 1989–1992 period was estimated to be 505 kmol km^{-2} a^{-1} upstream and 315 kmol km^{-2} a^{-1} downstream (Table 4). About 73% of this flux comes from weathering of the carbonate rocks upstream and 82% from weathering of the same rocks downstream, leaving silicate rocks contributing only 27% of the total flux upstream and 18% downstream. On the other hand, the HCO_3 flux comes mainly from weathering of the carbonate rocks: about 775 kmol km^{-2} a^{-1} were observed

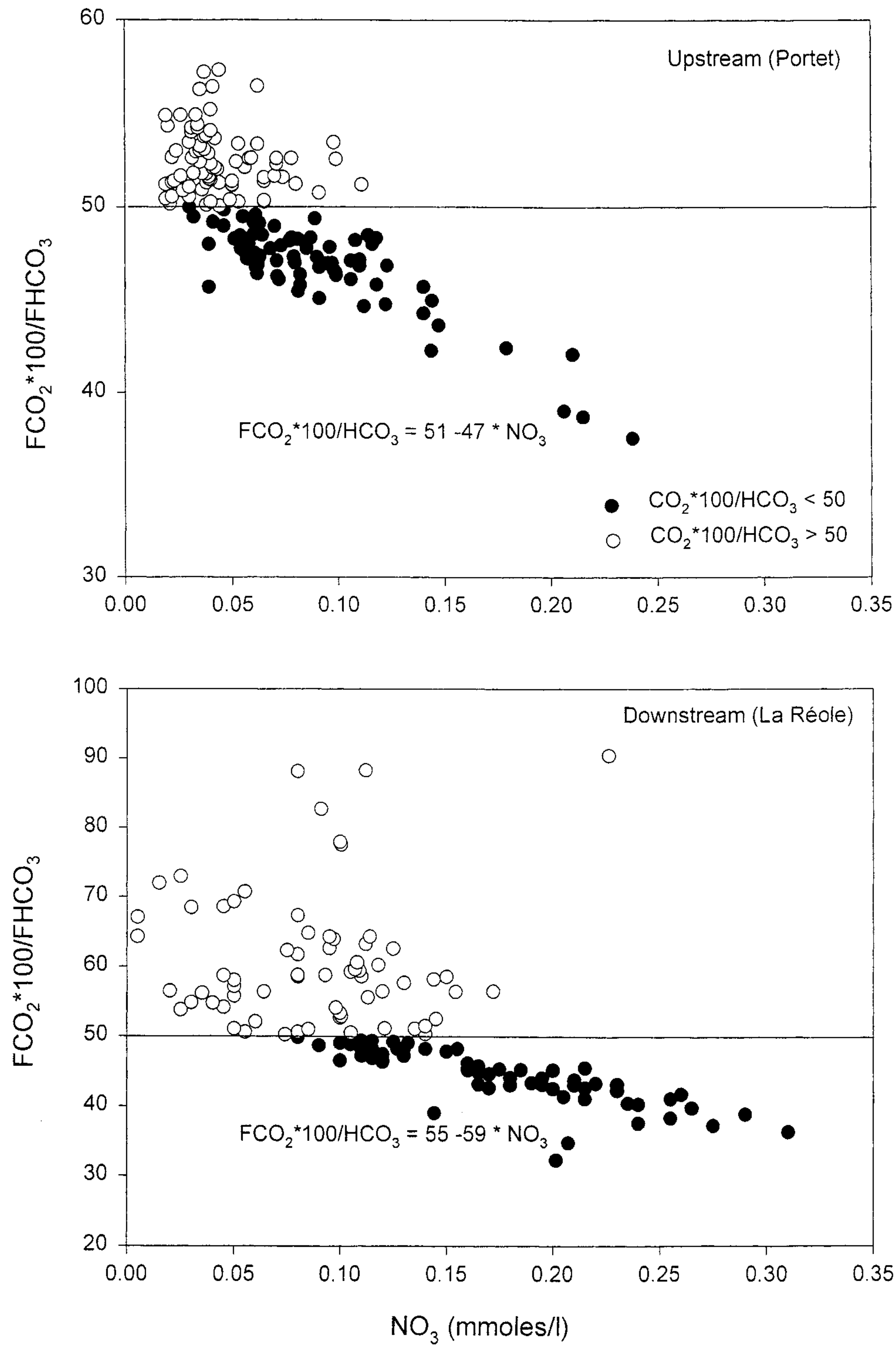


Fig. 7. Variations of the CO_2/HCO_3 ratio relative to NO_3 concentrations (mmol L^{-1}) in the Garonne waters during the 1989–1992 period.

upstream the Garonne river, and 504 kmol km^{-2} a^{-1} downstream (Table 4). The contribution of weathering of the silicate rocks to the total HCO_3 flux is only 19 kmol km^{-2} a^{-1}, or about 2.4%, upstream and 52 kmol km^{-2} a^{-1} or about 9.4%, downstream.

The relationship between the discharge and the ratio involving the consumed CO_2 flux for rock weathering and observed alkalinity in waters indicates that atmospheric CO_2 is not the unique weathering agent in the Garonne basin. Contribution of the atmospheric/soil CO_2 to the total river alkalinity decreases when the river discharge increases at the two stations Portet and La Réole, and it tends to an average contribution of 44% (Fig. 6). In unpolluted areas, this contribution varies between 100% for crystalline rocks corresponding to the hydrolysis of silicate minerals (Eqs. (7) and (8)), and 50% for carbonate rocks corresponding to carbonate dissolution (Eq. (9)).

The difference observed for the contribution of the atmospheric/soil CO_2 to the total river alkalinity in the Garonne basin (44% instead of 50%) may be attributed to carbonate dissolution by HNO_3 released by nitrifying N-fertilizers (Eq. (14)), as already suggested by Amiotte Suchet and Probst (1996); a good relationship being observed between the theoretical CO_2/HCO_3 ratio and the NO_3^- concentrations in the waters (Fig. 7). The increase of the HCO_3 flux corresponding to a CO_2/HCO_3 ratio below 50%, is correlated with an increase of the NO_3^- content in the waters (correlation coefficient of 0.77 upstream and of 0.62 downstream). For the same NO_3^- concentration, the CO_2/HCO_3 ratio decreases more rapidly downstream than upstream, confirming that weathering in the Garonne basin is most probably not only due to the action of CO_2, but also to HNO_3 produced by the fertilizers in the basin.

As can be seen in Eq. (12), calcite dissolution releases only 1 mol of HCO_3^-. This reaction produces alkalinity without consumption of atmospheric/soil CO_2, which may explain the long term changes of Ca, Mg and HCO_3 concentrations in the river waters. The changes cannot be directly related to discharge variations and/or to readjustments of calcite equilibrium, as the calcite-saturation coefficient remains always at about unity (Etchanchu and Probst, 1988). For some sub-basins, such as that of the Gers river (a tributary of the Garonne river originating in the Pyrénées mountains), this contribution drops to 37% (Semhi, 1996). By taking into account the equation of the carbonate dissolution by fertilizers (Eqs. (14) and (15)) and the CO_2/HCO_3 ratio (44% as average and 37% for the Gers river), it can be seen that 12–26% of carbonate dissolution could be due to HNO_3 induced by N-fertilizer spreading, rather than to natural weathering processes by carbonic acid. It supports previous estimations of Probst (1985) and Etchanchu and Probst (1988) that 30% of the total carbonate dissolution in the Garonne basin may be attributed to N-fertilizers. In terms of the exported flux of Ca + Mg to the oceans, 6–13% seem to have been produced by weathering induced by fertilizers used for agricultural purposes.

6. Conclusion

Nitrification of NH_4^+ from the fertilizers used in the Garonne basin produces nitrates. Increased use of these N-fertilizers is correlated with increased NO_3^- concentrations in the riverine fluxes, mainly leached from soils to the surface waters during heavy rains. The chemical composition of the Garonne waters during the 1989–1992 period, was controlled by basement rocks in the drainage basin consisting of silicate and carbonate rocks, and was used to make estimations of the atmospheric CO_2 flux consumed by weathering of these rocks.

In the Garonne drainage basin dominated by carbonate rocks, the CO_2/HCO_3 ratio of the river waters reaches a mean value of 44%. Part of the dissolved HCO_3 seems then not to be due to the action of atmospheric CO_2. On the other hand, a significant positive correlation was found between increase of the HCO_3 flux corresponding to a CO_2/HCO_3 ratio below 50%, and NO_3^- concentrations in the waters. However, nitrification of NH_4^+-fertilizers releases protons which may produce nitric reagents that induce carbonate dissolution supplying HCO_3^- ions in Garonne waters. Such a reaction explains the differences between the estimated contribution of atmospheric CO_2 to the total river alkalinity (CO_2/HCO_3 ratio of 44%) and the theoretical contribution (CO_2/HCO_3 ratio of 50%) corresponding to carbonate dissolution.

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