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To cite this version:

Anne-Sophie Perrin, A. Probst, Jean-Luc Probst. Impact of nitrogenous fertilizers on carbonate dissolution in small agricultural catchments : implications for weathering CO2 uptake at regional and global scales. Geochimica et Cosmochimica Acta, 2008, 72, pp.3105-3123. hal-00290659

HAL Id: hal-00290659

https://hal.science/hal-00290659v1

Submitted on 14 Mar 2024

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Impact of nitrogenous fertilizers on carbonate dissolution in small agricultural catchments: Implications for weathering CO_2 uptake at regional and global scales

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Abstract

The goal of this study was to highlight the occurrence of an additional proton-promoted weathering pathway of carbonate rocks in agricultural areas where N-fertilizers are extensively spread, and to estimate its consequences on riverine alkalinity and uptake of CO_2 by weathering. We surveyed 25 small streams in the calcareous molassic Gascogne area located in the Garonne river basin (south-western France) that drain cultivated or forested catchments for their major element compositions during different hydrologic periods. Among these catchments, the Hay and the Montoussé, two experimental catchments, were monitored on a weekly basis. Studies in the literature from other small carbonate catchments in Europe were dissected in the same way. In areas of intensive agriculture, the molar ratio $(Ca + Mg)/HCO_3$ in surface waters is significantly higher (0.7 on average) than in areas of low anthropogenic pressure (0.5). This corresponds to a decrease in riverine alkalinity, which can reach 80% during storm events. This relative loss of alkalinity correlates well with the NO_3^- content in surface waters. In cultivated areas, the contribution of atmospheric/soil CO_2 to the total riverine alkalinity ($CO_{2\ ATM\text{-}SOIL}/HCO_3$) is less than 50% (expected value for carbonate basins), and it decreases when the nitrate concentration increases. This loss of alkalinity can be attributed to the substitution of carbonic acid (natural weathering pathway) by protons produced by nitrification of N-fertilizers (anthropogenic weathering pathway) occurring in soils during carbonate dissolution. As a consequence of these processes, the alkalinity over the last 30 years shows a decreasing trend in the Save river (one of the main Garonne river tributaries, draining an agricultural catchment), while the nitrate and calcium plus magnesium contents are increasing.

We estimated that the contribution of atmospheric/soil CO_2 to riverine alkalinity decreased by about 7–17% on average for all the studied catchments. Using these values, the deficit of CO_2 uptake can be estimated as up to 0.22–0.53 and 12–29 Tg[1] yr^{-1} CO_2 on a country scale (France) and a global scale, respectively. These losses represent up to 5.7–13.4% and only 1.6–3.8% of the total CO_2 flux naturally consumed by carbonate dissolution, for France and on a global scale, respectively. Nevertheless, this loss of alkalinity relative to the $Ca + Mg$ content relates to carbonate weathering by protons from N-fertilizers nitrification, which is a net source of CO_2 for the atmosphere. This anthropogenic CO_2 source is not negligible since it could reach 6–15% of CO_2 uptake by natural silicate weathering and could consequently partly counterbalance this natural CO_2 sink.

1. INTRODUCTION

Over geological time, global carbon dioxide content and temperature of the atmosphere are regulated by adjusting

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[1] 1 Tg of carbon = 10^{12} g of C = 0.083 10^{12} mol of C.

the greenhouse effect via CO_2 uptake by the carbonate-silicate mineral weathering cycle (Ebelmen, 1845, 1847; Garrels et al., 1976; Walker et al., 1981; Berner et al., 1983; Mackenzie et al., 2004).

The amount of carbon (organic plus inorganic) eroded from the continents and transported by the rivers into the ocean averages 1 Gt C yr^{-1} (0.8 to 1.2 according to the literature). Dissolved inorganic carbon (DIC), particulate inorganic carbon (PIC), dissolved organic carbon (DOC), and particulate organic carbon (POC) riverine fluxes represent 38% (380 ± 76 Tg C yr^{-1}), 17% (170 ± 34 Tg C yr^{-1}), 25% (250 ± 50 Tg C yr^{-1}) and 20% (200 ± 40 Tg C yr^{-1}) of the total carbon river flux, respectively (see Amiotte-Suchet et al., 2003). Most riverine carbon fluxes originate from atmospheric/soil CO_2, except for PIC and half of the DIC, supplied, respectively, by erosion and dissolution of carbonates. As a whole, the flux of CO_2 uptake by organic (POC and DOC) and inorganic (71% of the DIC, i.e., DIC from silicate weathering plus half of DIC supplied by carbonate dissolution, see Amiotte-Suchet et al., 2003) erosion of the continents represents 720 ± 144 Tg C yr^{-1}, of which 62% is supplied by the erosion of soil organic matter while 38% is supplied by the chemical weathering of silicate and carbonate rocks.

With regard to atmospheric CO_2 content on a geological time scale (10^4–10^6 years), the flux of riverine organic carbon represents a net sink of CO_2 only if the organic carbon is buried in marine sediments. Indeed, part of the riverine organic carbon is mineralized (mainly the POC, the DOC being relatively conservative), releasing CO_2 into the atmosphere before reaching the ocean. For example, in the Garonne river, 50% of the POC flux is lost in the Gironde estuary, while all of the DOC flux reaches the Atlantic ocean (Veyssy et al., 1996).

Concerning inorganic carbon fluxes, atmospheric/soil CO_2 uptake by weathering of Ca and Mg silicates and release of dissolved Ca, Mg and bicarbonates into the rivers is followed by the burial of Ca and Mg as carbonates in marine sediments, representing a net sink of CO_2 for the atmosphere (e.g., Ebelmen, 1845, 1847; Garrels et al., 1976). This sink is naturally balanced by CO_2 release from volcanism and metamorphism on geological time scales. The fluxes of atmospheric/soil CO_2 uptake by rock weathering of the continents have been estimated from river fluxes of carbon, taking rock types into account (Probst, 1992; Amiotte-Suchet and Probst, 1993, 1995; Amiotte-Suchet et al., 2003). Global silicate weathering and CO_2 consumption rates have been deduced from the chemistry of large rivers (Gaillardet et al., 1999). Carbonate and other rock type weathering are not taken into account either because weathering reactions do not consume atmospheric CO_2 (e.g., evaporite dissolution) or because the calcite precipitation in the oceans equals the continental weathering flux (carbonates). Any disturbance of mineral weathering processes in nature, however, may affect the carbon cycle and the long-term global climate (Drever and Stillings, 1997).

Physical parameters have been extensively studied for their influence on chemical weathering rates, particularly lithology, climate (runoff and temperature) and relief (e.g., Amiotte-Suchet and Probst, 1993; White and Blum, 1995; Oliva et al., 2003). Biota may also play a role in mineral weathering processes due to CO_2 and protons sources through microbial and plant root activities and organic acids production (see e.g., Sposito, 1989; Haynes, 1990; Drever, 1994; Hinsinger et al., 2003).

In the present-day conditions of "anthropogenic forcing of the Earth Surface System" (Meybeck, 2002), the potential for acid anthropogenic inputs to catchments to considerably affect natural chemical weathering processes can no longer be ignored. The role of acid deposition (mainly sulphuric and nitric acids) on these processes has been investigated in small forested ecosystems (Pačes, 1986; Wright et al., 1988; Sverdrup and Warfvinge, 1995; Probst et al., 1992, 1995a; Probst et al., 2000; De Vries et al., 2003). Amiotte-Suchet et al. (1995) estimated that the decrease of atmospheric/soil CO_2 uptake by silicate weathering due to acid rain reached 73% at a small catchment scale in the Vosges Mountains (north-eastern France). On a global scale, it would represent less than 10% when considering only sulphuric acid deposition (Amiotte-Suchet et al., 1995; Lerman et al., 2007).

In this context, the impacts of other anthropogenic sources of protons, such as those released by sulfur mineral oxidation in mining areas or by N-fertilizer nitrification in agricultural catchments, would also deserve greater consideration.

Agricultural areas represent around 12% of land surface area on a global scale, but this percentage is higher in European countries (57% in France, for example), in North America and in Southeast Asia (Fig. 1).

In 2004–2005, 155 and 4 million tons of fertilizers ($N + P_2O_5 + K_2O$), about 60% of which was N-fertilizers (i.e., exactly 90 and 2.3 million tons of N, see FAO, 2000), were spread on soils at the world scale and in France, respectively. The world average annual increase in fertilizer consumption was 3.3% from 1961 to 1997, and FAO's study predicts a 1% increase per year until 2030 (FAO, 2000). This low annual increase prediction reflects a reduction in the crop production growth and a weak increase of fertilizer use in industrialized parts of the world. Nevertheless, higher fertilizer applications are expected in Asia and South America, although it should remain very low in Sub-Saharan Africa. In rural catchments, N-input includes the use of N-fertilizers, mismanagement of irrigated crops, disposal of livestock waste (Hallberg, 1989) and cultivation of virgin land (Ronen et al., 1988). In Norway, Hoyas et al. (1997) estimated that agricultural activities contribute approximately 85% of the total N-supply in a rural catchment, of which 65–70% originates from N-fertilizers.

Several problems have been pointed out concerning the impact of N-fertilizers on surface water and groundwater NO_3^- concentrations. Increasing N-input can indeed affect water quality, but it can also affect river ecology through shifts in plant and algal species composition, increased productivity, decreased species diversity, changes in food web structure, and the development of hypoxic and anoxic conditions in aquatic systems (Seitzinger and Kroeze, 1998). Despite this, only a few studies have been devoted to agriculture impacts on chemical weathering processes and

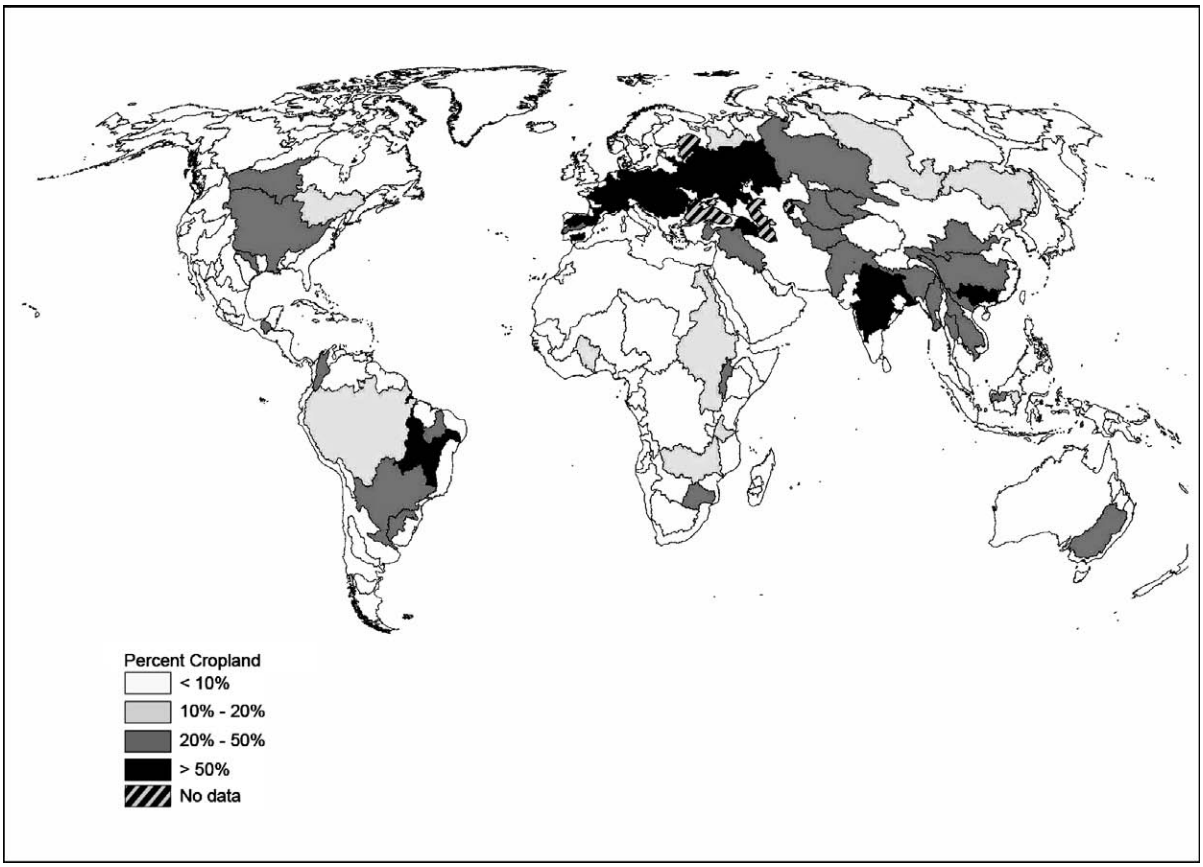

Fig. 1. World map of the percentages of cropland area by large river basins (adapted fromWorld Resources Institute-PAGE, 2000).

dissolved element fluxes exported by surface waters (Collins and Jenkins, 1996; Semhi et al., 2000; Pacheco and Van der Weijden, 2002). More recently, in the US, Raymond and Cole (2003), West and McBride (2005) and Oh and Raymond (2006) have underlined the influence of N-fertilizer nitrification on agricultural lime dissolution. The nitrification process of N-fertilizers liberates protons, which can weather minerals (Durand and Dutil, 1972; Faurie, 1977), as in natural conditions of forest soils, where litter nitrification has been shown to increase mineral weathering (Berthelin et al., 1985).

At the scale of small river basins, using river water chemical composition, Etchanchu and Probst (1988) and Semhi et al. (2000) estimated that the contribution of N-fertilizers to carbonate dissolution represents 30% and 12–26%, respectively, on two small agricultural carbonate basins in south-western France, the Girou and the Gers (subtributary and tributary of the Garonne river, respectively). For larger basins, such as the Garonne river basin, this contribution was estimated at 6% by Semhi et al. (2000). Moreover, fertilization practices might induce 6–13% of the Garonne river flux of $Ca^{2+} + Mg^{2+}$ exported to the oceans (Semhi et al., 2000).

No investigations have been performed on small monolithological catchments under agricultural pressure in various regions, which might help to better constrain the role of N-fertilizer inputs on chemical weathering.

This study aimed (i) to evaluate the impact of N-fertilizers on chemical weathering in 25 small catchments located on sedimentary bedrock (molasse type) from the Gascogne region (south-western France), where intensive cultivation of crops and N-fertilizer application are practiced; the water compositions of several streams and rivers in contrasting hydrological periods were considered; (ii) to investigate the role of fertilizers on carbonate chemical weathering in other cultivated European regions using the literature; (iii) to assess the impact of fertilizers on CO_2 uptake by weathering and on total riverine alkalinity in the studied areas; and (iv) to estimate the deficit of CO_2 uptake in agricultural areas underlain by carbonate bedrock at the scale of France and on a global scale.

The present-day deficit of CO_2 uptake due to weathering of continental rocks by strong acids (nitric or sulfuric acids) corresponds to an anthropogenic source of CO_2 for the atmosphere on a short time scale (decade-century).

Consequently, the objective of this study was also to estimate this CO_2 source on a global scale and to compare this flux to (i) other present-day anthropogenic CO_2 sources (e.g., fossil fuel combustion, deforestation) and (ii) global CO_2 uptake by natural carbonate dissolution and silicate

weathering, which represent a net sink of CO_2 for the atmosphere on a geological time scale.

2. STUDY AREA

2.1. Geomorphology, bedrock mineralogy and petrology

The study area is located in south-western France. The geomorphological area of the "Coteaux de Gascogne" is drained from the south to the north by a network of streams, all tributaries of the Garonne River (Fig. 2), in a fan pattern from their sources on the "Plateau de Lannemezan" to their confluences with the Garonne. This area lies on detrital sediments from the Pyrénées mountains. It is bound on the east by the Garonne River, on the south by the Pyrénées and on the west by the Atlantic Ocean (Etchanchu and Probst, 1988).

Throughout the Oligocene and Miocene, this basin served as an emergent zone of subsidence that received sandy, clay and calcareous sediments derived from the erosion of the Pyrénées, which were in an orogenic phase at that time. The heterogeneous materials were of low energetic value and produced a thick detrital formation of molasse type in the Miocene. From the Pleistocene onwards, the rivers became channelised, cutting broad valleys in the molasse deposits and leaving terraces of coarse alluvium (Revel, 1982; Revel and Guiresse, 1995). Erosion has produced a deeply undulating surface relief with frequently asymmetrical hills. Slopes vary between 0% and 20%, with 75–80% comprised between 4% and 10%. Crest lines dominate the main valleys from 60 to 100 m. The maximum elevation is close to 300 m; mean elevation decreases from the south to the north and from the east to the west.

The molasse, as defined by Cayeux (1935), is present in all of Aquitain basin with varying aspects. Clays, sandstones, limestones and marl mix in banks, with continuous lateral extent. Important variations in texture are noted in addition to carbonate content (60–90%). Induration is always low but with a crumbly consistency (Revel, 1982). Crouzel (1957) distinguished three cement types (always formed by clays and limestones) depending on the proportion and crystallinity of the constituents conferring different hardness to the bedrocks.

Skeletal elements are irregularly distributed; quartz grains are dominant, but other minerals appear, including feldspar, plagioclase, muscovite and tourmaline. Several bedrock fragments can be found, including Aquitaine and Pyrenean limestones, granites, gneisses, and shales.

2.2. Soil, land use and agricultural practices

In this area, which has been cultivated since the Middle Ages, mechanical erosion by ploughing has had a greater impact on downward soil displacement than water erosion, with a major impact on surface relief, especially on leveling and soil distribution (Guiresse and Revel, 1995). The S, BT, K and C horizons (Baize and Girard, 1992) may be brought to the surface, giving the currently tilled horizon its highly variable morphological characteristics. Due to the juxtaposition of patches of different colors in the present landscape, soil scientists have described the soil cover in this region as a mosaic (Revel and Guiresse, 1995). Very weak erosion has led to the development of calcic luvisols (UN FAO soil units) on the tertiary substratum and local rendosols on the hard calcareous sandstone beds. On the hillsides with very gentle slopes (less than 12%), the calcic cambisols (UN FAO soil units) have been subjected to moderate erosion. The short steep slopes (over 12%) have been worn away, often uncovering the calcareous K horizon, except in the former gullies. In contrast, in the valley bottoms, the accumulated materials have given rise to calcic colluvium at the base of the slopes (Revel and Guiresse, 1995). Non-calcic silty soils, locally named "boulbènes," represent less than 10% of the soils in this area. Calcic soils are dominated by a clay content ranging from 40% to 50%, while non calcic soils are silty (50–60%). In calcic and non-calcareous soils, respectively, pH ranges from 7.7 to 8.8 and 5.9 to 6.9, CEC values are composed between 20 and 30 and 10 and 20 cmol(+) kg^{-1} of dry soil with a saturation index (S/T) of 100% and 70–90% (Ca^{2+} ions contribution exceed

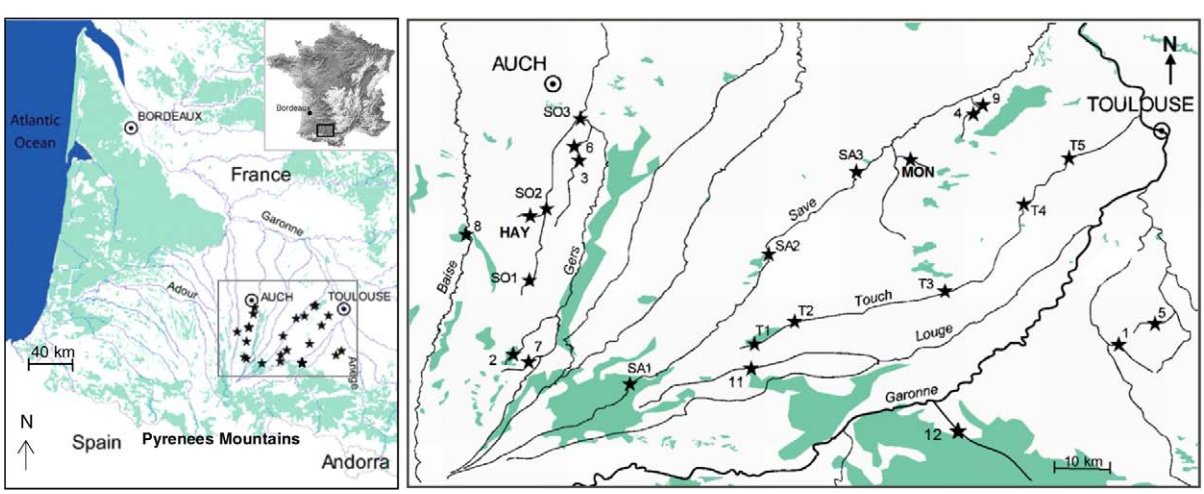

Fig. 2. Map of the studied area and locations of the different sampling points (star with reference number: see Table 1).

90% and 80%). In calcic soils, calcareous contents range between 3% and 46%, with 0.5–13% of reactive calcareous (a mean of 24% was determined by Crouzel and Meyer, 1977). The minerals encountered in the soils are mainly quartz, but feldspar (plagioclase and albite), calcite, zircon and less commonly monazite, chlorite, epidote, ilmenite, mica (muscovite), apatite, and tourmaline are also found. Concretions are commonly found composed of a clayey matrix mixed with manganese and iron oxides. Soil organic matter contents vary between 1% and 2.5% and the C/N ratio is less than 10, indicating a rapid mineralization rate. Bulk densities of soils range from 1.3 to 1.8.

Ninety percent of the surface of the Gascogne area is used for agricultural purposes, mostly corn and animal production (mainly cows) in the west and a rotation of wheat and sunflower in the east.

Farmers principally spread chemical fertilizers on soils, mainly compound fertilizers of the N-P-K type (as N, P_2O_5 and K_2O) and straight fertilizers such as ammonium nitrate (NH_4NO_3) and, to a lesser extent, urea ($CO(NH_2)_2$) and ammonium sulphate ($(NH_4)_2SO_4$). Typical amounts of chemical fertilizers used in this area are 670 kg ha^{-1} yr^{-1} (30%, 5% and 2% of N, P_2O_2 and K_2O, respectively) for wheat, 400 kg ha^{-1} yr^{-1} (22%, 4% and 5 % of N, P_2O_2 and K_2O) for sunflowers, 660 kg ha^{-1} yr^{-1} (21%, 14% and 13% of N, P_2O_2 and K_2O) for corn (maize), and 400 kg ha^{-1} yr^{-1} (0%, 16% and 26% of N, P_2O_2 and K_2O) for soy beans. Because soil pH and carbonate content are high, buffering with lime is not practiced.

2.3. Hydrology and climatology

The climatic conditions are oceanic with a gradient of 800–700 mm in mean annual precipitation (maximum in November–December and April–May) and a gradient of 500–600 mm (from west to east) mean annual evapotranspiration. The mean temperature is 12.7 °C with a minimum in January (5 °C in average) and a maximum in August (20 °C in average). The dry period runs from June to August (the month with the maximum water deficit), and the wet period runs from October to May (Ribeyreix-Claret, 2001). The hydrological regime of the rivers in this area is mainly pluvial regulated by rainfall (Etchanchu, 1988) with maximum discharge in February and low flows during the summer (July to September). These rivers are characterized by important interannual variations (Probst and Tardy, 1985). The Gascogne substratum is relatively impermeable due to its high expansive clay content. Consequently, river discharge is mainly supplied by surface and subsurface runoff, and groundwaters are limited to alluvial and colluvial phreatic aquifers. These aquifers are very limited and the small streams are sometimes dry in the summer.

3. MATERIALS AND METHODS

3.1. Sampling sites

3.1.1. Network of small catchments: spatial approach

We sampled a set of 25 streams (Fig. 2) of first to third Strahler's order (discharge from 0.3 to 1200 l s^{-1} during low water flow period) from the Gascogne region three to six times during the period 2002–2005 (see Table 1) in contrasting hydrological conditions: (i) March 2002, after a three months drought (30–50% water-height deficit compared to the mean from 1961 to 1990); (ii) February/March 2004 (high water flow), May 2004 (local storm events) and July 2004 (low water flow); and (iii) March 2005 (low water flow) and May 2005 (local storm events).

Among the sampling set, three major rivers (Save, Sousson and Touch) were sampled from upstream to downstream at 3–4 stations (Fig. 2).

Because forest areas are very scarce, only three forested catchments (deciduous trees) were selected; the others were cultivated for at least 90% of the surface, which is representative of the Gascogne area.

Sampling sites are all located at least 190 km from the ocean coast.

3.1.2. Experimental catchments: seasonal variation surveys

Among the 25 sampling sites, two experimental catchments, the Montoussé and the Hay, were monitored more intensively at their outlet on a weekly basis from December 2004 to April 2006 and from March 2005 to September 2006, respectively. Moreover, for the Montoussé catchment, rain waters were collected after each precipitation event in a polypropylene bottle.

With a length of 3 and 1.6 km width, the Montoussé catchment (328 ha) lies on a calcareous substratum and is composed of low elevation hills ranging from 173 m at the outlet to 268 m at the top. The Hay catchment, 2 km long by 0.8 km wide (145 ha) is located 50 km west of the Montoussé. Here, the slopes are gentler, and the substratum is composed of carbonate and non-carbonate molasse. In terms of land use, 90% of the Montoussé catchment is devoted to agriculture with a rotation of wheat (58%) and sunflower (38%) and marginally barley, garlic, grass and fallow. Forested (3%) and farmhouse (3%) areas represent the remaining surface. The Hay catchment is occupied by nearly 35% of forested areas, 32% irrigated corn, 10% grass, 5% soy, 5% sunflowers, 4% beans, 3% wheat and barley, 1% tobacco and 3% by farmhouses. In 2004–2005, the amount of N applied on soils was 140 and 126 N kg ha^{-1} yr^{-1}, respectively, in the Montoussé and Hay catchments.

3.2. Sampling and analytical methods

Conductivity and pH were measured in the field during sampling (Table 1). Water samples collected in PP plastic bottles were filtered in the lab through a 0.22 μm Millipore nitrocellulose filter. A non-acidified and an acidified sample (pH <3) were stored in the dark at 4 °C before analyses. Major cations were analyzed on acidified samples by atomic absorption spectrometry (AAS 5100 PC, Perkin-Elmer) after adding La (0.5%) for Ca^{2+} and Mg^{2+} analyses. In all cases, the standard ranges were checked using CRM BMOOS-01 (NWRI), and the error was minor to 5%. Major anion (NO_3^-, Cl^- and SO_4^{2-}) concentrations were measured with high performance liquid-ion chromatography (Dionex Chromatograph ICS 2000). The standard ranges were checked using CRM BMOOS-01 (NWRI), and the er-

Table 1
Characteristics and mean chemical composition of surface waters (stream waters or rainwaters) of the studied sites

Latitude/ longitude (Lambert II)	Ref. map	Watershed	Surface area (km^2)	Water discharge ($l\ s^{-1}$)	Date[a]	TDS ($mg\ l^{-1}$)	pH	Cond[d] ($\mu S\ cm^{-1}$ (25 °C)	Ca^{2+}[b]	Mg^{2+}[b]	Na^{+}[b]	K^{+}[b]	HCO_3^{-}[b]	NO_3^{-}[b]	Cl^{-}[b]	SO_4^{2-}[b]	SiO_2[b] ($mg\ l^{-1}$)	Land use[c]	Number of samples
									mmol l^{-1}										
Gascogne cultivated and forested areas																			
451.365/1821.645	SO1	Sousson @ Aujan	—	—	(2)(3)(4)(5)(6)	382	7.9	480	2.12	0.18	0.43	0.09	3.46	0.53	0.76	0.18	3.94	A	5
453.517/1832.962	SO2	Sousson @ Dareous	—	—	(2)(4)(5)(6)	425	8.1	555	2.27	0.19	0.46	0.15	3.66	0.56	0.85	0.19	2.80	A	4
458.020/1847.935	SO3	Sousson @ Auch	120	—	(2)(3)(4)(5)(6)	503	8	603	2.75	0.24	0.47	0.07	4.86	0.41	0.72	0.20	2.62	A	5
477.977/1810.610	T1	Touch @ Lilhac	—	10	(2)(4)(5)(6)	479	7.9	597	2.49	0.33	0.51	0.06	5.07	0.09	0.74	0.18	3.35	A	4
482.810/1814.225	T2	Touch @ Fabas	—	150	(3)(4)(5)(6)	433	8	545	2.24	0.39	0.47	0.08	4.56	0.24	0.63	0.17	2.46	A	4
500.825/1818.850	T3	Touch @ Savère	—	300	(2)(3)(4)(6)	391	7.9	628	2.37	0.65	0.57	0.06	4.70	0.30	0.81	0.23	2.85	A	4
510.422/1832.967	T4	Touch @ Lamasquère	—	800	(2)(3)(4)(5)(6)	395	8	611	1.59	0.43	0.64	0.06	3.31	0.22	0.7	0.25	1.92	A	5
515.884/1840.485	T5	Touch @ Plaisance du Touch	515	1100	(2)	415	—	—	1.65	0.50	1.14	0.05	3.37	0.45	1.05	0.45	2.23	A	1
462.987/1804.387	S1	Save @ Gorges	—	—	(2)(3)(4)(5)(6)	134	7.6	181	0.73	0.07	0.13	0.03	1.31	0.10	0.13	0.08	2.14	A	5
479.957/1825.327	S2	Save @ Anan	—	350	(2)(3)(4)(5)(6)	184	7.9	225	0.97	0.11	0.18	0.04	1.78	0.19	0.25	0.10	1.98	A	5
490.610/1838.677	S3	Save @ Cazaux	424	1200	(2)(3)(4)(5)(6)	277	7.9	—	1.33	0.26	0.31	0.05	2.62	0.19	0.37	0.13	1.91	A	5
521.435/1809.845	1	Vermeil	6.86	8.6	(2)(5)(6)	579	7.8	746	2.74	1.37	0.34	0.02	6.65	0.40	0.88	0.28	2.88	A	3
449.175/1809.550	2	Gèze @ Organ	1.30	7.9	(1)(2)(3)(4)(5)	96	7.5	140	0.44	0.07	0.18	0.03	0.75	0.16	0.25	0.04	3.14	A	4
457.235/1842.945	3	Naroque	2.09	10.1	(2)(3)(4)	462	7.9	477	2.56	0.22	0.35	0.03	4.46	0.44	0.63	0.22	2.59	A	3
504.605/1847.880	4	Mérenvielle @ Marguestaud	1.87	1.7	(1)(2)(3)(4)	701	8	815	3.02	0.95	1.08	0.07	6.27	0.64	1.72	0.44	4.87	A	4
525.775/1813.205	5	Jasse	3.25	3.6	(1)(2)(5)(6)	579	8.1	778	2.24	1.25	1.17	0.04	6.00	0.33	1.09	0.34	3.51	A	4
457.305/1843.159	6	Cédon	0.25	—	(2)(3)(4)(5)(6)	380	7.9	414	1.75	0.12	0.26	0.07	2.83	0.35	0.43	0.17	1.70	A	5
450.965/1808.280	7	Badet @ Carcy	2.11	9.7	(2)(3)(4)	164	—	254	0.92	0.11	0.29	0.09	1.46	0.32	0.4	0.09	3.21	A	3
444.029/1829.315	8	Baïse @ Forêt de Berdouès	10.09	40.7	(1)(2)	378	8	457	3.86	0.33	0.43	0.07	3.25	0.40	0.85	0.27	1.62	A	2
505.960/1848.885	9	Bombouride	2.04	2.6	(1)(2)	677	8	875	5.53	1.92	1.91	0.05	6.24	0.07	2.15	0.83	6.35	A	2
499.154/1863.069	10	Jordi	0.44	0.9	(1)	245	8	725	2.47	0.59	1.47	0.05	5.91	0.01	1.7	0.18	11.11	F	1
477.532/1805. 592	11	Mauboussin	1.18	0.6	(1)	138	7.9	477	2.03	0.19	0.29	0.03	4.47	<d.l.	0.44	0.17	7.85	F	1
440.106/1812.400	12	Coume de la Hille	0.7	0.3	(1)	170	8	535	2.07	0.33	0.62	0.05	4.61	<d.l.	1.02	0.15	7.60	F	1
Experimental catchments in the Gascogne area																			
453.115/1832.100	HAY	Hay	1.45	9	03/2005 to 09/2006	480	8	642	2.42	0.26	0.60	0.15	3.59	0.89	1.29	0.36	2.5	A	100
497.085/1840.494	MON	Montoussé: Streamwater	3.28	5	12/2004 to 04/2006	711	8.1	883	3.1	1.2	0.9	0.03	6.4	0.7	1.5	0.4	3.9	A	54
Other streams (literature data)		Rainwater[d]			01/2005 to 01/2006		5.6	24	0.008	0.003	0.024	0.004	0.030	0.054	0.035	0.014	0.260		
Meybeck (1986)		Carbonated catchments located in LAP[e] areas in France																F AM	57
Roy et al. (1999)		Seine River Basin																A, S	32
House and Warwick (1998)		Swale River Basin																A	15

d.l.: detection limit = 0.001.

[a] (1) March 2002, (2) February/March 2004, (3) May 2004, (4) July 2004, (5) March 2005, (6) May 2005.

[b] Mean concentration.

[c] A, Agriculture; F, Forest; AM, Alpine meadows; S, Spring.

[d] Mean volume-weighted concentration in rainwater ($n = 15$).

ror was minor to 5%. Alkalinity was determined by titration with HCl acid (DMS Titrino, Metrohm); the error was always less than 3%. The charge balance deviations of the samples were generally less than 5% (86% samples) and always less than 10%.

3.3. Calculation of CO_2 uptake by chemical weathering

The geochemical code MEGA ("Major Element Geochemical Approach") (Amiotte-Suchet, 1995; Amiotte-Suchet and Probst, 1996) was used to estimate the amount of atmospheric/soil CO_2 consumed during chemical weathering of the rocks, as used by Mortatti and Probst (2003) for the Amazon basin and by Semhi et al. (2000) for the Garonne basin. This model provides an estimate of the weathering contribution of each major mineral (Mg and Ca silicates, Na and K silicates, carbonates) to the riverine flux of major dissolved elements after correction of atmospheric inputs and, particularly, to discriminate between bicarbonate ions from atmospheric/soil CO_2 and carbonate dissolution. Pyrite, gypsum and halite, which are not present in the context of mollassic substratum, are not considered in the model calculation. Consequently, the amount of bicarbonate ions originating from atmospheric/soil CO_2 ($HCO_3^-{}_{CO_2}$) is calculated as follows:

$$HCO_3^-{}_{CO_2} = HCO_3^-{}_{\text{total riverine}} - HCO_3^-{}_{CaCO_3} \quad (1)$$

where the HCO_3 released by carbonate dissolution ($HCO_3^-{}_{CaCO_3}$) is equivalent to the $Ca^{2+} + Mg^{2+}$ molar flux released by carbonate dissolution according to the stoichiometric coefficient ratio of the carbonate dissolution reaction:

$$Ca_{(1-x)}Mg_xCO_3 + CO_2 + H_2O \rightarrow 2HCO_3^- + (1-x)Ca^{2+} + xMg^{2+}, \quad (2)$$

where the $Ca^{2+} + Mg^{2+}$ released by carbonate dissolution is obtained as the difference between the total $Ca^{2+} + Mg^{2+}$ and the $Ca^{2+} + Mg^{2+}$ from silicate weathering.

The amount of Ca^{2+} and Mg^{2+} originating from silicate weathering is calculated using the molar ratio $R_{sil} = (Na^+ + K^+)/(Ca^{2+} + Mg^{2+})$ in waters draining silicate rocks. This ratio was already calculated by Amiotte-Suchet and Probst (1996) as 0.5 for the river water draining carbonate-free molasse and alluvial sediments of the Garonne Basin. $Na^+ + K^+$ supplied by weathering of Na and K silicates is calculated from riverine dissolved silica according to the stoichiometric coefficient ratio of Na + K and silica released ($Na + K/SiO_2$ ratio = 1) during the feldspar hydrolysis reaction, as shown by Meybeck (1986) for the streamwater draining small French catchments on silicate rocks:

$$2NaAlSi_3O_8 + 2CO_2 + 2H_2O \rightarrow Al_2Si_4O_{10}(OH)_2 + 2Na^+ + 2HCO_3^- + 2SiO_2. \quad (3)$$

In the study area, this reaction corresponds to the dominant weathering processes and leads to the formation of 2:1 phyllosilicate (bisiallitization) in the soil profiles under the hydroclimatic conditions of this temperate region (Pedro, 1966; Tardy, 1971; Revel, 1982; Probst, 1986). K^+ originating from silicate weathering is negligible compared to the amount of K^+ supplied by atmospheric inputs and fertilizer applications.

The amount of riverine bicarbonate ions originating from atmospheric/soil CO_2 ($HCO_3^-{}_{CO_2}$) can be calculated from the riverine fluxes of $Ca^{2+} + Mg^{2+}$ and SiO_2 and from the molar ratio R_{sil} of stream waters draining carbonate-free molasse and alluvial deposits (Amiotte-Suchet and Probst, 1996) as follows:

$$HCO_3^-{}_{CO_2} = HCO_3^-{}_{\text{total riverine}} - [(Ca^{2+} + Mg^{2+})_{\text{total riverine}} - (SiO_{2\ \text{total riverine}}/R_{sil})]. \quad (4)$$

For our study area, where R_{sil} equals 0.5, Eq. (4) becomes

$$HCO_3^-{}_{CO_2} = HCO_3^-{}_{\text{total riverine}} - (Ca^{2+} + Mg^{2+})_{\text{total riverine}} + 2SiO_{2\ \text{total riverine}}. \quad (5)$$

3.4. Data in the literature

To enlarge our field of investigation, data from the literature were considered (Table 1). These concern stream waters from other carbonate regions in Europe, in cultivated areas and areas with low anthropogenic pressure. Low anthropogenic pressure (LAP) catchments refer to catchments without any town, village, large farms, intensive agriculture, or important roads, generally located in upstream areas at least 50 km from big cities (Meybeck, 1986). The characteristics of the watersheds are specified in Table 1.

4. RESULTS

4.1. Chemical composition of stream waters

In the Gascogne area (Table 1), stream waters are neutral (pH ranges from 7.5 to 8.1). Calcium and alkalinity (mainly corresponding to HCO_3^-) are dominant in this carbonate area. The range of concentrations is large, from 0.4 to 5.5 and 0.8 to 6.6 mmole l^{-1}, respectively. Silica, sodium and potassium concentrations are generally much lower, but they are indicators of silicate mineral weathering. Chloride is the most concentrated strong acid anion, followed by nitrate, which is generally significantly more important than sulfate, except in forested catchments. Streams draining cultivated areas in the Seine or Swale river basins present similar concentrations (Figs. 3 and 4). The water compositions of streams draining forested catchments in the Gascogne area are in the range of those draining "low anthropogenic pressure" catchments on carbonate bedrock in France (forested or not, Meybeck, 1986), particularly as regards Ca^{2+}, HCO_3^- and NO_3^-.

The chemical characteristics of stream water samples were compared using ternary diagrams (Piper, 1944), in which the relative abundance of each variable is expressed as the percentage of the sum of cations or anions (Figs. 3a, b and 4a, b, respectively) in milliequivalents per litre.

Fig. 3a represents the relative percentage of cations for the streams of the Gascogne area. Calcium is the dominant cation (54–88% of total cations), followed by Mg (5–38%),

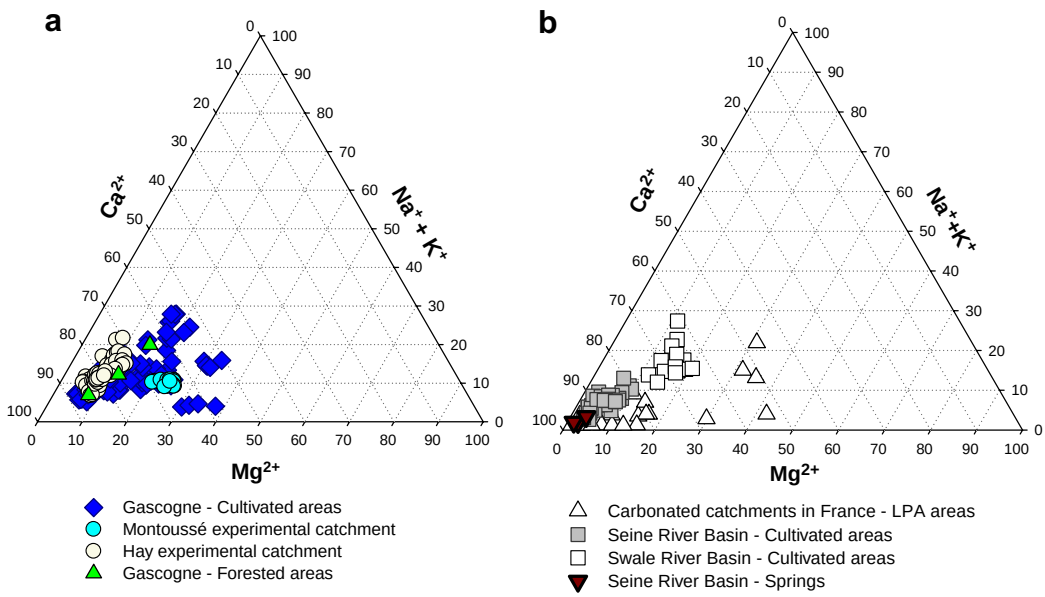

Fig. 3. Cation ternary diagram: (a) stream water samples from cultivated and forested areas of the Gascogne region and from the Montoussé and Hay experimental catchments; (b) stream water samples from carbonate areas with low anthropogenic pressure (LAP) in France (Meybeck, 1986), from cultivated areas and spring areas of the Seine basin (Roy et al., 1999), and from cultivated areas in the Swale basin (House and Warwick, 1998) compared to Gascogne cultivated catchments.

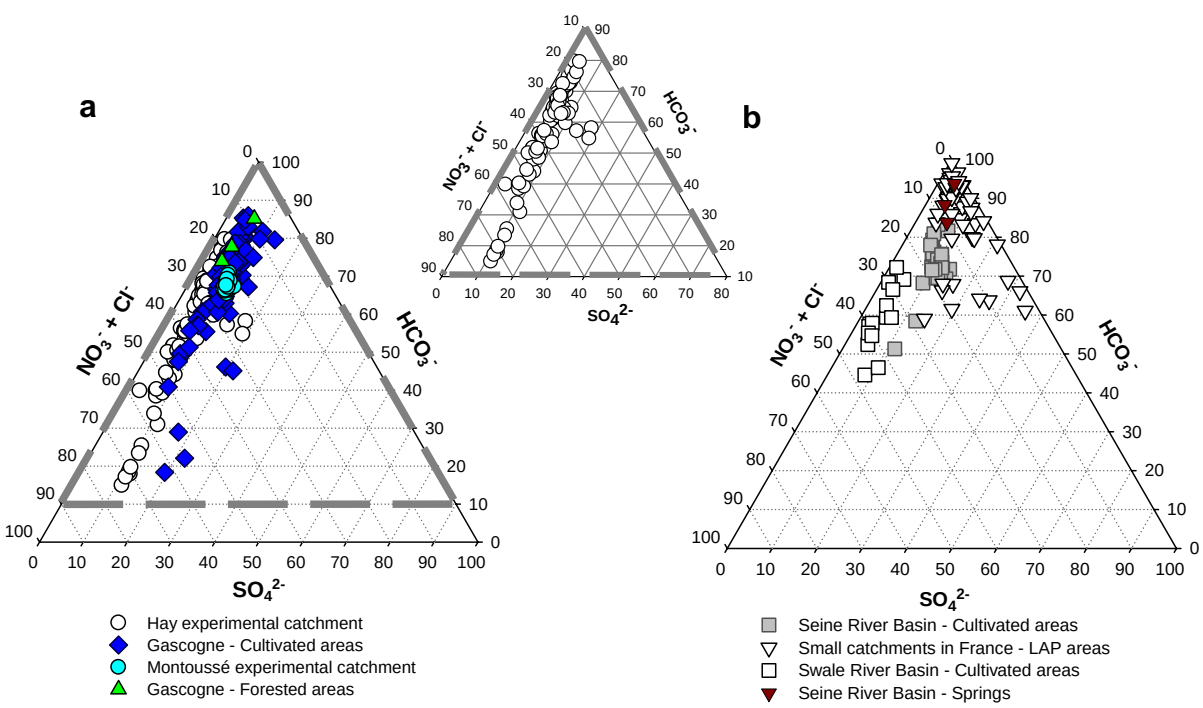

Fig. 4. Anion ternary diagram: (a) stream water samples from cultivated and forested areas of the Gascogne region and from the Montoussé and Hay experimental catchments, with a focus triangle on the Hay catchment data; (b) stream water samples from carbonate areas with low anthropogenic pressure (LAP) in France (Meybeck, 1986), from cultivated areas and spring areas of the Seine basin (Roy et al., 1999), and from cultivated areas in the Swale basin (House and Warwick, 1998), compared to Gascogne cultivated catchments.

indicating the high influence of carbonate dissolution, whatever the land use. Some streams present a higher $Na^+ + K^+$ contribution (up to 21–28%), resulting from silicate weathering. No significant relative changes in the water composition of cations are noticed in the Montoussé and Hay experimental catchments in relation to hydrological conditions. The other catchments used for comparison (Meybeck, 1986; House and Warwick, 1998; Roy et al., 1999) are located in the same part of the diagram (Fig. 3b), especially regarding the Ca^{2+} contribution.

Catchments with low anthropogenic pressure, however, cover a larger range of Mg^{2+} contributions. In particular, a few cultivated catchments from the Gascogne region and several French "pristine" catchments (Meybeck, 1986) present a higher relative Mg percentage, which might be explained by differences in the bedrock mineralogical composition (relative abundance of dolomite in the Gascogne area, see Cayeux, 1935).

Anion ternary diagrams (Fig. 4a) indicate that stream waters in the Gascogne region are dominated by HCO_3^- (16–86% of the total sum of anions), with $NO_3^- + Cl^-$ ranging from 7% to 85%. The sulfate contribution is low (generally less than 15%, except during the driest period in March 2002). The cluster of points lies between the HCO_3^- and $NO_3^- + Cl^-$ dominant respective poles, except for forested catchments (which mostly remain close to the HCO_3^- dominant pole). From these results, we can observe that the alkalinity is progressively replaced by strong acid anions. During summer storm events in the Hay experimental catchment, the $NO_3^- + Cl^-$ content becomes dominant (Fig. 4a focus) as a result of nitrate leaching from soils and increasing the sub-surface runoff contribution to stream water at the outlet, as mentioned by Probst (1985) in the same area. In particular, the maximum nitrate contribution corresponds to exceptional flood events that occur after the low water flow period of the summer, a period of intense mineralization in the soils. This pattern could not be detected in the Montoussé, probably due to less contrasting hydrological conditions and to a lower range of nitrate concentrations as well as to differences in agricultural practices, crop types and soil-bedrock compositions. As with the cations, anions in the Seine and Swale river basins (Fig. 4b) are located in the same area of the Piper's diagram as the Gascogne agricultural catchments, ranging along the same dominant axis (HCO_3^- and $NO_3^- + Cl^-$). The Seine springs (unpolluted catchments) and the majority of other French pristine streamwaters are located close to the bicarbonate endmember, particularly because nitrate and chloride concentrations are very low. Nevertheless, we can observe that some French unpolluted catchments (Meybeck, 1986) present higher sulfate contributions. These catchments, which are covered by coniferous forests, are probably affected by enhanced sulfuric acid inputs due to atmospheric pollution, as already shown for example by Probst et al. (1992) for the Strengbach catchment in the Vosges Mountains (France).

Box plots (Fig. 5) show the main statistical parameters for chloride, nitrate and sulfate concentrations in the different study areas. Chloride concentrations (Fig. 5a) are low in pristine catchments (median less than 0.25 mmol l^{-1}) except in the Gascogne forested catchments. In this case, only three forested samples are available, which can explain the high median value (1 mmol l^{-1}), but the values remain in the range of those measured for the set of cultivated catchments as well as for the experimental catchments of the Gascogne area (median greater than 1 mmol l^{-1}). In the cultivated catchments (Fig. 5a), chloride concentrations are, as a whole, significantly higher (median between 0.5 and 0.75 mmol l^{-1}) than in "pristine" catchments. According to Meybeck (1983, 1986), in the absence of evaporite outcrops, high chloride concentrations in streams can be mainly attributed to pollution sources. Pollution can be fertilizers rather than atmospheric deposits (see low Cl^- concentrations in Table 1), local industrial inputs (absence of industries in the surrounding of the sampling points) or sewage water contributions (very low population density of 30 inhabitants/km^2).

Nitrate concentrations (Fig. 5b) are very low in pristine catchments; the Gascogne area has median values less than 0.2 mmol l^{-1}. Nevertheless, the Seine springs present the same level of nitrate concentrations as the cultivated Swale basin. A potential diffuse source of pollution could be evoked. In the Gascogne region, the median nitrate concentration is 30 times higher in cultivated catchments than in pristine ones and up to 70 times higher in the two experimental catchments. Sulfate concentrations (Fig. 5c) are low in all catchments, with median concentrations less than 0.2 mmol l^{-1}, and no significant difference could be detected between cultivated and forested catchments. Nevertheless, the Montoussé streamwater is twice as concentrated in sulfate. This value is comparable to the median concentration of the Swale basins, for which the range of values is the largest (from 0.2 to 1.4 mmol l^{-1}).

Finally, these results clearly show that for carbonate areas, the nitrate content and its ratio to alkalinity are sig-

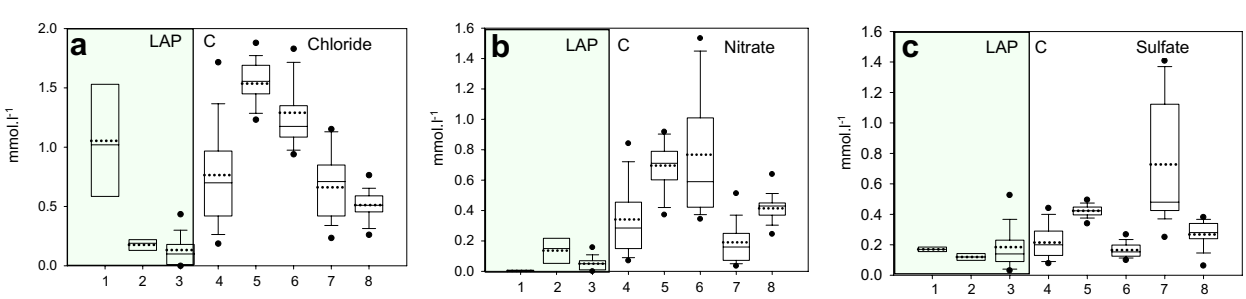

Fig. 5. Box Plot representing statistical values for chloride (a), nitrate (b) and sulfate (c). (LAP) means Low Anthropogenic Pressure areas: (1) Gascogne, $n = 3$; (2) Seine basin springs, $n = 3$; and (3) streams located in carbonate areas with LAP in France, $n = 57$ (Meybeck, 1986). (C) means cultivated areas: (4) Gascogne catchments, $n = 80$; (5) Montoussé experimental catchment, $n = 54$; (6) Hay experimental catchment, $n = 100$; (7) catchments located in cultivated areas in the Swale river basin, $n = 15$ (House and Warwick, 1998) and (8) Seine river basin, $n = 32$ (Roy et al., 1999). The median concentration (plain line), mean concentration (dotted line), 25th percentile (boundary of box closest to zero), 75th percentile (boundary of box farthest from zero), 90th percentile (points above the box) and 10th percentiles (points below the box) are shown.

nificantly higher in streamwaters draining cultivated catchments than in pristine ones.

4.2. Atmospheric inputs

Rainwater was collected during 15 events in the Montoussé catchment from January 2005 to January 2006. The mean volume-weighted concentrations of major elements are given in Table 1. Over this period, the ratio between annual rainfall and streamwater discharge indicates that elements in rainwater concentrate 3.9 times in the Montoussé brook. Using this ratio, the contribution of rainwater inputs to the total riverine concentrations of the different ions can be estimated at 1% for Ca^{2+}, 1% for Mg^{2+}, 10.4% for Na^{+}, 52.2% for K^{+}, 23.5% for NO_3^{-}, 10.5% for Cl^{-}, 27.4% for SO_4^{2-} and 2.4% for alkalinity. A significant amount of NH_4^{+} is supplied to the catchment by rainwater, but NH_4^{+} was not detected in streamwater; it is presumably nitrified in the catchment by soil bacteria and used by plants (Whitall et al., 2003).

Therefore, we might conclude that base cations (Ca^{2+}, Mg^{2+}) supplied by atmospheric inputs are low, except K^{+}. Na^{+} and Cl^{-} contributions are equivalent. Sulfate, nitrate and ammonium inputs are significant. The highest values are observed during local fertilizer spreading periods, which suggests that they partly originate from fertilizer inputs.

4.3. Relationship between $Ca^{2+} + Mg^{2+}$ and alkalinity in stream waters

As shown in Section 4.1 above, the streamwater chemical composition (Table 1, Figs. 3 and 4) of the studied catchments is mainly controlled by carbonate dissolution as atmospheric inputs of divalent base cations are very low. In pristine areas, the molar ratio between $Ca^{2+} + Mg^{2+}$ and bicarbonate ions released into the streamwaters averages 0.5 (Fig. 6a and b). This ratio indicates carbonate dissolution by natural weathering processes involving carbonic acid (Eq. 2).

For cultivated catchments, this ratio is between 0.5 and 1 with average values of 0.7 in the Gascogne area, the Seine River basin and the Swale River basin (Fig. 6a and b). In Fig. 6a, the weekly composition of the experimental Hay catchment shows a significant increase in $Ca^{2+} + Mg^{2+}$ over HCO_3^{-} during hydrological events.

This increase indicates that carbonic acid is probably not a unique weathering agent in these cultivated areas. Indeed, among the different sources of protons mentioned in the introduction, vegetation and crops as well as fertilizers may play a major role.

5. DISCUSSION

5.1. Role of vegetation

Concerning vegetation, as reported by Hinsinger et al. (2003), the main source of protons in the rhizosphere is due to root H^{+} or OH^{-} excretion, which counterbalances a net excess of cation or anion uptake, respectively. This process is stoichiometrically equivalent to charge imbalances (see e.g., Haynes, 1990). Nitrogen plays the most important role in the cation-anion balance as it is the nutrient that is taken up at the highest rate by most plant species (e.g., Marschner, 1995). In oxidizing conditions or under fertilization, nitrate is the major N form and its uptake by vegetation equals or slightly exceeds K, Ca and Mg up-

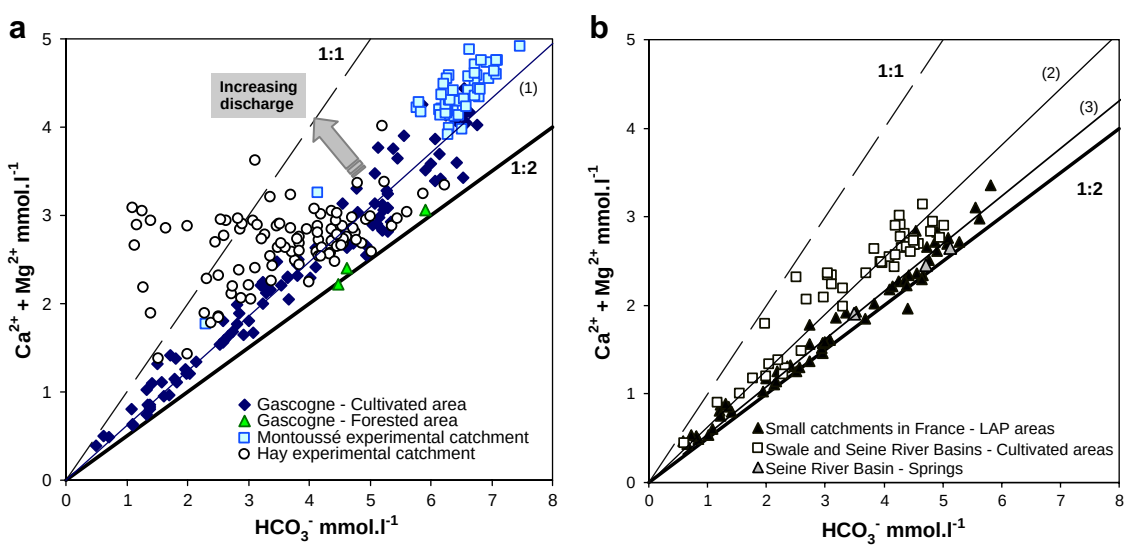

Fig. 6. Relationship between ($Ca^{2+} + Mg^{2+}$) and HCO_3^{-} concentrations in stream waters: (a) samples from cultivated and forested areas of the Gascogne and from the Montoussé and Hay experimental catchments; (b) samples from small carbonate catchments with low anthropogenic pressure (LAP) in France (Meybeck, 1986), from the cultivated and spring areas of the Seine river basin (Roy et al., 1999) and from the cultivated areas of the Swale river basin (House and Warwick, 1998). Regression equations are as follows: (1) cultivated catchments of the Gascogne $y = 0.6x$, $r^2 = 0.95$ ($p \leqslant 0.001$), $n = 80$; (2) cultivated catchments of the Swale river and Seine river basins: $y = 0.7x$, $r^2 = 0.89$ ($p \leqslant 0.001$), $n = 47$; (3) French streams with low anthropogenic pressure: $y = 0.5x$, $r^2 = 0.97$, $n = 57$ ($p \leqslant 0.001$). Theoretical line 1:2 (corresponding to expected $Ca^{2+} + Mg^{2+}/HCO_3^{-}$ ratio according to Eq. 2) is indicated.

take, leading to proton consumption by plant and hydroxide release into the soil (Jaillard et al., 2003).

Microbial communities contribute to the production of soil CO_2 (principally during the oxidation of soil organic matter), which is partly consumed during weathering reactions.

Low molecular weight organic compounds produced by vegetation, such as aliphatic acids and aldehydes, phenols, sugar acids, and amino acids, may accelerate weathering (Sposito, 1989; Fox and Comerford, 1990; Drever, 1994; Drever and Vance, 1994; Gwiazda and Broecker, 1994; Drever and Stillings, 1997). Nevertheless, Drever (1994) and Drever and Stillings (1997) suggested that the overall effect of organic ligands on the weathering rate of silicate minerals in nature is probably small, except perhaps in microenvironments adjacent to roots and fungal hyphae. Indeed, organic anion inputs are often very weak compared to other ion exchanges between roots and soil (Marschner, 1995; Hinsinger et al., 2003; Jaillard et al., 2003). Petersen and Böttger (1991) measured the excretion of organic anions by corn roots in the soil and determined that it does not exceed 0.3% of proton equivalents that are liberated via plant nutrient uptake.

Regarding the respective contribution of plant "proton-pump" and plant organic acid excretion to the proton mass balance in the soil as a whole, we consider in this study that the soil-vegetation system cannot be a net significant source of proton for these cultivated soils.

5.2. N-fertilizer role

Nitrification of N-fertilizers plays a key role in proton inputs to soils. After spreading, ammonium (NH_4^+) from nitrogenous fertilizers (usually in the form of NH_4NO_3 or less frequently $(NH_4)_2SO_4$, $(CO(NH_2)_2)$, NH_3, $(NH_4)_2PO_4$) is mainly oxidized in soil by autotrophic bacteria (like Nitrosomonas) during nitrification, resulting in nitrite (NO_2^-) and H^+ ions. Nitrite is, in turn, oxidized by another bacterium, such as Nitrobacter, resulting in nitrate (NO_3^-), which is available for plant uptake. As already shown by Faurie (1977) and others in Berthelin et al. (1985), protons are produced during the nitrification process (Eq. 6), which corresponds in the case of ammonium nitrate to Eq. (7):

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+; \quad (6)$$

$$NH_4NO_3 + 2O_2 \rightarrow 2NO_3^- + H_2O + 2H^+. \quad (7)$$

Carbonate soils can be considered an open system in equilibrium with calcite and with a gas phase of fixed P_{CO_2} (see Drever, 1997).

If we replace the carbonic acid in Eq. (2) ($CO_2 + H_2O \rightarrow H_2CO_3$) by nitric acid produced by nitrification processes (Eq. 7), the dissolution of carbonate rock becomes (Eq. 8).

$$Ca_{1-x}Mg_xCO_3 + NH_4NO_3 + 2O_2 \rightarrow (1-x)Ca^{2+} + xMg^{2+} + 2NO_3^- + 2H_2O + CO_2. \quad (8)$$

In Eq. (8), bicarbonate ions are not produced, and CO_2 is released (instead of being consumed like in Eq. 2). If protons from nitrification are added to the system, the $Ca^{2+} + Mg^{2+}$ concentration will increase; this additional cation input will be balanced by nitrate anions. As a result, HCO_3^- will decrease by transferring CO_2 to the gas phase, which will be released to the soil/atmosphere. Consequently, in surface waters, the ratio $Ca^{2+} + Mg^{2+}/HCO_3^-$ will increase to higher than 0.5 (ratio in LAP catchments), if the system is disturbed by input of protons from nitrification of N-fertilizers.

Weathering processes involving both carbonic acid (producing HCO_3^-) and protons from nitrification (without production of HCO_3^-) might explain the observed ratio (0.7 on average) for agricultural catchments.

5.3. Loss of alkalinity

"Loss" means loss compared to what the alkalinity ($HCO_3^-{}_{theoretical}$) would have been for the amount of Ca and Mg measured in the surface waters according to Eq. (2). For each sample, we must estimate the loss of alkalinity (ΔHCO_3^-) by calculating the difference between the theoretical ($HCO_3^-{}_{theoretical}$) and the measured alkalinities ($HCO_3^-{}_{measured}$) (Eq. 9):

$$\Delta HCO_3^- = HCO_3^-{}_{theoretical} - HCO_3^-{}_{measured} (mmol^{-1}). \quad (9)$$

$HCO_3^-{}_{theoretical}$ is deduced from measured $Ca^{2+} + Mg^{2+}$ concentrations (in mmol l^{-1}) using the theoretical molar ratio $[Ca^{2+} + Mg^{2+}]/[HCO_3^-] = 0.5$ according to natural carbonate dissolution by carbonic acid (Eq. 2).

ΔHCO_3^- (Fig. 7a and b) is positively correlated to NO_3^- concentrations (in mmol l^{-1}) measured in streamwaters draining cultivated catchments. Any deviation of the correlation is due to the presence of other strong acid anions (SO_4^{2-} or Cl^-), which may influence the charge balance. For LAP catchments, there is no correlation, as NO_3^- concentrations are very low.

According to Eqs. (2) (carbonate dissolution by carbonic acids) and (8) (if all the carbonate dissolution is controlled by NH_4 nitrification of NO_3NH_4), the ratio $\Delta HCO_3/NO_3^-$ equals one.

The slope of the relationship $\Delta HCO_3^- = f(NO_3^-)$ is similar for the cultivated areas (2.4 for the Gascogne area and 2.7 for the Seine and Swale basins), but it exceeds 1. This can be explained by the fact that the additive loss of alkalinity may be partly due to other acids as well (Amiotte-Suchet et al., 1995; Probst et al., 1995b).

In the Hay experimental catchment, contrasting hydrological conditions lead to a mean $\Delta HCO_3^-/NO_3^-$ ratio of 1.8, which is lower than for the other catchments. The highest alkalinity loss related to the highest NO_3^- concentration occurs during the storm events when nitrate leaching by subsurface runoff is the most important (Probst, 1985 and 1986), particularly when the storms occur after the dry season and when soil nitrification is high.

We notice in Fig. 7a that, for the Montoussé catchment, the relationship is not significant. This can be related to a lower range of NO_3^- concentrations in streamwaters compared to the Hay catchment, for example (Table 1), or to differences in nitrate behavior within the catchments (land use and agricultural practices) and stream discharge variations.

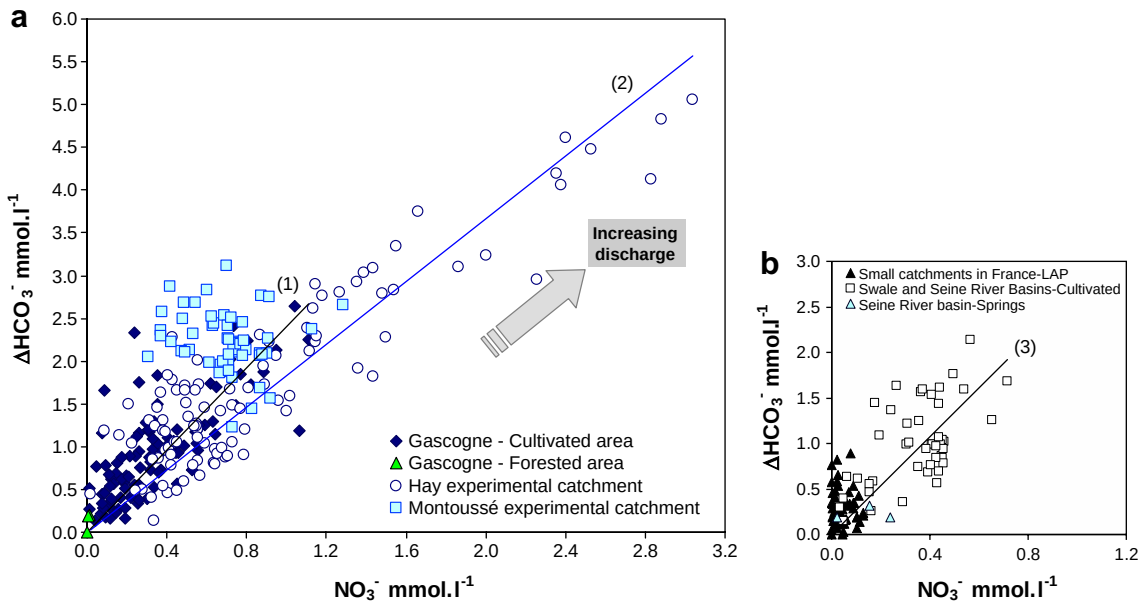

Fig. 7. Relationship between ΔHCO_3^- ($HCO_3^-{}_{theoretical} - HCO_3^-{}_{measured}$, mmol l^{-1}) and NO_3^- concentrations (mmol l^{-1}) in surface waters: (a) samples from cultivated and forested areas of the Gascogne and from the Montoussé and Hay experimental catchments; (b) samples from French catchments with low anthropogenic pressure (Meybeck, 1986), from the cultivated and spring areas of the Seine river basin (Roy et al., 1999) and from the cultivated areas of the Swale river basin (House and Warwick, 1998). Regression equations are as follows: (1) cultivated catchments of the Gascogne $y = 2.4x$, $r^2 = 0.43$ ($p \leqslant 0.001$), $n = 80$; (2) Hay experimental catchment $y = 1.8x$, $r^2 = 0.76$ ($p \leqslant 0.001$), $n = 100$; (3) cultivated catchments of the Swale and Seine basins: $y = 2.7x$, $r^2 = 0.21$ ($p \leqslant 0.001$), $n = 47$.

In cultivated carbonate areas in contrast to low anthropogenic pressure catchments, the relative alkalinity loss observed in surface waters is strongly related to nitrate concentration. As discussed above, this can be reasonably interpreted as a consequence of nitrogen fertilizer inputs in soils, which lead to proton release during nitrification and consequently to a substitution of alkalinity by nitrate.

5.4. Influence of N-fertilizers on atmospheric/soil CO_2 uptake by carbonate dissolution

In LAP (natural weathering pathways with carbonic acid), the contribution of atmospheric/soil CO_2 (CO_2 $_{ATM\text{-}SOIL}$) to the total riverine alkalinity reaches 100% in the case of silicate hydrolysis (Garrels and Mackenzie, 1971; Walker et al., 1981; Berner et al., 1983), in contrast to carbonate bedrock, whose contribution may not exceed 50%, according to the stoichiometric coefficients of the carbonate dissolution reaction (Eq. 2). According to Eq. (8), which corresponds to the dissolution of carbonate by nitric acid (anthropogenic weathering pathway), there is no uptake of atmospheric/soil CO_2 but, rather, a release. Consequently, the ratio between the CO_2 consumed by weathering and the HCO_3^- released (CO_2 $_{ATM\text{-}SOIL}$/total HCO_3^-) tends to 0%.

Fig. 8a and b represent the relationship between the estimated atmospheric/soil CO_2 contribution to the total riverine alkalinity calculated according to the method described in Section 3.3 and the nitrate concentration measured in the streamwaters considered in this paper.

In LAP catchments, the atmospheric CO_2 contribution remains at around 50% of the riverine alkalinity. Moreover, some samples from cultivated catchments are located above the expected theoretical value of 50% for carbonate bedrocks. Nevertheless, the corresponding streamwaters are draining bedrocks poor in carbonate minerals, as indicated by the water composition in Table 1 (low Ca and Mg contents, see samples 2, 6 and S1 to S3).

As seen in Fig. 8, the ratio CO_2 $_{ATM\text{-}SOIL}$/total HCO_3^- decreases when the nitrate concentration increases for cultivated catchments compared to unpolluted catchments. If we consider that this relationship is linear (CO_2 $_{ATM\text{-}SOIL}$/total $HCO_3^- = a[NO_3^-] + b$), when nitrate concentration is close to zero, the ratio CO_2 $_{ATM\text{-}SOIL}$/total HCO_3 equals 50% (natural conditions, Eq. 2), and the intercept b is 0.50. When the ratio tends to 0% (anthropogenic conditions), the nitrate concentration tends to 2 mmole.l^{-1} (Eq. 8) and the slope a is −0.25.

Consequently, the theoretical equation describing this relationship can be written as follows:

$$CO_2\ _{ATM\text{-}SOIL}/\text{total } HCO_3^- = -0.25[NO_3^-] + 0.50, \qquad (10)$$

where CO_2 $_{ATM\text{-}SOIL}$/total HCO_3^- is a molar ratio and $[NO_3^-]$ is in mmole.l^{-1}.

As seen in Fig. 8a and b, the clusters of points are, as a whole, well distributed along the theoretical line (Eq. 10), particularly in the case of the Gascogne and Seine rivers. If we change/add a source of protons (NH_4NO_3 nitrification) by another source from fertilizer, such as ammonium sulfate, organic fertilizer (manure, urea) or atmospheric acid inputs (Amiotte-Suchet et al., 1995), into Eq. (8), then the slope a and the corresponding nitrate concentration (Eq. 10) change. This is the case for the Swale river, for which the slope is steeper than the theoretical line.

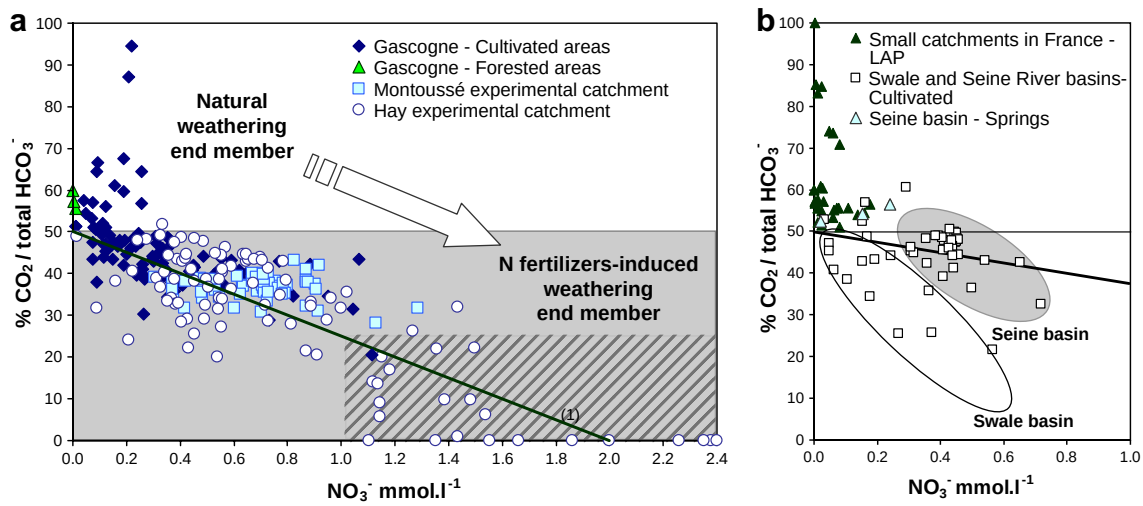

Fig. 8. Relationship between $CO_{2\ ATM\text{-}SOIL}$/total HCO_3^- ratio (%) and NO_3^- concentrations (mmol l^{-1}) in water: (a) samples from cultivated and forested areas of the Gascogne and in the Montoussé and Hay experimental catchments; (b) samples from French streams with low anthropogenic pressure (Meybeck, 1986), from the cultivated and spring areas of the Seine basin (Roy et al., 1999) and from the cultivated areas of the Swale basin (House and Warwick, 1998). (1) represents the theoretical line in the case of carbonate dissolution by protons from N-fertilizer nitrification. The equation is: $CO_{2\ ATM\text{-}SOIL}/\text{total } HCO_3^- = -0.25[NO_3^-] + 0.50$.

For the Gascogne area, the mean ratio $CO_{2\ ATM\text{-}SOIL}$/total HCO_3^- is $43 \pm 6\%$, which corresponds to a mean decrease of 7% compared to natural conditions (50%), with a maximum decrease of 30% (i.e., a ratio of $CO_{2\ ATM\text{-}SOIL}$/total HCO_3^- of 20%).

For the two experimental catchments, the mean ratio is $29 \pm 16\%$ and $37 \pm 3\%$ for the Hay and the Montoussé, i.e., a mean decrease of 21% and 13%, respectively. In the Hay catchment, however, a more important decrease is observed down to 50% (i.e., a ratio of $CO_{2\ ATM\text{-}SOIL}$/total HCO_3^- of 0%) during storm events (Fig. 8a). This pattern might be interpreted as a titration process of protons from N-fertilizers nitrification by carbonate dissolution, as can be clearly seen in Fig. 9, with an alkalinity loss reaching up to 80% when the molar ratio $NO_3/Ca + Mg$ is between 1 and 1.2.

As shown in Fig. 8b, a decrease of the ratio $CO_{2\ ATM\text{-}SOIL}$/total HCO_3^- is also observed when the nitrate concentration increases for streamwaters draining other cultivated carbonate areas in France (Seine river basin) and England (Swale river basin) as well as for the Gascogne rivers. The mean ratios of $CO_{2\ ATM\text{-}SOIL}$/total HCO_3 (respectively, $46 \pm 5\%$ and $41 \pm 11\%$ for the Seine and Swale rivers, i.e., a mean decrease of 4% and 9%) are close to the Gascogne values (ratio $43 \pm 6\%$, i.e., a mean decrease of 7%). These values are close to the average decrease of 6% (i.e., a ratio $CO_{2\ ATM\text{-}SOIL}$/total HCO_3^- of 44%) reported by Semhi et al. (2000) for the Garonne river for the period 1989–1992.

Moreover, in the same basin, new insight into major elements concentrations over the last 30 years registered by the Agence de l'Eau Adour-Garonne (French agency in charge of river water quality survey) illustrates a slight but significant decrease ($^{*}p \leqslant 0.05$, $N = 231$) of alkalinity concentration (−12.5%) over the period 1973–2003 in a major tributary of the Garonne river, the Save river. This river drains a 1150 km^2 carbonate basin in the Gascogne region,

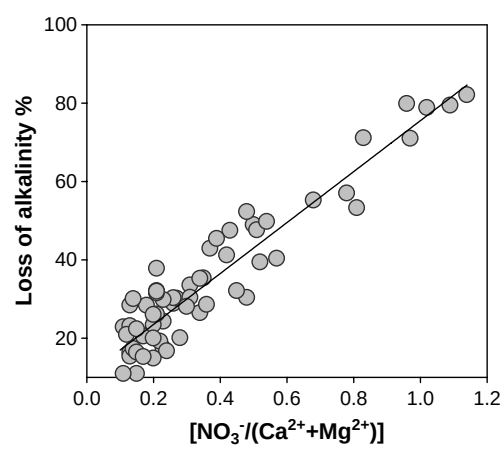

Fig. 9. Relationship between alkalinity loss (%) (expressed as $[HCO_3^-{}_{theoretical} - HCO_3^-{}_{measured}]/HCO_3^-{}_{theoretical}$) and $[NO_3^-/Ca^{2+} + Mg^{2+}]$ (moles.l^{-1}/moles. l^{-1}) at the outlet of the Hay experimental catchment.

mainly cultivated, in which one of the considered experimental catchments, the Montoussé, is included. Nitrate concentration significantly increased, however, ($^{***}p \leqslant 0.001$, $N = 275$) (Fig. 10) during the period 1973–2003 (+142%). Over the same period, the amount of N applied on land in this area was quasi doubled (84% increase), while fertilized surface underwent a 8% decrease (UNIFA, 2007). In the same time, discharge presents no significant trend. Discharge variations, however, clearly show two periods: a humid period during the first ten years and a drier period with low fluctuations during the twenty following years. These discharge changes might influence the general increasing or decreasing trends in concentration, but we notice that the major increase in nitrate and Ca + Mg (respectively, +142% and +16.5% over the period 1973–

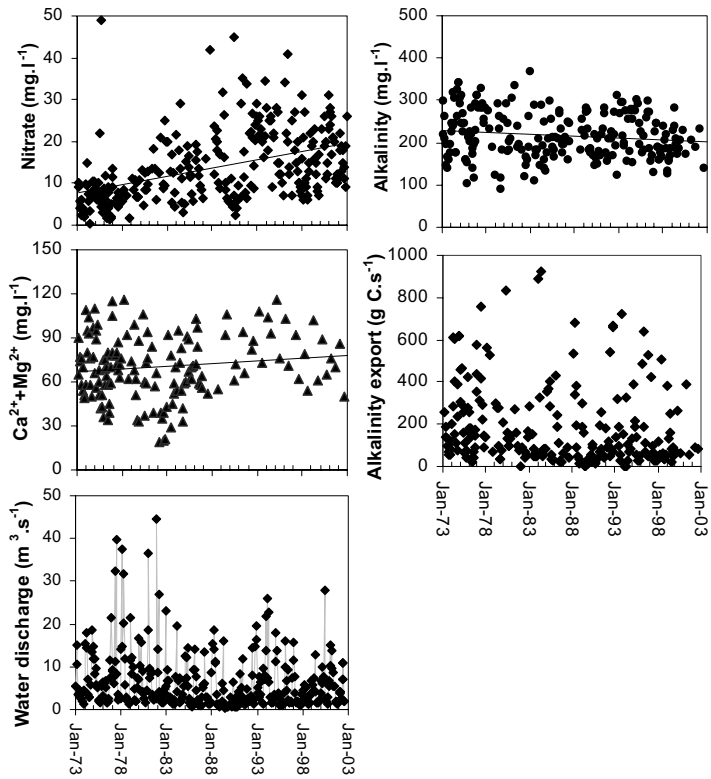

Fig. 10. Variations of bicarbonate, divalent cations ($Ca^{2+} + Mg^{2+}$), nitrate concentrations (mg l^{-1}), alkalinity export (g C s^{-1}) and discharge (m^3 s^{-1}) for the Save river (a main tributary of the Garonne river draining an intensively cultivated area) over the period 1973–2003. Lines represent linear regression trends over the time period (in the calculations, $\times$ is expressed in days from 01-01-1900): Alkalinity $= -2.8\ 10^{-3}x + 303.07$, $r^2 = 0.026$, $p \leqslant 0.05$, $n = 231$; $NO_3 = 1.2\ 10^{-3}x - 23.51$, $r^2 = 0.21$, $p \leqslant 0.001$, $n = 275$; $Ca + Mg = 10^{-3}x + 39.64$, $r^2 = 0.020$, $p < 0.10$, $n = 156$; $Q = -0.3\ 10^{-3}x + 17.20$, $r^2 = 0.033$, $p \leqslant 0.010$, $n = 364$. Data are from the French water agency Adour-Garonne.

2003) concentrations and a corresponding decrease in alkalinity are observed during the last twenty years when the discharge presents no increasing or decreasing trend. Moreover, the change in discharge could not affect the respective contribution of nitrate and alkalinity to the total anionic charge and consequently the loss of alkalinity. Hence, the observed decreasing trend of the alkalinity in the Save river can rather be considered a consequence of increasing input of N-fertilizer since 1970. Moreover, the increase of Ca + Mg concentrations (16.5%) in the Save river can be reasonably attributed to additional dissolution of the carbonate bedrock due to N-fertilizers (leading to the release of CO_2) and is on the same order of magnitude as the decreasing trend of HCO_3^- concentration (12.5%), as explained in Section 5.2.

In the Mississippi River, Raymond and Cole (2003) showed an increase of the alkalinity concentration and export for the period 1954 to 2001, which has been related to the increase in runoff and to land use, as attested by the impact of crop and forest area on alkalinity export for different sub-catchments. West and McBride (2005) attributed this increase of alkalinity to enhanced carbonate dissolution from agricultural liming by nitrogenous fertilizers inputs. It was estimated that 38% of carbonate dissolution in the Mississippi river basin could be related to nitric acid reaction (Personal communication by Probst, 2003 in West and McBride, 2005). Oh and Raymond (2006) estimated that, in the Ohio river basin (43% of agricultural areas), 17% of the export of total riverine bicarbonate is released by the dissolution of agricultural lime.

Finally, the main difference in alkalinity trends between the Gascogne rivers (decreasing trend) and the Mississippi river (increasing trend) can be attributed to:

- discharge trends (increasing for the Mississippi river and slightly decreasing or no trend for the Gascogne rivers),
- important inputs of lime in the Mississippi river basin (lime is easily dissolved by atmospheric carbonic acid and protons from N-fertilizers nitrification, leading to net alkalinity production).

Moreover, in the Garonne basin, soils are naturally carbonate-rich, and soil solutions and streamwaters are frequently oversaturated (HCO_3^- concentrations around 140 ppm in the Garonne river and the calcite saturation index SI > 1, see Etchanchu and Probst, 1988). The amount of alkalinity and of Ca^{2+} (and Mg^{2+}) drained in stream waters of the Gascogne area are mainly controlled by calcite precipitation conditions and favor the precipitation of calcium carbonate in the soil profile and the river bed. Nevertheless, in the river basins of this region, changes in carbonate weathering processes due to N-fertilizer can be observed through modifications of the relative proportion

between Ca^{2+} (and Mg^{2+}) and HCO_3^- (see Fig. 6). Consequently, we may expect that the dissolution of carbonate in carbonate-rich soils and in molasse bedrocks occurs by replacing atmospheric carbonic acid by protons from nitrification, leading to the replacement of alkalinity by nitrate, and consequently to a decrease in alkalinity concentration. In the Mississippi river basin, this process is perturbed by the dissolution of lime and by the increase of discharge, which mainly contribute to increasing the alkalinity concentration and export (and to an even greater extent calcium ions, as shown by Oh and Raymond (2006) for the Ohio river basin).

5.5. Implications for regional and global atmospheric CO_2 source/sink

The objectives of this section are to assess the possible impact of the dissolution of carbonate bedrock by nitric acid due the nitrification of N-fertilizers on the CO_2 balance, which has been observed for the Gascogne, the Seine and the Swale river basins at the scale of France and on a global scale.

As shown in the previous section, the ratio of $CO_{2\ ATM\text{-}SOIL}$/total HCO_3 decreases on average by about 4–9% for all the samples from the Gascogne, the Seine and the Swale river basins. This ratio, however, can reach 13% and 21% on average for the two experimental cultivated catchments based on intensive sampling surveys and as high as 50% during storm events.

Based on these results, we consider a minimum value to be 7% (average decrease for large river basins) and a maximum value to be 17% (average decrease for the two experimental catchments). The decrease of CO_2 uptake is calculated in this section on the basis of these minimum and maximum values, considering that the flux of alkalinity remains constant as could be observed for the Save basin, where the alkalinity presents low variations over the period 1983–2003 (Fig. 10). Consequently, the decrease of the ratio $CO_{2\ ATM\text{-}SOIL}$/total HCO_3^- could be mainly attributed for this basin to a decrease of the CO_2 flux due to the dissolution of carbonate minerals by anthropogenic protons in cultivated areas.

This decrease was estimated by coupling cropland areas and carbonate and shale outcrops on a country scale (in France) and a global scale. For the global scale, we crossed a global numerical map of lithology (Amiotte-Suchet et al., 2003) with a resolution of 1° by 1° (i.e., a square of about 111 km by 111 km at the equator) with a global cropland map (corresponding to four layers: Dryland cropland and pasture, Irrigated cropland and pasture, Cropland/grassland mosaic and Cropland/woodland mosaic) extracted from the USGS Global Land Cover Characteristics Data Base (Version 2.0) with a resolution of 1 km by 1 km (http://edcsns17.usgs.gov/glcc/globe_int.html). For France, we coupled this land cover map with a country map of carbonate soils with a resolution of 1 km by 1 km (INRA, 1998). All maps were projected on an Interrupted Goode Homolosine Projection to optimize surface estimates.

We thus estimated that 12.35×10^6 km^2 were cultivated on carbonate or shale rock types (respectively, 3.45×10^6 km^2 on carbonate rocks and 8.90×10^6 km^2 on shale outcrops).

Amiotte-Suchet et al. (2003) estimated that dissolution of carbonate rocks consumes 40% of total CO_2 uptake by continental weathering, even if its outcrop area represents only 13% of the total land area. Moreover, with 25% of the total land area surface, "shale" outcrops (with a carbonate content up to 50%) were also estimated to contribute to 40% of total CO_2 uptake by continental weathering. Nevertheless, as shown by Lerman et al. (2007) and Lerman and Wu (2007), CO_2 uptake by shales may differ since their mineral compositions (particularly the proportion of silicates and carbonates) vary. Moreover, since shales comprise evaporitic rocks, which cannot be separated, this estimate for shales must be considered a maximum value (Amiotte-Suchet et al., 2003). This assumption can also be counterbalanced by the fact that a lot of silicate outcrops contain traces of calcite, which can play a significant role in CO_2 consumption (Drever and Hurcomb, 1986; White et al., 2005).

In the calculations, we assumed that: (i) N-fertilizers are applied to all croplands; (ii) the loss of CO_2 consumption in soils varies between 7% and 17% as estimated in this study; and (iii) natural CO_2 consumption fluxes correspond to the values published by Amiotte-Suchet et al. (2003) for carbonates (478×10^3 moles km^{-2} yr^{-1}) and shales (251×10^3 moles km^{-2} yr^{-1}).

On a global scale, the decrease of the CO_2 flux consumed by cultivated area on carbonates (3.45×10^6 km^2) and shales (8.90×10^6 km^2) can be estimated, respectively, as 0.116 and 0.156×10^{12} moles yr^{-1} of CO_2 for minima (7% decrease) and 0.280 and 0.379×10^{12} moles yr^{-1} of CO_2 for maxima (17% decrease). The totals (carbonates plus shales) represent 0.270 to 0.659×10^{12} moles yr^{-1} of CO_2 uptake decrease for the minimum and maximum, respectively. Thus, N-fertilization in carbonate areas would lead to 1.6–3.8% loss of CO_2 consumption compared to the amount of CO_2 naturally consumed by weathering of carbonate plus shale rocks on a global scale (17.2×10^{12} moles of CO_2 yr^{-1}, according to Amiotte-Suchet et al., 2003), and to 1.3–3.1% loss compared to the amount of CO_2 consumed by overall weathering of continental rocks (21.5×10^{12} moles of CO_2 yr^{-1} according to Amiotte-Suchet et al., 2003, and 22×10^{12} moles of CO_2 yr^{-1} according to Lerman et al., 2007).

At the scale of France, the loss of CO_2 uptake was calculated in the same way. The loss is relatively higher (5.7–13.4% of total CO_2 naturally consumed by the dissolution of carbonate bedrock in France), since the proportion of cultivated land area on carbonate soils is greater. This decrease amounts to 5 to 12×10^9 moles of $CO_2 \times$ yr^{-1}, i.e., 0.22–0.53 Tg yr^{-1} CO_2 (0.06–0.14 Tg C yr^{-1}).

On a short time scale, carbonate dissolution by nitric acid in cultivated areas does not consume atmospheric CO_2, and it liberates additional Ca + Mg exported by the rivers to the oceans. The CO_2 released during this anthropogenic process can be partly/totally used to dissolve more carbonate in the soil, releasing calcium and alkalinity, as during natural weathering with carbonic acid.

On a geological time scale, the excess of Ca + Mg released into the rivers by anthropogenic carbonate dissolution can be precipitated as carbonate in the oceans, degassing CO_2 to the atmosphere. As a whole, this anthropogenic process represents a net source of CO_2 for the atmosphere.

On a global scale, we can estimate from the results of this study that the anthropogenic source of CO_2 due to the impact of fertilizer application on carbonate areas amounts to 0.27–0.66 $\times 10^{12}$ moles CO_2 yr^{-1}, i.e., 12–29 Tg yr^{-1} CO_2 (3.2–7.9 Tg C yr^{-1}).

Compared with other anthropogenic CO_2 sources (period 2000–2005: fossil fuel combustion (7.2 Gt C yr^{-1}), deforestation and land use changes (1.6 Gt C yr^{-1}) according to IPCC, 2007), this CO_2 flux appears relatively low.

Nevertheless, with regard to atmospheric CO_2 content, this source of CO_2 can be compared with atmospheric CO_2 uptake by silicate rock weathering (4.3 $\times 10^{12}$ moles of CO_2 yr^{-1} without shales and 12.9 $\times 10^{12}$ moles of CO_2 yr^{-1} with shales, Amiotte-Suchet et al., 2003), which represents a net sink of atmospheric CO_2, rather than with the CO_2 flux consumed by carbonate dissolution, which is counterbalanced by carbonate precipitation in the ocean. This anthropogenic source of CO_2 represents 2–5% (if shales in silicates are taken into account) to 6–15% (without shales) of the total CO_2 sink due to silicate weathering.

Moreover, in the US, West and McBride (2005) estimated that dissolution of agricultural lime by nitric acid from N-fertilizers leads to the release of 3.35 Tg yr^{-1} CO_2. This additional potential impact of nitrogenous fertilizers increases the imbalance of the CO_2 budget by releasing CO_2 to the atmosphere. These results highlight a potential strong imbalance in the C Cycle for carbonate outcrop areas as well as for non-carbonate areas, which receive agricultural liming and N-fertilizers.

6. CONCLUSION

Under natural environmental conditions, the dissolution of carbonates and the riverine transfer of calcium, magnesium and alkalinity to the ocean are mainly controlled by the presence of carbonic acid in the solution percolating through the soil. In carbonate cropland areas, nitrogen fertilizers influence the riverine alkalinity in agricultural catchments compared to low anthropogenic pressure catchments. The main results obtained in this study are the following:

- Riverine alkalinity compared to the $Ca^{2+} + Mg^{2+}$ concentration presents a significant decrease in agricultural catchments, as shown for 25 French small monolithological catchments in the Gascogne area (south-western France) as well as for other small carbonate watersheds in Europe.
- This decrease is particularly enhanced during storm events, as shown for the Hay experimental catchment in Gascogne.
- The alkalinity loss estimated in these agricultural catchments is significantly correlated with nitrate concentrations. Consequently, this alkalinity loss can be attributed to the dissolution of carbonates by proton inputs due to nitrification processes in soils after N-fertilizer spreading, which leads to the release of CO_2 to the soil/atmosphere.
- This loss of riverine alkalinity corresponds to a decrease of atmospheric/soil CO_2 uptake by weathering and its contribution to the total riverine alkalinity. For the studied catchments in France and Europe, this decrease was estimated on average between 7% and 17%, and it can reach up to 50% for some watersheds, such as the Hay experimental catchment during storm events.
- Temporal variations observed over the last 30 years for a larger river like the Save in the Gascogne area confirm the results obtained for small catchments and show that the alkalinity concentration presents a slight decreasing trend while the fluctuations of nitrate contents and calcium plus magnesium concentrations are increasing.

Using these results, we have estimated for the first time on a global scale that N-fertilizer application in carbonate cropland areas would decrease the atmospheric/soil CO_2 consumed by carbonate dissolution by about 1.4–3.4 Tg C yr^{-1} (i.e., 0.116–0.280 $\times 10^{12}$ moles yr^{-1} of CO_2 if only carbonate rocks are considered) to 3.2–7.9 Tg C yr^{-1} (i.e., 0.270 and 0.659 $\times 10^{12}$ moles yr^{-1} of CO_2 if shales are also taken into account), representing a non-negligible source of CO_2 for the atmosphere on a short time scale, and even more (up to 2 times) on a geological time scale, as the additional calcium plus magnesium released by anthropogenic nitric acid is precipitated in the ocean as carbonate. Compared to the CO_2 uptake by carbonate dissolution, this loss represents only 1.6–3.8% on a global scale and 5.7–13.4% for France. This anthropogenic CO_2 "source", however, corresponds on a global scale to 6–15% of the CO_2 sink due to CO_2 uptake by natural silicate weathering. Moreover, if we take into account the other anthropogenic CO_2 source due to the dissolution of agricultural lime in acid soils and the corresponding precipitation of carbonates in the ocean (see West and McBride, 2005), the impact of N-fertilizers on CO_2 sources could be higher. Indeed, West and McBride estimated that the CO_2 source due to the dissolution of agricultural lime by nitric acid and the corresponding precipitation of carbonates in the ocean (considering only 60% is precipitated) could represent 1.2–1.8 Tg C yr^{-1} for the US alone, according to the amount of applied aglime. If we add this aglime dissolution impact on a global scale to our estimate of carbonate dissolution by nitric acid, we reach a global anthropogenic source of 5–10 Tg C yr^{-1}, i.e., 10–20% of the CO_2 uptake by silicate weathering. This non-negligible anthropogenic source of carbon must be considered in models of the modern carbon cycle.

ACKNOWLEDGMENTS

Special thanks go to Gaël Durbe, Laure Gandois and Gérald Dermont from ECOLAB for their help in the field, for part of the analytical work and for discussions, to the technical staff of LMTG for chemical lab services (Maïté Carayon, Carole Causserand), to the "Association des Agriculteurs d'Auradé," the CACG (Compagnie d'Aménagement des Coteaux de Gascogne, particu-

larly Michel Peres and Bernard Balas) and to Pierrette Gouault and Eric Ceschia from the CESBIO, who facilitated access to the Montoussé catchment environmental data, and to Norbert Billet (CEBC-CNRS) for his help with GIS analyses. Finally, J.I. Drever and two anonymous reviewers are especially acknowledged for their very helpful comments. A.S. Perrin benefited from a FSE-CEE-CNRS fellowship. This work was supported by the INSU-CNRS (program ECCO-PNBC), the FEDER (EEC) and CPER (Région Midi-Pyrénées) funds within the framework of the IMAQUE ("IMpact of Agricultural practices on water QUality, soil, sediments and aquatic Ecosystem") project (ECOBAG network) and the French "Zone Atelier Adour-Garonne" (ZAAG) of the CNRS.

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