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Long-Term Effects of High Nitrogen Loads on Cation and Carbon Riverine Export in Agricultural Catchments

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S *Supporting Information*

ABSTRACT: The intensification of agriculture in recent decades has resulted in extremely high nitrogen inputs to ecosystems. One effect has been H^+ release through NH_4^+ oxidation in soils, which increases rock weathering and leads to acidification processes such as base-cation leaching from the soil exchange complex. This study investigated the evolution of cation concentrations over the past 50 years in rivers from the Armorican crystalline shield (Brittany, western France). On a regional scale, acidification has resulted in increased base-cation riverine exports (Ca^{2+}, Mg^{2+}, Na^+, K^+) correlated with the increased NO_3^- concentration. The estimated cation increase is 0.7 mmol(+)/L for Ca^{2+} + Mg^{2+} and 0.85 mmol(+)/L for total cations. According to mass balance, cation loss represents >30% of the base-cation exchange capacity of soils. Long-term acidification thus contributes to a decline in soil productivity. Estimates of the total organic nitrogen annually produced worldwide indicate that acidification may also constitute an additional carbon source in crystalline catchments if compensated by liming practices.
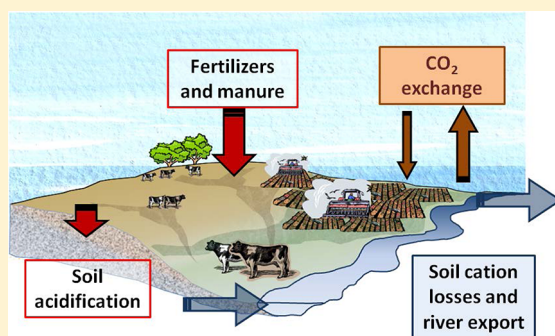
INTRODUCTION

The intensification of agriculture during the decades following World War II in the United States and Europe[1−3] led to a huge decrease in the number of farms and a correlated increase in their surface area. It also resulted in a massive use of chemical and organic fertilizers.[4−6] These practices have led to high nitrogen concentrations in soils and in surface water and groundwater (NO_3^- and NH_4^+).[7] Agricultural activities create many feedbacks such as increased atmospheric CO_2, NO_2, and NH_3 concentrations, increased plant C sequestration, and increased carbon storage in soils, although this point is still debated.[8,9] Agricultural practices may also influence rock weathering, which has direct and indirect consequences on carbon mass balance. These effects need to be assessed and compared with those of natural weathering.

The estimated global carbon transport by rivers is 0.8−1.6 Pg C year^{-1}.[10−13] The dissolved inorganic carbon exported by world rivers as a result of silicate and carbonate weathering represents a global carbon flux of 380 ± 76 Tg C year^{-1}.[11,14] Recent more local studies showed that acidification processes related to areas of intensive agriculture led to carbonate dissolution in limestone catchments.[15,16] This effect is apparent on very large scales[17,18] to more regional scales[19−21] as an increase in riverine cation concentrations and alkalinity.[17,20−22] On the basis of the limestone catchment surface area and fertilizer use, Perrin et al. calculated that, on a global scale,

nitrification-related carbonate weathering constituted a potential C source of 3.2−7.9 Tg year^{-1}.[16] Liming practices, which are intended to reduce the soil acidity generated by fertilizers, also constitute a potential carbon source through limestone dissolution.[20,23] However, the mechanisms of dissolution are complex and the "source" effect is strongly dependent on the reaction pathways and soil interactions.[24,25] Thus, the effects of liming are not easy to quantify.

The acidification processes and weathering mechanisms induced by fertilizer use in crystalline catchments (silicate rocks) have been little investigated, even though such catchments constitute about one-third of the continental area and about 20−30% of agricultural areas worldwide.[26] Crystalline rock weathering induced by intensive agriculture was previously investigated by examining chemical exports from two small catchments in Brittany.[27] After correction for the chemical inputs related to fertilizers, the base-cation export was shown to be extremely high. Analysis of the strontium isotopes in this system (soil leaching, minerals, waters) revealed that cations in river and ground waters were mainly derived from plagioclase and, to a lesser extent, biotite dissolution.[28]

Although regional scale river evolution as well as the effect of limestone catchments on the carbon cycle have been documented,[16,21] no studies of the effects of agricultural acidification in crystalline catchments have been carried out on a regional scale. Furthermore, whereas nitrate evolution during recent decades has been relatively well documented, the potential evolution of cations in rivers, as related to agricultural intensification, has not been investigated, although the effect of liming itself has been investigated.[20,23]

The aim of this paper was therefore to document large-scale adicification processes in silicate catchments related to intensive agriculture. The goal was (i) to quantify the cation export during the past 50 years, (ii) to determine the origin of the cations, and (iii) to analyze the link between cation export and agriculture nitrogen as well as lime inputs.

■ MATERIALS AND METHODS

Acidification Processes. The soil is a biogeochemical reactor with mineral (clays) and organic phases reacting with solutions as their negative charges adsorb and exchange cations. The sum of these negative charges constitutes the soil exchange complex or cation exchange capacity (CEC or $T = Ca^{2+} + Mg^{2+} + K^+ + Na^+ + Al^{3+} + H^+$). The S/T ratio corresponds to the proportion of alkaline and alkaline earth elements, or "base" cations ($S = Ca^{2+} + Mg^{2+} + K^+ + Na^+$) in the CEC. In soils, processes tending to increase acidity affect the negative charges of the CEC and lead to lower soil S/T ratios as a result of base-cation export. Base cations may either be taken up by the vegetation (exported by harvesting) or lixiviated in soil solution and streams. Base-cation lixiviation results from exchanges on the CEC with H^+ and Al^{3+} (refer to the Supporting Information Annex S1 for further details about chemical processes) produced in excess in soils (especially due to NH_4 mineralization, see below) or from the lixiviation of anions produced in excess in soils, especially nitrates, when they are not absorbed by plants. In this case, base cations are leached at the same time to maintain the charge equilibrium of the solutions.

We investigated the chemical reactions controlling cation fluxes in agricultural catchments and distinguished between CO_2-related and N-related reactions. We also examined the cation to HCO_3^- ratios that will be used later in the discussion. The chemical reactions and the cation to HCO_3^- ratios are described in the Supporting Information (SI Annex S1). Most of the nitrogen related to agriculture intensification is brought to the environment as ammonium in the form of NH_4NO_3 from chemical fertilizers or organic-bound NH_4^+ from manure or urea. The oxidation of ammonium into nitrate (nitrification, eq 1, SI Annex S1) produces two H^+, which initiates an acidification process.

In carbonated catchments, natural weathering is induced by atmospheric CO_2 and CO_2 produced from organic matter degradation in soils, leading to the conversion of $CaCO_3$ to 1 Ca^{2+} and 2 HCO_3^- (eq 2, SI Annex S1). The H^+ release from nitrification of NH_4^+ may also trigger carbonate rock weathering, leading to cation export (eq 3, SI Annex S1). This reaction leads to the conversion of 1 $CaCO_3$ to 1 Ca^{2+} and 1 HCO_3^-.

As in limestones, rock weathering may also result from CO_2 consumption in crystalline rock catchments. Both calcic and sodic plagioclases are common in crystalline rocks and are easily weatherable.[29,30] The weathering of Ca-plagioclase leads to kaolinite formation. In this case, the Ca^{2+} to HCO_3^- molar

ratio is 1/2 (eq 4, SI Annex S1). In the case of sodic plagioclase dissolution, smectite is formed instead of kaolinite, but the reaction is similar, and the Na^+ to HCO_3^- molar ratio is 1/1 (as for the Ca^{2+} to HCO_3^- molar(+) ratio). This reaction can be compared to the crystalline rock weathering induced by proton release as a result of nitrification (eq 5, SI Annex S1), which does not produce HCO_3^-.

Carbon Mass Balance. CO_2-induced carbonate weathering (eq 2, SI Annex S1) consumes 1 mol of CO_2 and produces 2 mol of HCO_3^-. One mole of HCO_3^- may in turn be converted to CO_2 in the ocean by the precipitation of 1 mol of carbonate (eq 2, from right to left). In this case the carbon mass balance between continents and oceans, on a global scale and in the long-term carbon cycle, is neutral, and carbonate dissolution therefore has no effect on the long-term atmospheric carbon stock. However, carbonate precipitation in the ocean is a rather slow process, which may only partially release the inorganic riverine carbon.[23] In the short term, carbonate dissolution may thus act as a carbon sink for atmospheric CO_2. As in the previous case, nitrification-induced carbonate weathering (eq 3, SI Annex S1) produces inorganic carbon, of which half may be converted to carbon dioxide, the other half remaining as dissolved inorganic carbon in river or ocean water. This reaction constitutes a direct carbon source.[16,23,24] CO_2-induced silicate weathering (eq 4, SI Annex S1) consumes 2 mol of CO_2 and produces 2 mol of HCO_3^-. Only half of the inorganic carbon can be released to the atmosphere (eq 6, SI Annex S1); thus, this reaction constitutes a carbon sink. Finally, nitrification-induced silicate weathering (eq 5, SI Annex S1) produces cations and does not produce HCO_3^-, so it does not interact with the carbon cycle.

Inclusion of the soil compartment makes the relationships between weathering reactions and carbon fluxes more complex. Carbonates are present in carbonated catchments but also in silicated catchments as a result of liming. The ionic products of N-induced carbonate dissolution can interact with reactive solid surfaces in the soil, and the cations released can be adsorbed on the soil exchange complex. These cations can then react with the CO_2 and transform carbon dioxide to inorganic carbon (eq 6, SI Annex S1).

Depending on the nature of cation release, carbonate dissolution may have different effects on the atmospheric carbon stock.[20] CO_2 consumption may also occur through eq 2 if the cations are exported with nitrates when they are not absorbed by plants. Thus, the cation to nitrate relationships need to be taken into account. Hamilton et al. showed that if the Ca^{2+} to HCO_3^- molar ratio is between 0.5 and 1, carbonate dissolution can be considered as a carbon sink, whereas if this ratio is >1, the HCO_3^- is converted to CO_2 and constitutes a carbon source.[24] However, this interpretation is valid only if no silicate dissolution occurs in parallel to carbonate dissolution.

Geology and Soils of Brittany. The magnitude of the acidification process on silicate catchments was first investigated by examining the chemical evolution of the main rivers of Brittany. The five river catchments cover an area of 14900 km^2 (55% of Brittany, Supporting Information Figure S1). The major river in this area is the Vilaine, which has a catchment of 10400 km^2 and represents 38% of Brittany. The whole Brittany region is composed of Proterozoic and Hercynian crystalline rocks, granites, and schists, mainly covered by Cambisols and Luvisols.[31] These soils are relatively acidic with a poorly developed exchange complex (CEC often <15 cmol(+)/kg) and unsaturated with base cations (S/T mostly <50%).[32]

Liming is therefore necessary to counteract biomass uptake and exportation by agriculture and to neutralize acidification associated with organic nitrogen application. The whole of Brittany is characterized by intensive agriculture, with 90% of the surface area devoted to farming. Livestock include more than 2 million cattle, 8 million pigs, and more than 60 million poultry (Source: Ministry for Agriculture, http://www.agreste. agriculture.gouv.fr). Together with the inorganic nitrogen fertilizers used for arable farming, the resulting agricultural nitrogen loads exceed 200 kg N ha^{-1} in a large part of Brittany. Nitrogen applications are mainly in the form of ammonitrate mineral fertilizers and organic slurry and manure.[27] Further details about the database and methods used and catchment characteristics can be found in the Supporting Information (Annex S2 and Table S1).

■ RESULTS

Evolution of Nitrate Concentrations. In many agricultural areas worldwide, high nitrogen loads have led to high nitrate concentrations in surface waters.[1,4,5,33] The temporal evolution of nitrate concentrations in the Vilaine (Figure 1) is
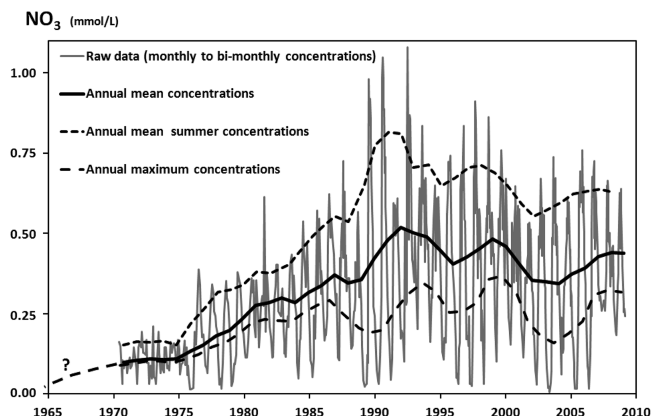

Figure 1. Temporal evolution of nitrate concentrations in the Vilaine River (3 years, smoothed data except raw data).

similar to that of the four other Brittany rivers (refer to Supporting Information Figure S2). The general trend is a clear increase. The Vilaine River drains a large catchment, and the nitrate concentrations exhibit broad variations (up to 0.10 mmol/L) due to seasonal cycles, which are characterized by low summer and high winter concentrations, irrespective of the amount of rainfall. The nitrogen concentration in precipitation remains low with regard to the river concentration, although nitrogen emissions to air related to agriculture provide fluxes that are not negligible. The nitrate variations in the Vilaine River result from differences in reservoir sources (runoff, shallow or deep aquifer), agricultural practices, soils, and in-stream biogeochemical processes. Nevertheless, the nitrate concentrations exhibit a clear increase from 1975 onward in all five rivers. A major increase in the mean annual concentrations of the Vilaine River is clearly apparent from 1975 until 1990–1992 (Figure 1). Between 1992 and the present, the annual mean concentrations are more stable, with two periods of lower NO$_3^-$ concentrations (1996 and 2002–2003) that correspond to drier years. Nitrate concentrations have been increasing in recent years. The annual maximum concentrations (90th percentile) peak during the early 1990s (Figure 1) and then show a slight decrease. The annual mean summer concen-

trations have been steadily increasing (Figure 1). A similar trend is apparent in the other rivers (Suppoting Information Figure S2).

This evolution can be related to the dramatic increase of fertilizer input in Europe, which rose from 2 to 11 billion tons per year between 1960 and the early 1990s, and has then remained almost stable up to now. In Brittany, mineral fertilizer use also increased during the same period (1950–1995) from 1.1 to 4.9 million tons and livestock increased from about 4 million cows and pigs and 12 million chickens in 1950 to almost 9 and 85 million, respectively, in 1990. During the same period, the annual consumption of mineral nitrogen increased from 60,000 to 300,000 t year^{-1}. The total amount of nitrogen, including both organic and inorganic nitrogen, therefore increased from about 50 to more than 200 kg ha^{-1} of spreading surface area. The concomitance of high NO$_3^-$ concentrations in the main rivers of Brittany with agricultural activities indicates that the agricultural pressure has effects on the whole region.

Evolution of Cation Concentrations. The temporal evolution in Ca^{2+} and Na$^+$ concentrations and the Na$^+$/Cl$^-$ ratio in the five rivers is presented in Figure 2. All of these rivers show an increase in Ca^{2+} and Na$^+$ during the 1980–1995 period, which was tested using Student's test between the 1975–1985 and either the 1990–1995 or the 2000–2005 concentrations ($t > 2$, $p = 0.05$). The increase ranged from 0.07 to 0.32 mmol/L and from 0.11 to 0.78 mmol/L for Ca^{2+} and Na$^+$, respectively. The highest Ca^{2+} concentrations, along with the highest nitrate concentrations, were measured in the Arguenon River (0.32 and 0.57 mmol/L, respectively). Although some Cl$^-$ may originate from agriculture[34] and mask the Na$^+$ increase, the Na$^+$/Cl$^-$ ratio increase was also tested with Student's test, which showed a significant increase (from 0.03 to 0.12) until 2005, highlighting a regional leaching of cations from soils and rocks. Moreover, the positive correlation between Ca^{2+} and NO$_3^-$ in the Vilaine River water during high flow periods (Figure 3) highlights the strong direct relationship between cations and nitrate. As NO$_3^-$ in rivers is directly linked to agriculture pressure, the leaching of cations as a result of acidification may also be directly linked to the deposition of N fertilizers in the different catchments. In the Vilaine catchment, the sum of major cations increased from 0.82 to 1.33 mmol L^{-1} between 1970–1980 and 1990–2010, which represents an increase of 0.51 mmol L^{-1}. This concentration represents an increase in the annual flux of weathering-derived cations of 1.1 kmol ha^{-1}. This value is much higher than in nonanthropized catchments with similar runoff and geology.[30,35] All five rivers show a similar chemical evolution of the major cations. This suggests that the geological silicate basement is not the main factor controlling river water chemistry in Brittany, as the rivers drain either granite or proterozoic schists, but rather that cation leaching throughout Brittany is controlled to a considerable extent by agricultural pressure including extensive liming.

Agricultural modifications during the second part of the 20th century have induced hydrology modifications observed as a base flow increase.[19,36] Such modifications are related to decreased evopotranspiration and increase of the groundwater and surface water contributions to streams related to increased irrigation and land use conversion to soybean. Although there was no specific investigation of the hydrology in Brittany, no clear increase in the Vilaine River flow can be observed for the 1970–2010 period such as the increase observed in the Mississippi River for the 1940–2010 period.[36] During the
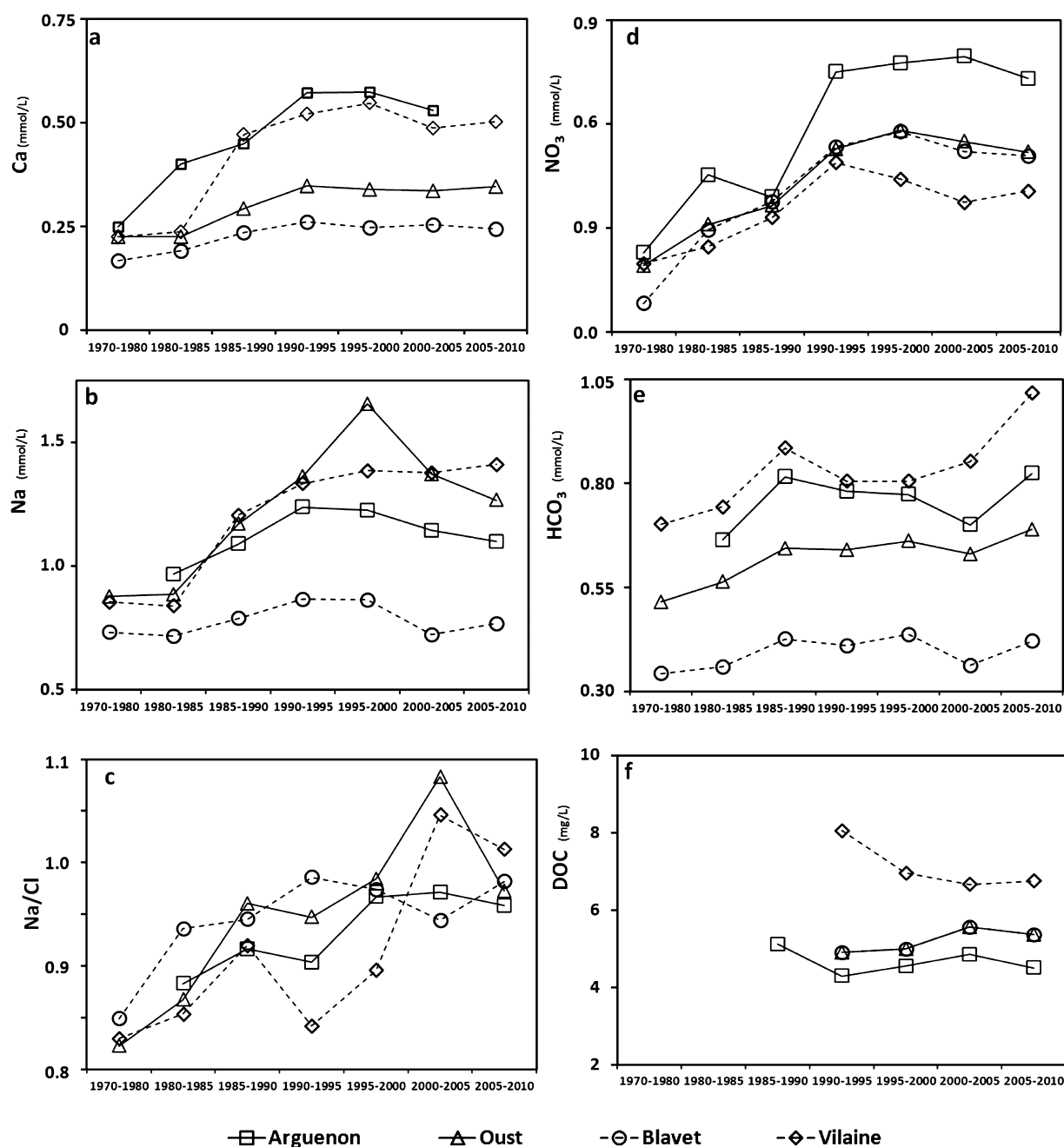
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Figure 2. Evolution of concentrations in the five studied rivers between 1975 and 2010: (a) Ca^{2+}; (b) Na^+; (c) Na^+/Cl^- ratios; (d) HCO_3^-; (e) NO_3^-; (f) dissolved organic carbon. (For clarity, the Aulne results have not been included because they are very close to the Blavet concentrations.)

period investigated in this study (the past 40 years), there was no major evolution of land use. The major evolution was related to the increase of the kettle and nitrogen input. The cation increase observed is mainly correlated to the nitrate increase. Although the nitrate to cation correlation may represent only covariable elements and does not demonstrate a strong direct link, the common increase of all the cations, simultaneously with the bicarbonate and nitrate increase, represents a major modification. Such modification is also contemporaneous to the N fertilizer increase, which clearly represents the major driver of the hydrobiogeochemical system evolution.[37]

Cations and HCO_3^- Relationships. The temporal evolution in HCO_3^- in the five rivers is presented in Figure 2. A more detailed view of the evolution is also provided for the

Vilaine River in the Supporting Information (Figure S3). During the 1970–2005 period, although the evolution is not linear, all of the rivers show a general HCO_3^- significant increase, which was tested using Student's test ($t > 2$, $p = 0.05$ except for the Arguenon River $p = 0.2$). The differences between the 1970–1980 and 2005–2010 periods range from 0.09 to 0.32 mmol/L. In the Vilaine River (Supporting Information Figure S3), a linear pH increase can also be observed except during the last years of the record. Both measurements indicate a large bicarbonate release during the last decades. The dissolved organic carbon measurements do not span the whole investigated period and do show relatively stable concentrations, although several rivers indicate a decrease during the 1985–1995 period.
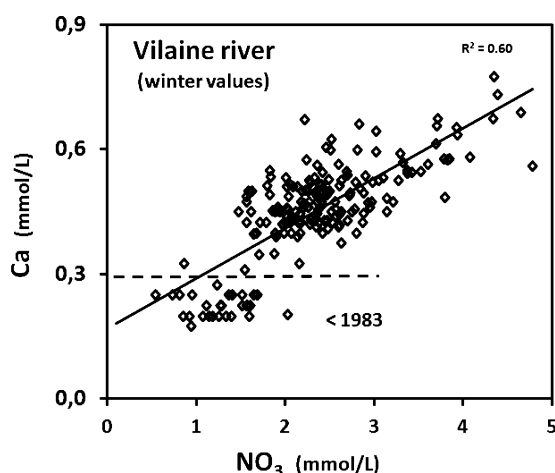
Figure 3. Ca^{2+} to NO_3^- molar concentrations in the Vilaine River during high flow periods (winter, 1975−2010).

The $Ca^{2+} + Mg^{2+}$ and Ca^{2+} to HCO_3^- concentrations in the Vilaine River are presented in Figure 4. The stoichiometry of the four reactions (2−5, Supporting Information Annex S1) is also shown as straight lines (lines 1−4 in Figure 4). The temporal evolution (as 5 year mean, i.e., Figure 2) is also presented. The $Ca^{2+} + Mg^{2+}$ concentrations (Figure 4a) are clearly much higher than the potential concentrations produced from CO_2-induced carbonate (line 1) and silicate weathering (line 3). They may be explained by a mixed origin of silicate (line 4) and carbonate (line 2) weathering induced by nitrification. In the Ca^{2+} versus HCO_3^- graph (Figure 4b) the Ca^{2+} concentrations are closer to the CO_2-induced carbonate or silicate dissolution (line 1), but a large shift is observed for a major part of the points toward the carbonate dissolution induced by nitrification (line 2). Consequently, the Mg^{2+} concentrations encountered in the rivers are mainly derived from silicate, ultimately derived from weathering resulting from nitrification, although Mg^{2+} may be leached from the soil exchange complex. This is confirmed by the temporal evolution of the Ca^{2+}/HCO_3^- and $Ca^{2+} + Mg^{2+}/HCO_3^-$ index (Supporting Information Figure S3), which shows values higher than the CO_2-induced reactions, especially during the 1985−2005 period.

All of the data indicate that a major evolution of the river chemistry has been observed during the past 40 years. This evolution is characterized by very large nitrate increases as well as pH and bicarbonate increases. Cations that derive from both carbon dioxide-induced and nitrification-induced reactions also show a clear shift during the same period, in relation to the nitrate evolution.

■ DISCUSSION

Origin of Cations in Rivers. The weathering of silicate minerals is one of the most important natural geochemical processes, releasing essential cations (Ca, Mg, K, Fe, and others) at the Earth's surface and increasing their availability for biota in soils and waters. In anthropogenized catchments, mineral and organic fertilizers constitute another major source of cations for both soils and waters. Chemical analyses of manure have revealed Ca^{2+} concentrations ranging from 20 to 40 g/kg. These concentrations are much lower than the NO_3^- concentrations, and the Ca^{2+}/NO_3^- mass ratio is 0.025−0.03.[27] From 1975 to the present day, the mean NO_3^-
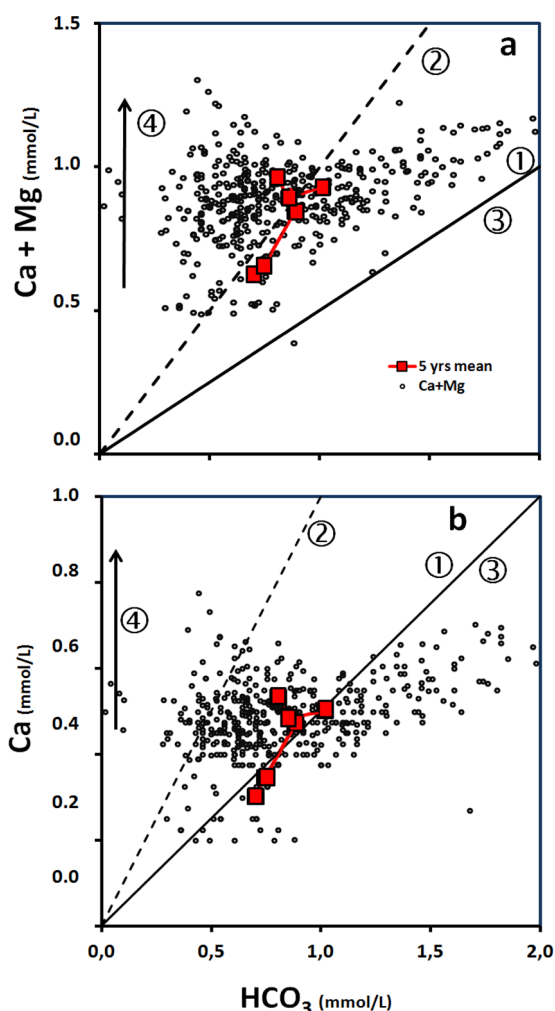

Figure 4. $Ca^{2+} + Mg^{2+}$ (a) and Ca^{2+} (b) versus HCO_3^- concentrations in the Vilaine River. The different lines represent the stoichiometric reaction of (1) dissolution of carbonate (eq 2), (2) dissolution of carbonate induced by nitrification (eq 3), (3) silicate weathering (eq 4), and (4) silicate weathering induced by nitrification (eq 5). Squares represent the 5-year mean of Figure 2.

concentrations in the Vilaine River increased by 0.4−0.5 mmol/L, which represents a Ca^{2+} source of 15−22.5 μmol/L. However, this Ca^{2+} increase induced by fertilizer leaching is much lower than the increase in Ca^{2+} concentrations observed in Brittany rivers. This suggests that, in addition to fertilizer leaching, another source of Ca^{2+} is leached from soils as a result of enhanced mineral weathering and/or soil exchange capacity desaturation.

Various mineral weathering processes may account for the neutralization of acidification in these silicate rock catchments, depending on the agricultural practices. Cations may originate from carbonates if liming operations are frequent, in which case, acidification can also constitute a carbon source. If cations are mainly produced through silicate weathering related to N acidification, they may have no influence on the carbon cycle. Liming operations to increase soil pH were important in Brittany during the 1970s and 1980s and are still frequent. The liming products mainly consist of a red alga (*Lithotamnium*) locally called "maerl" $(Ca_{(1-x)}Mg_xCO_3$ with x ranging from 1 to 3%). The current average annual liming level is roughly 2 mol of equivalent CaO h^{-1}. Considering that all of the added lime is

rapidly dissolved, the expected increase in Ca^{2+} concentration, taking into account an effective precipitation of 250−350 mm, is 0.7−1 mmol/L. This input could clearly explain the observed increase in Ca^{2+} in the investigated rivers. However, other potential reactions should also be considered.

As indicated under Results, although Ca may be explained by carbonate dissolution, Mg implies a silicate source. The influence of silicate weathering can also be investigated using the Na^+ concentrations. As Na^+ in rainfall is derived from the evaporation of seawater, the Na^+/Cl^- molar ratio of rainfall is similar to that of seawater and can be used to determine the Na^+ contribution from rainfall and from continental geogenic sources such as rock weathering and cation exchange on the adsorbing complex of soils. Because the Na^+ exchanged from clay is ultimately derived from silicate weathering and the Na^+ from anthropogenic sources is limited,[27] we can consider this Na^+ as a "continental", geogenic Na^+. Continental Na^+ is plotted against Ca^{2+} in Figure 5. The influence of silicate
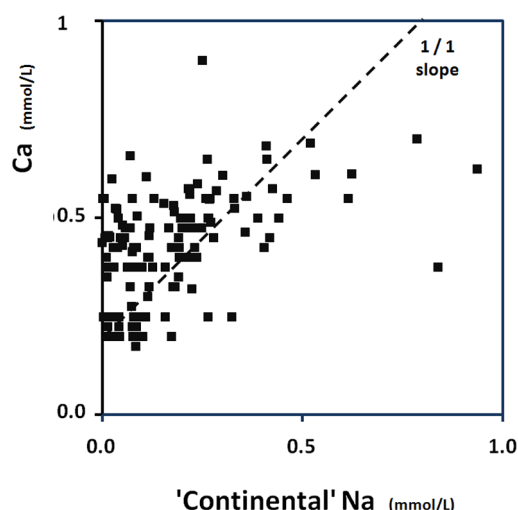

Figure 5. "Continental" Na^+ versus Ca^{2+} concentrations in the Vilaine River.

weathering is demonstrated by the high continental Na^+ concentrations. However, no clear relationships are apparent, and independent increases can be seen in both Ca^{2+} and Na^+, which suggests different potential mineral sources of the two cations. In silicate rocks, Na^+ is mainly derived from Na-plagioclase, a relatively ubiquitous mineral, which is quite easily weathered.[38] In addition, plagioclases may also constitute a Ca^{2+} source in soils and waters, as previously highlighted in Brittany,[28] which could explain the partial correlation between Na^+ and Ca^{2+}. Disseminated minor minerals such as calcite or apatite preserved in inclusions may also contribute to Ca^{2+}[35,38,39] but, in view of the very high cation concentrations, these mineral contributions are thought to remain negligible[28] compared to plagioclase and lime.

Mg^{2+} is not correlated to Na^+ (data not shown, $R^2 < 0.35$). It is only roughly correlated to Ca^{2+} (data not shown, $R^2 = 0.34$), and the relationships with carbonate are far from stoichiometric. Thus, although a slight carbonate contribution of Mg^{2+} probably occurs, the Mg^{2+} in river waters is thought to originate mainly from the weathering of magnesium silicate such as pyroxene (enstatite), amphibole (hornblende), or biotite. If all of the Mg^{2+}, K^+, and Na^+ are considered to originate from silicate weathering and all of the Ca^{2+} to come from carbonate

(maerl) weathering, the respective contributions of carbonate and silicate weathering to the increased cation export in the Vilaine River from 1980 to 1990 would be about 43 and 57% ($\Delta_{1990-1980}$ $Na^+ + K^+$ = 0.17 mmol ; $\Delta_{1990-1980}$ Mg^{2+} = 0.12 mmol ; $\Delta_{1990-1980}$ Ca^{2+} = 0.22 mmol). If a maximum of half of the Mg^{2+} and all the Ca^{2+} are attributed to magnesium calcite and/or dolomite dissolution, the carbonate contribution then becomes higher (55%) than the silicate contribution. As large volumes of easily weathered carbonates are added to agricultural soils every year, the carbonate contribution to cation riverine export is probably equal to or higher than the silicate contribution.

Cation riverine export is certainly related to a desaturation of the soil exchange complex (which is computed below), as base-cation mobilization and impoverishment in soils correspond to the mechanism of acidification. However, these exchangeable cations are originally and continuously produced by silicate/carbonate weathering.[28] Indeed, all cations show an extensive increase in river during the considered period, which requires larger sources than soil exchangeable store, as soils have moderate or low exchange complex. Although cation exchanges may have modified the cation relationships, the investigated data do not show evidence for typical cation ratios related to extensive cation exchange.

Quantification of Cation Loss. The mass balance of cation loss from the upper soil horizons of the Vilaine catchment over the pst 25 years was determined. We compared (1) the cation content of the current soil exchange capacity and its saturation with (2) the increase in riverine cation concentrations. This increase was computed as the difference between the river concentration before 1982 and the anthropogenic concentration after 1988. The 1982−1988 difference was considered to correspond to desaturation of the exchange complex and base-cation leaching. The details of the computation are provided in the Supporting Information (Annex S3). According to Pierson-Wickmann et al. data,[28] the total readily leached soil-exchangeable base cations can be calculated by considering the first 20 cm oil layer. The upper soil layer has a $Ca^{2+} + Mg^{2+}$ content of 93.5 kmol(+)/ha and a base-cation content of 120 kmol(+)/ha. The increases of $Ca^{2+} + Mg^{2+}$ and base cations in the Vilaine River between 1985 and 2010 (25 yea) correspond to 35 and 44 kmol(+)/ha, respectively. These increases in riverine export (and decreased base saturation) correspond to 30 and 37% of the estimated base-cation content of the upper soil horizons. This result can be linked with the IGCS database, which indicates over the past decade (1995−2005) a significant decrease of the exchangeable K^+ on the soil CEC, very low Na^+ contents, and a slight Mg^{2+} increase. The value computed here (30−37%) is close to values previously obtained in field experiments. Barak et al. obtained a 20% decline of the base-cation content of the soil exchange capacity after 30 years of fertilizer application at a rate of 168 kg/ha·year.[40] Schwab et al. also reported a base-cation loss of 33% from the soil exchange capacity after application of 224 kg/ha·year for 40 years.[41]

For several years, the organic nitrogen load has been limited to 170 kg/ha and the inputs in a large part of Brittany are as high as this, whereas the total nitrogen load (organic + mineral) exceeds 200 kg/ha. If it is assumed that the minimum $N-NH_4^+$ input has been 170 kg/ha during the past 25 years, the $Ca^{2+} + Mg^{2+}$ and base-cation losses correspond to 5 and 6%, respectively, of the acidity load computed from eq 1. This agrees with experimental evidence that N inputs of 168 kg/

ha·year for 30 years induced a base-cation loss equivalent to 8.5% of the acidity load.[40] Although cation loss has been partially compensated by liming (about 50% as computed above), these computations confirm that "anthropogenic" acidification related to farming intensification has led to considerable base-cation losses from the soil exchange capacity (decrease of base saturation).

Potential Effects of Acidification. *Soil Properties and Plant Productivity.* Base cations constitute essential nutrients for plant growth. A high base-cation content of the clay and organic matter complex implies that the soil exchange capacity is saturated in nutrients, which is a positive factor for soil fertility and enhances ecosystem productivity. As a first and direct order, a decrease in soil base saturation will also decrease soil productivity. A decrease in soil base cations may also be related to a decrease in soil-water pH. The soil pH in Brittany measured after KCl extraction is between 5 and 6 (78%) or below 5 (16.5%) (IGCS).[42] This value has remained relatively constant during the past 10 years due to the neutralizing effect of liming. However, it is quite low and indicates that the area remains highly sensitive to acidification processes. The soil-water pH ranges between 6 and 7 (78.5%) and between 5 and 6 (17%). The difference between pH_{water} and pH_{KCl} (1 pH unit) indicates that damage to the exchange complex, related to high Al^{3+} concentrations, might be a concern if the pH decreases still further due to the increased solubility of Al^{3+} below pH 5.[43]

The exchange capacity as a whole also measures the potential for ionic bonding, which is a parameter that influences soil structure and aggregate size.[44] A decrease in exchangeable base cations, especially Ca, may indirectly affect soil structure and water movements in soils. The role of calcium, as a flocculating agent forming the clay–humus complex and increasing soil aggregate stability, is particularly important. A decrease of exchangeable Ca^{2+} in soil could lead to clay leaching and then to a decrease in CEC at the soil surface and to formation of an impermeable hydromorphic horizon (Btg) deeper in the soil profile. All of these effects threaten the soil ecosystem, together with its chemical and physical properties and result in productivity decreases, which are contrary to the basis for N input.

Carbon Cycle. A second aspect of the impact of agricultural acidification is related to the global carbon cycle. Agriculture-induced acidification can constitute a carbon source in limestone catchments and represent 6–15% of the CO_2 uptake related to natural silicate weathering.[16] As indicated above, the N-induced weathering of silicates does not affect the carbon cycle. However, intensive liming in Brittany has resulted in high Ca^{2+}/HCO_3^- ratios and high Ca^{2+} concentrations tightly related to the NO_3^- concentrations in the major rivers. Both characteristics are indicative of rock weathering related to the use of carbonates from liming. This process releases some carbon as bicarbonate in river waters that is potentially released as CO_2 and constitutes a carbon source. Liming in crystalline catchments should be considered to induce CO_2 production, although, as observed previously, not all of the added lime can be accounted for in the GES computations.[23] The high Ca^{2+}/HCO_3^- and $(Ca^{2+} + Mg^{2+})/HCO_3^-$ indices (Supporting Information Figure S3) also may indicate a CO_2 release process in rivers.

In this study, the molar ratio of the Ca^{2+} flux to the organic nitrogen flux[37] in the Vilaine River during the past decade was about 0.54. The potential nitrogen fluxes derived from the FAO worldwide cattle estimates for the next decade (FAO database,

http://faostat.fao.org) range from 1.5×10^{13} to 2.5×10^{13} mol/year. Considering (i) that all of the Ca^{2+} originates from carbonate dissolution and represents a CO_2 production of half the Ca^{2+} flux and (ii) that 20–30% of the worldwide organic nitrogen flux is related to crystalline basement,[16] and taking into account (iii) the Ca^{2+}/N_{org} ratio obtained in this study, the calculated potential carbon source is 19–48 Tg. This is close to the value obtained by Perrin et al. for carbonate catchments.[16] Although this is only a rough estimate, it indicates the need for further evaluation of the potential agricultural carbon source.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The main rivers of Brittany that were investigated are located on a catchment map in Figure S1. Table S1 presents the catchment characteristics. Figure S2 presents the variation of NO_3^- concentrations in the five studied rivers between 1970 and 2010. Figure S3 presents the variation of element concentrations and pH in the Vilaine River between 1970 and 2010. In Annex S1, we present a description of the chemical reactions that occur in the soil and rivers as well as the cation to bicarbonate ratios for each of these reactions. Annex S2 presents the databases and chemical analysis used in this study, and Annex S3 details the quantification of cation loss presented in the second point of the discussion. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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