



# The contribution of agricultural lime to carbon dioxide emissions in the United States: dissolution, transport, and net emissions

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## Abstract

Agricultural lime (aglime) is commonly applied to soils in the eastern U.S. to increase soil pH. Aglime includes crushed limestone ( $\text{CaCO}_3$ ) and crushed dolomite ( $\text{MgCa}(\text{CO}_3)_2$ ). Following the supposition by the Intergovernmental Panel on Climate Change (IPCC) that all C in aglime is eventually released as  $\text{CO}_2$  to the atmosphere, the U.S. EPA estimated that 9 Tg (Teragram =  $10^{12}$  g =  $10^6$  metric tonne)  $\text{CO}_2$  was emitted from an approximate 20 Tg of applied aglime in 2001. A review of historic data on aglime production and use indicates that 30 Tg may better represent the annual U.S. consumption of aglime. More importantly, our review of terrestrial and ocean C dynamics indicates that it is unlikely that all C from aglime is released to the atmosphere following application to soils. On the contrary, the primary pathway for aglime dissolution is reaction with carbonic acid ( $\text{H}_2\text{CO}_3$ ) which results in uptake of  $\text{CO}_2$ . Depending on soil pH and nitrogen fertilizer use, a fraction of aglime may react with strong acid sources such as nitric acid ( $\text{HNO}_3$ ), thereby releasing  $\text{CO}_2$ . Data on soil leaching and river transport of calcium ( $\text{Ca}^{2+}$ ) and bicarbonate ( $\text{HCO}_3^-$ ) suggest that a significant portion of dissolved aglime constituents may leach through the soil and be transported by rivers to the ocean. Much of the fraction transported to the ocean will precipitate as  $\text{CaCO}_3$ . Bicarbonate remaining in the soil profile is expected to release  $\text{CO}_2$  following re-acidification of the soil over time. Our analysis indicates that net  $\text{CO}_2$  emissions from the application of aglime is 0.059 Mg C per Mg limestone and 0.064 Mg C per Mg dolomite. This is in contrast to IPCC estimates of 0.12 and 0.13 Mg C per Mg limestone and dolomite, respectively. Based on our best estimate, the application of 20–30 Tg of aglime in the U.S., consisting of 80% limestone and 20% dolomite, would have resulted in a net 4.4–6.6 Tg  $\text{CO}_2$  emissions in 2001.

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## 1. Introduction

Agricultural lime (aglime) is commonly used in the management of croplands and grasslands to decrease

soil acidity. Aglime is often applied in the form of crushed limestone ( $\text{CaCO}_3$ ) or crushed dolomite ( $\text{MgCa}(\text{CO}_3)_2$ ). In 2001, an estimated 16.1 Tg of limestone and 4.0 Tg of dolomite were applied in the U.S., collectively resulting in an estimated 9.0 Tg  $\text{CO}_2$  (2.4 Tg C) of aglime-derived carbon that was purportedly emitted to the atmosphere (EPA, 2004). These emissions constituted 1.7% of agricultural greenhouse gas emissions and 0.13% of total greenhouse gas emissions in the U.S. in 2001. These emissions are  $\text{CO}_2$  from the dissolution of carbonate rock and do not include emissions from the fossil fuels used to crush, deliver, and spread the crushed rock on agricultural fields. While the percent contribution of  $\text{CO}_2$  emissions from the dissolution of aglime to total U.S. greenhouse gas emissions is relatively small, the emissions from U.S. aglime alone are comparable to total  $\text{CO}_2$  emissions from Luxembourg and exceed the total national  $\text{CO}_2$  emissions from over half of UN member countries.

Total  $\text{CO}_2$  emissions attributable to the use of aglime in the U.S. are larger if we consider the energy used to produce, deliver, and spread the material. West and Marland (2002) estimate that production of crushed limestone and transport to the delivery site results in  $\text{CO}_2$  emissions of about 36 kg C per Mg of limestone. Fossil fuel combustion during application or spreading of aglime is expected to emit about 12 kg C  $\text{ha}^{-1}$  (West and Marland, 2002). Assuming a conservative application rate of 5 Mg crushed rock per hectare every 5 years, we estimate about 38 kg C  $\text{ha}^{-1} \text{yr}^{-1}$  from the production, transport, and application of aglime.

To derive a comparable per-hectare figure for dissolution of aglime, we use emissions coefficients developed by the Intergovernmental Panel on Climate Change (IPCC) for limestone and dolomite of 0.12 and 0.13 Mg C per Mg crushed rock, respectively (Houghton et al., 1997). These coefficients are also currently used in the annual Inventory of U.S. Greenhouse Gas Emissions and Sinks (EPA, 2004). Using the previously annualized application rate of about 1 Mg limestone  $\text{ha}^{-1} \text{yr}^{-1}$  results in average  $\text{CO}_2$  emissions of 120 kg C  $\text{ha}^{-1} \text{yr}^{-1}$  from the dissolution of the applied aglime. Total  $\text{CO}_2$  emissions from aglime are thus  $120 + 38 = 158$  kg C  $\text{ha}^{-1} \text{yr}^{-1}$ . If, for example, a continuous, no-till corn crop in the U.S. contributes 215 kg C  $\text{ha}^{-1} \text{yr}^{-1}$ , based on U.S. average production inputs in 1995 (West and Marland, 2002),

the application of aglime would thereby contribute 42% of the  $215 + 158 = 373$  kg C  $\text{ha}^{-1} \text{yr}^{-1}$  total annual  $\text{CO}_2$  emissions per hectare. Using the IPCC emissions coefficients, Robertson et al. (2000) estimated similarly that aglime contributed 35% and 47% of  $\text{CO}_2$  emissions from a conventionally tilled and no-till crop, respectively, in a corn–soybean–wheat rotation.

While the rate of  $\text{CO}_2$  release via dissolution of carbon contained in carbonate rock will vary depending on soil factors, climate regime, and the type of aglime applied (i.e., limestone or dolomite, fine or coarse textured), the IPCC and the estimates above assume that all of the C contained in these materials is eventually released to the atmosphere as  $\text{CO}_2$ . The IPCC emissions coefficients of 0.12 and 0.13 Mg C per Mg crushed rock are the mass fractions of C in limestone and dolomite, respectively. However, the assumption that all C in aglime is released to the atmosphere as  $\text{CO}_2$  seems unlikely based on current knowledge of carbonate dissolution and transport through soil. The objective of this analysis is to compile data on the use, dissolution, and transport of aglime, and to provide a first approximation of the ultimate fate of the carbon contained in aglime.

## 2. U.S. consumption of aglime

Aglime is applied to soils to raise soil pH and increase the fertility of croplands and grasslands. Quicklime ( $\text{CaO}$ ) and hydrated lime ( $\text{Ca}(\text{OH})_2$ ) were used for this purpose in the early 1900s, but use of these concentrated lime products declined rapidly, due to prohibitive production costs, in favor of crushed limestone and dolomite (Fig. 1a). The use of aglime on agricultural fields increased from the early 1900s to the late 1960s (Fig. 1b).

Currently available data indicate an approximate 10 Tg decrease in aglime use between 1980 and 2000 (U.S. Bureau of Mines, 1927–1996; U.S. Geological Survey, 1906–1927, 1997–2002). However, this apparent drop coincides with what appears to be a significant change in data collection and reporting. Aglime comprises 3–5% of the reported usage of crushed limestone and dolomite in the U.S., and the published tables for production of crushed limestone and dolomite were drastically restructured in the early 1980s. Specifically, between 1980 and 1983 aglime use is

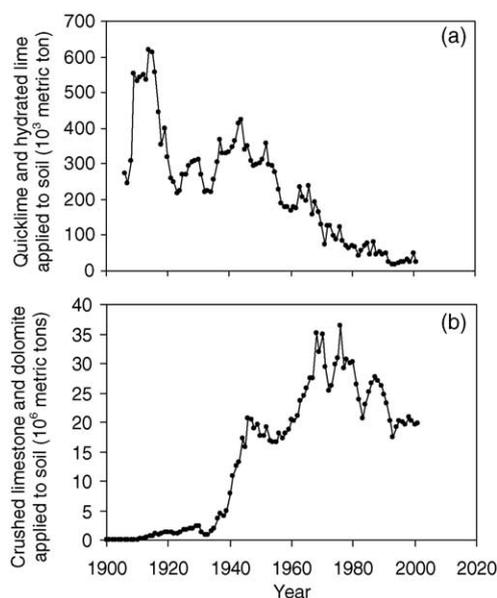


Fig. 1. Historic use of (a) lime (quicklime and hydrated lime) and (b) aglime (primarily crushed limestone) in the U.S. Data for even years from 1982 to 1992 are not available, and were estimated by averaging data from previous and latter years, respectively. Where quantities for unspecified uses of limestone and dolomite were provided, beginning in 1957, an estimate was made of the percentage used for agricultural purposes (see text for additional details). Data for agricultural limestone were separated into two categories for limestone and dolomite in 1983, but data is presented here as general agricultural lime (both limestone and dolomite) to remain consistent with earlier estimates of aglime use.

reported to have decreased from 30 Tg to about 21 Tg, while the “unspecified” category for use of crushed limestone and dolomite, representing data that is not broken down by end use and data that estimates the production from “nonrespondents”, increased from 2 to 102 Tg. The “unspecified” category continued to increase, up to 571 Tg in 2001, while the amount of reported aglime use decreased to 9.8 Tg. For this analysis, and in the absence of better information, we estimated the percentage of the “unspecified” category that was used for aglime application by distributing the “unspecified” category proportionally among all other categories for usage of crushed limestone and dolomite that are specified. This method is consistent with that used by the U.S. Geological Survey (V. Tepordei, U.S. Geological Survey, personal communication, 2003).

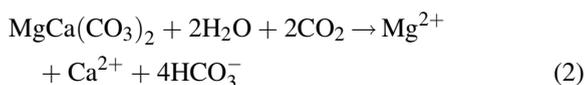
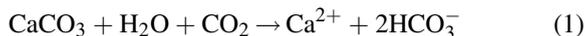
The reported decline in U.S. aglime use between 1980 and 2000 may also be questioned with respect to

U.S. nitrogen fertilizer use. We would expect rates of aglime use to follow nitrogen fertilizer use, because aglime is commonly used to offset soil acidification caused in part by nitrification. However, nitrogen fertilizer use between 1980 and 2000 maintained a rate of about  $12 \text{ Tg yr}^{-1}$ , with the exception of a 2 Tg decrease in the early and mid-1980s (USDA, 2003), causing further speculation regarding the substantial decrease in reported aglime use during this period.

While the data on U.S. aglime consumption are suspect, we base our initial analysis on the EPA (2004) estimate of 20 Tg of applied aglime in 2001, so that our results can be directly compared to the EPA (2004) emissions estimate of 9 Tg  $\text{CO}_2$ . However, we also apply our new emission coefficients to the more plausible estimate of 30 Tg of aglime applied in 2001, which is the value reported from 1980, before the reported usage of aglime dropped while the “unspecified” category substantially increased.

### 3. Application of aglime to soils

Following the application of aglime to soil, the dissolution of  $\text{CaCO}_3$  and  $\text{MgCa}(\text{CO}_3)_2$  can be characterized, respectively, as follows:

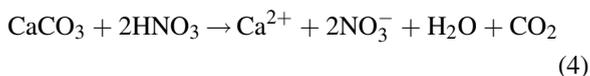


The reactions representing bicarbonate formation in solution (Eqs. (1) and (2)) produce two moles of  $\text{CO}_2$ -equivalent ( $2\text{HCO}_2^-$ ) for every mole of gaseous  $\text{CO}_2$  taken up. The resulting bicarbonate may either remain in the soil or be flushed through the soil profile. Bicarbonate remaining in the soil is expected to react with available  $\text{H}^+$  to form carbonic acid ( $\text{H}_2\text{CO}_3$ ), following acidification of the soil from subsequent annual nitrogen fertilizer applications and from continued organic matter inputs from crop residues. Carbonic acid in soil water is in equilibrium with soil  $\text{CO}_2$ , hence, reaction to carbonic acid yields  $\text{CO}_2$  that is released to the atmosphere. This latter equilibrium is as follows:



In the presence of nitrogen fertilizer, aglime will react with  $\text{H}^+$  produced during the nitrification process.

Oxidation of ammonia by the nitrifying bacteria *Nitrosomonas*, referred to as nitrification, results in nitrite ( $\text{NO}_2^-$ ) and  $\text{H}^+$  ions, thereby increasing soil acidity. Nitrite is in turn oxidized by another bacteria, *Nitrobacter*, resulting in nitrate ( $\text{NO}_3^-$ ) which is available for plant uptake. Nitrate and  $\text{H}^+$  also form nitric acid ( $\text{HNO}_3$ ). If calcium carbonate reacts with  $\text{HNO}_3$ ,  $\text{CO}_2$  is released as follows:



Eqs. (1), (2) and (4) represent two descriptions of the dissolution of aglime, with Eqs. (1) and (2) representing the prevailing chemistry when  $\text{CO}_2$  in soil solution ( $\text{H}_2\text{CO}_3$ ) is the primary contributor of  $\text{H}^+$ , and Eq. (4) representing the prevailing chemistry in a strong acid environment. These two pathways are also acknowledged in a conceptual model of carbonate dissolution proposed by Hamilton et al. (2002). Hamilton et al. (2002) illustrate the dissolution of calcium carbonate as a net sink for  $\text{CO}_2$  in soils with relatively high pH, in which  $\text{H}_2\text{CO}_3$  is the primary acid to react with carbonate minerals, but a net source of  $\text{CO}_2$  in soils with relatively low pH.

Accounting for the fate of the carbon in aglime during dissolution requires knowing the fraction of dissolution caused by  $\text{H}_2\text{CO}_3$  (Eqs. (1) and (2)), and the fraction caused by strong acids such as  $\text{HNO}_3$  (Eq. (4)). To a first approximation, the former reaction takes up one mole of  $\text{CO}_2$  for every mole of  $\text{CaCO}_3$  dissolved, while the latter reaction releases one mole of  $\text{CO}_2$  for every mole of  $\text{CaCO}_3$  dissolved. Semhi et al. (2000) developed a model which estimates the relative fractions of carbonate mineral dissolution by  $\text{H}_2\text{CO}_3$  and by  $\text{HNO}_3$ . Using measurements of major ion chemistry in the Garonne and Gers Rivers in France, the model estimated that approximately 6% and 12–26% of carbonate dissolution in the two rivers, respectively, could be due to  $\text{HNO}_3$  originating largely from the use of nitrogen fertilizers in adjacent watersheds. The percentage of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  in rivers, caused by the dissolution of aglime by  $\text{HNO}_3$ , depends in part on the amount of agricultural land and the rates of aglime and nitrogen fertilizer application in the surrounding watersheds. Preliminary analysis for the Mississippi River indicates that about 38% of carbonate dissolution occurring in the Mississippi River Basin in 2001 was due to reaction with nitric

acid (J.-L. Probst, UMR-CNRS/Université Paul Sabatier, personal communication, 2003).

#### 4. Leaching of aglime-derived bicarbonate through soils

Dissolution of aglime results in  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , and in  $\text{HCO}_3^-$  and  $\text{NO}_3^-$  depending on the path of dissolution. Some calcium is taken up by crops while the remainder may either remain in the upper soil profile, be transported to lower soil depths, or be flushed completely out of the soil. If transport through or out of the soil profile occurs, either  $\text{HCO}_3^-$  (from Eqs. (1) and (2)),  $\text{NO}_3^-$  (from Eq. (4)), or other available anions will accompany  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  to satisfy the charge balance. This is illustrated by Wong et al. (1992) by the chemically balanced solution of  $\text{Ca}^{2+}$  and  $\text{NO}_3^-$  found in drainage water following the application of calcium hydroxide as a liming agent and urea as a nitrogen fertilizer. The anion that accompanies  $\text{Ca}^{2+}$  through the soil profile depends on soil pH and the path of initial aglime dissolution.

In order to address the ultimate fate of C from the dissolution of aglime, we need to know how much  $\text{Ca}^{2+}$  is leached through the soil and whether this  $\text{Ca}^{2+}$  is retained lower in the soil profile or whether it has been flushed out of the soil profile and transported into rivers and the oceans. There have been a number of attempts to identify the location and distribution of  $\text{Ca}^{2+}$  following its application to soil surfaces. Brady and Weil (1996) estimated that  $115 \text{ kg ha}^{-1} \text{ yr}^{-1}$  of  $\text{Ca}^{2+}$  ( $288 \text{ kg ha}^{-1} \text{ yr}^{-1}$  of  $\text{CaCO}_3$ ) leaches from agricultural areas in humid temperate regions. In a high rainfall region of southeastern Nigeria, Friesen et al. (1982) found that after 3 years less than  $0.5 \text{ Mg ha}^{-1}$  of hydrated lime ( $\text{Ca}(\text{OH})_2$ -equivalent) had leached following treatments of 0–2 Mg hydrated lime  $\text{ha}^{-1}$ , but  $1.6 \text{ Mg ha}^{-1}$  leached from the surface following treatment of  $4 \text{ Mg ha}^{-1}$ . Nearly all  $\text{Ca}^{2+}$  initially applied was found in the top 90 cm, suggesting an accumulation of lime constituents in the soil profile. In a humid, tropical region in Puerto Rico, a number of limestone surface treatments (ranging from 0 to  $35 \text{ Mg limestone ha}^{-1}$  over a 2-year period) resulted in leaching from the 0 to 15 cm soil depth, with much of the leached  $\text{Ca}^{2+}$  accounted for in the top 60 cm of the soil profile (Pearson et al., 1962).

Other field experiments show an increased loss of  $\text{Ca}^{2+}$  from the soil profile. On a clay soil in the rainforest of Indonesia, Dierolf et al. (1997) observed a 5% retention of calcium in the 30–90 cm depth 2-year after lime application. An average 26% of calcium was unaccounted for in soil or crop biomass and was assumed to have leached below the 90 cm depth. Wong et al. (1992) measured a 27% loss of calcium from the soil profile following the application of  $1025 \text{ kg ha}^{-1}$  calcium hydroxide to monolith lysimeters in southeast Nigeria that were cropped for two growing seasons with maize and rice, respectively. Cuttle and James (1995) observed a 24% loss of calcium in drainage water from an improved pasture in Wales, U.K., 4 years following the application of  $8.8 \text{ Mg ha}^{-1}$  of lime.

The rate and total amount of leaching depend on the depth and amount of aglime incorporation, soil texture and porosity, and crop rooting depth. Leaching will also be influenced by the rate and type of nitrogen fertilizer, with higher leaching rates occurring with more acid-forming fertilizers (Pearson et al., 1962). The particle size and type of aglime can also influence leaching rates. Ritchey et al. (1980) illustrate the influence of the calcium source on leaching, with  $\text{CaCO}_3$  resulting in less leaching than gypsum ( $\text{CaSO}_4 \cdot 2(\text{H}_2\text{O})$ ) or calcium chloride ( $\text{CaCl}_2$ ). Marcos and González (1994) observed that calcium losses over a 5-year period increased with particle size of the applied limestone. While this may seem counter-intuitive, it has been interpreted by Domenech (1998) as being a result of the smaller contact surface between soil particles and large limestone particles, leading to less sorption of calcium to the soil exchange complex and hence a greater export by leaching.

The measured leaching rates discussed thus far are for a limited number of years following initial application of aglime and do not provide an accurate estimate of the total amount of calcium or bicarbonate leached out of the soil over time. Nordt et al. (2000) indicate that most soil inorganic carbon eventually leaches out of the soil in humid and sub-humid climate regions where precipitation equals or is greater than evapotranspiration. For this analysis, we assume a 50% leaching (transport factor) of calcium and associated bicarbonate or nitrate. We base this estimate on the 24–27% loss of calcium from three short-term (2–4 years) experiments, described pre-

viously, and assume an equivalent leaching rate over an additional 2+ years. We consider this to be a conservative assumption since Nordt et al. (2000) assume the eventual leaching of all bicarbonate over time. Additional long-term experiments, preferably including elemental mass balances for agricultural soil profiles, are clearly needed to substantiate the aforementioned estimates and the general leaching rate or transport factor we use here.

## 5. Transport of aglime-derived bicarbonate to the ocean

The fraction of calcium and bicarbonate dissolved from aglime that leaches through the soil profile presumably follows the hydrologic flow down rivers and into the oceans. Ludwig et al. (1996) estimate that about  $320 \text{ Tg C yr}^{-1}$  as bicarbonate is discharged from rivers to the world's oceans, with  $90 \text{ Tg C yr}^{-1}$  originating from carbonate mineral dissolution. This estimate is based on drainage intensity and rock type, and does not include bicarbonate contributions from aglime (J.-L. Probst, UMR-CNRS/Université Paul Sabatier, personal communication, 2003).

If application of aglime results in the leaching of bicarbonate, which is subsequently transported by rivers to the ocean, a historical increase in alkalinity should be observed in rivers that drain agricultural watersheds. Raymond and Cole (2003a) analyzed 849 alkalinity values from USGS data sets covering a 48-year period and concluded that, between 1954 and 2001, alkalinity export via the Mississippi River increased from  $11.0 \times 10^{12}$  to  $17.5 \times 10^{12} \text{ g C yr}^{-1}$ . Alkalinity export was positively correlated with the percent land area used for agricultural crops, with alkalinity export being four to nine times higher for cropland sites in the upper Mississippi and Ohio basins, respectively, than for non-cropland sites. Raymond and Cole (2003a) hypothesized that the increased export from cropland watersheds may be due to (i) tillage practices that increase contact between water and mineral soils, (ii) high cropland productivity that may increase organic acids in the soils, and (iii) the decreased ability of croplands to dilute surface runoff compared to forested watersheds. However, we propose here that a portion of the alkalinity increase in Mississippi River discharge

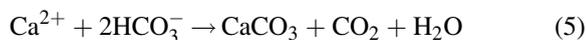
between 1954 and 2001 may be due to the increase in aglime use which occurred in this same time period (see Fig. 1) and which coincides with the historical increase in nitrogen fertilizer use. Mitsch et al. (2001) compiled data that illustrate a greater than 5 Tg yr<sup>-1</sup> increase in nitrogen fertilizer use in the Mississippi basin between 1955 and 1980, with use remaining at about 6.5 Tg yr<sup>-1</sup> between 1980 and 1995. Nitrate export from the Mississippi follows a similar trend, with an increase of about 1 Tg NO<sub>3</sub>-N in the annual flux between 1955 and 1980, and then remaining constant after 1980.

While there is no direct evidence that aglime applied to U.S. soils is eventually transported to the ocean, it is inferred from the following evidence: (1) nitrate concentration in the Mississippi River has increased, (2) the increase in nitrate is due to increased nitrogen fertilizer use, (3) aglime use has increased in the Mississippi Basin and its increase coincides with the increased use of nitrogen fertilizers, and (4) alkalinity (primarily HCO<sub>3</sub><sup>-</sup>) has also increased in the Mississippi River. Considering that aglime use in the Mississippi Basin accounts for nearly 75% of U.S. aglime use (U.S. Geological Survey, 1997–2002), we estimate that application of aglime in the Mississippi Basin between 1954 and 1980 increased by about 1.2 × 10<sup>12</sup> g C yr<sup>-1</sup>, or 83%. Raymond and Cole (2003a) estimate a 6.5 × 10<sup>12</sup> g C yr<sup>-1</sup> increase in bicarbonate export from the Mississippi River in this time period. With ~80% of the increased bicarbonate export probably due to increased discharge of water (Raymond and Cole, 2003b), 1.3 × 10<sup>12</sup> g C yr<sup>-1</sup> remains unaccounted for, and this unaccounted amount is of the same magnitude as the increase in aglime use in the Mississippi Basin.

While we can infer from the Mississippi River data that aglime constituents are eventually transported to the ocean, the time over which this occurs is uncertain. The length of time needed for leaching and transport of carbonate species is important in terms of C accounting and for understanding the impacts of aglime-derived CO<sub>2</sub> on the atmospheric CO<sub>2</sub> concentration. If leached carbonate remains in the lower soil profile or resides in the rivers or groundwater for a hundred years or more, current C accounting methods may consider this carbon to be “sequestered”. For our analysis here, we do not consider the time over which the dissolution and transport processes occur.

## 6. Fate of aglime-derived bicarbonate in ocean margins

An estimated 5.3 × 10<sup>15</sup> g CaCO<sub>3</sub> is produced in the world's oceans each year (Milliman, 1993). Calcite-precipitating organisms, including corals, foraminiferans, and coccolithophorid phytoplankton, are responsible for precipitating much of the ocean CaCO<sub>3</sub> (see Berry et al., 2002; Langer et al., 1997) as follows:



In freshwater, we would expect the release of one mole CO<sub>2</sub> per mole CaCO<sub>3</sub> precipitated (Eq. (5)). However, Ware et al. (1991) indicate that in seawater, 0.6 mol of CO<sub>2</sub> are actually released per mole of CaCO<sub>3</sub> precipitated. This is thought to be caused by the buffering effect of seawater, which is also responsible for the super-saturation of calcium and bicarbonate in the upper ocean and the necessity of calcite-secreting organisms to precipitate CaCO<sub>3</sub> through active physiological processes (see Broecker, 1974; Elderfield, 2002). It is also noted that CO<sub>2</sub> released during the formation of CaCO<sub>3</sub> by carbonate-secreting organisms may also be used by the same carbonate-precipitating organisms during photosynthesis (Murata and Takizawa, 2002), and that the increased availability of CO<sub>2</sub> may increase photosynthetic rates (Berry et al., 2002).

While some of the CaCO<sub>3</sub> precipitated in the ocean accumulates over time, a significant fraction of ocean CaCO<sub>3</sub> is dissolved in the upper water column, above 1000 m. Recent analyses of the ocean carbon budget indicate a dissolution rate of 50–80% for the deep ocean (Feely et al., 2004; Iglesias-Rodriguez et al., 2002). Coastal ocean dynamics differ from deep ocean dynamics in that CaCO<sub>3</sub> production rates are higher and dissolution rates are lower. Averaging the CaCO<sub>3</sub> accumulation rates in different neritic environments (Milliman, 1993; Iglesias-Rodriguez et al., 2002), weighted against the global CaCO<sub>3</sub> production for respective environments, indicates about a 40% global dissolution rate in ocean margins.

In our analysis, we use the 0.6:1.0 ratio of CO<sub>2</sub> loss to CaCO<sub>3</sub> precipitated in the ocean, and we estimate that 40% of the precipitated CaCO<sub>3</sub> will dissolve, thereby resulting in a net 60% accumulation of the precipitated CaCO<sub>3</sub> in the neritic ocean environment.

Interestingly, the balance between  $\text{CaCO}_3$  inputs and outputs does not appear to be in equilibrium and is also changing as atmospheric  $\text{CO}_2$  concentration increases. Milliman (1993) suggests that  $52 \times 10^{13}$  g  $\text{Ca yr}^{-1}$  are exported to the oceans from the world's rivers each year, with  $73 \times 10^{13}$  g  $\text{Ca}$  accumulating in shallow waters and  $56 \times 10^{13}$  g  $\text{Ca}$  accumulating in the deep oceans. With another  $12 \times 10^{13}$  of  $\text{Ca}$  input from subsea hydrothermal activity, there is a large apparent imbalance between input and output, and Milliman goes on to speculate about the geochemical significance of this apparent imbalance. With respect to increasing atmospheric  $\text{CO}_2$ , Sabine et al. (2004) estimate that with a doubling of atmospheric  $\text{CO}_2$  from preindustrial levels, there will be a 30% decrease in carbonate ion concentration and a 60% increase in hydrogen ion concentration in the ocean. This would result in a decreased capacity of the ocean to precipitate  $\text{CaCO}_3$ , thereby increasing the aglime-derived  $\text{CO}_2$  sequestered in the ocean.

## 7. Net $\text{CO}_2$ emissions from aglime applied to soil

While emissions inventories at the national and global scales (EPA, 2004; Bernoux et al., 2003; Houghton et al., 1997) presuppose that all C from aglime is lost to the atmosphere as  $\text{CO}_2$ , our synthesis of terrestrial and ocean carbonate dynamics indicates that 100% release as  $\text{CO}_2$  is unlikely. Conversely, if the  $\text{CaCO}_3$  were simply dissolved at one point and re-precipitated elsewhere there should be no net emission of  $\text{CO}_2$ . Involvement of nitric acid species and the apparent imbalance of the input and output of calcium in the ocean suggest that zero net emissions is also unlikely and that reality lies somewhere in between.

Consideration of aglime dissolution, transport, subsequent precipitation and dissolution in the ocean, and the evolution of these over time, is needed to approximate the net loss of  $\text{CO}_2$  following aglime application. The pathways of dissolution, transport, and net precipitation, previously outlined in this paper, are summarized here and modeled to provide an estimate of net  $\text{CO}_2$  loss following aglime application to soils. We illustrate the model using the EPA (2004) estimate of U.S. aglime application, 20 Tg in 2001, and also estimate  $\text{CO}_2$  emissions

based on the 30 Tg of aglime applied in the U.S. in 1980, which we believe more accurately represents current use.

Following application of 20 Tg of limestone to U.S. soils, we estimate that about 38% is dissolved by  $\text{HNO}_3$ , based on results from J.-L. Probst (UMR-CNRS/ Université Paul Sabatier, personal communication, 2003), thereby releasing 3.35 Tg of  $\text{CO}_2$ ; an estimated 62% is dissolved by  $\text{H}_2\text{CO}_3$  resulting in the uptake of 5.47 Tg  $\text{CO}_2$  (Fig. 2). In developing a first approximation for this analysis, we make the conservative assumption that 50% of the dissolved calcium is leached through the soil profile and transported to the ocean. Nitrate is leached with calcium that dissolved from aglime via Eq. (4), and  $\text{HCO}_3^-$  is leached with

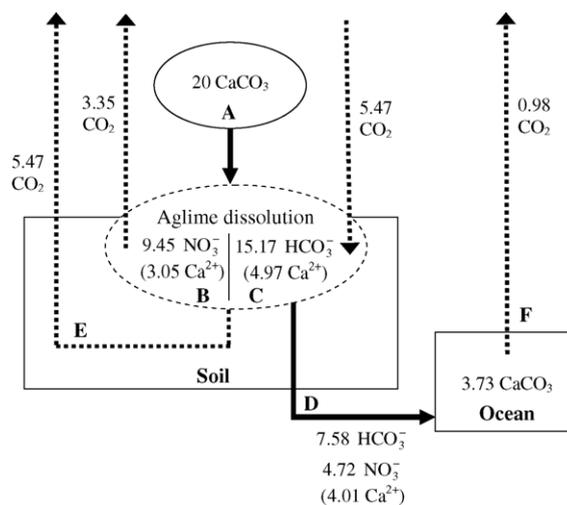


Fig. 2. Cumulative carbon accounting of annual U.S. aglime usage (in teragrams or  $10^{12}$  g). This model assumes all aglime is crushed limestone. Solid arrows illustrate the flows of  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$ , and  $\text{NO}_3^-$  associated with the dissolution and precipitation of  $\text{CaCO}_3$ . Dotted arrows illustrate fluxes of  $\text{CO}_2$  associated with the dissolution and precipitation of  $\text{CaCO}_3$ . (A) is the estimated amount of aglime applied in the U.S. in 2001 (EPA 2003). (B) represents 38% of aglime dissolution by  $\text{HNO}_3$ , resulting in the release of one mole  $\text{CO}_2$  per mole  $\text{CaCO}_3$  dissolved. (C) represents 62% of aglime dissolution by  $\text{H}_2\text{CO}_3$ , resulting in the uptake of 1 mol  $\text{CO}_2$  for every 2 mol of  $\text{HCO}_3^-$  produced. (D) represents 50% leaching of calcium through the soil profile, accompanied by an equivalent amount of  $\text{HCO}_3^-$  (7.58 Tg) and  $\text{NO}_3^-$  (4.72 Tg), and transported to the ocean. Bicarbonate remaining in the soil profile (E) is expected to react with available  $\text{H}^+$  to form carbonic acid, thereby releasing  $\text{CO}_2$  as the soil becomes more acidic over time. (F) represents the release of  $\text{CO}_2$  following a net 60% precipitation of  $\text{CaCO}_3$  in ocean margins, resulting in the release of 0.6 mol  $\text{CO}_2$  per mole  $\text{CaCO}_3$  precipitated.

Table 1  
Net CO<sub>2</sub> emissions from applied agricultural lime

	CO <sub>2</sub> emissions per unit aglime (Mg C/Mg crushed stone)		Estimated U.S. CO <sub>2</sub> emissions from aglime <sup>a</sup> (Tg CO <sub>2</sub> yr <sup>-1</sup> )	
	Limestone	Dolomite	Based on 20 Tg aglime	Based on 30 Tg aglime
Houghton et al. (1997)	0.120	0.130	9.0 <sup>b</sup>	13.4
This analysis	0.059	0.064	4.4	6.6

<sup>a</sup> Based on an approximate weighted average of 80% limestone and 20% dolomite.

<sup>b</sup> Represents current U.S. estimate used by EPA (2004).

calcium that dissolved from aglime via Eq. (1). Leaching and transport of bicarbonate and associated cations is the most uncertain factor in this analysis, and we are erring on the conservative side considering that Nordt et al. (2000) purport that most soil carbonates are eventually leached and transported to the ocean. Using a 50% transport factor, estimating 0.6 mol CO<sub>2</sub> released for every mole of CaCO<sub>3</sub> precipitated in the ocean (Ware et al., 1991; Sundquist, 1993), and assuming 40% dissolution of CaCO<sub>3</sub> in the ocean margins, we estimate a net 3.73 Tg accumulation of CaCO<sub>3</sub> in the coastal ocean and 0.98 Tg CO<sub>2</sub> released to the atmosphere (Fig. 2). Bicarbonate that does not fully leach out of the soil profile is expected to eventually release CO<sub>2</sub> (5.47 Tg CO<sub>2</sub>) as soil pH returns to its previously acidic condition due to fertilizer and organic matter inputs.

The net loss of CO<sub>2</sub> from this scenario is 4.33 Tg CO<sub>2</sub>, which is the difference between estimated uptake of atmospheric CO<sub>2</sub> (5.47 Tg) and releases of CO<sub>2</sub> (9.80 Tg). The estimated net loss of CO<sub>2</sub> is equivalent to 0.059 Mg C per Mg limestone (Table 1). Following a similar approach using dolomite instead of limestone results in an estimated net loss of 0.064 Mg C per Mg dolomite. Using these emissions factors with the estimated 20 Tg of aglime applied in 2001, of which approximately 80% was limestone and 20% was dolomite, results in a net 4.40 Tg CO<sub>2</sub> released to the atmosphere. This is about half of the CO<sub>2</sub> emissions from aglime estimated by EPA (2004) using the methodology outlined by Houghton et al. (1997) (Table 1). If the view is taken that the 1980 estimate of 30 Tg better represents the current annual application of aglime, while continuing to use an 80:20 ratio of limestone to dolomite, U.S. CO<sub>2</sub> emissions from aglime would equal 6.6 Tg.

## 8. Conclusions

The IPCC (Houghton et al., 1997) currently suggests that 100% of C in aglime is released as CO<sub>2</sub> to the atmosphere. Our review of the dissolution of aglime and the transport of aglime constituents to the ocean suggests that, as a current best estimate, there is a net CO<sub>2</sub> release of about 49%. This lower estimate is due in large part to the initial uptake of CO<sub>2</sub> during dissolution of aglime by H<sub>2</sub>CO<sub>3</sub>, which approximately offsets CO<sub>2</sub> releases during dissolution of aglime by HNO<sub>3</sub> and precipitation of CaCO<sub>3</sub> in coastal oceans. Our estimate indicates a 4.4 Tg CO<sub>2</sub> loss from 20 Tg of aglime applied in 2001, compared to a 9.0 Tg CO<sub>2</sub> loss estimated by EPA (2004) using IPCC emissions values (Houghton et al., 1997). Our estimate includes two uncertain factors which merit further research: (a) the fraction of aglime dissolved by HNO<sub>3</sub> as opposed to H<sub>2</sub>CO<sub>3</sub> and (b) the fraction of bicarbonate that is leached through the soil profile and transported to the ocean, and the time period over which leaching and transport occur. While more research is needed to quantify the loss of CO<sub>2</sub> resulting from aglime application, our analysis strongly suggests that not all C applied to soil as aglime is released to the atmosphere as CO<sub>2</sub>.

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## References

- Bernoux, M., Volkoff, B., da Conceição, M., Carvalho, S., Cerri, C.C., 2003. CO<sub>2</sub> emissions from liming of agricultural soils in Brazil. *Global Biogeochem. Cycles* 17, 104910.1029/2001GB001848.
- Berry, L., Taylor, A.R., Lucken, U., Ryan, K.P., Brownlee, C., 2002. Calcification and inorganic carbon acquisition in coccolithophores. *Funct. Plant Biol.* 29, 289–299.
- Brady, N.C., Weil, R.R., 1996. *The Nature and Properties of Soil*. Prentice-Hall, Upper Saddle River, New Jersey.
- Broecker, W.S., 1974. *Chemical Oceanography*. Harcourt Brace Jovanovich Inc., New York.
- Cuttle, S.P., James, A.R., 1995. Leaching of lime and fertilisers from a reseeded upland pasture on a stagnogley soil in mid-Wales. *Agric. Water Manage.* 28, 95–112.
- Dierolf, T.S., Arya, L.M., Yost, R.S., 1997. Water and cation movement in an Indonesian Ultisol. *Agron. J.* 89, 572–579.
- Domenech, E.M., 1998. Estudio lisimétrico del lavado de cationes en dos suelos de la provincial de Lugo. *Trabajos Compostelanos de Biología* 6, 57.
- Elderfield, H., 2002. Carbonate mysteries. *Science* 296, 1618–1621.
- EPA, 2004. Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990–2002, EPA 430-R-04-003. U.S. Environmental Protection Agency, Washington, DC.
- Feely, R.A., Sabine, C.L., Lee, K., Berelson, W., Kleypas, J., Fabry, V.J., Millero, F.J., 2004. Impact of anthropogenic CO<sub>2</sub> on the CaCO<sub>3</sub> system in the oceans. *Science* 305, 362–366.
- Friesen, D.K., Juo, A.S.R., Miller, M.H., 1982. Residual value of lime and leaching of calcium in a kaolinitic ultisol in the high rainfall tropics. *Soil Sci. Soc. Am. J.* 46, 1184–1189.
- Hamilton, S.K., Kurzman, A.L., Robertson, G.P., 2002. Liming of agricultural soils: a source or sink for CO<sub>2</sub>. Paper presented at the USDA Symposium on Natural Resource Management to Offset Greenhouse Gas Emissions. Raleigh, North Carolina, 19–21 November 2002. [Available at [http://chamaecyparis.sgccp.ncsu.edu/carbon2002/2002pres/Hamilton\\_Stephen.pdf](http://chamaecyparis.sgccp.ncsu.edu/carbon2002/2002pres/Hamilton_Stephen.pdf)].
- Houghton, J.T., Meira Filho, L.G., Lim, B., Tréanton, K., Mamaty, I., Bonduki, Y., Griggs, D.J., Callander, B.A. (Eds.), 1997. Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories. Hadley Centre Meteorological Office, United Kingdom.
- Iglesias-Rodriguez, M.D., Armstrong, R., Feely, R., Hood, R., Kleypas, J., Milliman, J.D., Sabine, C., Sarmiento, J., 2002. Progress made in study of ocean's calcium carbonate budget. *Eos* 83 (34) pp. 365, 374–375.
- Langer, M.R., Silk, M.T., Lipps, J.H., 1997. Global ocean carbonate and carbon dioxide production: the role of reef foraminifera. *J. Foraminiferal Res.* 27, 271–277.
- Ludwig, W., AmiotteSuchet, P., Probst, J.L., 1996. River discharges of carbon to the world's oceans: determining local inputs of alkalinity and of dissolved and particulate organic carbon. *Comptes Rendus De L Academie Des Sciences Serie II Fascicule A-Sciences De La Terre et Des Planetes* 323, 1007–1014.
- Marcos, M.L.F., González, A.P., 1994. Cation leaching from two soils located in lysimeters since 1988–1990 in a long-term experiment. *Agrochimica* 38, 341–354.
- Milliman, J.D., 1993. Production and accumulation of calcium carbonate in the ocean—budget of a nonsteady state. *Global Biogeochem. Cycles* 7, 927–957.
- Mitsch, W.J., Day Jr., J.W., Gilliam, J.W., Groffman, P.M., Hey, D.L., Randall, G.W., Wang, N., 2001. Reducing nitrogen loading to the Gulf of Mexico from the Mississippi River Basin: Strategies to counter a persistent ecological problem. *Bioscience* 51, 373–388.
- Murata, A., Takizawa, T., 2002. Impact of a coccolithophorid bloom on the CO<sub>2</sub> system in surface waters of the eastern Bering Sea shelf. *Geophys. Res. Lett.* 29, 1547.
- Nordt, L.C., Wilding, L.P., Drees, L.R., 2000. Pedogenic carbon transformations in leaching soil systems: implications for the global C cycle. In: Lal, R., Kimble, J.M., Eswaran, H., Stewart, B.A. (Eds.), *Global Climate Change and Pedogenic Carbonates*. CRC Press, Boca Raton, FL, pp. 43–64.
- Pearson, R.W., Abruna, F., Vicente-Chandler, J., 1962. Effect of lime and nitrogen applications on downward movement of calcium and magnesium in two humid tropical soils of Puerto Rico. *Soil Sci.* 93, 77–82.
- Raymond, P.A., Cole, J.J., 2003a. Increase in the export of alkalinity from North America's largest river. *Science* 301, 88–91.
- Raymond, P.A., Cole, J.J., 2003b. Response to Jones, J.J., Stanley, E.H., Mulholland, P.J., Increased alkalinity in the Mississippi. *Science* 302, 985.
- Ritchey, K.D., Souza, D.M.G., Lobato, D., Correa, O., 1980. Calcium leaching to increase rooting depth in a Brazilian Savannah Oxisol. *Agron. J.* 72, 40–44.
- Robertson, G.P., Paul, E.A., Harwood, R.R., 2000. Greenhouse gases in intensive agriculture: contributions of individual gases to the radiative forcing of the atmosphere. *Science* 289, 1922–1924.
- Sabine, C.L., Feely, R.A., Gruber, N., Key, R.M., Lee, K., Bullister, J.L., Wanninkhof, R., Wong, C.S., Wallace, D.W.R., Tilbrook, B., Millero, F.J., Peng, T.-H., Kozyr, A., Ono, T., Rios, A.F., 2004. The oceanic sink for anthropogenic CO<sub>2</sub>. *Science* 305, 367–371.
- Semhi, K., Suchet, P.A., Clauer, N., Probst, J.-L., 2000. Impact of nitrogen fertilizers on the natural weathering-erosion process and fluvial transport in the Garonne basin. *Appl. Geochem.* 15, 865–878.

- Sundquist, E.T., 1993. The global carbon dioxide budget. *Science* 259, 934–941.
- U.S. Bureau of and Mines, 1927–1996. *Mineral Resources of the United States*. U.S. Department of the Interior, Bureau of Mines, Washington, DC.
- USDA, 2003. *Agricultural Resources and Environmental Indicators*, Agricultural Handbook No. AH722. U.S. Department of Agriculture, Economic Research Service, Natural Resources and Environment Division, Washington, DC [Available at <http://www.ers.usda.gov/publications/arei/arei2001>].
- U.S. Geological and Survey, 1906–1927. *Mineral Resources of the United States*. U.S. Department of the Interior, U.S. Geological Survey, Washington, DC.
- U.S. Geological Survey, 1997–2002. *Minerals Yearbook*, vol. 1. U.S. Department of the Interior, U.S. Geological Survey, Washington, DC.
- Ware, J.R., Smith, S.V., Reaka-Kudla, M.L., 1991. Coral reefs: sources or sinks of atmospheric CO<sub>2</sub>? *Coral Reefs* 11, 127–130.
- West, T.O., Marland, G., 2002. A synthesis of carbon sequestration, carbon emissions, and net carbon flux in agriculture: comparing tillage practices in the United States. *Agric. Ecosyst. Environ.* 91, 217–232.
- Wong, M.T.F., Vanderkuijjs, A.C.B.M., Juo, A.S.R., 1992. Leaching loss of calcium, magnesium, potassium and nitrate derived from soil, lime and fertilizers as influenced by urea applied to undisturbed lysimeters in south-east Nigeria. *Fert. Res.* 31, 281–289.