



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 (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 CO_2 to the atmosphere, the U.S. EPA estimated that 9 Tg (Teragram = 10^{12} g = 10^6 metric tonne) 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 (H_2CO_3) which results in uptake of CO_2 . Depending on soil pH and nitrogen fertilizer use, a fraction of aglime may react with strong acid sources such as nitric acid (HNO_3), thereby releasing CO_2 . Data on soil leaching and river transport of calcium (Ca^{2+}) and bicarbonate (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 CaCO_3 . Bicarbonate remaining in the soil profile is expected to release CO_2 following re-acidification of the soil over time. Our analysis indicates that net 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 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 (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 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 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 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 CO_2 emissions from Luxembourg and exceed the total national CO_2 emissions from over half of UN member countries.

Total 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 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 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 CO_2 emissions of 120 kg C $\text{ha}^{-1} \text{yr}^{-1}$ from the dissolution of the applied aglime. Total CO_2 emissions from aglime are thus $120 + 38 = 158 \text{ kg C ha}^{-1} \text{yr}^{-1}$. 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 $215 + 158 = 373 \text{ kg C ha}^{-1} \text{yr}^{-1}$ total annual CO_2 emissions per hectare. Using the IPCC emissions coefficients, Robertson et al. (2000) estimated similarly that aglime contributed 35% and 47% of CO_2 emissions from a conventionally tilled and no-till crop, respectively, in a corn–soybean–wheat rotation.

While the rate of 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 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 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 (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

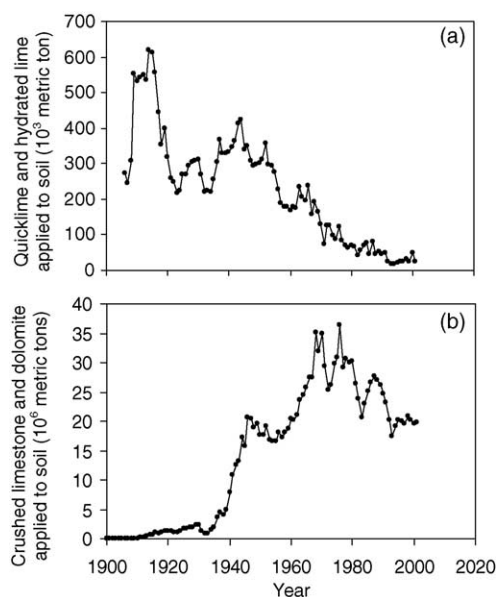


Fig. 1. Historic use of (a) lime (quicklime and hydrated lime) and (b) aglime (primarily crushed limestone) in the U.S. Data for even years from 1982 to 1992 are not available, and were estimated by averaging data from previous and latter years, respectively. Where quantities for unspecified uses of 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).

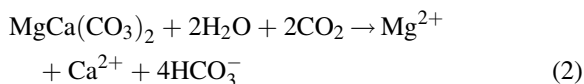
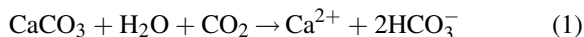
The reported decline in U.S. aglime use between 1980 and 2000 may also be questioned with respect to

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 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.

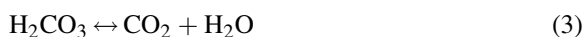
While the data on U.S. aglime consumption are suspect, we base our initial analysis on the EPA (2004) estimate of 20 Tg of applied aglime in 2001, so that our results can be directly compared to the EPA (2004) emissions estimate of 9 Tg CO_2 . However, we also apply our new emission coefficients to the 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 CaCO_3 and $\text{MgCa}(\text{CO}_3)_2$ can be characterized, respectively, as follows:

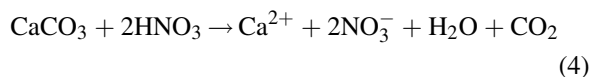


The reactions representing bicarbonate formation in solution (Eqs. (1) and (2)) produce two moles of CO_2 -equivalent (2HCO_2^-) for every mole of gaseous CO_2 taken up. The resulting bicarbonate may either remain in the soil or be flushed through the soil profile. Bicarbonate remaining in the soil is expected to react with available H^+ to form carbonic acid (H_2CO_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 CO_2 , hence, reaction to carbonic acid yields CO_2 that is released to the atmosphere. This latter equilibrium is as follows:



In the presence of nitrogen fertilizer, aglime will react with H^+ produced during the nitrification process.

Oxidation of ammonia by the nitrifying bacteria *Nitrosomonas*, referred to as nitrification, results in nitrite (NO_2^-) and H^+ ions, thereby increasing soil acidity. Nitrite is in turn oxidized by another bacteria, *Nitrobacter*, resulting in nitrate (NO_3^-) which is available for plant uptake. Nitrate and H^+ also form nitric acid (HNO_3). If calcium carbonate reacts with HNO_3 , 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 CO_2 in soil solution (H_2CO_3) is the primary contributor of 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 CO_2 in soils with relatively high pH, in which H_2CO_3 is the primary acid to react with carbonate minerals, but a net source of 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 H_2CO_3 (Eqs. (1) and (2)), and the fraction caused by strong acids such as HNO_3 (Eq. (4)). To a first approximation, the former reaction takes up one mole of CO_2 for every mole of CaCO_3 dissolved, while the latter reaction releases one mole of CO_2 for every mole of CaCO_3 dissolved. Semhi et al. (2000) developed a model which estimates the relative fractions of carbonate mineral dissolution by H_2CO_3 and by 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 HNO_3 originating largely from the use of nitrogen fertilizers in adjacent watersheds. The percentage of Ca^{2+} and HCO_3^- in rivers, caused by the dissolution of aglime by 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 Ca^{2+} and Mg^{2+} , and in HCO_3^- and 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 HCO_3^- (from Eqs. (1) and (2)), NO_3^- (from Eq. (4)), or other available anions will accompany Ca^{2+} and Mg^{2+} to satisfy the charge balance. This is illustrated by Wong et al. (1992) by the chemically balanced solution of Ca^{2+} and 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 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 Ca^{2+} is leached through the soil and whether this 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 Ca^{2+} following its application to soil surfaces. Brady and Weil (1996) estimated that $115 \text{ kg ha}^{-1} \text{ yr}^{-1}$ of Ca^{2+} ($288 \text{ kg ha}^{-1} \text{ yr}^{-1}$ of 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 Mg ha^{-1} of hydrated lime ($\text{Ca}(\text{OH})_2$ -equivalent) had leached following treatments of 0–2 $\text{Mg hydrated lime ha}^{-1}$, but 1.6 Mg ha^{-1} leached from the surface following treatment of 4 Mg ha^{-1} . Nearly all 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 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 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 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 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 CaCO_3 resulting in less leaching than gypsum ($\text{CaSO}_4 \cdot 2(\text{H}_2\text{O})$) or calcium chloride (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 Tg C yr^{-1} as bicarbonate is discharged from rivers to the world's oceans, with 90 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 11.0×10^{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

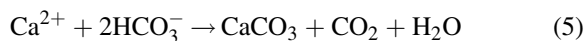
between 1954 and 2001 may be due to the increase in aglime use which occurred in this same time period (see Fig. 1) and which coincides with the historical increase in nitrogen fertilizer use. Mitsch et al. (2001) compiled data that illustrate a greater than 5 Tg yr⁻¹ increase in nitrogen fertilizer use in the Mississippi basin between 1955 and 1980, with use remaining at about 6.5 Tg yr⁻¹ between 1980 and 1995. Nitrate export from the Mississippi follows a similar trend, with an increase of about 1 Tg NO₃-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 HCO₃⁻) 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 × 10¹² g C yr⁻¹, or 83%. Raymond and Cole (2003a) estimate a 6.5 × 10¹² g C yr⁻¹ 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 × 10¹² g C yr⁻¹ 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 CO₂ on the atmospheric CO₂ 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 × 10¹⁵ g CaCO₃ 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 CaCO₃ (see Berry et al., 2002; Langer et al., 1997) as follows:



In freshwater, we would expect the release of one mole CO₂ per mole CaCO₃ precipitated (Eq. (5)). However, Ware et al. (1991) indicate that in seawater, 0.6 mol of CO₂ are actually released per mole of CaCO₃ 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 CaCO₃ through active physiological processes (see Broecker, 1974; Elderfield, 2002). It is also noted that CO₂ released during the formation of CaCO₃ 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 CO₂ may increase photosynthetic rates (Berry et al., 2002).

While some of the CaCO₃ precipitated in the ocean accumulates over time, a significant fraction of ocean CaCO₃ 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 CaCO₃ production rates are higher and dissolution rates are lower. Averaging the CaCO₃ accumulation rates in different neritic environments (Milliman, 1993; Iglesias-Rodriguez et al., 2002), weighted against the global CaCO₃ 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 CO₂ loss to CaCO₃ precipitated in the ocean, and we estimate that 40% of the precipitated CaCO₃ will dissolve, thereby resulting in a net 60% accumulation of the precipitated CaCO₃ in the neritic ocean environment.

Interestingly, the balance between CaCO_3 inputs and outputs does not appear to be in equilibrium and is also changing as atmospheric CO_2 concentration increases. Milliman (1993) suggests that 52×10^{13} g Ca yr^{-1} are exported to the oceans from the world's rivers each year, with 73×10^{13} g Ca accumulating in shallow waters and 56×10^{13} g Ca accumulating in the deep oceans. With another 12×10^{13} of 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 CO_2 , Sabine et al. (2004) estimate that with a doubling of atmospheric 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 CaCO_3 , thereby increasing the aglime-derived CO_2 sequestered in the ocean.

7. Net 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 CO_2 , our synthesis of terrestrial and ocean carbonate dynamics indicates that 100% release as CO_2 is unlikely. Conversely, if the CaCO_3 were simply dissolved at one point and re-precipitated elsewhere there should be no net emission of 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 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 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 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 HNO_3 , based on results from J.-L. Probst (UMR-CNRS/ Université Paul Sabatier, personal communication, 2003), thereby releasing 3.35 Tg of CO_2 ; an estimated 62% is dissolved by H_2CO_3 resulting in the uptake of 5.47 Tg 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 HCO_3^- is leached with

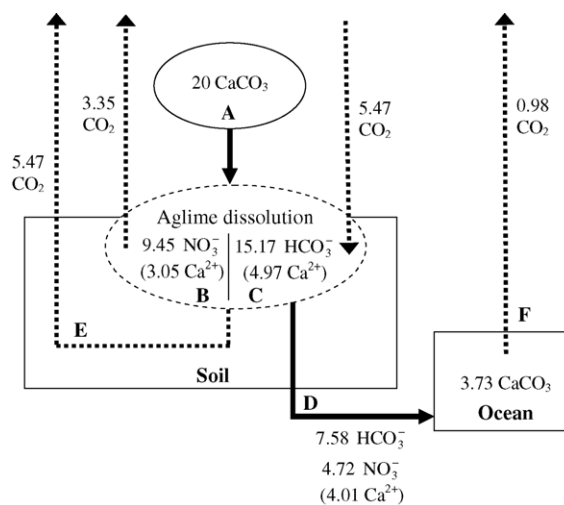


Fig. 2. Cumulative carbon accounting of annual U.S. aglime usage (in teragrams or 10^{12} g). This model assumes all aglime is crushed limestone. Solid arrows illustrate the flows of Ca^{2+} , HCO_3^- , and NO_3^- associated with the dissolution and precipitation of CaCO_3 . Dotted arrows illustrate fluxes of CO_2 associated with the dissolution and precipitation of 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 HNO_3 , resulting in the release of one mole CO_2 per mole CaCO_3 dissolved. (C) represents 62% of aglime dissolution by H_2CO_3 , resulting in the uptake of 1 mol CO_2 for every 2 mol of HCO_3^- produced. (D) represents 50% leaching of calcium through the soil profile, accompanied by an equivalent amount of HCO_3^- (7.58 Tg) and NO_3^- (4.72 Tg), and transported to the ocean. Bicarbonate remaining in the soil profile (E) is expected to react with available H^+ to form carbonic acid, thereby releasing CO_2 as the soil becomes more acidic over time. (F) represents the release of CO_2 following a net 60% precipitation of CaCO_3 in ocean margins, resulting in the release of 0.6 mol CO_2 per mole CaCO_3 precipitated.

Table 1
Net CO₂ emissions from applied agricultural lime

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

^a Based on an approximate weighted average of 80% limestone and 20% dolomite.

^b 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 CO₂ released for every mole of CaCO₃ precipitated in the ocean (Ware et al., 1991; Sundquist, 1993), and assuming 40% dissolution of CaCO₃ in the ocean margins, we estimate a net 3.73 Tg accumulation of CaCO₃ in the coastal ocean and 0.98 Tg CO₂ released to the atmosphere (Fig. 2). Bicarbonate that does not fully leach out of the soil profile is expected to eventually release CO₂ (5.47 Tg CO₂) as soil pH returns to its previously acidic condition due to fertilizer and organic matter inputs.

The net loss of CO₂ from this scenario is 4.33 Tg CO₂, which is the difference between estimated uptake of atmospheric CO₂ (5.47 Tg) and releases of CO₂ (9.80 Tg). The estimated net loss of CO₂ 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 CO₂ released to the atmosphere. This is about half of the CO₂ 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. CO₂ 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 CO₂ 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 CO₂ release of about 49%. This lower estimate is due in large part to the initial uptake of CO₂ during dissolution of aglime by H₂CO₃, which approximately offsets CO₂ releases during dissolution of aglime by HNO₃ and precipitation of CaCO₃ in coastal oceans. Our estimate indicates a 4.4 Tg CO₂ loss from 20 Tg of aglime applied in 2001, compared to a 9.0 Tg CO₂ 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 HNO₃ as opposed to H₂CO₃ 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 CO₂ resulting from aglime application, our analysis strongly suggests that not all C applied to soil as aglime is released to the atmosphere as CO₂.

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