## Update of the CO<sub>2</sub> Emission Factor from Agricultural Liming

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Limestone (CaCO<sub>3</sub>) is added to increase soil pH or reduce soil acidification. When CaCO<sub>3</sub> comes in contact with strong acid sources such as nitric acid in the soil, chemical reaction (1) is triggered and some of the CaCO<sub>3</sub> degrades, releasing CO<sub>2</sub> emissions. The rate and ultimate magnitude of degradation of applied limestone depends on the soil conditions, soil type, climate regime, and the type of mineral applied (US EPA 2014). The limestone can also be dissolved into calcium bicarbonate with the presence of carbonic acid (H<sub>2</sub>CO<sub>3</sub>) that forms when the soil moisture uptakes the atmospheric  $CO_2$  emissions, as shown in chemical reaction (2). The bicarbonate may leach through the soil and be transported by rivers to the oceans. For the bicarbonate that remains in the soil, it can be subject to soil re-acidification via chemical reaction (3), and thus no  $CO_2$  emissions are generated as a net effect of chemical reactions of (2) and (3). For the bicarbonate that is leached and transported to oceans, however, government agencies understand its fate differently: The U.S. Environmental Protection Agency (EPA) adopted the finding that much of this leached bicarbonate is precipitated back to CaCO<sub>3</sub> in the ocean by calcite-precipitating organisms, including corals, foraminiferans, and coccolithophorid phytoplankton (West and McBride 2005), while the United States Department of Agriculture (USDA) assumes that it will be sequestered for decades to centuries.

$$CaCO_3 + 2HNO_3 \rightarrow H_2O + CO_2 + Ca(NO_3)_2 \tag{1}$$

$$CaCO_3+H_2O + CO_2 \rightarrow Ca(HCO_3)_2$$

$$Ca(HCO_3)_2 \rightarrow CaCO_3+H_2O+CO_2$$
(2)
(3)

$$a(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2 \tag{3}$$

In determining the CO<sub>2</sub> emissions from limestone application, government agencies have adopted different approaches that differ in the magnitude of degradation of applied limestone and the fate of the bicarbonate that is produced with an uptake of atmospheric  $CO_2$  emissions in the soil. The EPA has adopted the findings that net CO<sub>2</sub> emissions from agricultural application of limestone is 0.059 gram carbon per gram of limestone, or 49.2% of the limestone is acidified and releases CO<sub>2</sub> emissions and the remaining does not produce net CO<sub>2</sub> emissions or uptake atmospheric  $CO_2$  emissions (0.216 g  $CO_2$ /g  $CaCO_3$ ). On the other hand, in their recently released report on methodology for estimating greenhouse gas (GHG) emissions in the agriculture and forestry sector (U.S. Department of Agriculture 2014), the USDA made an assumption that only one third of the limestone is acidified directly to CO<sub>2</sub> and two thirds of the limestone is dissolved in the presence of carbonic acid ( $H_2CO_3$ ) as a result of uptake of atmospheric  $CO_2$  emissions by the soil, as shown in chemical reaction (2), and the resultant bicarbonate is leached to the ocean where it will be sequestered for decades to centuries. Therefore, the USDA approach leads to a net carbon sink from the addition of limestone (-0.147 g CO<sub>2</sub>/g CaCO<sub>3</sub>) because half of the carbon in the bicarbonate leached and sequestered comes from uptake of atmospheric CO<sub>2</sub> emissions.

We decided to take the EPA's approach to estimate the CO<sub>2</sub> emission factor from agricultural liming as the EPA has explained in their 2014 GHG emission inventory that the lime dissolution rate was based on liming occurring in the Mississippi River basin, where the vast majority of all U.S. liming takes place. U.S. liming that does not occur in the Mississippi River basin tends to

occur under similar soil and rainfall regimes, and thus the emission factor is appropriate for use across the United States (US EPA 2014). On the other hand, the USDA approach lacks resolution at the farm scale, because the method of estimation is based on stream-gauge data that are collected at the watershed scale (U.S. Department of Agriculture 2014). Besides, the USDA does not clarify the scientific basis that supports their assumption on the relative magnitudes of limestone that is acidified to  $CO_2$  emissions to bicarbonate, which has a direct impact on the estimated overall  $CO_2$  emissions from agricultural liming. With the EPA's approach, we updated the  $CO_2$  emission factor from agricultural liming from previous 0.44 g  $CO_2/g$  CaCO<sub>3</sub> to 0.216 g  $CO_2/g$  CaCO<sub>3</sub> in GREET1\_2014.

## References:

- U.S. Department of Agriculture. 2014. "Quantifying Greenhouse Gas Fluxes in Agriculture and Forestry: Methods for Entity-Scale Inventory."
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