Updating Parametric Assumptions on Nitrogen Fertilizers in GREET2015

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This memo documents Argonne's updates on three parametric assumptions regarding nitrogen fertilizers in GREET2015.

1. Nitrous oxide emission rate for nitric acid production

Nitrous oxide (N_2O) is emitted during the production of nitric acid (HNO_3). Virtually all of the nitric acid produced in the United States is manufactured by the catalytic oxidation of ammonia, as shown in Reactions 1 through 3 (U.S. Environmental Protection Agency, 1999a). N_2O is formed as a byproduct of the high temperature catalytic oxidation of ammonia and is released from reactor vents into the atmosphere (U.S. Environmental Protection Agency, 2015a). The amount of N_2O formed depends on combustion conditions in the oxidizing unit, catalyst compositions, catalyst age, and burner design. Reactions 4 through 6 show the formation of N_2O at HNO_3 plants (U.S. Environmental Protection Agency, 2010).

Ammonia Oxidation: $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$ (1)
Nitric Oxide Oxidation: $2NO + O_2 \rightarrow 2NO_2$ (2)
Absorption: $3NO_2 + H_2O \rightarrow 2HNO_3 + NO$ (3)

$$2\ NH_3 + 2\ O_2 \rightarrow N_2O + 3\ H_2O \quad (4)$$

$$2\ NH_3 + 8\ NO \rightarrow 5\ N_2O + 3\ H_2O \quad (5)$$

$$4\ NH_3 + 4\ NO + 3\ O_2 \rightarrow 4\ N_2O + 6\ H_2O \quad (6)$$

Nitric acid facilities also produce nitrogen oxide (NO_x) emissions. Currently, these facilities employ controls for NO_x emissions. As such, a combination of non-selective catalytic reduction (NSCR) and selective catalytic reduction (SCR) technologies are employed by the U.S. industry. In the process of destroying NO_x, NSCR systems are also very effective at destroying N_2O. However, neither SCR nor extended absorption is known to reduce N_2O emissions (U.S. Environmental Protection Agency, 2015a).

Starting 2010, process N_2O emissions and nitric acid production data were available directly from EPA's Greenhouse Gas Reporting Program (GHGRP), which collected and aggregated reported facility-level data (U.S. Environmental Protection Agency, 2015b). In the U.S., all HNO_3 facilities producing weak HNO_3 (30-70% in concentration) are required to report annual GHG emissions data to EPA as per requirement of the GHGRP. These facilities calculate process emissions using a site-specific emission factor developed through annual performance testing under typical operating conditions or by directly measuring N_2O emissions using monitoring equipment. As of 2013, 35 facilities made reportings to EPA, including a known single high-strength HNO_3 production facility in the U.S. (U.S. Environmental Protection Agency, 2015b).

Using the 2010 GHGRP data, emission factors for production with abatement and without abatement, on average, were calculated to be 3,300 and 5,980 g N_2O/metric ton of pure HNO_3 produced, respectively. The emission factors were used in conjunction with existing estimates on the share of production with and without N_2O abatement technology to estimate N_2O emissions prior to 2010 in EPA's latest GHG emission inventory (U.S. Environmental Protection Agency, 2015a).

Table 1 shows the annual N_2O emissions and HNO_3 production from all HNO_3 production facilities in the U.S. from 2010 to 2013 as extracted from the GHGRP. Accordingly, we calculated annual N_2O emission factors. Compared to 2010, the emission reduction in 2013 may reflect the increase in adoption of N_2O emission abatement technologies.

Table 1. N_2O emissions for nitric acid production in the U.S., 2010-2013

Year	N_2O emissions, 1000 metric tons	HNO_3 production, 1000 metric tons	Emission factor, g N_2O/short ton HNO_3
2010	39	7,444	4,753
2011	37	7,606	4,413
2012	35	7,453	4,260
2013	36	7,572	4,313

The new N_2O emission factor of 4,313 g/short ton of pure HNO_3 production, which represents the most recent industrial emission performance, replaces the old one in GREET2014, which was 7,916 grams/short ton, based on the 1996 IPCC good practice guidelines.

2. Natural gas consumption for ammonia production

Ammonia is synthesized from nitrogen and hydrogen that consumes energy, as shown in Equation (7).

$$N_2 + 3H_2 \rightarrow 2NH_3 \qquad (7)$$

The nitrogen used in the process is taken from the air. In the U.S., the hydrogen source is mostly derived from steam methane reforming of natural gas (NG) (U.S. Environmental Protection

Agency, 2009). About 32 mmBtu of NG (low-heating value [LHV] based) is consumed to produce one short ton of ammonia (Johnson et al., 2013). Ammonia manufacture relies on natural gas as both a feedstock and a fuel. Natural gas can make up 70-85% of the cost of producing ammonia (PotashCorp, 2015).

Therefore, ammonia plants are concentrated in areas with abundant supplies of natural gas. A majority of ammonia plants in the U.S. are located in Louisiana, Texas and Oklahoma (The Ammonia Industry, 2015), near the large fields of NG in the southern Gulf region. Other ammonia plants in the U.S. are mostly centered in Midwest states of Iowa, Nebraska, Indiana, Ohio, and Illinois to benefit from proximity to key customers of the ammonia products (The Ammonia Industry, 2015).

Normally, NG feedstock first makes its way to regional hubs, e.g., the Henry Hub in Louisiana, after which NG may be transmitted to a variety of users including industrial ammonia plants. Information on NG supplies to ammonia plants, however, is rarely reported in public domain, and thus requires estimation. For ammonia plants in the Gulf region and the southwest states of Louisiana, Texas, and Oklahoma, we assumed that an NG pipeline transportation distance of 200 miles is needed to send the Gulf Coast NG to the regional Henry Hub; For ammonia plants in the Midwest, abundant NG can be transmitted via pipelines connecting (1) Western Canada; (2) the area of East Texas, Louisiana, Gulf of Mexico, and Arkansas; and (3) the area of southwestern Texas, the Texas and Oklahoma panhandles, western Arkansas, and southwestern Kansas, which account for about 41%, 28%, and 17% of the total pipeline capacity feeding into the Midwest Region (U.S. Energy Information Administration, 2015) . In addition, abundant shale gas from the Appalachian basins is transmitted to Midwest NG markets via pipeline systems like the eastern segment of the Rockies Express Pipeline (TallGrass Energy, 2015). We estimated a distance of 1,090 miles for pipeline NG transmission to the Midwest states, as shown in Table 2. After the NG supplied from different origins reaches the local transportation corridors, it continues its way to the local ammonia plants by local NG transmission pipeline. CF Industries, a major ammonia producer in the U.S., has its largest plant located at Louisiana, which likely receives NG transmitted from the nearby Henry Hub about 100 miles away. Here, we assume that the transmitted NG eventually reaches ammonia plants with 100 miles of local pipelines. Combining the NG pipeline regional and local transmission distances, we estimate that the NG feedstock is transmitted by pipeline with an average distance of 575 miles to the ammonia plants in the U.S., without going through any local distribution systems. This compares to a total transportation and distribution distance of 680 miles of NG pipelines for use in ammonia plants in the U.S. previously estimated in GREET2014.

Table 2. Estimated transportation and distribution distances by pipeline of NG feedstock for ammonia plants in the U.S.

	Production capacity of ammonia plants, % of U.S. total	NG pipeline transmission to regional hub, miles	NG pipeline transmission from regional hub to plants, miles
Gulf Coast ammonia plants	68	200	100
Midwest ammonia plants			

From western Canada	9	1,300	100
From Southwestern U.S.	6	1,000	100
From Southwestern Panhandle	3	1,300	100
From the Appalachian basins	3	400	100
Ammonia plants elsewhere	11	1,000	100
Average for all ammonia plants in the U.S.	100	475	100

3. Classification of ammonia sulfate

According to Johnson et al. (2013), the total nitrogen fertilizer application in the U.S. consists of a small amount of ammonia sulfate, about 2% of the total use. Ammonia sulfate is produced in an exothermic reaction between ammonia and sulfuric acid. However, ammonia sulfate nowadays is mostly derived as a by-product of removing SO_2 from stack gases at coal-fired power plants, metal smelting facilities, and at refineries which conform to SO_2 emission regulations (IHS Inc, 2015). Ammonia sulfate may also be derived as a coke oven or caprolactam by-product (U.S. Environmental Protection Agency, 1999), or produced through the reaction of ammonia and spent sulfuric acid as byproducts of other industrial processes (IPNI, 2015). Previously in GREET2014, we treated ammonia sulfate the same as ammonia nitrate that requires an energy consumption of about 0.84 MJ/kg from the reaction between ammonia and nitric acid (Johnson et al., 2013). In GREET2015 we treat ammonia sulfate as an industrial byproduct with no energy- and emission-burden.

Reference

The Ammonia Industry, 2015. Ammonia Capacity in North America.

IHS Inc, 2015. Chemical Economics Handbook: Ammonium Sulfate.

IPNI, 2015. Nutrient Source Specifics: Ammonium Sulfate.

Johnson, M.C., Palou-Rivera, I., Frank, E., 2013. Energy consumption during the manufacture of nutrients for algae cultivation. Algal Res. 2, 426–436.

PotashCorp, 2015. Basics of Nitrogen.

TallGrass Energy, 2015. Rockies Express Pipeline (REX).

U.S. Energy Information Administration, 2015. Major Natural Gas Transportation Corridors.

U.S. Environmental Protection Agency, 2015a. Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2013.

U.S. Environmental Protection Agency, 2015b. Greenhouse Gas Reporting Program.

U.S. Environmental Protection Agency, 2010. AVAILABLE AND EMERGING TECHNOLOGIES FOR REDUCING GREENHOUSE GAS EMISSIONS FROM THE NITRIC ACID PRODUCTION INDUSTRY.

U.S. Environmental Protection Agency, 2009. Technical Support Document for the Ammonia Production Sector: Proposed Rule for Mandatory Reporting of Greenhouse Gases.

U.S. Environmental Protection Agency, 1999a. Emissions Factors & AP 42, Compilation of Air Pollutant Emission Factors: 8.8 Nitric Acid.

U.S. Environmental Protection Agency, 1999b. Emissions Factors & AP 42, Compilation of Air Pollutant Emission Factors: 8.4 Ammonium Sulfate.