Technical Support Document for the Ammonia Production Sector: Proposed Rule for Mandatory Reporting of Greenhouse Gases

Office of Air and Radiation U.S. Environmental Protection Agency

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1. Industry Description

Ammonia is a major industrial chemical that is mainly used as fertilizer, directly applied as anhydrous ammonia, or further processed into urea, ammonium nitrates, ammonium phosphates, and other nitrogen compounds. Ammonia also is used to produce plastics, synthetic fibers and resins, and explosives. There has been a decrease in ammonia manufacture in recent years due to several factors, including market fluctuations and increasing natural gas prices. Ammonia manufacture relies on natural gas as both a feedstock and a fuel, and as such, domestic manufacturers are competing with imports from countries with lower natural gas prices. If natural gas prices remain high, domestically manufactured ammonia will likely continue to decrease with increasing ammonia imports (EEA 2004).

Total estimated U.S. production of ammonia was approximately 8 million metric tons in 2006, ranging from around 22,000 metric tons to nearly 1.5 million metric tons across 24 operational facilities (USGS Mineral Yearbook 2006). Facility-level ammonia and urea production capacity data are presented in Table 1.

Emissions of CO_2 occur during the production of synthetic ammonia, primarily through the use of natural gas as a feedstock. One nitrogen production plant located in Kansas produces ammonia from petroleum coke feedstock, but the other ammonia manufacturing plants produce ammonia from natural gas. In a few plants a portion of the CO_2 produced is captured and used to produce urea or methanol. The brine electrolysis process for production of ammonia does not lead to process-based CO_2 emissions.

Company	Plant Location	Year End Ammonia Capacity (metric tons) ^{a,b}	Year End Urea Capacity (metric tons) ^{a,b,f}
Agrium Inc.	Borger, TX	490,000	89,727
Agrium Inc.	Finley, WA ^c	180,000	0
Agrium Inc.	Kenai, AK	280,000	215,444
CF Industries Inc.	Donaldsonville, LA	2,040,000	2,020,095
Coffeyville Resources LLC	Coffeyville, KS	375,000	172,306
Dyno Nobel ASA	Cheyenne, WY	174,000	92,079
Dyno Nobel ASA	St. Helens, OR	101,000	103,182
El Dorado Chemical Co.	Cherokee, AL	175,000	197,418
Green Valley Chemical Corp.	Creston, IA	32,000	0
Honeywell International Inc.	Hopewell, VA	530,000	0
Koch Nitrogen Co.	Beatrice, NE	265,000	61,748
Koch Nitrogen Co.	Dodge City, KS	280,000	73,984
Koch Nitrogen Co.	Enid, OK	930,000	346,527
Koch Nitrogen Co.	Fort Dodge, IA	350,000	160,402
Koch Nitrogen Co.	Sterlington, LA	1,110,000	0

Table 1. U.S. Producers of Ammonia and Urea (metric tons per year)

Company	Plant Location	Year End Ammonia Capacity (metric tons) ^{a,b}	Year End Urea Capacity (metric tons) ^{a,b,f}
Mosaic Co., The	Faustina (Donaldsonville), LA	508,000	0
Nitromite Fertilizer (Valero Energy Corp.)	Dumas, TX ^d	128,000	0
PCS Nitrogen Inc.	Augusta, GA	688,000	454,521
PCS Nitrogen Inc.	Geismar, LA ^c	483,000	337,688
PCS Nitrogen Inc.	Lima, OH	542,000	370,826
Rentech Energy Midwest Corp. ^e	East Dubuque, IL	278,000	120,329
Shoreline Chemical	Gordon, GA	31,000	0
Terra Industries Inc.	Beaumont, TX ^c	231,000	0
Terra Industries Inc.	Port Neal, IA	336,000	226,942
Terra Industries Inc.	Verdigris, OK	953,000	495,614
Terra Industries Inc.	Woodward, OK	399,000	94,008
Terra Industries Inc.	Yazoo City, MS	454,000	158,284
Total		12,700,000	5,791,125

Note: Estimated operating capacity based on 7-day-per-week full production.

^a Data are rounded to no more than three significant digits; may not add to totals shown.

^b Engineering design capacity adjusted for 340 days per year of effective production capability.

^c These facilities no longer manufacture ammonia but rather use imported ammonia to produce upgrade products such as nitric acid and urea ammonium nitrate (UAN).

^d Closed in 2006.

^e Purchased from Royster-Clark Inc. in 2006.

^f It was assumed that those facilities that had urea capacity in 2004 continued to have urea capacity in 2006 and that those facilities that did not have urea capacity in 2004 continued not to have urea capacity in 2006.

Source: Ammonia capacity: USGS Minerals Yearbook 2006

(http://minerals.usgs.gov/minerals/pubs/commodity/nitrogen/myb1-2006-nitro.xls). Urea capacity: IFDC 2005. North America Fertilizer Capacity. Market Information Unit. Market Development Division. September 2005.

2006 urea capacity values were estimated by adjusting data from IFDC 2005 using the relative relationship of 2004 urea to ammonia capacities.

2. Total Emissions

According to the U.S. Greenhouse Gas Inventory, total CO_2 process emissions from ammonia production were 11.8 million metric tons of CO_2 equivalents (mtCO_2e) (U.S. EPA 2008) in 2006. These estimates were based on national-level production data. Emissions have decreased 28 percent since 1990, and 2006 emissions were 4 percent lower than the previous year (U.S. EPA 2008). Emissions of CO_2 from on-site combustion are not currently accounted for separately in the U.S. Inventory. However, the processing of ammonia requires boilers and other equipment that use natural gas and other fuels, and hence, results in emissions from combustion as well as the ammonia manufacturing process.

According to facility specific production estimates, national emissions from ammonia manufacturing were estimated to be 14.6 mtCO₂e. These emissions include both process related

 CO_2 emissions and on-site stationary combustion emissions (CO_2 , CH_4 , and N_2O) from 24 manufacturing facilities across the United States. Process-related emissions account for 7.6 million mtCO2e, or 52 percent of the total, while on-site stationary combustion emissions account for the remaining 7.0 million mtCO2e emissions.

2.1 Process Emissions

Ammonia is produced using either natural gas or petroleum coke, although the industry predominantly uses natural gas. There are five principal process steps in synthetic ammonia production from natural gas feedstock. The primary reforming step converts CH_4 to CO_2 , carbon monoxide (CO), and H_2 in the presence of a catalyst. Only 30 to 40 percent of the CH_4 feedstock to the primary reformer is converted to CO and CO_2 . The secondary reforming step converts the remaining CH_4 feedstock to CO and CO_2 . The CO in the process gas from the secondary reforming step (representing approximately 15 percent of the process gas) is converted to CO_2 in the process gas by the shift conversion process, and the hydrogen is combined with the nitrogen (N_2) in the process gas stream during the ammonia synthesis step. The CO_2 is included in a waste gas stream with other process impurities and is absorbed by a scrubber solution. In regenerating the scrubber solution, CO_2 is released.

The conversion process for conventional steam reforming of CH₄, including primary and secondary reforming and the shift conversion process is approximately as follows:

(catalyst) 0.88 CH₄ + 1.26 Air + 1.24 H₂O \longrightarrow 0.88 CO₂ + N₂ + 3 H₂ N₂ + 3 H₂ \rightarrow 2 NH₃

To produce synthetic ammonia from petroleum coke, the petroleum coke is gasified and converted to CO_2 and H_2 . These gases are separated, and the H_2 is used as a feedstock to the ammonia production process, where it is reacted with N_2 to form ammonia.

Not all of the CO_2 generated in the production of ammonia is emitted directly to the atmosphere. At some production plants, both ammonia and CO_2 are used as raw materials in the production of urea $[CO(NH_2)_2]$, which is another type of nitrogenous fertilizer that contains carbon as well as nitrogen. The carbon in the consumed urea is assumed to be released into the environment as CO_2 during use. Therefore, the CO_2 generated by ammonia production that is subsequently captured and used to produce other materials is not included in this source category.

2.2 Stationary Combustion

Combustion emissions from ammonia manufacturing plants result from the combustion of natural gas and fuel oil. Combustion sources include primary reformers and boilers. The feedstock (raw material) used in ammonia production is not necessarily the same as the fuel used for energy (combustion) in ammonia production. For example, although one facility produces ammonia from petroleum coke, this same facility combusts natural gas for its stationary sources.

In addition, although other fuels may be combusted for energy, MECS data for NAICS code 325311, "Nitrogenous Fertilizers" which includes ammonia manufacturing, indicates 98 percent of the total fuel energy consumption (i.e., excluding purchased electricity) is natural gas.

3. Review of Existing Programs and Methodologies

Existing reporting programs and methodologies for ammonia manufacture include IPCC, WRI/WBCSD Protocol, DOE 1605(b), and Climate Registry. They are described below.

3.1 2006 IPCC Guidelines

The 2006 IPCC Guidelines consider three different methods for calculating total emissions from ammonia production, including process emissions from feedstock and stationary combustion emissions from fuel combustion (IPCC 2006, Table 3.1). Note that the 2006 IPCC Guidelines for ammonia production use the term "fuel" in referring to the combined "fuel" (i.e., energy) natural gas and "feedstock" (i.e., raw material) natural gas, and provides a single Tier 1 emission factor to estimate the total CO_2 emissions from natural gas consumption in ammonia production. In Table 2, "fuel" (stationary combustion) and "feedstock" (process) CO_2 emissions from ammonia production are estimated separately. The Tier 1 method uses a default emission factor per unit of output multiplied by production activity data. The equation is as follows:

$$E_{CO2} = AP x FR x CCF x COF x 44/12 - R_{CO2}$$

E _{CO2}	= emissions of CO ₂ (kg)
AP	= production of ammonia (metric tons)
FR	= fuel requirement per unit of output (GJ/metric tons ammonia produced)
CCF	= carbon content of the fuel (kg C/GJ)
COF	= carbon oxidation factor of the fuel (fraction)
R_{CO_2}	= CO_2 recovered for downstream use (kg)

The Tier 2 method estimates total fuel requirement for each fuel type by using the equation below:

$$TFR_i = \Sigma (AP_{ij} \times FR_{ij})$$

Where:

TFR _i	= total fuel requirement for fuel type i (GJ)
AP_{ij}	= ammonia production using fuel type i in process type j (metric tons)
FR_{ij}	 fuel requirement per unit of output for fuel type i in process type j (GJ/metric tons ammonia produced)

Ammonia production, fuel type, and process type is obtained from producers and default factors are used for fuel requirement per unit of output. Default carbon content of fuel and carbon oxidation factor are used for Tier 2. Emissions are estimated using the equation below:

$$E_{CO2} = \Sigma (TFR_i \times CCF \times COF \times 44/12) - R_{CO2}$$

Where:

 E_{CO2} = emissions of CO_2 (kg)

 TFR_i = total fuel requirement for fuel type i (GJ)

CCF = carbon content of the fuel (kg C/GJ)

COF = carbon oxidation factor of the fuel (fraction)

 $R_{CO2} = CO_2$ recovered for downstream use (kg)

For Tier 3 estimates, total fuel requirement must be obtained from producers.

3.2 2008 U.S. Inventory of Greenhouse Gas Emissions and Sinks

The U.S. Inventory estimates emissions for ammonia production according to the following equation:

 CO_2 Emissions = $AP_{PC} * CC_{PC} + AP_{NG} * CC_{NG}$

AP_{PC}	=Ammonia production from petroleum coke (tons ammonia)
CC _{PC}	=Carbon content of petroleum coke (3.57 ton CO_2 /ton ammonia produced)
AP_{NG}	=Ammonia production from natural gas (tons ammonia)
CC _{NG}	= Carbon content of natural gas (1.2 ton CO_2 /ton ammonia produced)

The U.S. Inventory also estimates emissions from urea consumed for industrial processes (does not include urea applied to agricultural lands) and reports this estimate along with the ammonia production estimate.

3.3 WRI/WBCSD Protocol

The World Resource Institute and World Business Council for Sustainable Development's Greenhouse Gas Protocol follows IPCC's Tier 2 approach and IPCC's Tier 3 if sufficient data are available.

3.4 The Climate Registry

This protocol has two different methodologies. The Tier A1 method uses direct measurement, either through CEMS or periodic direct measurements. The Tier A2 is a mass balance approach using the same equation as used for Tier 1 of the 2006 IPCC Guidelines:

Emissions = [Σ (TFR x CCF x COF x 44/12) for each fuel type] - REC_{CO2}

Where:

TFR	= total feedstock requirement for each fuel type, GJ (see calculation below)
CCF	= carbon content factor for each fuel type, kg C/GJ
COF	= carbon oxidation factor for each fuel type, fraction
REC _{CO2}	= CO_2 recovered for downstream use (e.g., urea production), kg
Note: CO	² recovery includes CO ₂ for urea production and carbon capture and storage (CCS) only.

TFR = Σ (PRODamm x FR) for each fuel type and process type

PRODamm	= ammonia production for each fuel type and process type, tons
FR	= fuel requirement for each fuel type and process type, GJ/ton ammonia production

3.5 Technical Guidelines Voluntary Reporting of Greenhouse Gases (1605(b)) Program

This protocol has three different methodologies. The "A" rated method is direct measurement of emissions, either by using a continuous emission monitoring system (CEMS) or by periodic direct measurements. The "B" rated method is based on calculation, using measurement of feedstock and its carbon content. The mass balance approach is based on the carbon content and consumption data for feedstock. Reporters can use default carbon content values from EIA 2003 if plant-specific data is not available. The "C" rated method is based on calculation, using quantity of ammonia produced. If no plant-specific information is available, reporters can use a default emission factor of 1.26 metric ton CO₂/metric ton ammonia produced.

Table 2. CO₂ Emissions Coefficients for U.S. Natural Gas as provided by DOE's Voluntary Reporting of Greenhouse Gases Technical Guidelines for Ammonia

HHV Btu content per Standard Cubic Foot	Emissions Coefficient (metric tons carbon per billion Btu)		
	CO ₂	Carbon	
975-1,000	54.01	14.73	
1,000-1,025	52,91	14.43	
1,025-1,050	53.06	14.47	
1,050-1,075	53.46	14.58	
1,075-1,100	53.72	14.65	

Source: U.S. DOE 2007.

4. Options for Reporting Threshold

Several alternative emission and capacity threshold options for reporting facility-level GHG emissions from the ammonia manufacturing sector were analyzed. This section describes the reporting options considered and associated emissions and the coverage of ammonia manufacturing facilities under each option.

4.1 Options Considered

4.1.1 Emissions Thresholds

For the reporting of process CO_2 emissions from ammonia production, threshold options considered included emissions-based thresholds of 100,000 metric tons of CO_2e (mt CO_2e), 25,000 mt CO_2e , 10,000 mt CO_2e , and 1,000 mt CO_2e for both combustion and process emissions. The results of the threshold analysis incorporating these four threshold options are summarized in Table 3.

Threshold	Process	Combustion	Total		Emissions Covered		Facilities Covered	
Level (metric tons CO ₂ e)	Emissions (metric tons CO ₂ e/yr)	Emissions (metric tons CO ₂ e /yr)	National Emissions (metric tons CO ₂ e)	Number of Facilities	metric tons CO₂e/yr	Percent	Number	Percent
100,000	7,499,174	6,950,345	14,543,007	24	14,449,519	99%	22	92%
25,000	7,553,606	6,989,401	14,543,007	24	14,543,007	100%	24	100%
10,000	7,553,606	6,989,401	14,543,007	24	14,543,007	100%	24	100%
1,000	7,553,606	6,989,401	14,543,007	24	14,543,007	100%	24	100%

Table 3	Threshold	Analysis	for	Ammonia
Table J.	Theshold	Allalysis	101	Ammonia

The IPCC Tier 1 method was used to determine process CO_2 emissions from the facilities presented in Table 1, because production capacity was the only facility-level data available. A default process emission factor of 1.2 metric tons CO_2 /metric tons ammonia produced was obtained from the *Inventory of U.S. Greenhouse Gas Emissions and Sinks 1990-2006* (U.S. EPA 2008) for those facilities that use natural gas as feedstock for the steam reforming process. An emission factor of 3.57 was used for the one facility that manufactures ammonia from petroleum coke. This emission factor was determined by dividing the total CO_2 produced by this plant from petroleum coke consumption (assuming 90 percent of the petroleum coke consumed is carbon) by the total ammonia produced at the plant for the years 2000, 2001, and 2002. It should be noted that the CO_2 emission factor for ammonia production in the 2006 IPCC Guidelines includes CO_2 emissions from both fuel natural gas and feedstock natural gas, while the CO_2 emission factor in the previous IPCC Guidelines, and the CO_2 emission factor used in the 1990-2006 U.S. Inventory, account for only feedstock natural gas but not fuel natural gas.

Facility-level production was calculated by using facility-level capacity data as shown in Table 1 and multiplying by a capacity factor of 72 percent, which is the capacity utilization reported for U.S. ammonia producers in 2006 (USGS 2007). Estimated facility-level production was then multiplied by the default emission factor in order to determine estimated facility process emissions. The facilities are presented in Table 3.

Plant	Plant location	Capacity (Metric tons)	Production (Metric tons)
Agrium Inc.	Borger, TX	490,000	352,800
Agrium Inc.	Finley, WA ^b	180,000	0
Agrium Inc.	Kenai, AK	280,000	201,600
CF Industries Inc.	Donaldsonville, LA	2,040,000	1,468,800
Coffeyville Resources LLC	Coffeyville, KS	375,000	279,000
Dyno Nobel ASA	Cheyenne, WY	174,000	125,280
Dyno Nobel ASA	St. Helens, OR	101,000	72,720
El Dorado Chemical Co.	Cherokee, AL	175,000	126,000
Green Valley Chemical Corp.	Creston, IA	32,000	23,040
Honeywell International Inc.	Hopewell, VA	530,000	381,600
Koch Nitrogen Co.	Beatrice, NE	265,000	190,800
Koch Nitrogen Co.	Dodge City, KS	280,000	201,600
Koch Nitrogen Co.	Enid, OK	930,000	669,600
Koch Nitrogen Co.	Fort Dodge, IA	350,000	252,000
Koch Nitrogen Co.	Sterlington, LA	1,110,000	799,200
Mosaic Co., The	Faustina (Donaldsonville), LA	508,000	365,760
Nitromite Fertilizer (Valero Energy Corp.)	Dumas, TX ^c	128,000	53,760
PCS Nitrogen Inc.	Augusta, GA	688,000	495,360

Table 3. Ammonia Facilities With Capacity and Production Data

Plant	Plant location	Capacity (Metric tons)	Production (Metric tons)
PCS Nitrogen Inc.	Geismar, LA ^b	483,000	0
PCS Nitrogen Inc.	Lima, OH	542,000	390,240
Rentech Energy Midwest Corp. ^d	East Dubuque, IL	278,000	200,160
Shoreline Chemical	Gordon, GA	31,000	22,320
Terra Industries	Beaumont, TX	231,000	0
Terra Industries Inc.	Port Neal, IA	336,000	241,920
Terra Industries Inc.	Verdigris, OK	953,000	686,160
Terra Industries Inc.	Woodward, OK	399,000	287,280
Terra Industries Inc.	Yazoo City, MS	454,000	326,880
Total		12,700,000	8,213,880

^a Emission estimates presented here differ from those published in the U.S. Greenhouse Gas Emissions and Sinks 1990-2006 (U.S. EPA 2008). Emission estimates presented here were calculated using a bottom up approach based on facility level data whereas emission estimates found in the U.S. Greenhouse Gas Emissions and Sinks 1990-2006 are calculated using a top down approach based on national production data.

^b These facilities no longer manufacture ammonia but rather use imported ammonia to produce upgrade products such as nitric acid and UAN.

^c Closed in 2006.

^d Purchased from Royster-Clark Inc. in 2006.

Source: Ammonia capacity: USGS Minerals Yearbook 2006

(http://minerals.usgs.gov/minerals/pubs/commodity/nitrogen/myb1-2006-nitro.xls). Production was estimated using a factor of 72% from USGS 2007. The USGS Mineral Yearbook for 2006 states that ammonia producers in the US operated at about 72% of design capacity in 2006. This value includes capacities at plants that operated during any part of the year and does not include plants that were idle for all of 2006. Process emission estimates were calculated using estimated production values and an emission factor for natural gas from U.S. EPA 2008. An emission factor for petroleum coke was used for Coffeyville Resources LLC as their primary feedstock is petroleum coke.

In order to determine CO_2 emissions from combustion related to the ammonia production process, region-specific energy intensities for fossil fuel combustion were used. It was assumed that each facility used natural gas as its combustible fuel based on MECS data for NAICS code 325311.

Total ammonia plant energy intensity by region was obtained from Phylipsen et al., 2002. National average energy intensity values for feedstock energy and electricity were obtained from Lawrence Berkeley National Laboratories (LBNL) 2000 and were 19.4 million Btu per ton (MMBtu/ton) and 0.43 MMBtu/ton respectively. In order to obtain energy intensity by region for combustion alone, national average feedstock and electricity energy intensities for ammonia production were subtracted from regional total ammonia plant energy intensity from Phylipsen et al., 2002. These values can be seen in Table 4. For those facilities that were not captured among the regions available in Phylipsen et al., 2002, a national value of 15.9 MMBtu/metric tons obtained from Lawrence Berkeley National Laboratory 2002 was used.

	Data obtained from Phylipsen et al. (MMBtu/ton)	Adjusted to represent for only Combustion (MMBtu/ton)	Energy Intensity for fuel combustion (MMBtu/Mt)
Southeast U.S. (Mississippi)	33.7	13.9	15.3
South Central U.S. (Texas/Louisiana)	34.2	14.4	15.8
North Central U.S. (Oklahoma and the mid-west)	35.5	15.7	17.3
National U.S.			15.9

Table 4. Energy Intensity Values for Ammonia Production

Source: Phylipsen, D. et al., 2002. National U.S.: LBNL 2000.

Methane and N_2O emission factors for stationary combustion, shown in Table 5, were derived from Table 2.3 of the 2006 IPCC Guidelines for National Greenhouse Gas Inventories (IPCC 2006) for Manufacturing Industries and Construction. Industrial source emission factors, shown in Table 6, were derived from Table 2.7 of 2006 IPCC Guidelines for National Greenhouse Gas Inventories (IPCC 2006).

Table 5. Default Emission Factors for Stationary Combustion in Manufacturing Industries and Construction

Fuel	CH₄ Default Emission Factor (kg/TJ)	N₂O Default Emission Factor (kg/TJ)
Natural Gas	1	0.1

Source: From Table 2.3 of 2006 IPCC Guidelines for National Greenhouse Gas Inventories.

Basic Technology	Configuration	Emission factors (kg/TJ energy input)	
		CH ₄	N ₂ O
Liquid Fuels			
Residual Fuel Oil Boilers		3	0.3
Gas/Diesel Oil Boilers		0.2	0.4
Large Stationary Diesel Oil Engines>600 hp (447 kW)		4	NA
Liquefied Petroleum Gases Boilers		0.9	4
Solid Fuels			
Other Bituminous/Sub-big. Overfeed Stoker Boilers		1	0.7
Other Bituminous/Sub-Bit. Underfeed Stoker Boilers		14	0.7
Other Bituminous/Sub- bituminous Pulverized	Dry Bottom, wall fired	0.7	0.5
	Dry Bottom, tangentially fired	0.7	1.4
	Wet Bottom	0.9	1.4
Other Bituminous Spreader Stokers		1	0.7
Other Bituminous/Sub-bit. Fluidized Bed Combustor		1	61
Natural Gas			
Boilers		1	1
Gas-Fired Gas Turbines >3MW		4	1
Natural Gas-fired	2-Stroke Lean Burn	693	NA
Reciprocating Engines	4-Stroke Lean Burn	597	NA
	4-Stroke Rich Burn	110	NA
Biomass			
Wood/Wood Waste Boilers		11	7

Table 6. Industrial Source Emission Factors

Source: From Table 2.7 of 2006 IPCC Guidelines for National Greenhouse Gas Inventories.

4.1.2 Capacity Thresholds

Capacity based thresholds are not presented here because all but one plant exceeds the highest emissions-based thresholds. Capacity based thresholds will capture a similar number of facilities and amount of emissions.

4.1.3 No Emissions Threshold

The no emissions threshold includes all ammonia production facilities included in this Technical Support Document regardless of their emissions or capacity.

4.2 Analysis of Emissions and Facilities Covered Per Option

4.2.1 Emissions Thresholds

At the threshold levels of 1,000 metric tons, 10,000 metric tons, and 25,000 metric tons, all facilities exceed the threshold, therefore covering 100% of total emissions. However, at the 100,000 metric tons level, two facilities do not exceed the threshold – the Gordon, GA facility of Shoreline Chemical Millennium Inorganic Chemicals Inc., which produces an estimated 45,000 metric tons CO_2 emissions per year, and the Creston, IA facility of Green Valley Chemical Corp, which produces an estimated 49,000 metric tons CO_2 emissions per year. At the 100,000 metric tons threshold level, 99 percent of emissions would be covered.

4.2.2 Capacity Threshold

Capacity based thresholds were not analyzed.

4.2.3 No Emissions Threshold

The no emissions threshold includes all ammonia production facilities included in this Technical Support Document regardless of their emissions or capacity.

5. Options for Monitoring Methods

Four separate monitoring methods were considered for this technical support document: a simplified emission calculation (Option 1), a mass balance (Option 2), a facility specific calculation (Option 3), and direct measurement (Option 4). All of these options require annual reporting.

5.1 Option 1: Simplified Emissions Calculation

A simplified emissions calculation approach would use IPCC's Tier 1 methodology for estimating emissions, using facility-specific production data and a default emission factor. The equation used for this method can be found in Section 3.1 "Existing Relevant Reporting Programs/Methodologies."

5.2 Option 2: Mass Balance

A mass balance approach uses default carbon content values for pipeline quality natural gas (from the U.S. DOE). Using default carbon content for fuel would not provide the same level of accuracy as using facility-specific carbon contents. This approach is consistent with IPCC Tier 2, DOE 1605 (b) and The Climate Registry "B" rated estimation methods.

5.3 Option 3: Facility Specific Calculation

If the facility does not use CEMS, an alternative hybrid method is proposed based on the IPCC Tier 2 method guidance for determining CO_2 emissions from ammonia production. This method calculates process emissions through facility-level data collection on the consumption of the generally natural gas feedstock, the carbon content of the feedstock, and the quantity of CO_2 sent for downstream use, i.e., urea production. Separate equations are proposed for gaseous, liquid, or solid feedstocks.

For gaseous feedstocks, the following equation would be used to calculate CO₂ emissions:

$$CO_2 = \left(\sum_{1}^{n} \frac{44}{12} * (Fdstk)_n * (CC)_n * \frac{MW}{MVC} - (R_{CO2})_n\right) * 0.001$$

Where:

CO_2	 Annual CO₂ mass emissions arising from feedstock consumption (metric tons)
(Fdstk) _n	= Volume of the gaseous feedstock used in month n (scf of feedstock)
(CC) _n	 Average carbon content of the gaseous feedstock, from the analysis results for month n (kg C per kg of feedstock)
MW	= Molecular weight of the gaseous feedstock (kg/kg-mole)
MVC	 Molar volume conversion factor (849.5 scf per kg-mole at standard conditions)
n	= Months per year
44/12	= Ratio of molecular weights, CO ₂ to carbon
0.001	= Conversion factor from kg to metric tons
$(R_{CO2})_n$	 CO₂ recovered for downstream use for month n (urea or methanol production, CO₂ capture), kg CO₂

For calculating CO₂ emissions from liquid feedstocks, the following equation would be used:

$$CO_2 = \left(\sum_{1}^{n} \frac{44}{12} * (Fdstk)_n * (CC)_n - (R_{CO2})_n\right) * 0.001$$

CO ₂	 Annual CO₂ mass emissions arising from feedstock consumption (metric tons)
(Fdstk) _n =	= Volume of the liquid feedstock used in month "n" (gallons of feedstock)
(CC) _n	 Average carbon content of the gaseous feedstock, from the analysis results for month "n" (kg C per gallon of feedstock)
n	= Months per year
44/12	= Ratio of molecular weights, CO_2 to carbon
0.001	= Conversion factor from kg to metric tons
$(R_{CO2})_n$	= CO_2 recovered for downstream use for month "n" (urea or methanol production, CO_2 capture), kg CO_2 .

For solid feedstocks, emissions of CO₂ would be calculated using the following equation:

$$CO_2 = \left(\sum_{1}^{n} \frac{44}{12} * (Fdstk)_n * (CC)_n - (R_{CO2})_n\right) * 0.001$$

Where:

CO_2	 Annual CO₂ mass emissions arising from feedstock consumption (metric tons)
(Fdstk) _n =	= Mass of the solid feedstock used in month "n" (kg of feedstock)
(CC) _n	 Average carbon content of the solid feedstock, from the analysis results for month "n" (kg C per kg of feedstock)
n	= Months per year
44/12	= Ratio of molecular weights, CO_2 to carbon
0.001	= Conversion factor from kg to metric tons
$(\mathbf{R}_{\mathrm{CO2}})_{\mathrm{n}}$	= CO_2 recovered for downstream use for month "n" (urea or methanol production, CO_2 capture), kg CO_2 .

5.4 Option 4: Direct Measurement

Direct measurement constitutes either measurements of the GHG concentration in the stack gas and the flow rate of the stack gas using a Continuous Emissions Monitoring System (CEMS), or periodic measurement of the GHG concentration in the stack gas and the flow rate of the stack gas using periodic stack testing. Under either a CEMS approach or a stack testing approach, the emissions measurement data would be reported annually.

Elements of a CEMS include a platform and sample probe within the stack to withdraw a sample of the stack gas, an analyzer to measure the concentration of the GHG (e.g., CO_2) in the stack gas, and a flow meter within the stack to measure the flow rate of the stack gas. The emissions are calculated from the concentration of GHGs in the stack gas and the flow rate of the stack gas. The CEMS continuously withdraws and analyzes a sample of the stack gas and continuously measures the GHG concentration and flow rate of the stack gas.

For direct measurement using stack testing, sampling equipment would be periodically brought to the site and installed temporarily in the stack to withdraw a sample of the stack gas and measure the flow rate of the stack gas. Similar to CEMS, for stack testing the emissions are calculated from the concentration of GHGs in the stack gas and the flow rate of the stack gas. The difference between stack testing and continuous monitoring is that the CEMS data provide a continuous measurement of the emissions while a stack testing would be appropriate for those facilities where both inputs (such as feedstock and fuel) and process operating parameters remain relatively consistent over time. In cases where there is the potential for significant variations in the process input characteristics or operating conditions, continuous measurements would be needed to accurately record changes in the actual GHG emissions from the sources resulting from any process variations.

6. Procedures for Estimating Missing Data

Options and considerations for missing data vary depending on the proposed monitoring method. Each option would require a complete record of all measured parameters as well as parameters determined from company records that are used in the GHG emissions calculations (e.g., carbon contents, monthly fuel consumption, etc.).

6.1 Procedures for Option 1: Simplified Emission Calculation

If facility-specific production data is missing for one year, an average value using the production data from the year prior and the year after the missing year may be calculated. Default emission factors are readily available through IPCC guidelines (IPCC 2006).

6.2 **Procedures for Option 2: Mass Balance**

Default emission factors are readily available through the Department of Energy (IPCC 2006).

6.3 Procedures for Option 3: Facility Specific Calculation

For process sources that use the hybrid approach, the following data would be needed: fuel type, fuel consumption, fuel molecular weight (for gaseous fuels), fuel carbon content, and amount of CO₂ recovered for downstream use. In general, the substitute data value could be the arithmetic average of the quality-assured values of that same parameter immediately preceding and immediately following the missing data incident. If no quality-assured data are available prior to the missing data incident, the substitute data value could be the first quality-assured value obtained after the missing data period could be used. For missing oil or gas flow rates, standard missing data procedures in section 2.4.2 of appendix D to part 75 apply. For missing records of solid fuel usage, the substitute data would be the best available estimate of fuel consumption, based on all available process data.

6.4 Procedures for Option 4: Direct Measurement

6.4.1 Continuous Emission Monitoring Data (CEMS)

For options involving direct measurement of CO_2 emissions using CEMS, Part 75 establishes procedures for the management of missing data. Specifically, the procedures for managing missing CO_2 concentration data are specified in §75.35. In general, missing data from the operation of the CEMS may be replaced with substitute data to determine the CO_2 emissions during the period for which CEMS data are missing. Section 75.35(a) requires the owner or operator of a unit with a CO_2 CEMS to substitute for missing CO_2 pollutant concentration data using the procedures specified in paragraphs (b) and (d) of §75.35; paragraph (b) covers operation of the system during the first 720 quality-assured operation hours for the CEMS, and paragraph (d) covers operation of the system after the first 720 quality-assured operating hours are completed.

During the first 720 quality-assured monitor operating hours following initial certification at a particular unit or stack location, the owner or operator would be required to substitute CO_2 pollutant concentration data according to the procedures in §75.31(b). That is, if prior quality-assured data exist, the owner or operator would be required to substitute for each hour of missing data, the average of the data recorded by a certified monitor for the operating hour immediately preceding and immediately following the hour for which data are missing. If there are no prior

quality-assured data, the owner or operator would have to substitute the maximum potential CO_2 concentration for the missing data.

Following the first 720 quality-assured monitor operating hours, the owner or operator would have to follow the same missing data procedures for SO_2 specified in §75.33(b). The specific methods used to estimate missing data would depend on the monitor data availability and the duration of the missing data period.

6.4.2 Stack Testing Data

For options involving direct measurement of CO_2 flow rates or direct measurement of CO_2 emissions using stack testing, "missing data" is not generally anticipated. Stack testing conducted for the purposes of compliance determination is subject to quality assurance guidelines and data quality objectives established by the U.S. EPA, including the Clean Air Act National Stack Testing Guidance published in 2005 (EPA 2005). The 2005 EPA Guidance Document indicates that stack tests should be conducted in accordance with a pre-approved site-specific test plan to ensure that a complete and representative test is conducted. Results of stack tests that do not meet pre-established quality assurance guidelines and data quality objectives would generally not be acceptable for use in emissions reporting.

7. QA/QC Requirements

Facilities might be required to conduct quality assurance and quality control of the production and consumption data, supplier information (e.g., carbon contents), and emission estimates reported. Facilities could be encouraged to prepare an in-depth quality assurance and quality control plan which would include checks on production data, the carbon content information received from the supplier and from the lab analysis, and calculations performed to estimate GHG emissions. Several examples of QA/QC procedures are listed below.

7.1 Stationary Emissions

Facilities could follow the guidelines given by the Stationary Combustion Source TSD.

7.2 Process Emissions

Options and considerations for QA/QC will vary depending on the proposed monitoring method. Each option would require unique QA/QC measures appropriate to the particular methodology employed to ensure proper emission monitoring and reporting.

7.2.1 Continuous Emission Monitoring System (CEMS)

For units using CEMS to measure CO_2 emissions, the equipment could be tested for accuracy and calibrated as necessary by a certified third party vendor. These procedures should be consistent in stringency and data reporting and documentation adequacy with the QA/QC procedures for CEMS described in Part 75 of the Acid Rain Program.

7.2.2 Stack Test Data

EPA could apply current EPA regulations for performance testing under 40 CFR § 63.7(c)(2)(i) that state that before conducting a required performance test, the owner/operator is required to develop a site-specific test plan and, if required, submit the test plan for approval. The test plan

is required to include "a test program summary, the test schedule, data quality objectives, and both an internal and external quality assurance (QA) program" to be applied to the stack test. Data quality objectives are defined under 40 CFR § 63.7(c)(2)(i) as "the pre-test expectations of precision, accuracy, and completeness of data." Under 40 CFR § 63.7(c)(2)(ii), the internal QA program is required to include, "at a minimum, the activities planned by routine operators and analysts to provide an assessment of test data precision; an example of internal QA is the sampling and analysis of replicate samples." Under 40 CFR § 63.7(c)(2)(iii) the external QA program is required to include, "at a minimum, application of plans for a test method performance audit (PA) during the performance test." In addition, according to the 2005 Guidance Document, a site-specific test plan should generally include chain of custody documentation from sample collection through laboratory analysis including transport, and should recognize special sample transport, handling, and analysis instructions necessary for each set of field samples (US EPA 2005).

7.2.3 Equipment Maintenance

For units using flow meters to directly measure the flow rate of fuels, raw materials, products, or process byproducts, flow meters could be required to be calibrated on a scheduled basis in accordance with equipment manufacturer specifications and standards. Flow meter calibration is generally conducted at least annually. A written record of procedures needed to maintain the flow meters in proper operating condition and a schedule for those procedures should be part of the QA/QC plan for the capture or production unit.

An equipment maintenance plan should be developed as part of the QA/QC plan. Elements of a maintenance plan for equipment include the following:

- Conduct regular maintenance of equipment, e.g. flow meters.
 - Keep a written record of procedures needed to maintain the monitoring system in proper operating condition and a schedule for those procedures;
 - Keep a record of all testing, maintenance, or repair activities performed on any monitoring system or component in a location and format suitable for inspection. A maintenance log may be used for this purpose. The following records could be maintained: date, time, and description of any testing, adjustment, repair, replacement, or preventive maintenance action performed on any monitoring system and records of any corrective actions associated with a monitor's outage period. Additionally, any adjustment that recharacterizes a system's ability to record and report emissions data must be recorded (e.g., changing of flow monitor or moisture monitoring system polynomial coefficients, K factors or mathematical algorithms, changing of temperature and pressure coefficients and dilution ratio settings), and a written explanation of the procedures used to make the adjustment(s) shall be kept (EPA 2003).

For units using CEMS to measure CO_2 flow rates or CO_2 emissions, the equipment might be required to be tested for accuracy and calibrated as necessary by a certified third party vendor. These procedures should be consistent in stringency and data reporting and documentation adequacy with the QA/QC procedures for CEMS described in Part 75 of the Acid Rain Program (EPA 2008a).

7.3 Data Management

Data management procedures could be included in the QA/QC Plan. Elements of the data management procedures plan might include:

- Check for temporal consistency in production data, carbonate content data, and emission estimates. A monitoring error is probable if differences between annual data cannot be explained by:
 - Changes in activity levels,
 - Changes concerning fuels or input material,
 - Changes concerning the emitting process (e.g. energy efficiency improvements) (European Commission 2007).
- Determine the "reasonableness" of the emission estimate by comparing it to previous year's estimates and relative to national emission estimate for the industry:
 - Comparison of data on fuel or input material consumed by specific sources with fuel or input material purchasing data and data on stock changes,
 - Comparison of fuel or input material consumption data with fuel or input material purchasing data and data on stock changes,
 - Comparison of emission factors that have been calculated or obtained from the fuel or input material supplier, to national or international reference emission factors of comparable fuels or input materials
 - Comparison of emission factors based on fuel analyses to national or international reference emission factors of comparable fuels, or input materials,
 - Comparison of measured and calculated emissions (European Commission 2007).
- Maintain data documentation, including comprehensive documentation of data received through personal communication:
 - Check that changes in data or methodology are documented

8. Types of Emission Information to be Reported

Information reported may vary depending on the monitoring method selected. However, all facility owners and operators would submit their process CO_2 emissions data and combustion related CO_2 , CH_4 , and N_2O data. For reporting options for emissions (CO_2 , CH_4 , and N_2O) from stationary combustion, refer to EPA-HQ-OAR-2008-0508-004. However, some monitoring options discussed later in section 6 will capture total greenhouse emissions at ammonia production facilities (process and combustion) and we have noted where the monitoring option will sufficiently meet or be consistent with reporting options discussed in the stationary fuel combustion technical support document.

8.1 Other Information to be Reported

In addition, facility owners and operator could submit the following additional data on an annual basis. These data are the basis for calculations and would be needed to understand the emissions data and verify the reasonableness of the reported emissions. The data could include: the total quantity of feedstock consumed for ammonia manufacturing, the quantity of CO_2 captured for use and the end use, if known, the total amount of fuel used to determine CO_2 , CH_4 , and N_2O

from stationary fuel combustion units at ammonia manufacturing facilities, the monthly analyses of carbon content for each feedstock used in ammonia manufacturing, and monthly urea, methanol, and hydrogen production.

The following sections describe data that could be required for specific monitoring options.

8.1.1 Option 1: Simplified Emissions Calculation

For the simplified emissions calculation, the facility should report its ammonia production in addition to GHG emissions.

8.1.2 Option 2: Mass Balance

For the mass balance approach, the facility should report its ammonia production in addition to GHG emissions.

8.1.3 Option 3: Facility Specific Calculation

For the facility-specific calculation method, the facility would report its production data, fuel type, fuel consumption, carbon content of fuel, and quantity of carbon recovered for downstream use.

8.1.4 Option 4: Direct Measurement

For options based on direct measurement, either using a CEMS or through stack testing, the GHG emissions are directly measured at the point of emission.

8.1.4.1 CEMS

For direct measurement using CEMS, the facility would report the GHG emissions measured by the CEMS for each monitored emission point and would also report the monitored GHG concentrations in the stack gas and the monitored stack gas flow rate for each monitored emission point. These data would illustrate how the monitoring data were used to estimate the GHG emissions.

The following data could be reported to support direct measurement of emissions using CEMS:

- The unit ID number (if applicable);
- A code representing the type of unit;
- Maximum product production rate and maximum raw material input rate (in units of metric tons per hour);
- Each type of raw material used and each type of product produced in the unit during the report year;
- The calculated CO₂, CH₄, and N₂O emissions for each type of raw material used and product produced, expressed in metric tons of each gas and in metric tons of CO₂e;
- A code representing the method used to calculate the CO₂ emissions for each type of raw material used (e.g., part 75, Tier 1, Tier 2, etc.);
- If applicable, a code indicating which one of the monitoring and reporting methodologies in part 75 of this chapter was used to quantify the CO₂ emissions;
- The calculated CO₂ emissions from sorbent (if any), expressed in metric tons; and

• The total GHG emissions from the unit for the reporting year, i.e., the sum of the CO₂, CH₄, and N₂O emissions across all raw material and product types, expressed in metric tons of CO₂e.

8.1.4.2 Stack Testing

For direct measurement using stack testing, the facility would report the GHG emissions measured during the stack test, the measured GHG concentrations in the stack gas, the monitored stack gas flow rate for each monitored emission point, and the time period during which the stack test was conducted. The facility should also report the process operating conditions (e.g., raw material feed rates) during the time period during which the test was conducted.

8.2 Additional Data to be Retained Onsite

Facilities could be required to retain data concerning monitoring of GHG emissions onsite for a period of 5 years from the reporting year. For CEMS, these data could include CEMS monitoring system data including continuous-monitored GHG concentrations and stack gas flow rates, and calibration and quality assurance records. For stack testing these data could include stack test reports and associated sampling and chemical analytical data for the stack test. Process data, including process raw material and product feed rates and carbon contents, could also be retained on site. The EPA could use such data to conduct trend analyses and potentially to develop process or activity-specific emission factors for the process.

9. References

IFDC (2005). International Fertilizer Development Center. North America Fertilizer Capacity. Market Information Unit. Market Development Division. September 2005.

IPCC (2006). 2006 IPCC Guidelines for National Greenhouse Gas Inventories. The National Greenhouse Gas Inventories Programme, The Intergovernmental Panel on Climate Change, H.S. Eggleston, L. Buenida, K. Miwa, T Ngara, and K. Tanabe (eds.). Hayama, Kanagawa, Japan.

LBNL (2000). Worrell, E., D. Phylipsen, D. Einstein, and N. Martin, April 2000. Lawrence Berkeley National Laboratory (LBNL), Environmental Energy Technologies Division. Energy Use and Energy Intensity in the U.S. Chemical Industry. http://www.energystar.gov/ia/business/industry/industrial LBNL-44314.pdf

Official Journal of the European Union, August 31, 2007. Commission Decision of 18 July 2007, "Establishing guidelines for the monitoring and reporting of greenhouse gas emissions pursuant to Directive 2003/87/EC of the European Parliament and of the Council. Available at <u>http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2007:229:0001:0085:EN:PDF</u>.

Part 75, Appendix B1, Available at http://www.epa.gov/airmarkt/spm/rule/001000000B.htm.

Phylipsen, D., K. Blok, E. Worrell, and J. de Beer, 2002. Benchmarking the energy efficiency of the Dutch industry: an assessment of the expected effect on energy consumption and CO_2 emissions. Energy Policy 30 (2002) 663–679.

U.S. DOE (2007). Technical Guidelines Voluntary Reporting of Greenhouse Gases (1605(b)) Program. Available at <u>http://www.pi.energy.gov/enhancingGHGregistry/documents/January2007_1605bTechnicalGuid</u> elines.pdf.

U.S. EPA (2005). Clean Air Act National Stack Testing Guidance, U.S. Environmental Protection Agency Office of Enforcement and Compliance Assurance, September 30, 2005, Page 11. <u>www.epa.gov/compliance/resources/policies/monitoring/caa/stacktesting.pdf</u>

U.S. EPA (2007). Climate Leaders, Inventory Guidance, Design Principles Guidance, Chapter 7 "Managing Inventory Quality". Available at: http://www.epa.gov/climateleaders/documents/resources/design_princ_ch7.pdf.

U.S. EPA (2008). *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2006*. U.S. Environmental Protection Agency, Washington D.C. USEPA #430-R-08-005.

USGS (2007). 2006 Minerals Yearbook: Nitrogen. U.S. Geological Survey, Reston, VA. Available at http://minerals.usgs.gov/minerals/pubs/commodity/nitrogen/myb1-2006-nitro.pdf.