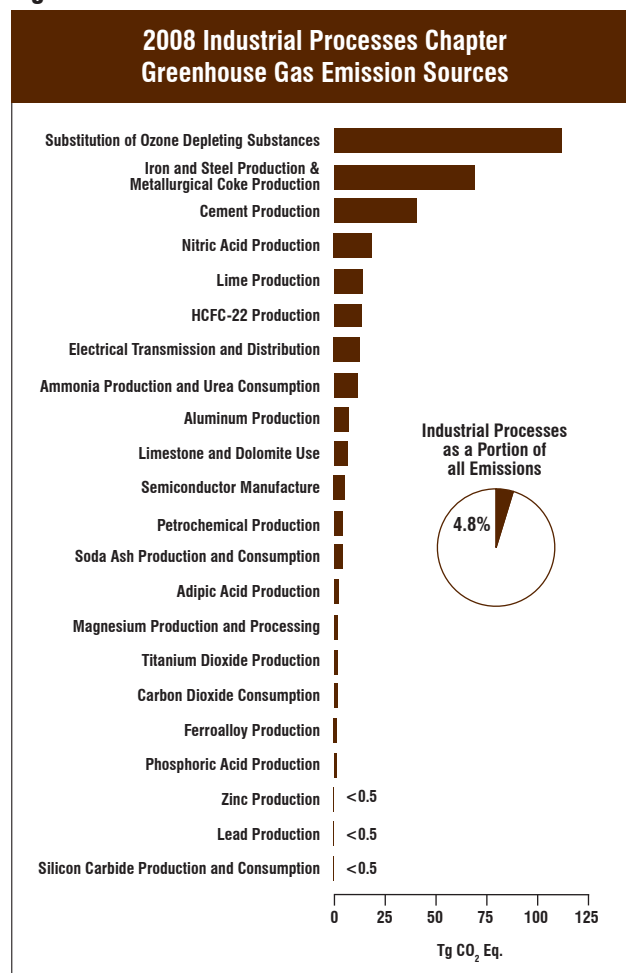


## 4. Industrial Processes

**G**reenhouse gas emissions are produced as the by-products of various non-energy-related industrial activities. That is, these emissions are produced from an industrial process itself and are not directly a result of energy consumed during the process. For example, raw materials can be chemically transformed from one state to another. This transformation can result in the release of greenhouse gases such as carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), or nitrous oxide (N<sub>2</sub>O). The processes addressed in this chapter include iron and steel production and metallurgical coke production, cement production, lime production, ammonia production and urea consumption, limestone and dolomite consumption (e.g., flux stone, flue gas desulfurization, and glass manufacturing), soda ash production and use, aluminum production, titanium dioxide production, CO<sub>2</sub> consumption, ferroalloy production, phosphoric acid production, zinc production, lead production, petrochemical production, silicon carbide production and consumption, nitric acid production, and adipic acid production (see Figure 4-1).

In addition to the three greenhouse gases listed above, there are also industrial sources of man-made fluorinated compounds called hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulfur hexafluoride (SF<sub>6</sub>). The present contribution of these gases to the radiative forcing effect of all anthropogenic greenhouse gases is small; however, because of their extremely long lifetimes, many of them will continue to accumulate in the atmosphere as long as emissions continue. In addition, many of these gases have high global warming potentials; SF<sub>6</sub> is the most potent greenhouse gas the Intergovernmental Panel on Climate Change (IPCC) has evaluated. Usage of HFCs for the substitution of ozone depleting substances is growing rapidly, as they are the primary substitutes for ozone depleting substances (ODSs), which are being phased-out under the *Montreal Protocol on Substances that Deplete the Ozone Layer*. In addition to their use as ODS substitutes, HFCs, PFCs, SF<sub>6</sub>, and other fluorinated compounds are employed and emitted by a number of other industrial sources in the United States. These industries include aluminum production, HCFC-22 production, semiconductor manufacture, electric power transmission and distribution, and magnesium metal production and processing.

**Figure 4-1**



In 2008, industrial processes generated emissions of 334.5 teragrams of CO<sub>2</sub> equivalent (Tg CO<sub>2</sub> Eq.), or 5 percent of total U.S. greenhouse gas emissions. CO<sub>2</sub> emissions from all industrial processes were 162.1 Tg CO<sub>2</sub> Eq. (162,111 Gg) in 2008, or 3 percent of total U.S. CO<sub>2</sub> emissions. CH<sub>4</sub> emissions from industrial processes resulted in emissions of approximately 1.6 Tg CO<sub>2</sub> Eq. (75 Gg) in 2008, which was less than 1 percent of U.S. CH<sub>4</sub> emissions. N<sub>2</sub>O emissions from adipic acid and nitric acid production were 21.1 Tg CO<sub>2</sub> Eq. (68 Gg) in 2008, or 7 percent of total U.S. N<sub>2</sub>O emissions. In 2008 combined emissions of HFCs, PFCs and SF<sub>6</sub> totaled 149.7 Tg CO<sub>2</sub> Eq. Overall, emissions from industrial processes increased by 5 percent from 1990 to 2008 despite decreases in emissions from several industrial processes, such as iron and steel production and metallurgical coke production, ammonia production and urea consumption, and adipic acid production. The increase in overall emissions was primarily driven by a rise in the emissions from the use of substitutes for ozone depleting substances.

Table 4-1 summarizes emissions for the Industrial Processes chapter in units of Tg CO<sub>2</sub> Eq., while unweighted native gas emissions in Gg are provided in Table 4-2. The source descriptions that follow in the chapter are presented in the order as reported to the UNFCCC in the common reporting format tables, corresponding generally to: mineral products, chemical production, metal production, and emissions from the uses of HFCs, PFCs, and SF<sub>6</sub>.

Methodological recalculations were applied to the entire time-series to ensure time-series consistency from 1990 through 2008. Details on the emission trends through time are described in more detail in the Methodology section, above.

## QA/QC and Verification Procedures

Tier 1 quality assurance and quality control procedures have been performed for all industrial process sources. For industrial process sources of CO<sub>2</sub> and CH<sub>4</sub> emissions, a detailed plan was developed and implemented. This plan was based on U.S. strategy, but was tailored to include specific procedures recommended for these sources. Two types of checks were performed using this plan (1) general, or Tier 1, procedures that focus on annual procedures and checks to be used when gathering, maintaining, handling, documenting, checking and archiving the data, supporting documents, and files, and (2) source-category specific, or

Tier 2, procedures that focus on procedures and checks of the emission factors, activity data, and methodologies used for estimating emissions from the relevant Industrial Processes sources. Examples of these procedures include, among others, checks to ensure that activity data and emission estimates are consistent with historical trends; that, where possible, consistent and reputable data sources are used across sources; that interpolation or extrapolation techniques are consistent across sources; and that common datasets and factors are used where applicable.

The general method employed to estimate emissions for industrial processes, as recommended by the IPCC, involves multiplying production data (or activity data) for each process by an emission factor per unit of production. The uncertainty in the emission estimates is therefore generally a function of a combination of the uncertainties surrounding the production and emission factor variables. Uncertainty of activity data and the associated probability density functions for industrial processes CO<sub>2</sub> sources were estimated based on expert assessment of available qualitative and quantitative information. Uncertainty estimates and probability density functions for the emission factors used to calculate emissions from this source were devised based on IPCC recommendations.

Activity data is obtained through a survey of manufacturers conducted by various organizations (specified within each source); the uncertainty of the activity data is a function of the reliability of plant-level production data and is influenced by the completeness of the survey response. The emission factors used were either derived using calculations that assume precise and efficient chemical reactions, or were based upon empirical data in published references. As a result, uncertainties in the emission coefficients can be attributed to, among other things, inefficiencies in the chemical reactions associated with each production process or to the use of empirically-derived emission factors that are biased; therefore, they may not represent U.S. national averages. Additional assumptions are described within each source.

The uncertainty analysis performed to quantify uncertainties associated with the 2008 inventory estimates from industrial processes continues a multi-year process for developing credible quantitative uncertainty estimates for these source categories using the IPCC Tier 2 approach. As the process continues, the type and the characteristics of

**Table 4-1: Emissions from Industrial Processes (Tg CO<sub>2</sub> Eq.)**

Gas/Source	1990	1995	2000	2005	2006	2007	2008
<b>CO<sub>2</sub></b>	<b>191.5</b>	<b>192.6</b>	<b>187.7</b>	<b>167.0</b>	<b>171.5</b>	<b>174.0</b>	<b>162.1</b>
Iron and Steel Production and Metallurgical Coke Production	102.6	95.7	88.1	67.7	70.5	72.8	69.0
<i>Iron and Steel Production</i>	97.1	90.7	83.7	63.9	66.9	69.0	63.7
<i>Metallurgical Coke Production</i>	5.5	5.0	4.4	3.8	3.7	3.8	5.3
Cement Production	33.3	36.8	41.2	45.9	46.6	45.2	41.1
Lime Production	11.5	13.3	14.1	14.4	15.1	14.6	14.3
Ammonia Production & Urea Consumption	16.8	17.8	16.4	12.8	12.3	14.0	11.8
Limestone and Dolomite Use	5.1	6.7	5.1	6.8	8.0	7.7	6.6
Aluminum Production	6.8	5.7	6.1	4.1	3.8	4.3	4.5
Soda Ash Production and Consumption	4.1	4.3	4.2	4.2	4.2	4.1	4.1
Petrochemical Production	3.3	4.1	4.5	4.2	3.8	3.9	3.4
Titanium Dioxide Production	1.2	1.5	1.8	1.8	1.8	1.9	1.8
Carbon Dioxide Consumption	1.4	1.4	1.4	1.3	1.7	1.9	1.8
Ferroalloy Production	2.2	2.0	1.9	1.4	1.5	1.6	1.6
Phosphoric Acid Production	1.5	1.5	1.4	1.4	1.2	1.2	1.2
Zinc Production	0.9	1.0	1.1	0.5	0.5	0.4	0.4
Lead Production	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Silicon Carbide Production and Consumption	0.4	0.3	0.2	0.2	0.2	0.2	0.2
<b>CH<sub>4</sub></b>	<b>1.9</b>	<b>2.1</b>	<b>2.2</b>	<b>1.8</b>	<b>1.7</b>	<b>1.7</b>	<b>1.6</b>
Petrochemical Production	0.9	1.1	1.2	1.1	1.0	1.0	0.9
Iron and Steel Production and Metallurgical Coke Production	1.0	1.0	0.9	0.7	0.7	0.7	0.6
<i>Iron and Steel Production</i>	1.0	1.0	0.9	0.7	0.7	0.7	0.6
<i>Metallurgical Coke Production</i>	+	+	+	+	+	+	+
Ferroalloy Production	+	+	+	+	+	+	+
Silicon Carbide Production and Consumption	+	+	+	+	+	+	+
<b>N<sub>2</sub>O</b>	<b>34.7</b>	<b>38.6</b>	<b>26.3</b>	<b>22.6</b>	<b>21.5</b>	<b>24.2</b>	<b>21.1</b>
Nitric Acid Production	18.9	21.0	20.7	17.6	17.2	20.5	19.0
Adipic Acid Production	15.8	17.6	5.5	5.0	4.3	3.7	2.0
<b>HFCs</b>	<b>36.9</b>	<b>62.2</b>	<b>103.2</b>	<b>119.3</b>	<b>121.8</b>	<b>127.4</b>	<b>126.9</b>
Substitution of Ozone Depleting Substances <sup>a</sup>	0.3	29.0	74.3	103.2	107.7	110.1	113.0
HCFC-22 Manufacture	36.4	33.0	28.6	15.8	13.8	17.0	13.6
Semiconductor Manufacturing HFCs	0.2	0.3	0.3	0.2	0.3	0.3	0.3
<b>SF<sub>6</sub></b>	<b>32.6</b>	<b>27.9</b>	<b>19.1</b>	<b>17.8</b>	<b>17.0</b>	<b>16.1</b>	<b>16.1</b>
Electrical Transmission and Distribution	26.6	21.4	15.0	14.0	13.2	12.7	13.1
Magnesium Production and Processing	5.4	5.6	3.0	2.9	2.9	2.6	2.0
Semiconductor Manufacturing SF <sub>6</sub>	0.5	0.9	1.1	1.0	1.0	0.8	1.1
<b>PFCs</b>	<b>20.8</b>	<b>15.6</b>	<b>13.5</b>	<b>6.2</b>	<b>6.0</b>	<b>7.5</b>	<b>6.7</b>
Aluminum Production	18.5	11.8	8.6	3.0	2.5	3.8	2.7
Semiconductor Manufacturing PFCs	2.2	3.8	4.9	3.2	3.5	3.6	4.0
<b>Total</b>	<b>318.3</b>	<b>339.1</b>	<b>351.9</b>	<b>334.7</b>	<b>339.7</b>	<b>350.9</b>	<b>334.5</b>

+ Does not exceed 0.05 Tg CO<sub>2</sub> Eq.

<sup>a</sup> Small amounts of PFC emissions also result from this source.

Note: Totals may not sum due to independent rounding.

the actual probability density functions underlying the input variables are identified and better characterized (resulting in development of more reliable inputs for the model, including accurate characterization of correlation between variables),

based primarily on expert judgment. Accordingly, the quantitative uncertainty estimates reported in this section should be considered illustrative and as iterations of ongoing efforts to produce accurate uncertainty estimates.

**Table 4-2: Emissions from Industrial Processes (Gg)**

Gas/Source	1990	1995	2000	2005	2006	2007	2008
<b>CO<sub>2</sub></b>	<b>191,498</b>	<b>192,580</b>	<b>187,715</b>	<b>167,034</b>	<b>171,543</b>	<b>174,005</b>	<b>162,111</b>
Iron and Steel Production and Metallurgical Coke Production	102,564	95,748	88,110	67,731	70,539	72,802	69,010
<i>Iron and Steel Production</i>	97,066	90,711	83,728	63,882	66,857	68,996	63,729
<i>Metallurgical Coke Production</i>	5,498	5,037	4,381	3,849	3,682	3,806	5,281
Cement Production	33,278	36,847	41,190	45,910	46,562	45,229	41,147
Lime Production	11,533	13,325	14,088	14,379	15,100	14,595	14,330
Ammonia Production & Urea Consumption	16,831	17,796	16,402	12,849	12,300	13,968	11,755
Limestone and Dolomite Use	5,127	6,683	5,056	6,768	8,035	7,702	6,617
Aluminum Production	6,831	5,659	6,086	4,142	3,801	4,251	4,477
Soda Ash Production and Consumption	4,141	4,304	4,181	4,228	4,162	4,140	4,111
Petrochemical Production	3,311	4,101	4,479	4,181	3,837	3,931	3,449
Titanium Dioxide Production	1,195	1,526	1,752	1,755	1,836	1,930	1,809
Carbon Dioxide Consumption	1,416	1,422	1,421	1,321	1,709	1,867	1,780
Ferroalloy Production	2,152	2,036	1,893	1,392	1,505	1,552	1,599
Phosphoric Acid Production	1,529	1,513	1,382	1,386	1,167	1,166	1,187
Zinc Production	929	993	1,115	506	513	411	402
Lead Production	285	298	311	266	270	267	264
Silicon Carbide Production and Consumption	375	329	248	219	207	196	175
<b>CH<sub>4</sub></b>	<b>88</b>	<b>100</b>	<b>104</b>	<b>86</b>	<b>83</b>	<b>82</b>	<b>75</b>
Petrochemical Production	41	52	59	51	48	48	43
Iron and Steel Production and Metallurgical Coke Production	46	47	44	34	35	33	31
<i>Iron and Steel Production</i>	46	47	44	34	35	33	31
<i>Metallurgical Coke Production</i>	+	+	+	+	+	+	+
Ferroalloy Production	1	1	1	+	+	+	+
Silicon Carbide Production and Consumption	1	1	1	+	+	+	+
<b>N<sub>2</sub>O</b>	<b>112</b>	<b>125</b>	<b>85</b>	<b>73</b>	<b>70</b>	<b>78</b>	<b>68</b>
Nitric Acid Production	61	68	67	57	56	66	61
Adipic Acid Production	51	57	18	16	14	12	7
<b>HFCs</b>	<b>M</b>	<b>M</b>	<b>M</b>	<b>M</b>	<b>M</b>	<b>M</b>	<b>M</b>
Substitution of Ozone Depleting Substances <sup>a</sup>	M	M	M	M	M	M	M
HCFC-22 Production	3	3	2	1	1	1	1
Semiconductor Manufacturing HFCs	+	+	+	+	+	+	+
<b>SF<sub>6</sub></b>	<b>1</b>	<b>1</b>	<b>1</b>	<b>1</b>	<b>1</b>	<b>1</b>	<b>1</b>
Electrical Transmission and Distribution	1	1	1	1	1	1	1
Magnesium Production and Processing	+	+	+	+	+	+	+
Semiconductor Manufacturing SF <sub>6</sub>	+	+	+	+	+	+	+
<b>PFCs</b>	<b>M</b>	<b>M</b>	<b>M</b>	<b>M</b>	<b>M</b>	<b>M</b>	<b>M</b>
Aluminum Production	M	M	M	M	M	M	M
Semiconductor Manufacturing PFCs	M	M	M	M	M	M	M

+ Does not exceed 0.5 Gg.  
M (Mixture of gases).  
<sup>a</sup> Small amounts of PFC emissions also result from this source.  
Note: Totals may not sum due to independent rounding.

The correlation among data used for estimating emissions for different sources can influence the uncertainty analysis of each individual source. While the uncertainty analysis

recognizes very significant connections among sources, a more comprehensive approach that accounts for all linkages will be identified as the uncertainty analysis moves forward.

## 4.1. Cement Production (IPCC Source Category 2A1)

Cement production is an energy- and raw-material-intensive process that results in the generation of CO<sub>2</sub> from both the energy consumed in making the cement and the chemical process itself.<sup>1</sup> Cement is produced in 37 states and Puerto Rico. Carbon dioxide emitted from the chemical process of cement production is the second largest source of industrial CO<sub>2</sub> emissions in the United States.

During the cement production process, calcium carbonate (CaCO<sub>3</sub>) is heated in a cement kiln at a temperature of about 1,450°C (2,400°F) to form lime (i.e., calcium oxide or CaO) and CO<sub>2</sub> in a process known as calcination or calcining. A very small amount of carbonates other than CaCO<sub>3</sub> and non-carbonates are also present in the raw material; however, for calculation purposes all of the raw material is assumed to be CaCO<sub>3</sub>. Next, the lime is combined with silica-containing materials to produce clinker (an intermediate product), with the earlier by-product CO<sub>2</sub> being released to the atmosphere. The clinker is then allowed to cool, mixed with a small amount of gypsum, and potentially other materials (e.g., slag) and used to make portland cement.<sup>2</sup>

In 2008, U.S. clinker production—including Puerto Rico—totaled 79,572 thousand metric tons (USGS 2009b). The resulting emissions of CO<sub>2</sub> from 2008 cement production were estimated to be 41.1 Tg CO<sub>2</sub> Eq. (41,147 Gg) (see Table 4-3).

After falling in 1991 by two percent from 1990 levels, cement production emissions grew every year through 2006, and then decreased from 2006 to 2008. Overall, from 1990 to 2008, emissions increased by 24 percent. Cement continues to be a critical component of the construction industry; therefore, the availability of public construction funding, as well as overall economic growth, have had considerable influence on cement production.

<sup>1</sup> The CO<sub>2</sub> emissions related to the consumption of energy for cement manufacture are accounted for under CO<sub>2</sub> from Fossil Fuel Combustion in the Energy chapter.

<sup>2</sup> Approximately six percent of total clinker production is used to produce masonry cement, which is produced using plasticizers (e.g., ground limestone, lime) and portland cement. CO<sub>2</sub> emissions that result from the production of lime used to create masonry cement are included in the Lime Manufacture source category (van Oss 2008c).

**Table 4-3: CO<sub>2</sub> Emissions from Cement Production (Tg CO<sub>2</sub> Eq. and Gg)**

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	33.3	33,278
1995	36.8	36,847
2000	41.2	41,190
2005	45.9	45,910
2006	46.6	46,562
2007	45.2	45,229
2008	41.1	41,147

### Methodology

Carbon dioxide emissions from cement production are created by the chemical reaction of carbon-containing minerals (i.e., calcining limestone) in the cement kiln. While in the kiln, limestone is broken down into CO<sub>2</sub> and lime with the CO<sub>2</sub> released to the atmosphere. The quantity of CO<sub>2</sub> emitted during cement production is directly proportional to the lime content of the clinker. During calcination, each mole of CaCO<sub>3</sub> (i.e., limestone) heated in the clinker kiln forms one mole of lime (CaO) and one mole of CO<sub>2</sub>:



Carbon dioxide emissions were estimated by applying an emission factor, in tons of CO<sub>2</sub> released per ton of clinker produced, to the total amount of clinker produced. The emission factor used in this analysis is the product of the average lime fraction for clinker of 65 percent (van Oss 2008c) and a constant reflecting the mass of CO<sub>2</sub> released per unit of lime. This calculation yields an emission factor of 0.51 tons of CO<sub>2</sub> per ton of clinker produced, which was determined as follows:

$$\begin{aligned} \text{EF}_{\text{Clinker}} &= 0.65 \text{ CaO} \times \left[ \frac{44.01 \text{ g/mole CO}_2}{56.08 \text{ g/mole CaO}} \right] \\ &= 0.51 \text{ tons CO}_2/\text{ton clinker} \end{aligned}$$

During clinker production, some of the clinker precursor materials remain in the kiln as non-calcinated, partially calcinated, or fully calcinated cement kiln dust (CKD). The emissions attributable to the calcinated portion of the CKD are not accounted for by the clinker emission factor. The IPCC recommends that these additional CKD CO<sub>2</sub> emissions should be estimated as two percent of the CO<sub>2</sub> emissions

**Table 4-4: Clinker Production (Gg)**

Year	Clinker
1990	64,355
1995	71,257
2000	79,656
2005	88,783
2006	90,045
2007	87,466
2008	79,572

calculated from clinker production.<sup>3</sup> Total cement production emissions were calculated by adding the emissions from clinker production to the emissions assigned to CKD (IPCC 2006).<sup>4</sup>

The 1990 through 2007 activity data for clinker production (see Table 4-4) were obtained through the *USGS Mineral Yearbook: Cement* (US Bureau of Mines 1990 through 1993, USGS 1995 through 2009a). The 2008 activity data were obtained through the USGS Mineral Industry Survey (2009b). The data were compiled by USGS through questionnaires sent to domestic clinker and cement manufacturing plants.

## Uncertainty and Time-Series Consistency

The uncertainties contained in these estimates are primarily due to uncertainties in the lime content of clinker and in the percentage of CKD recycled inside the cement kiln. Uncertainty is also associated with the assumption

that all calcium-containing raw materials are CaCO<sub>3</sub> when a small percentage likely consists of other carbonate and non-carbonate raw materials. The lime content of clinker varies from 60 to 67 percent (van Oss 2008b). CKD loss can range from 1.5 to 8 percent depending upon plant specifications. Additionally, some amount of CO<sub>2</sub> is reabsorbed when the cement is used for construction. As cement reacts with water, alkaline substances such as calcium hydroxide are formed. During this curing process, these compounds may react with CO<sub>2</sub> in the atmosphere to create calcium carbonate. This reaction only occurs in roughly the outer 0.2 inches of surface area. Because the amount of CO<sub>2</sub> reabsorbed is thought to be minimal, it was not estimated.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-5. Cement Production CO<sub>2</sub> emissions were estimated to be between 35.8 and 46.7 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level. This indicates a range of approximately 13 percent below and 13 percent above the emission estimate of 41.2 Tg CO<sub>2</sub> Eq.

Methodological recalculations were applied to the entire time series to ensure time-series consistency from 1990 through 2008. Details on the emission trends through time are described in more detail in the Methodology section, above.

## Planned Improvements

Future improvements to the cement source category involve continued research into emission factors for clinker production and CKD. Research has been conducted into the accuracy and appropriateness of default emission factors

**Table 4-5: Tier 2 Quantitative Uncertainty Estimates for CO<sub>2</sub> Emissions from Cement Production (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2008 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Cement Production	CO <sub>2</sub>	41.2	35.8	46.7	-13%	+13%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

<sup>3</sup> Default IPCC clinker and CKD emission factors were verified through expert consultation with the Portland Cement Association (PCA 2008) and van Oss (2008a).

<sup>4</sup> The 2 percent CO<sub>2</sub> addition associated with CKD is included in the emission estimate for completeness. The cement emission estimate also includes an assumption that all raw material is limestone (CaCO<sub>3</sub>) when in fact a small percentage is likely composed of non-carbonate materials. Together these assumptions may result in a small emission overestimate (van Oss 2008c).

and reporting methodology used by other organizations. As these methodologies continue to develop, the cement source category will be updated with any improvements to IPCC assumptions for clinker and CKD emissions.

## 4.2. Lime Production (IPCC Source Category 2A2)

Lime is an important manufactured product with many industrial, chemical, and environmental applications. Its major uses are in steel making, flue gas desulfurization (FGD) systems at coal-fired electric power plants, construction, and water purification. For U.S. operations, the term “lime” actually refers to a variety of chemical compounds. These include calcium oxide (CaO), or high-calcium quicklime; calcium hydroxide (Ca(OH)<sub>2</sub>), or hydrated lime; dolomitic quicklime ([CaO•MgO]); and dolomitic hydrate ([Ca(OH)<sub>2</sub>•MgO] or [Ca(OH)<sub>2</sub>•Mg(OH)<sub>2</sub>]).

Lime production involves three main processes: stone preparation, calcination, and hydration. CO<sub>2</sub> is generated during the calcination stage, when limestone—mostly calcium carbonate (CaCO<sub>3</sub>)—is roasted at high temperatures in a kiln to produce CaO and CO<sub>2</sub>. The CO<sub>2</sub> is given off as a gas and is normally emitted to the atmosphere. Some of the CO<sub>2</sub> generated during the production process, however, is recovered at some facilities for use in sugar refining and precipitated calcium carbonate (PCC) production.<sup>5</sup> In certain additional applications, lime reabsorbs CO<sub>2</sub> during use.

Lime production in the United States—including Puerto Rico—was reported to be 19,838 thousand metric tons in 2008 (USGS 2009b). This resulted in estimated CO<sub>2</sub> emissions of 14.3 Tg CO<sub>2</sub> Eq. (or 14,330 Gg) (see Table 4-6 and Table 4-7).

The contemporary lime market is approximately distributed across five end-use categories as follows: metallurgical uses, 36 percent; environmental uses, 30 percent; chemical and industrial uses, 22 percent; construction uses, 10 percent; and refractory dolomite, 1 percent. In the construction sector, lime is used to improve durability in

<sup>5</sup> PCC is obtained from the reaction of CO<sub>2</sub> with calcium hydroxide. It is used as a filler and/or coating in the paper, food, and plastic industries.

**Table 4-6: CO<sub>2</sub> Emissions from Lime Production (Tg CO<sub>2</sub> Eq. and Gg)**

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	11.5	11,533
1995	13.3	13,325
2000	14.1	14,088
2005	14.4	14,379
2006	15.1	15,100
2007	14.6	14,595
2008	14.3	14,330

**Table 4-7: Potential, Recovered, and Net CO<sub>2</sub> Emissions from Lime Production (Gg)**

Year	Potential	Recovered <sup>a</sup>	Net Emissions
1990	12,004	471	11,533
1995	14,019	694	13,325
2000	14,872	784	14,088
2005	15,131	752	14,379
2006	15,825	725	15,100
2007	15,264	669	14,595
2008	14,977	647	14,330

<sup>a</sup> For sugar refining and PCC production.  
Note: Totals may not sum due to independent rounding.

plaster, stucco, and mortars, as well as to stabilize soils. In 2008, the amount of lime used for construction decreased by 14 percent from 2007 levels (USGS 2009b).

Lime production in 2008 decreased by 2 percent compared to 2007, owing mostly to a downturn in major markets including construction and steel (USGS 2009b). Overall, from 1990 to 2008, lime production has increased by 24 percent (USGS 1992 through 2007 & 2009a, USGS 2009b). Annual consumption for industrial and chemical and metallurgical consumption decreased slightly or were essentially unchanged (USGS 2009b). The environmental sector exhibited a slight increase in lime use consumption compared with 2007 levels due to the nearly 6 percent increase in consumption for flue gas desulfurization (USGS 2009b).

## Methodology

During the calcination stage of lime production, CO<sub>2</sub> is given off as a gas and normally exits the system with the stack gas. To calculate emissions, the amounts of high-calcium and dolomitic lime produced were multiplied by their respective emission factors. The emission factor is the product of a constant reflecting the mass of CO<sub>2</sub> released per unit of lime and the average calcium plus magnesium oxide (CaO + MgO) content for lime (95 percent for both types of lime) (IPCC 2006). The emission factors were calculated as follows:

For high-calcium lime:

$$[(44.01 \text{ g/mole CO}_2) \div (56.08 \text{ g/mole CaO})] \times (0.95 \text{ CaO/lime}) = 0.75 \text{ g CO}_2/\text{g lime}$$

For dolomitic lime:

$$[(88.02 \text{ g/mole CO}_2) \div (96.39 \text{ g/mole CaO})] \times (0.95 \text{ CaO/lime}) = 0.87 \text{ g CO}_2/\text{g lime}$$

Production was adjusted to remove the mass of chemically combined water found in hydrated lime, determined according to the molecular weight ratios of H<sub>2</sub>O to (Ca(OH)<sub>2</sub> and [Ca(OH)<sub>2</sub>•Mg(OH)<sub>2</sub>]) (IPCC 2000). These factors set the chemically combined water content to 24.3 percent for high-calcium hydrated lime, and 27.2 percent for dolomitic hydrated lime.

Lime emission estimates were multiplied by a factor of 1.02 to account for lime kiln dust (LKD), which is produced as a by-product during the production of lime (IPCC 2006).

Lime emission estimates were further adjusted to account for PCC producers and sugar refineries that recover CO<sub>2</sub> emitted by lime production facilities for use as an input into production or refining processes. For CO<sub>2</sub> recovery by sugar refineries, lime consumption estimates from USGS

were multiplied by a CO<sub>2</sub> recovery factor to determine the total amount of CO<sub>2</sub> recovered from lime production facilities. According to industry surveys, sugar refineries use captured CO<sub>2</sub> for 100 percent of their CO<sub>2</sub> input (Lutter 2009). CO<sub>2</sub> recovery by PCC producers was determined by multiplying estimates for the percentage CO<sub>2</sub> of production weight for PCC production at lime plants by a CO<sub>2</sub> recovery factor based on the amount of purchased CO<sub>2</sub> by PCC manufacturers (Prillaman 2008 and 2009). As data were only available starting in 2007, CO<sub>2</sub> recovery for the period 1990 through 2006 was extrapolated by determining a ratio of PCC production at lime facilities to lime consumption for PCC (USGS 2002 through 2007 & 2009a, USGS 2009b).

Lime production data (high-calcium- and dolomitic-quicklime, high-calcium- and dolomitic-hydrated, and dead-burned dolomite) for 1990 through 2008 (see Table 4-8) were obtained from USGS (1992 through 2007 & 2009a, 2009b). Natural hydraulic lime, which is produced from CaO and hydraulic calcium silicates, is not produced in the United States (USGS 2009b). Total lime production was adjusted to account for the water content of hydrated lime by converting hydrate to oxide equivalent, based on recommendations from the *IPCC Good Practice Guidance* and is presented in Table 4-9 (USGS 1992 through 2007 & 2009a, USGS 2009b, IPCC 2000). The CaO and CaO•MgO contents of lime were obtained from the IPCC (IPCC 2006). Since data for the individual lime types (high calcium and dolomitic) was not provided prior to 1997, total lime production for 1990 through 1996 was calculated according to the three year distribution from 1997 to 1999. Lime consumed by PCC producers and sugar refineries were obtained from USGS (1992 through 2007 & 2009a, 2009b).

**Table 4-8: High-Calcium- and Dolomitic-Quicklime, High-Calcium- and Dolomitic-Hydrated, and Dead-Burned-Dolomite Lime Production (Gg)**

Year	High-Calcium Quicklime	Dolomitic Quicklime	High-Calcium Hydrated	Dolomitic Hydrated	Dead-Burned Dolomite
1990	11,166	2,234	1,781	319	342
1995	13,165	2,635	2,027	363	308
2000	14,300	3,000	1,550	421	200
2005	14,100	2,990	2,220	474	200
2006	15,000	2,950	2,370	409	200
2007	14,700	2,700	2,240	352	200
2008	14,900	2,310	2,070	358	200



**Table 4-9: Adjusted Lime Production<sup>a</sup> (Gg)**

Year	High-Calcium	Dolomitic
1990	12,514	2,809
1995	14,700	3,207
2000	15,473	3,506
2005	15,781	3,535
2006	16,794	3,448
2007	16,396	3,156
2008	16,467	2,771

<sup>a</sup> Minus water content of hydrated lime.

## Uncertainty and Time-Series Consistency

The uncertainties contained in these estimates can be attributed to slight differences in the chemical composition of these products and recovery rates for sugar refineries and PCC manufacturers located at lime plants. Although the methodology accounts for various formulations of lime, it does not account for the trace impurities found in lime, such as iron oxide, alumina, and silica. Due to differences in the limestone used as a raw material, a rigid specification of lime material is impossible. As a result, few plants produce lime with exactly the same properties.

In addition, a portion of the CO<sub>2</sub> emitted during lime production will actually be reabsorbed when the lime is consumed. As noted above, lime has many different chemical, industrial, environmental, and construction applications. In many processes, CO<sub>2</sub> reacts with the lime to create calcium carbonate (e.g., water softening). CO<sub>2</sub> reabsorption rates vary, however, depending on the application. For example, 100 percent of the lime used to produce precipitated calcium carbonate reacts with CO<sub>2</sub>; whereas most of the lime used in steel making reacts with impurities such as silica, sulfur, and aluminum compounds. A detailed accounting of lime use in the United States and further research into the associated processes are required to quantify the amount of CO<sub>2</sub> that is reabsorbed.<sup>6</sup>

<sup>6</sup> Representatives of the National Lime Association estimate that CO<sub>2</sub> reabsorption that occurs from the use of lime may offset as much as a quarter of the CO<sub>2</sub> emissions from calcination (Males 2003).

In some cases, lime is generated from calcium carbonate by-products at pulp mills and water treatment plants.<sup>7</sup> The lime generated by these processes is not included in the USGS data for commercial lime consumption. In the pulping industry, mostly using the Kraft (sulfate) pulping process, lime is consumed in order to causticize a process liquor (green liquor) composed of sodium carbonate and sodium sulfide. The green liquor results from the dilution of the smelt created by combustion of the black liquor where biogenic C is present from the wood. Kraft mills recover the calcium carbonate “mud” after the causticizing operation and calcine it back into lime—thereby generating CO<sub>2</sub>—for reuse in the pulping process. Although this re-generation of lime could be considered a lime manufacturing process, the CO<sub>2</sub> emitted during this process is mostly biogenic in origin, and therefore is not included in Inventory totals (Miner and Upton 2002).

In the case of water treatment plants, lime is used in the softening process. Some large water treatment plants may recover their waste calcium carbonate and calcine it into quicklime for reuse in the softening process. Further research is necessary to determine the degree to which lime recycling is practiced by water treatment plants in the United States.

Uncertainties also remain surrounding recovery rates used for sugar refining and PCC production. The recovery rate for sugar refineries is based on two sugar beet processing and refining facilities located in California that use 100 percent recovered CO<sub>2</sub> from lime plants (Lutter 2009). This analysis assumes that all sugar refineries located on-site at lime plants also use 100 percent recovered CO<sub>2</sub>. The recovery rate for PCC producers located on-site at lime plants is based on the 2008 value for PCC manufactured at commercial lime plants, given by the National Lime Association (Prillaman 2009).

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-10. Lime CO<sub>2</sub> emissions were estimated to be between 13.2 and 15.6 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level. This indicates a range of approximately 8 percent below and 9 percent above the emission estimate of 14.3 Tg CO<sub>2</sub> Eq.

<sup>7</sup> Some carbide producers may also regenerate lime from their calcium hydroxide by-products, which does not result in emissions of CO<sub>2</sub>. In making calcium carbide, quicklime is mixed with coke and heated in electric furnaces. The regeneration of lime in this process is done using a waste calcium hydroxide (hydrated lime) [CaC<sub>2</sub> + 2H<sub>2</sub>O → C<sub>2</sub>H<sub>2</sub> + Ca(OH)<sub>2</sub>], not calcium carbonate [CaCO<sub>3</sub>]. Thus, the calcium hydroxide is heated in the kiln to simply expel the water [Ca(OH)<sub>2</sub> + heat → CaO + H<sub>2</sub>O] and no CO<sub>2</sub> is released.

**Table 4-10: Tier 2 Quantitative Uncertainty Estimates for CO<sub>2</sub> Emissions from Lime Production (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2008 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Lime Production	CO <sub>2</sub>	14.3	13.2	15.6	-8%	+9%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

## Planned Improvements

Future improvements to the lime source category involve continued research into CO<sub>2</sub> recovery associated with lime use during sugar refining and precipitate calcium carbonate (PCC) production. Currently, two sugar refining facilities in California have been identified to capture CO<sub>2</sub> produced in lime kilns located on the same site as the sugar refinery (Lutter, 2009). Currently, data on CO<sub>2</sub> production by these lime facilities is unavailable. Future work will include research to determine the number of sugar refineries that employ the carbonation technique, the percentage of these that use captured CO<sub>2</sub> from lime production facilities, and the amount of CO<sub>2</sub> recovered per unit of lime production. Future research will also aim to improve estimates of CO<sub>2</sub> recovered as part of the PCC production process using estimates of PCC production and CO<sub>2</sub> inputs rather than lime consumption by PCC facilities.

## 4.3. Limestone and Dolomite Use (IPCC Source Category 2A3)

Limestone (CaCO<sub>3</sub>) and dolomite (CaCO<sub>3</sub>MgCO<sub>3</sub>)<sup>8</sup> are basic raw materials used by a wide variety of industries, including construction, agriculture, chemical, metallurgy,

glass production, and environmental pollution control. Limestone is widely distributed throughout the world in deposits of varying sizes and degrees of purity. Large deposits of limestone occur in nearly every state in the United States, and significant quantities are extracted for industrial applications. For some of these applications, limestone is sufficiently heated during the process and generates CO<sub>2</sub> as a byproduct. Examples of such applications include limestone used as a flux or purifier in metallurgical furnaces, as a sorbent in flue gas desulfurization systems for utility and industrial plants, or as a raw material in glass manufacturing and magnesium production.

In 2008, approximately 14,795 thousand metric tons of limestone and 1,283 thousand metric tons of dolomite were consumed during production for these emissive applications. Overall, usage of limestone and dolomite resulted in aggregate CO<sub>2</sub> emissions of 6.6 Tg CO<sub>2</sub> Eq. (6,617 Gg) (see Table 4-11 and Table 4-12). Overall, emissions have increased 31 percent overall from 1990 through 2008.

## Methodology

Carbon dioxide emissions were calculated by multiplying the quantity of limestone or dolomite consumed by the average C content, 12.0 percent for limestone and 13.0

**Table 4-11: CO<sub>2</sub> Emissions from Limestone & Dolomite Use (Tg CO<sub>2</sub> Eq.)**

Activity	1990	1995	2000	2005	2006	2007	2008
Flux Stone	2.6	3.2	2.1	2.7	4.5	2.0	1.0
Glass Making	0.2	0.5	0.4	0.4	0.7	0.3	0.4
FGD	1.4	1.7	1.8	3.0	2.1	3.2	3.8
Magnesium Production	0.1	0.1	0.1	0.0	0.0	0.0	0.0
Other Miscellaneous Uses	0.8	1.2	0.7	0.7	0.7	2.2	1.5
<b>Total</b>	<b>5.1</b>	<b>6.7</b>	<b>5.1</b>	<b>6.8</b>	<b>8.0</b>	<b>7.7</b>	<b>6.6</b>

Notes: Totals may not sum due to independent rounding. "Other miscellaneous uses" include chemical stone, mine dusting or acid water treatment, acid neutralization, and sugar refining.

<sup>8</sup> Limestone and dolomite are collectively referred to as limestone by the industry, and intermediate varieties are seldom distinguished.

**Table 4-12: CO<sub>2</sub> Emissions from Limestone & Dolomite Use (Gg)**

Activity	1990	1995	2000	2005	2006	2007	2008
Flux Stone	2,593	3,198	2,104	2,650	4,492	1,959	974
Limestone	2,304	2,027	1,374	1,096	1,917	1,270	568
Dolomite	289	1,171	730	1,554	2,575	689	407
Glass Making	217	525	371	425	747	333	387
Limestone	189	421	371	405	717	333	387
Dolomite	28	103	0	20	31	0	0
Flue Gas Desulfurization	1,433	1,719	1,787	2,975	2,061	3,179	3,801
Magnesium Production	64	73	73	0	0	0	0
Other Miscellaneous Uses	819	1,168	722	718	735	2,231	1,455
<b>Total</b>	<b>5,127</b>	<b>6,683</b>	<b>5,056</b>	<b>6,768</b>	<b>8,035</b>	<b>7,702</b>	<b>6,617</b>

Notes: Totals may not sum due to independent rounding. "Other miscellaneous uses" include chemical stone, mine dusting or acid water treatment, acid neutralization, and sugar refining.

percent for dolomite (based on stoichiometry), and converting this value to CO<sub>2</sub>. This methodology was used for flux stone, glass manufacturing, flue gas desulfurization systems, chemical stone, mine dusting or acid water treatment, acid neutralization, and sugar refining and then converting to CO<sub>2</sub> using a molecular weight ratio. Flux stone used during the production of iron and steel was deducted from the Limestone and Dolomite Use estimate and attributed to the Iron and Steel Production estimate.

Traditionally, the production of magnesium metal was the only other significant use of limestone and dolomite that produced CO<sub>2</sub> emissions. At the start of 2001, there were two magnesium production plants operating in the United States and they used different production methods. One plant produced magnesium metal using a dolomitic process that resulted in the release of CO<sub>2</sub> emissions, while the other plant produced magnesium from magnesium chloride using a CO<sub>2</sub>-emissions-free process called electrolytic reduction.

However, the plant utilizing the dolomitic process ceased its operations prior to the end of 2001, so beginning in 2002 there were no emissions from this particular sub-use.

Consumption data for 1990 through 2008 of limestone and dolomite used for flux stone, glass manufacturing, flue gas desulfurization systems, chemical stone, mine dusting or acid water treatment, acid neutralization, and sugar refining (see Table 4-13) were obtained from the USGS *Minerals Yearbook: Crushed Stone Annual Report* (1995 through 2007a, 2009b, 2010) and the U.S. Bureau of Mines (1991 & 1993a). The production capacity data for 1990 through 2008 of dolomitic magnesium metal (see Table 4-14) also came from the USGS (1995 through 2007b, 2008, 2009a) and the U.S. Bureau of Mines (1990 through 1993b). The last plant in the United States that used the dolomitic production process for magnesium metal closed in 2001. The USGS does not mention this process in the 2008 *Minerals Yearbook: Magnesium*; therefore, it is assumed that this process

**Table 4-13: Limestone and Dolomite Consumption (Thousand Metric Tons)**

Activity	1990	1995	2000	2005	2006	2007	2008
Flux Stone	6,737	8,586	6,283	7,022	11,030	5,305	3,253
Limestone	5,804	5,734	4,151	3,165	5,208	3,477	1,970
Dolomite	933	2,852	2,132	3,857	5,822	1,827	1,283
Glass Making	489	1,174	843	962	1,693	757	879
Limestone	430	958	843	920	1,629	757	879
Dolomite	59	216	0	43	64	0	0
Flue Gas Desulfurization	3,258	3,908	4,061	6,761	4,683	7,225	8,639
Other Miscellaneous Uses	1,835	2,654	1,640	1,632	1,671	5,057	3,307
<b>Total</b>	<b>12,319</b>	<b>16,321</b>	<b>12,826</b>	<b>16,377</b>	<b>19,078</b>	<b>18,344</b>	<b>16,077</b>

Notes: "Other miscellaneous uses" includes chemical stone, mine dusting or acid water treatment, acid neutralization, and sugar refining. Zero values for limestone and dolomite consumption for glass making result during years when the USGS reports that no limestone or dolomite are consumed for this use.

**Table 4-14: Dolomitic Magnesium Metal Production Capacity (Metric Tons)**

Year	Production Capacity
1990	35,000
1995	40,000
2000	40,000
2005	0
2006	0
2007	0
2008	0

Note: Production capacity for 2002, 2003, 2004, 2005, 2006, and 2007 amounts to zero because the last U.S. production plant employing the dolomitic process shut down mid-2001 (USGS 2002b through 2008b).

continues to be non-existent in the United States (USGS 2009a). During 1990 and 1992, the USGS did not conduct a detailed survey of limestone and dolomite consumption by end-use. Consumption for 1990 was estimated by applying the 1991 percentages of total limestone and dolomite use constituted by the individual limestone and dolomite uses to 1990 total use. Similarly, the 1992 consumption figures were approximated by applying an average of the 1991 and 1993 percentages of total limestone and dolomite use constituted by the individual limestone and dolomite uses to the 1992 total.

Additionally, each year the USGS withholds data on certain limestone and dolomite end-uses due to confidentiality agreements regarding company proprietary data. For the purposes of this analysis, emissive end-uses that contained withheld data were estimated using one of the following techniques: (1) the value for all the withheld data points for limestone or dolomite use was distributed evenly to all withheld end-uses; (2) the average percent of total limestone or dolomite for the withheld end-use in the preceding and succeeding years; or (3) the average fraction of total limestone or dolomite for the end-use over the entire time period.

There is a large quantity of crushed stone reported to the USGS under the category “unspecified uses.” A portion of this consumption is believed to be limestone or dolomite used for emissive end uses. The quantity listed for “unspecified uses” was, therefore, allocated to each reported end-use

according to each end uses fraction of total consumption in that year.<sup>9</sup>

## Uncertainty and Time Series Consistency

The uncertainty levels presented in this section arise in part due to variations in the chemical composition of limestone. In addition to calcium carbonate, limestone may contain smaller amounts of magnesia, silica, and sulfur, among other minerals. The exact specifications for limestone or dolomite used as flux stone vary with the pyrometallurgical process and the kind of ore processed. Similarly, the quality of the limestone used for glass manufacturing will depend on the type of glass being manufactured.

The estimates below also account for uncertainty associated with activity data. Large fluctuations in reported consumption exist, reflecting year-to-year changes in the number of survey responders. The uncertainty resulting from a shifting survey population is exacerbated by the gaps in the time series of reports. The accuracy of distribution by end use is also uncertain because this value is reported by the manufacturer and not the end user. Additionally, there is significant inherent uncertainty associated with estimating withheld data points for specific end uses of limestone and dolomite. The uncertainty of the estimates for limestone used in glass making is especially high; however, since glass making accounts for a small percent of consumption, its contribution to the overall emissions estimate is low. Lastly, much of the limestone consumed in the United States is reported as “other unspecified uses;” therefore, it is difficult to accurately allocate this unspecified quantity to the correct end-uses.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-15. Limestone and Dolomite Use CO<sub>2</sub> emissions were estimated to be between 6.4 and 7.9 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level. This indicates a range of approximately 3 percent below and 20 percent above the emission estimate of 6.6 Tg CO<sub>2</sub> Eq.

Methodological recalculations were applied to the entire time series to ensure time-series consistency from 1990 through 2008. Details on the emission trends through time are described in more detail in the Methodology section, above.

<sup>9</sup> This approach was recommended by USGS.

**Table 4-15: Tier 2 Quantitative Uncertainty Estimates for CO<sub>2</sub> Emissions from Limestone and Dolomite Use (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2008 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			(Tg CO <sub>2</sub> Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Limestone and Dolomite Use	CO <sub>2</sub>	6.6	6.4	7.9	-3%	+20%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

## Recalculations

Beginning in 2007, USGS began reporting a single value for “unspecified uses.” A portion of this consumption is believed to be limestone or dolomite used for emissive end uses. The quantity listed for “unspecified uses” was, therefore, allocated to each reported end-use in 2007 according to each end-use’s fraction of total consumption in that year. This recalculation resulted in an increase in 2007 emissions by 25 percent relative to the previous Inventory.

Additionally, the dolomitic magnesium metal production capacity value for the years 1992 through 1995 was updated to reflect data from USGS (1995 through 1996) and the U.S. Bureau of Mines (1992 through 1993b).

## Planned Improvements

Future improvements to the limestone and dolomite source category involve research into the availability of limestone and dolomite end-use data. If sufficient data are available, limestone and dolomite used as process materials in source categories included in future inventories (e.g., glass production, other process use of carbonates) may be removed from this section and will be reported under the appropriate source categories. Additionally, future improvements include revisiting the methodology to distribute withheld data across emissive end-uses for all years to improve consistency of calculations.

## 4.4. Soda Ash Production and Consumption (IPCC Source Category 2A4)

Soda ash (sodium carbonate, Na<sub>2</sub>CO<sub>3</sub>) is a white crystalline solid that is readily soluble in water and strongly alkaline. Commercial soda ash is used as a raw material in a variety of industrial processes and in many familiar consumer products such as glass, soap and detergents, paper, textiles, and food. It is used primarily as an alkali, either in glass manufacturing or simply as a material that reacts with and neutralizes acids or acidic substances. Internationally, two types of soda ash are produced, natural and synthetic. The United States produces only natural soda ash and is second only to China in total soda ash production. Trona is the principal ore from which natural soda ash is made.

Only two states produce natural soda ash: Wyoming and California. Of these two states, only net emissions of CO<sub>2</sub> from Wyoming were calculated due to specifics regarding the production processes employed in the state.<sup>10</sup> During

<sup>10</sup> In California, soda ash is manufactured using sodium carbonate bearing brines instead of trona ore. To extract the sodium carbonate, the complex brines are first treated with CO<sub>2</sub> in carbonation towers to convert the sodium carbonate into sodium bicarbonate, which then precipitates from the brine solution. The precipitated sodium bicarbonate is then calcined back into sodium carbonate. Although CO<sub>2</sub> is generated as a by-product, the CO<sub>2</sub> is recovered and recycled for use in the carbonation stage and is not emitted. A third state, Colorado, produced soda ash until the plant was idled in 2004. The lone producer of sodium bicarbonate no longer mines trona in the state. For a brief time, NaHCO<sub>3</sub> was produced using soda ash feedstocks mined in Wyoming and shipped to Colorado. Because the trona is mined in Wyoming, the production numbers given by the USGS included the feedstocks mined in Wyoming and shipped to Colorado. In this way, the sodium bicarbonate production that took place in Colorado was accounted for in the Wyoming numbers.

**Table 4-16: CO<sub>2</sub> Emissions from Soda Ash Production and Consumption (Tg CO<sub>2</sub> Eq.)**

Year	Production	Consumption	Total
1990	1.4	2.7	4.1
1995	1.6	2.7	4.3
2000	1.5	2.7	4.2
2005	1.7	2.6	4.2
2006	1.6	2.5	4.2
2007	1.7	2.5	4.1
2008	1.7	2.4	4.1

Note: Totals may not sum due to independent rounding.

**Table 4-17: CO<sub>2</sub> Emissions from Soda Ash Production and Consumption (Gg)**

Year	Production	Consumption	Total
1990	1,431	2,710	4,141
1995	1,607	2,698	4,304
2000	1,529	2,652	4,181
2005	1,655	2,573	4,228
2006	1,626	2,536	4,162
2007	1,675	2,465	4,140
2008	1,733	2,378	4,111

Note: Totals may not sum due to independent rounding.

the production process used in Wyoming, trona ore is treated to produce soda ash. CO<sub>2</sub> is generated as a byproduct of this reaction, and is eventually emitted into the atmosphere. In addition, CO<sub>2</sub> may also be released when soda ash is consumed.

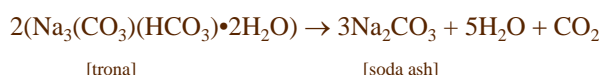
In 2008, CO<sub>2</sub> emissions from the production of soda ash from trona were approximately 1.7 Tg CO<sub>2</sub> Eq. (1,733 Gg). Soda ash consumption in the United States generated 2.4 Tg CO<sub>2</sub> Eq. (2,378 Gg) in 2008. Total emissions from soda ash production and consumption in 2008 were 4.1 Tg CO<sub>2</sub> Eq. (4,111 Gg) (see Table 4-16 and Table 4-17). Emissions have remained relatively constant with some fluctuations since 1990. These fluctuations were strongly related to the behavior of the export market and the U.S. economy. Emissions in 2008 decreased by approximately 0.7 percent from the previous year, and have also decreased overall by 0.7 percent since 1990.

The United States represents about one-fourth of total world soda ash output. Based on final 2007 reported data, the estimated distribution of soda ash by end-use in 2008 was glass making, 49 percent; chemical production, 30 percent; soap and detergent manufacturing, 8 percent; distributors, 5 percent; flue gas desulfurization, 2 percent; water treatment, 2 percent; pulp and paper production, 2 percent; and miscellaneous, 3 percent (USGS 2009).

Although the United States continues to be a major supplier of world soda ash, China, which surpassed the United States in soda ash production in 2003, is the world's leading producer. While Chinese soda ash production appears to be stabilizing, U.S. competition in Asian markets is expected to continue. Despite this competition, U.S. soda ash production is expected to increase by about 0.5 percent annually (USGS 2008).

## Methodology

During the production process, trona ore is calcined in a rotary kiln and chemically transformed into a crude soda ash that requires further processing. CO<sub>2</sub> and water are generated as by-products of the calcination process. CO<sub>2</sub> emissions from the calcination of trona can be estimated based on the following chemical reaction:



Based on this formula, approximately 10.27 metric tons of trona are required to generate one metric ton of CO<sub>2</sub>, or an emission factor of 0.097 metric tons CO<sub>2</sub> per metric ton trona (IPCC 2006). Thus, the 17.8 million metric tons of trona mined in 2008 for soda ash production (USGS 2008) resulted in CO<sub>2</sub> emissions of approximately 1.7 Tg CO<sub>2</sub> Eq. (1,733 Gg).

**Table 4-18: Soda Ash Production and Consumption (Gg)**

Year	Production <sup>a</sup>	Consumption
1990	14,700	6,530
1995	16,500	6,500
2000	15,700	6,390
2005	17,000	6,200
2006	16,700	6,110
2007	17,200	5,940
2008	17,800	5,730

<sup>a</sup> Soda ash produced from trona ore only.

**Table 4-19: Tier 2 Quantitative Uncertainty Estimates for CO<sub>2</sub> Emissions from Soda Ash Production and Consumption (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2008 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			(Tg CO <sub>2</sub> Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Soda Ash Production and Consumption	CO <sub>2</sub>	4.1	4.0	4.9	-2%	+20%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Once produced, most soda ash is consumed in glass and chemical production, with minor amounts in soap and detergents, pulp and paper, flue gas desulfurization and water treatment. As soda ash is consumed for these purposes, additional CO<sub>2</sub> is usually emitted. In these applications, it is assumed that one mole of C is released for every mole of soda ash used. Thus, approximately 0.113 metric tons of C (or 0.415 metric tons of CO<sub>2</sub>) are released for every metric ton of soda ash consumed.

The activity data for trona production and soda ash consumption (see Table 4-18) were taken from USGS (1994 through 2008). Soda ash production and consumption data were collected by the USGS from voluntary surveys of the U.S. soda ash industry.

### Uncertainty and Time-Series Consistency

Emission estimates from soda ash production have relatively low associated uncertainty levels in that reliable and accurate data sources are available for the emission factor and activity data. The primary source of uncertainty, however, results from the fact that emissions from soda ash consumption are dependent upon the type of processing employed by each end-use. Specific information characterizing the emissions from each end-use is limited. Therefore, there is uncertainty surrounding the emission factors from the consumption of soda ash.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-19. Soda Ash Production and Consumption CO<sub>2</sub> emissions were estimated to be between 4.0 and 4.9 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level. This indicates a range of approximately 2 percent below and 20 percent above the emission estimate of 4.1 Tg CO<sub>2</sub> Eq.

Methodological recalculations were applied to the entire time series to ensure time-series consistency from 1990 through 2008. Details on the emission trends through time

are described in more detail in the Methodology section, above.

### Planned Improvements

Future inventories are anticipated to estimate emissions from glass production and other use of carbonates. These inventories will extract soda ash consumed for glass production and other use of carbonates from the current soda ash consumption emission estimates and include them under those sources.

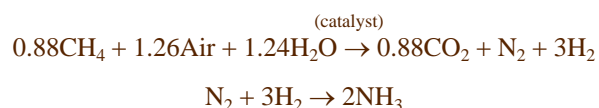
## 4.5. Ammonia Production (IPCC Source Category 2B1) and Urea Consumption

Emissions of CO<sub>2</sub> occur during the production of synthetic ammonia, primarily through the use of natural gas as a feedstock. The natural gas-based, naphtha-based, and petroleum coke-based processes produce CO<sub>2</sub> and hydrogen (H<sub>2</sub>), the latter of which is used in the production of ammonia. One N production plant located in Kansas is producing ammonia from petroleum coke feedstock. In some plants the CO<sub>2</sub> produced is captured and used to produce urea. The brine electrolysis process for production of ammonia does not lead to process-based CO<sub>2</sub> emissions.

There are five principal process steps in synthetic ammonia production from natural gas feedstock. The primary reforming step converts CH<sub>4</sub> to CO, carbon monoxide (CO), and H<sub>2</sub> in the presence of a catalyst. Only 30 to 40 percent of the CH<sub>4</sub> feedstock to the primary reformer is converted to CO and CO<sub>2</sub>. The secondary reforming step converts the remaining CH<sub>4</sub> feedstock to CO and CO<sub>2</sub>. The CO in the process gas from the secondary reforming step (representing approximately 15 percent of the process gas) is converted to CO<sub>2</sub> in the presence of a catalyst, water, and air in the shift

conversion step. Carbon dioxide is removed from the process gas by the shift conversion process, and the hydrogen gas is combined with the nitrogen (N<sub>2</sub>) gas in the process gas during the ammonia synthesis step to produce ammonia. The CO<sub>2</sub> is included in a waste gas stream with other process impurities and is absorbed by a scrubber solution. In regenerating the scrubber solution, CO<sub>2</sub> is released.

The conversion process for conventional steam reforming of CH<sub>4</sub>, including primary and secondary reforming and the shift conversion processes, is approximately as follows:



To produce synthetic ammonia from petroleum coke, the petroleum coke is gasified and converted to CO<sub>2</sub> and H<sub>2</sub>. These gases are separated, and the H<sub>2</sub> is used as a feedstock to the ammonia production process, where it is reacted with N<sub>2</sub> to form ammonia.

Not all of the CO<sub>2</sub> produced in the production of ammonia is emitted directly to the atmosphere. Both ammonia and CO<sub>2</sub> are used as raw materials in the production of urea [CO(NH<sub>2</sub>)<sub>2</sub>], which is another type of nitrogenous fertilizer that contains C as well as N. The chemical reaction that produces urea is:



Urea is consumed for a variety of uses, including as a nitrogenous fertilizer, in urea-formaldehyde resins, and as a deicing agent (TIG 2002). The C in the consumed urea is assumed to be released into the environment as CO<sub>2</sub> during use. Therefore, the CO<sub>2</sub> produced by ammonia production that is subsequently used in the production of urea is still emitted during urea consumption. The majority of CO<sub>2</sub> emissions associated with urea consumption are those that result from its use as a fertilizer. These emissions are accounted for in the Cropland Remaining Cropland section of the Land Use, Land-Use Change, and Forestry chapter. Carbon dioxide emissions associated with other uses of urea are accounted for in this chapter. Net emissions of CO<sub>2</sub> from ammonia production in 2008 were 11.8 Tg CO<sub>2</sub> Eq. (11,755 Gg), and are summarized in Table 4-20 and Table 4-21. Emissions of CO<sub>2</sub> from urea consumed for non-fertilizer purposes in 2008 totaled 3.9 Tg CO<sub>2</sub> Eq. (3,871 Gg), and are summarized in Table 4-20 and Table 4-21. The decrease in ammonia production in recent years is due to several factors, including market fluctuations and high natural gas prices. Ammonia production relies on natural gas as both a feedstock and a fuel, and as such, domestic producers are competing with imports from countries with lower gas prices. If natural gas prices remain high, it is likely that domestically produced ammonia will continue to decrease with increasing ammonia imports (EEA 2004).

**Table 4-20: CO<sub>2</sub> Emissions from Ammonia Production and Urea Consumption (Tg CO<sub>2</sub> Eq.)**

Source	1990	1995	2000	2005	2006	2007	2008
Ammonia Production	13.0	13.5	12.2	9.2	8.8	9.1	7.9
Urea Consumption <sup>a</sup>	3.8	4.3	4.2	3.7	3.5	4.9	3.9
<b>Total</b>	<b>16.8</b>	<b>17.8</b>	<b>16.4</b>	<b>12.8</b>	<b>12.3</b>	<b>14.0</b>	<b>11.8</b>

<sup>a</sup> Urea Consumption is for non-fertilizer purposes only. Urea consumed as a fertilizer is accounted for in the Land Use, Land-Use Change, and Forestry chapter. Note: Totals may not sum due to independent rounding.

**Table 4-21: CO<sub>2</sub> Emissions from Ammonia Production and Urea Consumption (Gg)**

Source	1990	1995	2000	2005	2006	2007	2008
Ammonia Production	13,047	13,541	12,172	9,196	8,781	9,074	7,885
Urea Consumption <sup>a</sup>	3,784	4,255	4,231	3,653	3,519	4,894	3,871
<b>Total</b>	<b>16,831</b>	<b>17,796</b>	<b>16,402</b>	<b>12,849</b>	<b>12,300</b>	<b>13,968</b>	<b>11,755</b>

<sup>a</sup> Urea Consumption is for non-fertilizer purposes only. Urea consumed as a fertilizer is accounted for in the Land Use, Land-Use Change, and Forestry chapter. Note: Totals may not sum due to independent rounding.



## Methodology

The calculation methodology for non-combustion CO<sub>2</sub> emissions from production of nitrogenous fertilizers from natural gas feedstock is based on a CO<sub>2</sub> emission factor published by the European Fertilizer Manufacturers Association (EFMA). The selected EFMA factor is based on ammonia production technologies that are similar to those employed in the U.S. The CO<sub>2</sub> emission factor (1.2 metric tons CO<sub>2</sub>/metric ton NH<sub>3</sub>) is applied to the percent of total annual domestic ammonia production from natural gas feedstock. Emissions from fuels consumed for energy purposes during the production of ammonia are accounted for in the Energy chapter. Emissions of CO<sub>2</sub> from ammonia production are then adjusted to account for the use of some of the CO<sub>2</sub> produced from ammonia production as a raw material in the production of urea. For each ton of urea produced, 8.8 of every 12 tons of CO<sub>2</sub> are consumed and 6.8 of every 12 tons of ammonia are consumed (IPCC 2006, EFMA 2000). The CO<sub>2</sub> emissions reported for ammonia production are therefore reduced by a factor of 0.73 multiplied by total annual domestic urea production. Total CO<sub>2</sub> emissions resulting from nitrogenous fertilizer production do not change as a result of this calculation, but some of the CO<sub>2</sub> emissions are attributed to ammonia production and some of the CO<sub>2</sub> emissions are attributed to urea consumption. Those CO<sub>2</sub> emissions that result from the use of urea as a fertilizer are accounted for in the Land Use, Land-Use Change, and Forestry chapter.

The total amount of urea consumed for non-agricultural purposes is estimated by deducting the quantity of urea fertilizer applied to agricultural lands, which is obtained directly from the Land Use, Land-Use Change, and Forestry

Chapter and is reported in Table 4-22, from total U.S. production. Total urea production is estimated based on the amount of urea produced plus the sum of net urea imports and exports. Carbon dioxide emissions associated with urea that is used for non-fertilizer purposes are estimated using a factor of 0.73 tons of CO<sub>2</sub> per ton of urea consumed.

All ammonia production and subsequent urea production are assumed to be from the same process—conventional catalytic reforming of natural gas feedstock, with the exception of ammonia production from petroleum coke feedstock at one plant located in Kansas. The CO<sub>2</sub> emission factor for production of ammonia from petroleum coke is based on plant specific data, wherein all C contained in the petroleum coke feedstock that is not used for urea production is assumed to be emitted to the atmosphere as CO<sub>2</sub> (Bark 2004). Ammonia and urea are assumed to be manufactured in the same manufacturing complex, as both the raw materials needed for urea production are produced by the ammonia production process. The CO<sub>2</sub> emission factor (3.57 metric tons CO<sub>2</sub>/metric ton NH<sub>3</sub>) is applied to the percent of total annual domestic ammonia production from petroleum coke feedstock.

The emission factor of 1.2 metric ton CO<sub>2</sub>/metric ton NH<sub>3</sub> for production of ammonia from natural gas feedstock was taken from the EFMA Best Available Techniques publication, Production of Ammonia (EFMA 1995). The EFMA reported an emission factor range of 1.15 to 1.30 metric ton CO<sub>2</sub>/metric ton NH<sub>3</sub>, with 1.2 metric ton CO<sub>2</sub>/metric ton NH<sub>3</sub> as a typical value. Technologies (e.g., catalytic reforming process) associated with this factor are found to closely resemble those employed in the U.S. for use of natural gas as a feedstock. The EFMA reference also

**Table 4-22: Ammonia Production, Urea Production, Urea Net Imports, and Urea Exports (Gg)**

Year	Ammonia Production	Urea Production	Urea Applied as Fertilizer	Urea Imports	Urea Exports
1990	15,425	7,450	3,296	1,860	854
1995	15,788	7,370	3,623	2,936	881
2000	14,342	6,910	4,382	3,904	663
2005	10,143	5,270	4,779	5,026	536
2006	9,962	5,410	4,985	5,029	656
2007	10,393	5,590	5,191	6,546	271
2008	9,571	5,240	5,191	5,459	230

indicates that more than 99 percent of the CH<sub>4</sub> feedstock to the catalytic reforming process is ultimately converted to CO<sub>2</sub>. The emission factor of 3.57 metric ton CO<sub>2</sub>/metric ton NH<sub>3</sub> for production of ammonia from petroleum coke feedstock was developed from plant-specific ammonia production data and petroleum coke feedstock utilization data for the ammonia plant located in Kansas (Bark 2004). As noted earlier, emissions from fuels consumed for energy purposes during the production of ammonia are accounted for in the Energy chapter. Ammonia production data (see Table 4-22) was obtained from Coffeyville Resources (Coffeyville 2005, 2006, 2007a, 2007b, 2009) and the Census Bureau of the U.S. Department of Commerce (U.S. Census Bureau 1991 through 1994, 1998 through 2009) as reported in *Current Industrial Reports Fertilizer Materials and Related Products* annual and quarterly reports. Urea-ammonia nitrate production was obtained from Coffeyville Resources (Coffeyville 2005, 2006, 2007a, 2007b, 2009). Urea production data for 1990 through 2008 were obtained from the *Minerals Yearbook: Nitrogen* (USGS 1994 through 2010). Import data for urea were obtained from the U.S. Census Bureau *Current Industrial Reports Fertilizer Materials and Related Products* annual and quarterly reports for 1997 through 2008 (U.S. Census Bureau 1998 through 2009), The Fertilizer Institute (TFI 2002) for 1993 through 1996, and the United States International Trade Commission Interactive Tariff and Trade DataWeb (U.S. ITC 2002) for 1990 through 1992 (see Table 4-22). Urea export data for 1990 through 2008 were taken from U.S. Fertilizer Import/Exports from USDA Economic Research Service Data Sets (U.S. Department of Agriculture 2009).

## Uncertainty and Time-Series Consistency

The uncertainties presented in this section are primarily due to how accurately the emission factor used represents an average across all ammonia plants using natural gas feedstock. Uncertainties are also associated with natural gas

feedstock consumption data for the U.S. ammonia industry as a whole, the assumption that all ammonia production and subsequent urea production was from the same process—conventional catalytic reforming of natural gas feedstock, with the exception of one ammonia production plant located in Kansas that is manufacturing ammonia from petroleum coke feedstock. It is also assumed that ammonia and urea are produced at collocated plants from the same natural gas raw material.

Such recovery may or may not affect the overall estimate of CO<sub>2</sub> emissions depending upon the end use to which the recovered CO<sub>2</sub> is applied. Further research is required to determine whether byproduct CO<sub>2</sub> is being recovered from other ammonia production plants for application to end uses that are not accounted for elsewhere.

Additional uncertainty is associated with the estimate of urea consumed for non-fertilizer purposes. Emissions associated with this consumption are reported in this source category, while those associated with consumption as fertilizer are reported in Cropland Remaining Cropland section of the Land Use, Land-Use Change, and Forestry chapter. The amount of urea used for non-fertilizer purposes is estimated based on estimates of urea production, net urea imports, and the amount of urea used as fertilizer. There is uncertainty associated with the accuracy of these estimates as well as the fact that each estimate is obtained from a different data source.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-23. Ammonia Production and Urea Consumption CO<sub>2</sub> emissions were estimated to be between 10.4 and 13.1 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level. This indicates a range of approximately 11 percent below and 11 percent above the emission estimate of 11.8 Tg CO<sub>2</sub> Eq.

Methodological recalculations were applied to the entire time series to ensure time-series consistency from 1990

**Table 4-23: Tier 2 Quantitative Uncertainty Estimates for CO<sub>2</sub> Emissions from Ammonia Production and Urea Consumption (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2008 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Ammonia Production and Urea Consumption	CO <sub>2</sub>	11.8	10.4	13.1	-11%	+11%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

through 2008. Details on the emission trends through time are described in more detail in the Methodology section, above.

## Planned Improvements

Planned improvements to the Ammonia Production and Urea Consumption source category include updating emission factors to include both fuel and feedstock CO<sub>2</sub> emissions and incorporating CO<sub>2</sub> capture and storage. Methodologies will also be updated if additional ammonia-production plants are found to use hydrocarbons other than natural gas for ammonia production. Additional efforts will be made to find consistent data sources for urea consumption and to report emissions from this consumption appropriately as defined by the *2006 IPCC Guidelines for National Greenhouse Gas Inventories* (IPCC 2006).

## 4.6. Nitric Acid Production (IPCC Source Category 2B2)

Nitric acid (HNO<sub>3</sub>) is an inorganic compound used primarily to make synthetic commercial fertilizers. It is also a major component in the production of adipic acid—a feedstock for nylon—and explosives. Virtually all of the nitric acid produced in the United States is manufactured by the catalytic oxidation of ammonia (EPA 1997). During this reaction, N<sub>2</sub>O is formed as a by-product and is released from reactor vents into the atmosphere.

Currently, the nitric acid industry controls for emissions of NO and NO<sub>2</sub> (i.e., NO<sub>x</sub>). As such, the industry in the United States uses a combination of non-selective catalytic reduction (NSCR) and selective catalytic reduction (SCR) technologies. In the process of destroying NO<sub>x</sub>, NSCR systems are also very effective at destroying N<sub>2</sub>O. However, NSCR units are generally not preferred in modern plants because of high energy costs and associated high gas temperatures. NSCRs were widely installed in nitric plants built between 1971 and 1977. Approximately 17 percent of nitric acid plants use NSCR and they represent 7.6 percent of estimated national production (EPA 2010). The remaining 92.4 percent of production occurs using SCR or extended absorption, neither of which is known to reduce N<sub>2</sub>O emissions.

**Table 4-24: N<sub>2</sub>O Emissions from Nitric Acid Production (Tg CO<sub>2</sub> Eq. and Gg)**

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	18.9	61
1995	21.0	68
2000	20.7	67
2005	17.6	57
2006	17.2	56
2007	20.5	66
2008	19.0	61

Nitrous oxide emissions from this source were estimated to be 19.0 Tg CO<sub>2</sub> Eq. (61 Gg) in 2008 (see Table 4-24). Emissions from nitric acid production have increased by 0.7 percent since 1990, with the trend in the time series closely tracking the changes in production. Emissions decreased 7.4 percent between 2007 and 2008. Emissions have decreased by 15.3 percent since 1997, the highest year of production in the time series.

## Methodology

Nitrous oxide emissions were calculated by multiplying nitric acid production by the amount of N<sub>2</sub>O emitted per unit of nitric acid produced. The emission factor was determined as a weighted average of two known emission factors: 2 kg N<sub>2</sub>O/metric ton HNO<sub>3</sub> produced at plants using non-selective catalytic reduction (NSCR) systems and 9 kg N<sub>2</sub>O/metric ton HNO<sub>3</sub> produced at plants not equipped with NSCR (IPCC 2006). In the process of destroying NO<sub>x</sub>, NSCR systems destroy 80 to 90 percent of the N<sub>2</sub>O, which is accounted for in the emission factor of 2 kg N<sub>2</sub>O/metric ton HNO<sub>3</sub>. Approximately 17 percent of HNO<sub>3</sub> plants in the United States are equipped with NSCR representing 7.6 percent of estimated national production (EPA 2010). Hence, the emission factor is equal to  $(9 \times 0.924) + (2 \times 0.076) = 8.5$  kg N<sub>2</sub>O per metric ton HNO<sub>3</sub>.

Nitric acid production data for 1990 through 2002 were obtained from the U.S. Census Bureau, Current Industrial Reports (2006). Production data for 2003 were obtained from the U.S. Census Bureau, Current Industrial Reports (2008). Production data for 2004 through 2008 were obtained from

**Table 4-25: Nitric Acid Production (Gg)**

Year	Gg
1990	7,195
1995	8,019
2000	7,900
2005	6,711
2006	6,572
2007	7,827
2008	7,245

the U.S. Census Bureau, Current Industrial Reports (2009) (see Table 4-25).

### Uncertainty and Time-Series Consistency

The overall uncertainty associated with the 2008 N<sub>2</sub>O emissions estimate from nitric acid production was calculated using the IPCC Guidelines for National Greenhouse Gas Inventories (2006) Tier 2 methodology. Uncertainty associated with the parameters used to estimate N<sub>2</sub>O emissions included that of production data, the share of U.S. nitric acid production attributable to each emission abatement technology, and the emission factors applied to each abatement technology type.

The results of this Tier 2 quantitative uncertainty analysis are summarized in Table 4-26. Nitrous oxide emissions from nitric acid production were estimated to be between 11.3 and 27.5 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level. This indicates a range of approximately 41 percent below to 45 percent above the 2008 emissions estimate of 19.0 Tg CO<sub>2</sub> Eq.

Methodological recalculations were applied to the entire time series to ensure time-series consistency from 1990 through 2008. Details on the emission trends through time are described in more detail in the Methodology section, above.

**Table 4-26: Tier 2 Quantitative Uncertainty Estimates for N<sub>2</sub>O Emissions from Nitric Acid Production (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2008 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Nitric Acid Production	N <sub>2</sub> O	19.0	11.3	27.5	-41%	+45%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

### Recalculations Discussion

Historical estimates for N<sub>2</sub>O emissions from nitric acid production have been revised relative to the previous inventory based on updated information from US EPA (2010) on abatement technologies in use and based on revised production data published by the U.S. Census Bureau (2009). The previous Inventory assumed that approximately 5 percent of facilities accounting for less than 1 percent of national production were equipped with NSCR systems (EPA 2008). The current Inventory assumes that approximately 17 percent of facilities accounting for roughly 8 percent of national production were equipped with NSCR systems (EPA 2010). This change resulted in a decrease in the weighted average emission factor of 0.5 kg N<sub>2</sub>O/metric ton HNO<sub>3</sub> (5.5 percent). Additionally, national nitric acid production values for 2006 and 2007 have been updated relative to the previous Inventory. Revised production in 2006 resulted in a negligible decrease in emissions of less than 0.01 Tg CO<sub>2</sub> Eq. (0.01 percent). Revised production in 2007 resulted in a small increase in emissions of 0.01 Tg CO<sub>2</sub> Eq. (0.06 percent). Overall, changes relative to the previous Inventory resulted in an average annual decrease in emissions of 1.1 Tg CO<sub>2</sub> Eq. (5.5 percent) for the period 1990 through 2007.

### 4.7. Adipic Acid Production (IPCC Source Category 2B3)

Adipic acid production is an anthropogenic source of N<sub>2</sub>O emissions. Worldwide, few adipic acid plants exist. The United States and Europe are the major producers. In 2008, the United States had two companies in three locations accounting for 34 percent of world production (VA DEQ 2009; CW 2007). Eight European producers account for a combined 38 percent of world production (CW 2007). Adipic acid is a white crystalline solid used in the manufacture of synthetic fibers, plastics, coatings, urethane foams, elastomers, and synthetic lubricants. Commercially, it is the

**Table 4-27: N<sub>2</sub>O Emissions from Adipic Acid Production (Tg CO<sub>2</sub> Eq. and Gg)**

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	15.8	51
1995	17.6	57
2000	5.5	18
2005	5.0	16
2006	4.3	14
2007	3.7	12
2008	2.0	7

most important of the aliphatic dicarboxylic acids, which are used to manufacture polyesters. 84 percent of all adipic acid produced in the United States is used in the production of nylon 6,6; nine percent is used in the production of polyester polyols; four percent is used in the production of plasticizers; and the remaining four percent is accounted for by other uses, including unsaturated polyester resins and food applications (ICIS 2007). Food grade adipic acid is used to provide some foods with a “tangy” flavor (Thiemens and Trogler 1991).

Adipic acid is produced through a two-stage process during which N<sub>2</sub>O is generated in the second stage. The first stage of manufacturing usually involves the oxidation of cyclohexane to form a cyclohexanone/cyclohexanol mixture. The second stage involves oxidizing this mixture with nitric acid to produce adipic acid. N<sub>2</sub>O is generated as a by-product of the nitric acid oxidation stage and is emitted in the waste gas stream (Thiemens and Trogler 1991). Process emissions from the production of adipic acid vary with the types of technologies and level of emission controls employed by a facility. In 1990, two of the three major adipic acid-producing plants had N<sub>2</sub>O abatement technologies in place and, as of 1998, the three major adipic acid production facilities had control systems in place (Reimer et al. 1999).<sup>11</sup> One small plant, which last operated in April 2006 and represented approximately two percent of production, did not control for N<sub>2</sub>O (VA DEQ 2009; ICIS 2007; VA DEQ 2006).

Nitrous oxide emissions from adipic acid production were estimated to be 2.0 Tg CO<sub>2</sub> Eq. (7 Gg) in 2008 (see Table 4-27). National adipic acid production has increased by approximately 34 percent over the period of 1990 through

2008, to roughly one million metric tons. Over the same period, emissions have been reduced by 87 percent due to the widespread installation of pollution control measures in the late 1990s and because the smallest of the four facilities ceased production of adipic acid in April 2006 (VA DEQ 2009).

## Methodology

Due to confidential business information, plant names are not provided in this section. The four adipic acid-producing plants will henceforth be referred to as Plants 1 through 4.

For Plants 1 and 2, 1990 to 2008 emission estimates were obtained directly from the plant engineer and account for reductions due to control systems in place at these plants during the time series (Desai 2010). These estimates were based on continuous emissions monitoring equipment installed at the two facilities. For Plants 3 and 4, N<sub>2</sub>O emissions were calculated by multiplying adipic acid production by an emission factor (i.e., N<sub>2</sub>O emitted per unit of adipic acid produced) and adjusting for the percentage of N<sub>2</sub>O released as a result of plant-specific emission controls. On the basis of experiments, the overall reaction stoichiometry for N<sub>2</sub>O production in the preparation of adipic acid was estimated at approximately 0.3 metric tons of N<sub>2</sub>O per metric ton of product (IPCC 2006). Emissions are estimated using the following equation:

$$\begin{aligned} \text{N}_2\text{O emissions} = & \{ \text{production of adipic acid} \\ & [\text{metric tons (MT) of adipic acid}] \times \\ & (0.3 \text{ MT N}_2\text{O /MT adipic acid}) \times \\ & [1 - (\text{N}_2\text{O destruction factor} \times \text{abatement system utility factor})] \end{aligned}$$

The “N<sub>2</sub>O destruction factor” represents the percentage of N<sub>2</sub>O emissions that are destroyed by the installed abatement technology. The “abatement system utility factor” represents the percentage of time that the abatement equipment operates during the annual production period. Overall, in the United States, two of the plants employ catalytic destruction (Plants 1 and 2), one plant employs thermal destruction (Plant 3), and the smallest plant used no N<sub>2</sub>O abatement equipment (Plant 4). For Plant 3, which uses thermal destruction and for which no reported plant-specific emissions are available, the N<sub>2</sub>O abatement system destruction factor is assumed to be 98.5 percent, and the abatement system utility factor is assumed to be 97 percent (IPCC 2006).

<sup>11</sup> During 1997, the N<sub>2</sub>O emission controls installed by the third plant operated for approximately a quarter of the year.

From 1990 to 2003, plant-specific production data were estimated for Plant 3 where direct emission measurements were not available. In order to calculate plant-specific production for this plant, national adipic acid production was allocated to the plant level using the ratio of known plant capacity to total national capacity for all U.S. plants. The estimated plant production for this plant was then used for calculating emissions as described above. For 2004 and 2006, actual plant production data were obtained and used for emission calculations (CW 2007; CW 2005). For 2005, interpolated national production was used for calculating emissions. Updated production data were not available for Plant 3 in 2007 or 2008; therefore, production values in 2007 and 2008 were proxied using 2006 data.

For Plant 4, which last operated in April 2006 (VA DEQ 2009), plant-specific production data were obtained across the timeseries from 1990 through 2008 (VA DEQ 2010). The plant-specific production data were then used for calculating emissions as described above.

National adipic acid production data (see Table 4-28) for 1990 through 2002 were obtained from the American Chemistry Council (ACC 2003). Production for 2004 and 2006 were obtained from Chemical Week, Product Focus: Adipic Acid (CW 2005, 2007). National production for 2003 was calculated through linear interpolation between 2002 and 2004 reported national production data. 2005 national production was proxied using 2004 reported national production. National production in 2006 represents the sum of annual production at Plants 1, 2, and 3 and 3.5 months of production at Plant 4, resulting in estimated national production of 989 Gg (VA DEQ, 2009; CW 2005, 2007). Updated national production data were not available for 2007 or 2008; therefore, national production in 2007 and 2008 represents the sum of production at the three plants still in operation (Plants 1, 2, and 3) resulting in estimated national production of 985 Gg in 2007 and 2008, respectively (VA DEQ, 2009; CW 2005, 2007).

Plant capacities for 1990 through 1994 were obtained from *Chemical and Engineering News*, “Facts and Figures” and “Production of Top 50 Chemicals” (C&EN 1992 through 1995). Plant capacities for 1995 and 1996 were kept the same as 1994 data. The 1997 plant capacities were taken from *Chemical Market Reporter* “Chemical Profile: Adipic Acid” (CMR 1998). The 1998 plant capacities for all four

**Table 4-28: Adipic Acid Production (Gg)**

Year	Gg
1990	735
1995	830
2000	925
2005	1,002
2006	990
2007	985
2008	985

plants and 1999 plant capacities for three of the plants were obtained from *Chemical Week*, “Product Focus: Adipic Acid/Adiponitrile” (CW 1999). Plant capacities for 2000 for three of the plants were updated using *Chemical Market Reporter*, “Chemical Profile: Adipic Acid” (CMR 2001). For 2001 through 2005, the plant capacities for three plants were kept the same as the year 2000 capacities. Plant capacity for 1999 to 2005 for the one remaining plant was kept the same as 1998. For 2004 to 2008, although some plant capacity data are available (CW 1999, CMR 2001, ICIS 2007), they are not used to calculate plant-specific production for these years because plant-specific production data for 2004 and 2006 are also available and are used in our calculations instead (CW 2005, CW 2007).

## Uncertainty and Time-Series Consistency

The overall uncertainty associated with the 2008 N<sub>2</sub>O emission estimate from adipic acid production was calculated using the *IPCC Guidelines for National Greenhouse Gas Inventories* (2006) Tier 2 methodology. Uncertainty associated with the parameters used to estimate N<sub>2</sub>O emissions included that of company specific production data, emission factors for abated and unabated emissions, and company-specific historical emissions estimates.

The results of this Tier 2 quantitative uncertainty analysis are summarized in Table 4-29. Nitrous oxide emissions from adipic acid production were estimated to be between 1.3 and 2.9 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level. This indicates a range of approximately 37 percent below to 41 percent above the 2008 emission estimate of 2.0 Tg CO<sub>2</sub> Eq.

Methodological recalculations were applied to the entire time series to ensure time-series consistency from 1990

**Table 4-29: Tier 2 Quantitative Uncertainty Estimates for N<sub>2</sub>O Emissions from Adipic Acid Production (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2008 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			(Tg CO <sub>2</sub> Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Adipic Acid Production	N <sub>2</sub> O	2.0	1.3	2.9	-37%	+41%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

through 2008. Details on the emission trends through time are described in more detail in the Methodology section, above.

## Planned Improvements

Improvement efforts will be focused on obtaining direct measurement data from facilities. If they become available, cross verification with top-down approaches will provide a useful Tier 2 level QC check. Also, additional information on the actual performance of the latest catalytic and thermal abatement equipment at plants with continuous emission monitoring may support the re-evaluation of current default abatement values.

## 4.8. Silicon Carbide Production (IPCC Source Category 2B4) and Consumption

Carbon dioxide and CH<sub>4</sub> are emitted from the production<sup>12</sup> of silicon carbide (SiC), a material used as an industrial abrasive. To make SiC, quartz (SiO<sub>2</sub>) is reacted with C in the form of petroleum coke. A portion (about 35 percent) of the C contained in the petroleum coke is retained in the SiC. The remaining C is emitted as CO<sub>2</sub>, CH<sub>4</sub>, or CO.

Carbon dioxide is also emitted from the consumption of SiC for metallurgical and other non-abrasive applications. The USGS reports that a portion (approximately 50 percent) of SiC is used in metallurgical and other non-abrasive applications, primarily in iron and steel production (USGS 2006).

<sup>12</sup> Silicon carbide is produced for both abrasive and metallurgical applications in the United States. Production for metallurgical applications is not available and therefore both CH<sub>4</sub> and CO<sub>2</sub> estimates are based solely upon production estimates of silicon carbide for abrasive applications.

Carbon dioxide from SiC production and consumption in 2008 were 0.2 Tg CO<sub>2</sub> Eq. (175 Gg) (USGS 2009). Approximately 52 percent of these emissions resulted from SiC production while the remainder results from SiC consumption. CH<sub>4</sub> emissions from SiC production in 2008 were 0.01 Tg CO<sub>2</sub> Eq. CH<sub>4</sub> (0.4 Gg) (see Table 4-30 and Table 4-31).

## Methodology

Emissions of CO<sub>2</sub> and CH<sub>4</sub> from the production of SiC were calculated by multiplying annual SiC production by the emission factors (2.62 metric tons CO<sub>2</sub>/metric ton SiC for CO<sub>2</sub> and 11.6 kg CH<sub>4</sub>/metric ton SiC for CH<sub>4</sub>) provided by the 2006 IPCC Guidelines for National Greenhouse Gas Inventories (IPCC 2006).

Emissions of CO<sub>2</sub> from silicon carbide consumption were calculated by multiplying the annual SiC consumption (production plus net imports) by the percent used in metallurgical and other non-abrasive uses (50 percent) (USGS 2006). The total SiC consumed in metallurgical and other non-abrasive uses was multiplied by the C content of SiC (31.5 percent), which was determined according to the molecular weight ratio of SiC.

Production data for 1990 through 2008 were obtained from the *Minerals Yearbook: Manufactured Abrasives* (USGS 1991a through 2005a, 2007) and the 2009 *Mineral Commodity Summary: Manufactured Abrasives* (USGS 2009). Silicon carbide consumption by major end use was obtained from the *Minerals Yearbook: Silicon* (USGS 1991b through 2005b) (see Table 4-32) for years 1990 through 2004 and from the USGS Minerals Commodity Specialist for 2005 and 2006 (Corathers 2006, 2007). Silicon carbide consumption by major end use data for 2008 are proxied using 2007 data due to unavailability of data at time of publication. Net imports for the entire time series were obtained from the U.S. Census Bureau (2005 through 2009).

**Table 4-30: CO<sub>2</sub> and CH<sub>4</sub> Emissions from Silicon Carbide Production and Consumption (Tg CO<sub>2</sub> Eq.)**

Gas	1990	1995	2000	2005	2006	2007	2008
CO <sub>2</sub>	0.4	0.3	0.2	0.2	0.2	0.2	0.2
CH <sub>4</sub>	+	+	+	+	+	+	+
<b>Total</b>	<b>0.4</b>	<b>0.3</b>	<b>0.3</b>	<b>0.2</b>	<b>0.2</b>	<b>0.2</b>	<b>0.2</b>

+ Does not exceed 0.05 Tg CO<sub>2</sub> Eq.  
Note: Totals may not sum due to independent rounding.

**Table 4-31: CO<sub>2</sub> and CH<sub>4</sub> Emissions from Silicon Carbide Production and Consumption (Gg)**

Gas	1990	1995	2000	2005	2006	2007	2008
CO <sub>2</sub>	375	329	248	219	207	196	175
CH <sub>4</sub>	1	1	1	+	+	+	+

+ Does not exceed 0.5 Gg.

## Uncertainty and Time-Series Consistency

There is uncertainty associated with the emission factors used because they are based on stoichiometry as opposed to monitoring of actual SiC production plants. An alternative would be to calculate emissions based on the quantity of petroleum coke used during the production process rather than on the amount of silicon carbide produced. However, these data were not available. For CH<sub>4</sub>, there is

also uncertainty associated with the hydrogen-containing volatile compounds in the petroleum coke (IPCC 2006). There is also some uncertainty associated with production, net imports, and consumption data as well as the percent of total consumption that is attributed to metallurgical and other non-abrasive uses.

**Table 4-32: Production and Consumption of Silicon Carbide (Metric Tons)**

Year	Production	Consumption
1990	105,000	172,465
1995	75,400	227,395
2000	45,000	225,070
2005	35,000	220,149
2006	35,000	199,937
2007	35,000	179,741
2008	35,000	144,928

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-33. Silicon carbide production and consumption CO<sub>2</sub> emissions were estimated to be between 9 percent below and 9 percent above the emission estimate of 0.2 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level. Silicon carbide production CH<sub>4</sub> emissions were estimated to be between 9 percent below and 9 percent above the emission estimate of 0.01 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level.

Methodological recalculations were applied to the entire time series to ensure time-series consistency from 1990 through 2008. Details on the emission trends through time are described in more detail in the Methodology section, above.

**Table 4-33: Tier 2 Quantitative Uncertainty Estimates for CH<sub>4</sub> and CO<sub>2</sub> Emissions from Silicon Carbide Production and Consumption (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2008 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup> (Tg CO <sub>2</sub> Eq.)			
			Lower Bound	Upper Bound	Lower Bound (%)	Upper Bound (%)
Silicon Carbide Production and Consumption	CO <sub>2</sub>	0.18	0.16	0.19	-9%	+9%
Silicon Carbide Production	CH <sub>4</sub>	+	+	+	-9%	+9%

+ Does not exceed 0.05 Tg CO<sub>2</sub> Eq. or 0.5 Gg.  
<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.



## Planned Improvements

Future improvements to the carbide production source category include continued research to determine if calcium carbide production and consumption data are available for the United States. If these data are available, calcium carbide emission estimates will be included in this source category.

## 4.9. Petrochemical Production (IPCC Source Category 2B5)

The production of some petrochemicals results in the release of small amounts of CH<sub>4</sub> and CO<sub>2</sub> emissions. Petrochemicals are chemicals isolated or derived from petroleum or natural gas. Methane emissions are presented here from the production of carbon black, ethylene, ethylene dichloride, and methanol, while CO<sub>2</sub> emissions are presented here for only carbon black production. The CO<sub>2</sub> emissions from petrochemical processes other than carbon black are currently included in the Carbon Stored in Products from Non-Energy Uses of Fossil Fuels Section of the Energy chapter. The CO<sub>2</sub> from carbon black production is included here to allow for the direct reporting of CO<sub>2</sub> emissions from the process and direct accounting of the feedstocks used in the process.

Carbon black is an intense black powder generated by the incomplete combustion of an aromatic petroleum or coal-based feedstock. Most carbon black produced in the United States is added to rubber to impart strength and abrasion resistance, and the tire industry is by far the largest consumer. Ethylene is consumed in the production processes

of the plastics industry including polymers such as high, low, and linear low density polyethylene (HDPE, LDPE, LLDPE), polyvinyl chloride (PVC), ethylene dichloride, ethylene oxide, and ethylbenzene. Ethylene dichloride is one of the first manufactured chlorinated hydrocarbons with reported production as early as 1795. In addition to being an important intermediate in the synthesis of chlorinated hydrocarbons, ethylene dichloride is used as an industrial solvent and as a fuel additive. Methanol is an alternative transportation fuel as well as a principle ingredient in windshield wiper fluid, paints, solvents, refrigerants, and disinfectants. In addition, methanol-based acetic acid is used in making PET plastics and polyester fibers.

Emissions of CO<sub>2</sub> and CH<sub>4</sub> from petrochemical production in 2008 were 3.4 Tg CO<sub>2</sub> Eq. (3,449 Gg) and 0.9 Tg CO<sub>2</sub> Eq. (43 Gg), respectively (see Table 4-34 and Table 4-35), totaling 4.4 Tg CO<sub>2</sub> Eq. There has been an overall increase in CO<sub>2</sub> emissions from carbon black production of four percent since 1990. CH<sub>4</sub> emissions from petrochemical production increased by approximately six percent since 1990.

## Methodology

Emissions of CH<sub>4</sub> were calculated by multiplying annual estimates of chemical production by the appropriate emission factor, as follows: 11 kg CH<sub>4</sub>/metric ton carbon black, 1 kg CH<sub>4</sub>/metric ton ethylene, 0.4 kg CH<sub>4</sub>/metric ton ethylene dichloride,<sup>13</sup> and 2 kg CH<sub>4</sub>/metric ton methanol. Although the production of other chemicals may also result in CH<sub>4</sub> emissions, insufficient data were available to estimate their emissions.

**Table 4-34: CO<sub>2</sub> and CH<sub>4</sub> Emissions from Petrochemical Production (Tg CO<sub>2</sub> Eq.)**

Gas	1990	1995	2000	2005	2006	2007	2008
CO <sub>2</sub>	3.3	4.1	4.5	4.2	3.8	3.9	3.4
CH <sub>4</sub>	0.9	1.1	1.2	1.1	1.0	1.0	0.9
<b>Total</b>	<b>4.2</b>	<b>5.2</b>	<b>5.7</b>	<b>5.3</b>	<b>4.8</b>	<b>4.9</b>	<b>4.4</b>

**Table 4-35: CO<sub>2</sub> and CH<sub>4</sub> Emissions from Petrochemical Production (Gg)**

The emission factor obtained from IPCC/UNEP/OECD/IEA (1997).

Gas	1990	1995	2000	2005	2006	2007	2008
CO <sub>2</sub>	3,311	4,101	4,479	4,181	3,837	3,931	3,449
CH <sub>4</sub>	41	52	59	51	48	48	43

Emission factors were taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997). Annual production data (see Table 4-36) were obtained from the American Chemistry Council's *Guide to the Business of Chemistry* (ACC 2002, 2003, 2005 through 2009) and the International Carbon Black Association (Johnson 2003, 2005 through 2009).

Almost all carbon black in the United States is produced from petroleum-based or coal-based feedstocks using the "furnace black" process (European IPPC Bureau 2004). The furnace black process is a partial combustion process in which a portion of the carbon black feedstock is combusted to provide energy to the process. Carbon black is also produced in the United States by the thermal cracking of acetylene-containing feedstocks ("acetylene black process") and by the thermal cracking of other hydrocarbons ("thermal black process"). One U.S. carbon black plant produces carbon black using the thermal black process, and one U.S. carbon black plant produces carbon black using the acetylene black process (The Innovation Group 2004).

The furnace black process produces carbon black from "carbon black feedstock" (also referred to as "carbon black oil"), which is a heavy aromatic oil that may be derived as a byproduct of either the petroleum refining process or the metallurgical (coal) coke production process. For the production of both petroleum-derived and coal-derived carbon black, the "primary feedstock" (i.e., carbon black feedstock) is injected into a furnace that is heated by a "secondary feedstock" (generally natural gas). Both the natural gas secondary feedstock and a portion of the carbon black feedstock are oxidized to provide heat to the production process and pyrolyze the remaining carbon black feedstock to carbon black. The "tail gas" from the furnace black process contains CO<sub>2</sub>, carbon monoxide, sulfur compounds, CH<sub>4</sub>, and non-CH<sub>4</sub> volatile organic compounds. A portion of the tail gas is generally burned for energy recovery to heat the downstream carbon black product dryers. The remaining

tail gas may also be burned for energy recovery, flared, or vented uncontrolled to the atmosphere.

The calculation of the C lost during the production process is the basis for determining the amount of CO<sub>2</sub> released during the process. The C content of national carbon black production is subtracted from the total amount of C contained in primary and secondary carbon black feedstock to find the amount of C lost during the production process. It is assumed that the C lost in this process is emitted to the atmosphere as either CH<sub>4</sub> or CO<sub>2</sub>. The C content of the CH<sub>4</sub> emissions, estimated as described above, is subtracted from the total C lost in the process to calculate the amount of C emitted as CO<sub>2</sub>. The total amount of primary and secondary carbon black feedstock consumed in the process (see Table 4-37) is estimated using a primary feedstock consumption factor and a secondary feedstock consumption factor estimated from U.S. Census Bureau (1999, 2004, and 2007) data. The average carbon black feedstock consumption factor for U.S. carbon black production is 1.69 metric tons of carbon black feedstock consumed per metric ton of carbon black produced. The average natural gas consumption factor for U.S. carbon black production is 321 normal cubic meters of natural gas consumed per metric ton of carbon black produced. The amount of C contained in the primary and secondary feedstocks is calculated by applying the respective C contents of the feedstocks to the respective levels of feedstock consumption (EIA 2003, 2004).

For the purposes of emissions estimation, 100 percent of the primary carbon black feedstock is assumed to be derived from petroleum refining byproducts. Carbon black feedstock derived from metallurgical (coal) coke production (e.g., creosote oil) is also used for carbon black production; however, no data are available concerning the annual consumption of coal-derived carbon black feedstock. Carbon black feedstock derived from petroleum refining byproducts is assumed to be 89 percent elemental C (Srivastava et al. 1999). It is assumed that 100 percent of the tail gas produced from the carbon black production process is combusted

**Table 4-36: Production of Selected Petrochemicals (Thousand Metric Tons)**

Chemical	1990	1995	2000	2005	2006	2007	2008
Carbon Black	1,307	1,619	1,769	1,651	1,515	1,552	1,362
Ethylene	16,541	21,214	24,970	23,954	25,000	25,392	22,539
Ethylene Dichloride	6,282	7,829	9,866	11,260	9,736	9,566	8,981
Methanol	3,785	4,992	5,221	2,336	1,123	1,068	1,136

**Table 4-37: Carbon Black Feedstock (Primary Feedstock) and Natural Gas Feedstock (Secondary Feedstock) Consumption (Thousand Metric Tons)**

Activity	1990	1995	2000	2005	2006	2007	2008
Primary Feedstock	2,213	2,741	2,993	2,794	2,564	2,627	2,305
Secondary Feedstock	284	352	384	359	329	337	296

and that none of the tail gas is vented to the atmosphere uncontrolled. The furnace black process is assumed to be the only process used for the production of carbon black because of the lack of data concerning the relatively small amount of carbon black produced using the acetylene black and thermal black processes. The carbon black produced from the furnace black process is assumed to be 97 percent elemental C (Othmer et al. 1992).

### Uncertainty and Time-Series Consistency

The CH<sub>4</sub> emission factors used for petrochemical production are based on a limited number of studies. Using plant-specific factors instead of average factors could increase the accuracy of the emission estimates; however, such data were not available. There may also be other significant sources of CH<sub>4</sub> arising from petrochemical production activities that have not been included in these estimates.

The results of the quantitative uncertainty analysis for the CO<sub>2</sub> emissions from carbon black production calculation are based on feedstock consumption, import and export data, and carbon black production data. The composition of carbon black feedstock varies depending upon the specific refinery production process, and therefore the assumption that carbon black feedstock is 89 percent C gives rise to uncertainty. Also, no data are available concerning the consumption of coal-derived carbon black feedstock, so CO<sub>2</sub> emissions from the utilization of coal-based feedstock are not included in the emission estimate. In addition, other data sources indicate that the amount of petroleum-based feedstock used

in carbon black production may be underreported by the U.S. Census Bureau. Finally, the amount of carbon black produced from the thermal black process and acetylene black process, although estimated to be a small percentage of the total production, is not known. Therefore, there is some uncertainty associated with the assumption that all of the carbon black is produced using the furnace black process.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-38. Petrochemical production CO<sub>2</sub> emissions were estimated to be between 2.5 and 4.6 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level. This indicates a range of approximately 27 percent below to 32 percent above the emission estimate of 3.4 Tg CO<sub>2</sub> Eq. Petrochemical production CH<sub>4</sub> emissions were estimated to be between 0.6 and 1.2 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level. This indicates a range of approximately 30 percent below to 30 percent above the emission estimate of 0.9 Tg CO<sub>2</sub> Eq.

Methodological recalculations were applied to the entire time series to ensure time-series consistency from 1990 through 2008. Details on the emission trends through time are described in more detail in the Methodology section, above.

### Recalculations Discussion

Carbon black feedstock consumption and natural gas consumption were updated to include 2006 data. The inclusion of this data changed the carbon black feedstock average consumption factor from 1.43 metric tons of carbon black feedstock consumed per metric ton of carbon black

**Table 4-38: Tier 2 Quantitative Uncertainty Estimates for CH<sub>4</sub> Emissions from Petrochemical Production and CO<sub>2</sub> Emissions from Carbon Black Production (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2008 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			Lower Bound	Upper Bound	Lower Bound (%)	Upper Bound (%)
Petrochemical Production	CO <sub>2</sub>	3.4	2.5	4.6	-27%	+32%
Petrochemical Production	CH <sub>4</sub>	0.9	0.6	1.2	-30%	+30%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

produced to 1.69 metric tons of carbon black feedstock consumed per metric ton of carbon black produced and natural gas feedstock average consumption factor from 341 normal cubic meters of natural gas consumed per metric ton of carbon black produced to 321 normal cubic meters of natural gas consumed per metric ton of carbon black produced. The change in these factors increased CO<sub>2</sub> emissions by approximately 50 percent across the time series relative to the previous Inventory.

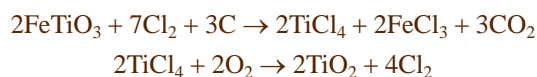
## Planned Improvements

Future improvements to the petrochemicals source category include research into the use of acrylonitrile in the United States, revisions to the carbon black CH<sub>4</sub> and CO<sub>2</sub> emission factors, and research into process and feedstock data to obtain Tier 2 emission estimates from the production of methanol, ethylene, propylene, ethylene dichloride, and ethylene oxide.

## 4.10. Titanium Dioxide Production (IPCC Source Category 2B5)

Titanium dioxide (TiO<sub>2</sub>) is a metal oxide manufactured from titanium ore, and is principally used as a pigment. Titanium dioxide is a principal ingredient in white paint, and is also used as a pigment in the manufacture of white paper, foods, and other products. There are two processes for making TiO<sub>2</sub>: the chloride process and the sulfate process. The chloride process uses petroleum coke and chlorine as raw materials and emits process-related CO<sub>2</sub>. The sulfate process does not use petroleum coke or other forms of C as a raw material and does not emit CO<sub>2</sub>.

The chloride process is based on the following chemical reactions:



The C in the first chemical reaction is provided by petroleum coke, which is oxidized in the presence of the chlorine and FeTiO<sub>3</sub> (the Ti-containing ore) to form CO<sub>2</sub>. The majority of U.S. TiO<sub>2</sub> was produced in the United States through the chloride process, and a special grade of “calcined” petroleum coke is manufactured specifically for this purpose.

**Table 4-39: CO<sub>2</sub> Emissions from Titanium Dioxide (Tg CO<sub>2</sub> Eq. and Gg)**

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	1.2	1,195
1995	1.5	1,526
2000	1.8	1,752
2005	1.8	1,755
2006	1.8	1,836
2007	1.9	1,930
2008	1.8	1,809

Emissions of CO<sub>2</sub> in 2008 were 1.8 Tg CO<sub>2</sub> Eq. (1,809 Gg), which represents an increase of 51 percent since 1990 (see Table 4-39).

## Methodology

Emissions of CO<sub>2</sub> from TiO<sub>2</sub> production were calculated by multiplying annual TiO<sub>2</sub> production by chloride-process-specific emission factors.

Data were obtained for the total amount of TiO<sub>2</sub> produced each year. For years previous to 2004, it was assumed that TiO<sub>2</sub> was produced using the chloride process and the sulfate process in the same ratio as the ratio of the total U.S. production capacity for each process. As of 2004, the last remaining sulfate-process plant in the United States had closed; therefore, 100 percent of post-2004 production uses the chloride process (USGS 2005). An emission factor of 0.4 metric tons C/metric ton TiO<sub>2</sub> was applied to the estimated chloride-process production. It was assumed that all TiO<sub>2</sub> produced using the chloride process was produced using petroleum coke, although some TiO<sub>2</sub> may have been produced with graphite or other C inputs. The amount of petroleum coke consumed annually in TiO<sub>2</sub> production was calculated based on the assumption that the calcined petroleum coke used in the process is 98.4 percent C and 1.6 percent inert materials (Nelson 1969).

The emission factor for the TiO<sub>2</sub> chloride process was taken from the *2006 IPCC Guidelines for National Greenhouse Gas Inventories* (IPCC 2006). Titanium dioxide production data and the percentage of total TiO<sub>2</sub> production capacity that is chloride process for 1990 through 2007 (see Table 4-40) were obtained through the *Minerals Yearbook: Titanium Annual Report* (USGS 1991 through 2008). The

**Table 4-40: Titanium Dioxide Production (Gg)**

Year	Gg
1990	979
1995	1,250
2000	1,400
2005	1,310
2006	1,370
2007	1,440
2008	1,350

2008 production value is from the 2009 *Mineral Commodity Summary Report* (USGS 2009). Because the 2008 capacity value was unavailable at the time of publication, the 2007 capacity value was used. Percentage chloride-process data were not available for 1990 through 1993, and data from the 1994 *USGS Minerals Yearbook* were used for these years. Because a sulfate-process plant closed in September 2001, the chloride-process percentage for 2001 was estimated based on a discussion with Joseph Gambogi (2002). By 2002, only one sulfate plant remained online in the United States and this plant closed in 2004 (USGS 2005).

### Uncertainty and Time-Series Consistency

Although some TiO<sub>2</sub> may be produced using graphite or other C inputs, information and data regarding these practices were not available. Titanium dioxide produced using graphite inputs, for example, may generate differing amounts of CO<sub>2</sub> per unit of TiO<sub>2</sub> produced as compared to that generated through the use of petroleum coke in production. While the most accurate method to estimate emissions would be to base calculations on the amount of reducing agent used in each process rather than on the amount of TiO<sub>2</sub> produced, sufficient data were not available to do so.

Also, annual TiO<sub>2</sub> is not reported by USGS by the type of production process used (chloride or sulfate). Only the

percentage of total production capacity by process is reported. The percent of total TiO<sub>2</sub> production capacity that was attributed to the chloride process was multiplied by total TiO<sub>2</sub> production to estimate the amount of TiO<sub>2</sub> produced using the chloride process (since, as of 2004, the last remaining sulfate-process plant in the United States closed). This assumes that the chloride-process plants and sulfate-process plants operate at the same level of utilization. Finally, the emission factor was applied uniformly to all chloride-process production, and no data were available to account for differences in production efficiency among chloride-process plants. In calculating the amount of petroleum coke consumed in chloride-process TiO<sub>2</sub> production, literature data were used for petroleum coke composition. Certain grades of petroleum coke are manufactured specifically for use in the TiO<sub>2</sub> chloride process; however, this composition information was not available.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-41. Titanium dioxide consumption CO<sub>2</sub> emissions were estimated to be between 1.6 and 2.0 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level. This indicates a range of approximately 12 percent below and 13 percent above the emission estimate of 1.8 Tg CO<sub>2</sub> Eq.

Methodological recalculations were applied to the entire time series to ensure time-series consistency from 1990 through 2008. Details on the emission trends through time are described in more detail in the Methodology section, above.

### Planned Improvements

Future improvements to TiO<sub>2</sub> production methodology include researching the significance of titanium-slag production in electric furnaces and synthetic-rutile production using the Becher process in the United States. Significant use of these production processes will be included in future estimates.

**Table 4-41: Tier 2 Quantitative Uncertainty Estimates for CO<sub>2</sub> Emissions from Titanium Dioxide Production (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2008 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Titanium Dioxide Production	CO <sub>2</sub>	1.8	1.6	2.0	-12%	+13%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

## 4.11. Carbon Dioxide Consumption (IPCC Source Category 2B5)

Carbon dioxide is used for a variety of commercial applications, including food processing, chemical production, carbonated beverage production, and refrigeration, and is also used in petroleum production for enhanced oil recovery (EOR). Carbon dioxide used for EOR is injected into the underground reservoirs to increase the reservoir pressure to enable additional petroleum to be produced.

For the most part, CO<sub>2</sub> used in non-EOR applications will eventually be released to the atmosphere, and for the purposes of this analysis CO<sub>2</sub> used in commercial applications other than EOR is assumed to be emitted to the atmosphere. CO<sub>2</sub> used in EOR applications is discussed in the Energy Chapter under “Carbon Capture and Storage, including Enhanced Oil Recovery” and is not discussed in this section.

Carbon dioxide is produced from naturally occurring CO<sub>2</sub> reservoirs, as a by-product from the energy and industrial production processes (e.g., ammonia production, fossil fuel combustion, ethanol production), and as a by-product from the production of crude oil and natural gas, which contain naturally occurring CO<sub>2</sub> as a component. Only CO<sub>2</sub> produced from naturally occurring CO<sub>2</sub> reservoirs and used in industrial applications other than EOR is included in this analysis. Neither by-product CO<sub>2</sub> generated from energy nor industrial production processes nor CO<sub>2</sub> separated from crude oil and natural gas are included in this analysis for a number of reasons. Carbon dioxide captured from biogenic sources (e.g., ethanol production plants) is not included in the Inventory. Carbon dioxide captured from crude oil and gas production is used in EOR applications and is therefore reported in the Energy Chapter. Any CO<sub>2</sub> captured from industrial or energy production processes (e.g., ammonia plants, fossil fuel combustion) and used in non-EOR applications is assumed to be emitted to the atmosphere. The CO<sub>2</sub> emissions from such capture and use are therefore accounted for under Ammonia Production, Fossil Fuel Combustion, or other appropriate source category.<sup>14</sup>

Carbon dioxide is produced as a by-product of crude oil and natural gas production. This CO<sub>2</sub> is separated from the

crude oil and natural gas using gas processing equipment, and may be emitted directly to the atmosphere, or captured and reinjected into underground formations, used for EOR, or sold for other commercial uses. A further discussion of CO<sub>2</sub> used in EOR is described in the Energy Chapter under the text box titled “Carbon Dioxide Transport, Injection, and Geological Storage.” The only CO<sub>2</sub> consumption that is accounted for in this analysis is CO<sub>2</sub> produced from naturally-occurring CO<sub>2</sub> reservoirs that is used in commercial applications other than EOR.

There are currently two facilities, one in Mississippi and one in New Mexico, producing CO<sub>2</sub> from naturally occurring CO<sub>2</sub> reservoirs for use in both EOR and in other commercial applications (e.g., chemical manufacturing, food production). There are other naturally occurring CO<sub>2</sub> reservoirs, mostly located in the western U.S. Facilities are producing CO<sub>2</sub> from these natural reservoirs, but they are only producing CO<sub>2</sub> for EOR applications, not for other commercial applications (Allis et al. 2000). Carbon dioxide production from these facilities is discussed in the Energy Chapter.

In 2008, the amount of CO<sub>2</sub> produced by the Mississippi and New Mexico facilities for commercial applications and subsequently emitted to the atmosphere were 1.8 Tg CO<sub>2</sub> Eq. (1,780 Gg) (see Table 4-42). This amount represents a decrease of 5 percent from the previous year and an increase of 26 percent since 1990. This increase was due to an increase in production at the Mississippi facility, despite the decrease in the percent of the facility’s total reported production that was used for commercial applications.

**Table 4-42: CO<sub>2</sub> Emissions from CO<sub>2</sub> Consumption (Tg CO<sub>2</sub> Eq. and Gg)**

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	1.4	1,416
1995	1.4	1,422
2000	1.4	1,421
2005	1.3	1,321
2006	1.7	1,709
2007	1.9	1,867
2008	1.8	1,780

<sup>14</sup> There are currently four known electric power plants operating in the U.S. that capture CO<sub>2</sub> for use as food-grade CO<sub>2</sub> or other industrial processes; however, insufficient data prevents estimating emissions from these activities as part of Carbon Dioxide Consumption.

## Methodology

Carbon dioxide emission estimates for 1990 through 2008 were based on production data for the two facilities currently producing CO<sub>2</sub> from naturally-occurring CO<sub>2</sub> reservoirs for use in non-EOR applications. Some of the CO<sub>2</sub> produced by these facilities is used for EOR and some is used in other commercial applications (e.g., chemical manufacturing, food production). It is assumed that 100 percent of the CO<sub>2</sub> production used in commercial applications other than EOR is eventually released into the atmosphere.

Carbon dioxide production data for the Jackson Dome, Mississippi facility and the percentage of total production that was used for EOR and in non-EOR applications were obtained from the Advanced Resources Institute (ARI 2006, 2007) for 1990 to 2000 and from the Annual Reports for Denbury Resources (Denbury Resources 2002 through 2009) for 2001 to 2007 (see Table 4-43). Denbury Resources reported the average CO<sub>2</sub> production in units of MMCF CO<sub>2</sub> per day for 2001 through 2008 and reported the percentage of the total average annual production that was used for EOR. Carbon dioxide production data for the Bravo Dome, New Mexico facility were obtained from the Advanced Resources International, Inc. (ARI 1990 - 2009). The percentage of total production that was used for EOR and in non-EOR applications were obtained from the New Mexico Bureau of Geology and Mineral Resources (Broadhead 2003 and New Mexico Bureau of Geology and Mineral Resources 2006).

## Uncertainty and Time-Series Consistency

Uncertainty is associated with the number of facilities that are currently producing CO<sub>2</sub> from naturally occurring

CO<sub>2</sub> reservoirs for commercial uses other than EOR, and for which the CO<sub>2</sub> emissions are not accounted for elsewhere. Research indicates that there are only two such facilities, which are in New Mexico and Mississippi; however, additional facilities may exist that have not been identified. In addition, it is possible that CO<sub>2</sub> recovery exists in particular production and end-use sectors that are not accounted for elsewhere. Such recovery may or may not affect the overall estimate of CO<sub>2</sub> emissions from that sector depending upon the end use to which the recovered CO<sub>2</sub> is applied. Further research is required to determine whether CO<sub>2</sub> is being recovered from other facilities for application to end uses that are not accounted for elsewhere.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-44. Carbon dioxide consumption CO<sub>2</sub> emissions were estimated to be between 1.4 and 2.3 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level. This indicates a range of approximately 24 percent below to 27 percent above the emission estimate of 1.8 Tg CO<sub>2</sub> Eq.

Methodological recalculations were applied to the entire time series to ensure time-series consistency from 1990 through 2008. Details on the emission trends through time are described in more detail in the Methodology section, above.

## Planned Improvements

Future improvements to the Carbon Dioxide Consumption source category include research into CO<sub>2</sub> capture for industrial purposes at electric power plants. Currently, four plants have been identified that capture CO<sub>2</sub> for these purposes, but insufficient data prevents including them in the current emission estimate.

**Table 4-43: CO<sub>2</sub> Production (Gg CO<sub>2</sub>) and the Percent Used for Non-EOR Applications for Jackson Dome and Bravo Dome**

Year	Jackson Dome CO <sub>2</sub> Production (Gg)	Jackson Dome % Used for Non-EOR	Bravo Dome CO <sub>2</sub> Production (Gg)	Bravo Dome % Used for Non-EOR
1990	1,353	100%	6,301	1%
1995	1,353	100%	6,862	1%
2000	1,353	100%	6,834	1%
2005	4,678	27%	5,799	1%
2006	6,610	25%	5,613	1%
2007	9,529	19%	5,605	1%
2008	12,312	14%	5,605	1%

**Table 4-44: Tier 2 Quantitative Uncertainty Estimates for CO<sub>2</sub> Emissions from CO<sub>2</sub> Consumption (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2008 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
CO <sub>2</sub> Consumption	CO <sub>2</sub>	1.8	1.4	2.3	-24%	+27%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

## 4.12. Phosphoric Acid Production (IPCC Source Category 2B5)

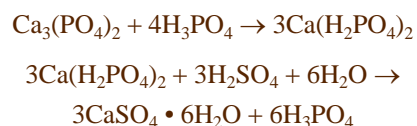
Phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) is a basic raw material in the production of phosphate-based fertilizers. Phosphate rock is mined in Florida, North Carolina, Idaho, Utah, and other areas of the United States and is used primarily as a raw material for phosphoric acid production. The production of phosphoric acid from phosphate rock produces byproduct gypsum (CaSO<sub>4</sub>•2H<sub>2</sub>O), referred to as phosphogypsum.

The composition of natural phosphate rock varies depending upon the location where it is mined. Natural phosphate rock mined in the United States generally contains inorganic C in the form of calcium carbonate (limestone) and also may contain organic C. The chemical composition of phosphate rock (francolite) mined in Florida is:

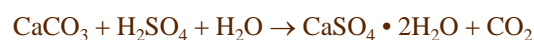


The calcium carbonate component of the phosphate rock is integral to the phosphate rock chemistry. Phosphate rock can also contain organic C that is physically incorporated into the mined rock but is not an integral component of the phosphate rock chemistry. Phosphoric acid production from natural phosphate rock is a source of CO<sub>2</sub> emissions, due to the chemical reaction of the inorganic C (calcium carbonate) component of the phosphate rock.

The phosphoric acid production process involves chemical reaction of the calcium phosphate (Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>) component of the phosphate rock with sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and recirculated phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) (EFMA 2000). The primary chemical reactions for the production of phosphoric acid from phosphate rock are:



The limestone (CaCO<sub>3</sub>) component of the phosphate rock reacts with the sulfuric acid in the phosphoric acid production process to produce calcium sulfate (phosphogypsum) and CO<sub>2</sub>. The chemical reaction for the limestone-sulfuric acid reaction is:



Total marketable phosphate rock production in 2008 was 30.2 million metric tons (USGS 2009). Approximately 87 percent of domestic phosphate rock production was mined in Florida and North Carolina, while approximately 13 percent of production was mined in Idaho and Utah. Data on the 2008 imports of phosphate rock were unavailable at the time of publication. The 2007 value of 2.7 million metric tons of crude phosphate rock was therefore assumed as the 2008 value. The vast majority, 99 percent, of imported phosphate rock is sourced from Morocco (USGS 2005). Marketable phosphate rock production, including domestic production and imports for consumption, increased by approximately 4 percent between 2007 and 2008. However, over the 1990 to 2008 period, production has decreased by 24 percent. Total CO<sub>2</sub> emissions from phosphoric acid production were 1.2 Tg CO<sub>2</sub> Eq. (1,187 Gg) in 2008 (see Table 4-45).

**Table 4-45: CO<sub>2</sub> Emissions from Phosphoric Acid Production (Tg CO<sub>2</sub> Eq. and Gg)**

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	1.5	1,529
1995	1.5	1,513
2000	1.4	1,382
2005	1.4	1,386
2006	1.2	1,167
2007	1.2	1,166
2008	1.2	1,187



## Methodology

Carbon dioxide emissions from production of phosphoric acid from phosphate rock are calculated by multiplying the average amount of calcium carbonate contained in the natural phosphate rock by the amount of phosphate rock that is used annually to produce phosphoric acid, accounting for domestic production and net imports for consumption.

The CO<sub>2</sub> emissions calculation methodology is based on the assumption that all of the inorganic C (calcium carbonate) content of the phosphate rock reacts to CO<sub>2</sub> in the phosphoric acid production process and is emitted with the stack gas. The methodology also assumes that none of the organic C content of the phosphate rock is converted to CO<sub>2</sub> and that all of the organic C content remains in the phosphoric acid product.

From 1993 to 2004, the USGS *Mineral Yearbook: Phosphate Rock* disaggregated phosphate rock mined annually in Florida and North Carolina from phosphate rock mined annually in Idaho and Utah, and reported the annual amounts of phosphate rock exported and imported for consumption (see Table 4-46). For the years 1990, 1991, 1992, 2005, 2006, and 2007 only nationally aggregated mining data was reported by USGS. For these years, the breakdown of phosphate rock mined in Florida and North Carolina, and the amount mined in Idaho and Utah, are approximated using 1993 to 2004 data. Data for domestic production of phosphate rock, exports of phosphate rock (primarily from Florida and North Carolina), and imports of phosphate rock for consumption for 1990 through 2007 were obtained from USGS *Minerals Yearbook: Phosphate Rock* (USGS 1994 through 2008). From 2004 through 2007, the USGS reported no exports of phosphate rock from U.S. producers (USGS 2005 through 2008). Since 2008 data were unavailable at the time of publication, the 2007 values and assumptions outlined above were used as approximates for

2008. The 2008 value for phosphate rock production was available (USGS 2009).

The carbonate content of phosphate rock varies depending upon where the material is mined. Composition data for domestically mined and imported phosphate rock were provided by the Florida Institute of Phosphate Research (FIPR 2003). Phosphate rock mined in Florida contains approximately 1 percent inorganic C, and phosphate rock imported from Morocco contains approximately 1.46 percent inorganic C. Calcined phosphate rock mined in North Carolina and Idaho contains approximately 0.41 percent and 0.27 percent inorganic C, respectively (see Table 4-47).

Carbonate content data for phosphate rock mined in Florida are used to calculate the CO<sub>2</sub> emissions from consumption of phosphate rock mined in Florida and North Carolina (87 percent of domestic production) and carbonate content data for phosphate rock mined in Morocco are used to calculate CO<sub>2</sub> emissions from consumption of imported phosphate rock. The CO<sub>2</sub> emissions calculation is based on the assumption that all of the domestic production of phosphate rock is used in uncalcined form. As of 2006, the USGS noted that one phosphate rock producer in Idaho produces calcined phosphate rock; however, no production data were available for this single producer (USGS 2006). Carbonate content data for uncalcined phosphate rock mined in Idaho and Utah (13 percent of domestic production) were not available, and carbonate content was therefore estimated from the carbonate

## Uncertainty and Time-Series Consistency

Phosphate rock production data used in the emission calculations were developed by the USGS through monthly and semiannual voluntary surveys of the active phosphate rock mines during 2008. For previous years in the time

**Table 4-46: Phosphate Rock Domestic Production, Exports, and Imports (Gg)**

Location	1990	1995	2000	2005	2006	2007	2008
U.S. Production <sup>a</sup>	49,800	43,720	37,370	36,100	30,100	29,700	30,200
FL & NC	42,494	38,100	31,900	31,227	26,037	25,691	26,123
ID & UT	7,306	5,620	5,470	4,874	4,064	4,010	4,077
Exports—FL & NC	6,240	2,760	299	–	–	–	–
Imports—Morocco	451	1,800	1,930	2,630	2,420	2,670	2,750
<b>Total U.S. Consumption</b>	<b>44,011</b>	<b>42,760</b>	<b>39,001</b>	<b>38,730</b>	<b>32,520</b>	<b>32,370</b>	<b>32,950</b>

– Assumed equal to zero.

<sup>a</sup> USGS does not disaggregate production data regionally (FL & NC and ID & UT) for 1990, 2005, 2006, and 2007. Data for those years are estimated based on the remaining time series distribution.

**Table 4-47: Chemical Composition of Phosphate Rock (Percent by Weight)**

Composition	Central Florida	North Florida	North Carolina (calcined)	Idaho (calcined)	Morocco
Total Carbon (as C)	1.60	1.76	0.76	0.60	1.56
Inorganic Carbon (as C)	1.00	0.93	0.41	0.27	1.46
Organic Carbon (as C)	0.60	0.83	0.35	–	0.10
Inorganic Carbon (as CO <sub>2</sub> )	3.67	3.43	1.50	1.00	5.00

– Assumed equal to zero.  
Source: FIPR (2003).

series, USGS provided the data disaggregated regionally; however, beginning in 2006 only total U.S. phosphate rock production were reported. Regional production for 2007 was estimated based on regional production data from previous years and multiplied by regionally-specific emission factors. Regional production for 2008 was not yet available at the time of publication. There is uncertainty associated with the degree to which the estimated 2007 regional production data represents actual production in those regions. Total U.S. phosphate rock production data are not considered to be a significant source of uncertainty because all the domestic phosphate rock producers report their annual production to the USGS. Data for exports of phosphate rock used in the emission calculation are reported by phosphate rock producers and are not considered to be a significant source of uncertainty. Data for imports for consumption are based on international trade data collected by the U.S. Census Bureau. These U.S. government economic data are not considered to be a significant source of uncertainty.

An additional source of uncertainty in the calculation of CO<sub>2</sub> emissions from phosphoric acid production is the carbonate composition of phosphate rock; the composition of phosphate rock varies depending upon where the material is mined, and may also vary over time. Another source of uncertainty is the disposition of the organic C content of the phosphate rock. A representative of the FIPR indicated that in the phosphoric acid production process, the organic C content of the mined phosphate rock generally remains in the phosphoric acid product, which is what produces the color of the phosphoric acid product (FIPR 2003a). Organic C is therefore not included in the calculation of CO<sub>2</sub> emissions from phosphoric acid production.

A third source of uncertainty is the assumption that all domestically-produced phosphate rock is used in phosphoric acid production and used without first being calcined. Calcination of the phosphate rock would result in conversion

of some of the organic C in the phosphate rock into CO<sub>2</sub>. However, according to the USGS, only one producer in Idaho is currently calcining phosphate rock, and no data were available concerning the annual production of this single producer (USGS 2005). For available years, total production of phosphate rock in Utah and Idaho combined amounts to approximately 13 percent of total domestic production on average (USGS 1994 through 2005).

Finally, USGS indicated that approximately 7 percent of domestically-produced phosphate rock is used to manufacture elemental phosphorus and other phosphorus-based chemicals, rather than phosphoric acid (USGS 2006). According to USGS, there is only one domestic producer of elemental phosphorus, in Idaho, and no data were available concerning the annual production of this single producer. Elemental phosphorus is produced by reducing phosphate rock with coal coke, and it is therefore assumed that 100 percent of the carbonate content of the phosphate rock will be converted to CO<sub>2</sub> in the elemental phosphorus production process. The calculation for CO<sub>2</sub> emissions is based on the assumption that phosphate rock consumption, for purposes other than phosphoric acid production, results in CO<sub>2</sub> emissions from 100 percent of the inorganic C content in phosphate rock, but none from the organic C content.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-48. Phosphoric acid production CO<sub>2</sub> emissions were estimated to be between 1.0 and 1.4 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level. This indicates a range of approximately 18 percent below and 19 percent above the emission estimate of 1.2 Tg CO<sub>2</sub> Eq.

Methodological recalculations were applied to the entire time series to ensure time-series consistency from 1990 through 2008. Details on the emission trends through time are described in more detail in the Methodology section, above.

**Table 4-48: Tier 2 Quantitative Uncertainty Estimates for CO<sub>2</sub> Emissions from Phosphoric Acid Production (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2008 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			(Tg CO <sub>2</sub> Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Phosphoric Acid Production	CO <sub>2</sub>	1.2	1.0	1.4	-18%	+19%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

## Planned Improvements

Currently, data sources for the carbonate content of the phosphate rock are limited. If additional data sources are found, this information will be incorporated into future estimates.

## 4.13. Iron and Steel Production (IPCC Source Category 2C1) and Metallurgical Coke Production

The production of iron and steel is an energy-intensive process that also generates process-related emissions of CO<sub>2</sub> and CH<sub>4</sub>. In the United States, steel is produced through both primary and secondary processes. Historically, primary production—based on the use of a basic oxygen furnace (BOF) with pig iron as the primary feedstock—has been the dominant method. But secondary production through the use of electric arc furnaces (EAFs) has increased significantly in recent years due to the economic advantages steel recycling, which has been driven by the increased availability of scrap steel. Total production of crude steel in the United States increased steadily from approximately 47,116,000 tons in 2001 to 62,835,000 tons in 2007. But due to the decrease in demand caused by the global economic downturn, crude steel production in the United States decreased to 58,191,000 tons in 2008.

Metallurgical coke is used widely during the production of iron and steel. The production of metallurgical coke from coking coal occurs both on-site at “integrated” iron and steel plants and off-site at “merchant” coke plants. Metallurgical coke is produced by heating coking coal in a coke oven in a low-oxygen environment. The process drives off the volatile components of the coking coal and produces coal (metallurgical) coke. Carbon containing byproducts of the metallurgical coke manufacturing process include coke oven gas, coal tar, coke breeze (small-grade coke oven coke with

particle size <5mm) and light oil. Coke oven gas is recovered and used for underfiring the coke ovens and within the iron and steel mill. Small amounts of coke oven gas are also sold as synthetic natural gas outside of iron and steel mills (and are accounted for in the Energy chapter). Coal tar is used as a raw material to produce anodes used for primary aluminum production, electric arc furnace (EAF) steel production, and other electrolytic processes, and also is used in the production of other coal tar products. Light oil is sold to petroleum refiners who use the material as an additive for gasoline. The metallurgical coke production process produces CO<sub>2</sub> emissions and fugitive CH<sub>4</sub> emissions.

Iron is produced by first reducing iron oxide (iron ore) with metallurgical coke in a blast furnace to produce pig iron (impure or crude iron containing about 3 to 5 percent carbon by weight). Inputs to the blast furnace include natural gas, fuel oil, and coke oven gas. The carbon in the metallurgical coke used in the blast furnace combines with oxides in the iron ore in a reducing atmosphere to produce blast furnace gas containing carbon monoxide (CO) and CO<sub>2</sub>. The CO is then converted and emitted as CO<sub>2</sub> when combusted to either pre-heat the blast air used in the blast furnace or for other purposes at the steel mill. Iron may be introduced into the blast furnace in the form of raw iron ore, pellets (9-16mm iron-containing spheres), briquettes, or sinter. Pig iron is used as a raw material in the production of steel, which contains about 1 percent carbon by weight. Pig iron is also used as a raw material in the production of iron products in foundries. The pig iron production process produces CO<sub>2</sub> emissions and fugitive CH<sub>4</sub> emissions.

Iron can also be produced through the direct reduction process; wherein, iron ore is reduced to metallic iron in the solid state at process temperatures less than 1000°C. Direct reduced iron production results in process emissions of CO<sub>2</sub> and emissions of CH<sub>4</sub> through the consumption of natural gas used during the reduction process.

Sintering is a thermal process by which fine iron-bearing particles, such as air emission control system dust, are baked, which causes the material to agglomerate into roughly one-inch pellets that are then recharged into the blast furnace for pig iron production. Iron ore particles may also be formed into larger pellets or briquettes by mechanical means, and then agglomerated by heating. The agglomerate is then crushed and screened to produce an iron-bearing feed that is charged into the blast furnace. The sintering process produces CO<sub>2</sub> and fugitive CH<sub>4</sub> emissions through the consumption of carbonaceous inputs (e.g., coke breeze) during the sintering process.

Steel is produced from varying levels of pig iron and scrap steel in specialized BOF and EAF steel-making furnaces. Carbon inputs to BOF steel-making furnaces include pig iron and scrap steel as well as natural gas, fuel oil, and fluxes (e.g., limestone, dolomite). In a BOF, the carbon in iron and scrap steel combines with high-purity oxygen to reduce the carbon content of the metal to the amount desired for the specified grade of steel. EAFs use carbon electrodes, charge carbon and other materials (e.g., natural gas) to aid in melting metal inputs (primarily recycled scrap steel), which are refined and alloyed to produce the desired grade of steel. Carbon dioxide emissions occur in BOFs through the reduction process. In EAFs, CO<sub>2</sub> emissions result primarily from the consumption of carbon electrodes and also from the consumption of supplemental materials used to augment the melting process.

In addition to the production processes mentioned above, CO<sub>2</sub> is also generated at iron and steel mills through the consumption of process by-products (e.g., blast furnace gas, coke oven gas) used for various purposes including heating, annealing, and electricity generation.<sup>15</sup> Process by-products sold for use as synthetic natural gas are deducted and reported in the Energy chapter (emissions associated with natural gas and fuel oil consumption for these purposes are reported in the Energy chapter).

<sup>15</sup> Emissions resulting from fuel consumption for the generation of electricity are reported in the Energy chapter. Some integrated iron and steel mills have on-site electricity generation for which fuel is used. Data are not available concerning the amounts and types of fuels used in iron and steel mills to generate electricity. Therefore all of the fuel consumption reported at iron and steel mills is assumed to be used within the iron and steel mills for purposes other than electricity consumption, and the amounts of any fuels actually used to produce electricity at iron and steel mills are not subtracted from the electricity production emissions value used in the Energy chapter, therefore some double-counting of electricity-related CO<sub>2</sub> emissions may occur.

The majority of CO<sub>2</sub> emissions from the iron and steel production process come from the use of metallurgical coke in the production of pig iron and from the consumption of other process by-products at the iron and steel mill, with smaller amounts evolving from the use of flux and from the removal of carbon from pig iron used to produce steel. Some carbon is also stored in the finished iron and steel products.

According to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories (IPCC 2006), the production of metallurgical coke from coking coal is considered to be an energy use of fossil fuel and the use of coke in iron and steel production is considered to be an industrial process source. Therefore, the Guidelines suggest that emissions from the production of metallurgical coke should be reported separately in the Energy source, while emissions from coke consumption in iron and steel production should be reported in the industrial process source. However, the approaches and emission estimates for both metallurgical coke production and iron and steel production are both presented here because the activity data used to estimate emissions from metallurgical coke production have significant overlap with activity data used to estimate iron and steel production emissions. Further, some by-products (e.g., coke oven gas) of the metallurgical coke production process are consumed during iron and steel production, and some by-products of the iron and steel production process (e.g., blast furnace gas) are consumed during metallurgical coke production. Emissions associated with the consumption of these by-products are attributed to point of consumption. As an example, CO<sub>2</sub> emissions associated with the combustion of coke oven gas in the blast furnace during pig iron production are attributed to pig iron production. Emissions associated with fuel consumption downstream of the iron and steelmaking furnaces, such as natural gas used for heating and annealing purposes, are reported in the Energy chapter.

### **Metallurgical Coke Production**

Emissions of CO<sub>2</sub> and CH<sub>4</sub> from metallurgical coke production in 2008 were 5.3 Tg CO<sub>2</sub> Eq. (5,281 Gg) and less than 0.05 Tg CO<sub>2</sub> Eq. (less than 0.5 Gg), respectively (see Table 4-49 and Table 4-50), totaling 5.3 Tg CO<sub>2</sub> Eq. Emissions increased in 2008, but have decreased overall since 1990. In 2008, domestic coke production decreased by 3.4 percent and has decreased overall since 1990. Coke production in 2008 was 25 percent lower than in 2000 and 43 percent below 1990. Overall, emissions from metallurgical

**Table 4-49: CO<sub>2</sub> and CH<sub>4</sub> Emissions from Metallurgical Coke Production (Tg CO<sub>2</sub> Eq.)**

Gas	1990	1995	2000	2005	2006	2007	2008
CO <sub>2</sub>	5.5	5.0	4.4	3.8	3.7	3.8	5.3
CH <sub>4</sub>	+	+	+	+	+	+	+
<b>Total</b>	<b>5.5</b>	<b>5.0</b>	<b>4.4</b>	<b>3.8</b>	<b>3.7</b>	<b>3.8</b>	<b>5.3</b>

+ Does not exceed 0.05 Tg CO<sub>2</sub> Eq.

**Table 4-50: CO<sub>2</sub> and CH<sub>4</sub> Emissions from Metallurgical Coke Production (Gg)**

Gas	1990	1995	2000	2005	2006	2007	2008
CO <sub>2</sub>	5,498	5,037	4,381	3,849	3,682	3,806	5,281
CH <sub>4</sub>	+	+	+	+	+	+	+

+ Does not exceed 0.5 Gg.

coke production have declined by 4 percent (0.2 Tg CO<sub>2</sub> Eq.) from 1990 to 2008.

### Iron and Steel Production

Emissions of CO<sub>2</sub> and CH<sub>4</sub> from iron and steel production in 2008 were 63.7 Tg CO<sub>2</sub> Eq. (63,729 Gg) and 0.6 Tg CO<sub>2</sub> Eq. (30.8 Gg), respectively (see Table 4-51 through Table 4-54), totaling 64.4 Tg CO<sub>2</sub> Eq. Emissions decreased in 2008 and have decreased overall since 1990 due to restructuring of the industry, technological improvements, and increased scrap steel utilization. CO<sub>2</sub> emission estimates

include emissions from the consumption of carbonaceous materials in the blast furnace, EAF, and BOF as well as blast furnace gas and coke oven gas consumption for other activities at the steel mill.

In 2008, domestic production of pig iron decreased by 7 percent. Overall, domestic pig iron production has declined since the 1990s. Pig iron production in 2008 was 30 percent lower than in 2000 and 32 percent below 1990. While CO<sub>2</sub> emissions from steel production have increased by 2 percent (0.1 Tg CO<sub>2</sub> Eq.) since 1990, overall CO<sub>2</sub> emissions from

**Table 4-51: CO<sub>2</sub> Emissions from Iron and Steel Production (Tg CO<sub>2</sub> Eq.)**

Process	1990	1995	2000	2005	2006	2007	2008
Sinter Production	2.4	2.5	2.2	1.7	1.4	1.4	1.3
Iron Production	47.9	38.8	33.8	19.6	23.9	27.3	25.7
Steel Production	7.5	8.6	7.9	8.5	8.9	9.4	7.6
Other Activities <sup>a</sup>	39.3	40.9	39.9	34.2	32.6	31.0	29.1
<b>Total</b>	<b>97.1</b>	<b>90.7</b>	<b>83.7</b>	<b>63.9</b>	<b>66.9</b>	<b>69.0</b>	<b>63.7</b>

<sup>a</sup> Includes emissions from blast furnace gas and coke oven gas combustion for activities at the steel mill other than consumption in blast furnace, EAFs, or BOFs.

Note: Totals may not sum due to independent rounding.

**Table 4-52: CO<sub>2</sub> Emissions from Iron and Steel Production (Gg)**

Process	1990	1995	2000	2005	2006	2007	2008
Sinter Production	2,448	2,512	2,158	1,663	1,418	1,383	1,299
Iron Production	47,886	38,791	33,808	19,576	23,931	27,265	25,699
Steel Production	7,476	8,557	7,885	8,491	8,925	9,384	7,594
Other Activities <sup>a</sup>	39,256	40,850	39,877	34,152	32,583	30,964	29,137
<b>Total</b>	<b>97,066</b>	<b>90,711</b>	<b>83,728</b>	<b>63,882</b>	<b>66,857</b>	<b>68,996</b>	<b>63,729</b>

<sup>a</sup> Includes emissions from blast furnace gas and coke oven gas combustion for activities at the steel mill other than consumption in blast furnace, EAFs, or BOFs.

Note: Totals may not sum due to independent rounding.

**Table 4-53: CH<sub>4</sub> Emissions from Iron and Steel Production (Tg CO<sub>2</sub> Eq.)**

Process	1990	1995	2000	2005	2006	2007	2008
Sinter Production	+	+	+	+	+	+	+
Iron Production	1.0	1.0	0.9	0.7	0.7	0.7	0.6
<b>Total</b>	<b>1.0</b>	<b>1.0</b>	<b>0.9</b>	<b>0.7</b>	<b>0.7</b>	<b>0.7</b>	<b>0.6</b>

+ Does not exceed 0.05 Tg CO<sub>2</sub> Eq.  
Note: Totals may not sum due to independent rounding.

**Table 4-54: CH<sub>4</sub> Emissions from Iron and Steel Production (Gg)**

Process	1990	1995	2000	2005	2006	2007	2008
Sinter Production	0.9	0.9	0.7	0.6	0.5	0.5	0.4
Iron Production	44.7	45.8	43.1	33.5	34.1	32.7	30.4
<b>Total</b>	<b>45.6</b>	<b>46.7</b>	<b>43.8</b>	<b>34.1</b>	<b>34.6</b>	<b>33.2</b>	<b>30.8</b>

Note: Totals may not sum due to independent rounding.

iron and steel production have declined by 34 percent (33.3 Tg CO<sub>2</sub> Eq.) from 1990 to 2008.

## Methodology

Emission estimates presented in this chapter are based on the methodologies provided by the *2006 IPCC Guidelines for National Greenhouse Gas Inventories* (IPCC 2006), which call for a mass balance accounting of the carbonaceous inputs and outputs during the iron and steel production process and the metallurgical coke production process.

### Metallurgical Coke Production

Coking coal is used to manufacture metallurgical (coal) coke that is used primarily as a reducing agent in the production of iron and steel, but is also used in the production of other metals including lead and zinc (see Lead Production and Zinc Production in this chapter). Emissions associated with producing metallurgical coke from coking coal are estimated and reported separately from emissions that result from the iron and steel production process. To estimate emission from metallurgical coke production, a Tier 2 method provided by the *2006 IPCC Guidelines for National Greenhouse Gas Inventories* (IPCC 2006) was utilized. The amount of carbon contained in materials produced during the metallurgical coke production process (i.e., coke, coke breeze, coke oven gas, and coal tar) is deducted from the amount of carbon contained in materials consumed during the metallurgical coke production process (i.e., natural gas, blast furnace gas, coking coal). Light oil, which is produced during the metallurgical coke production process, is excluded from

the deductions due to data limitations. The amount of carbon contained in these materials is calculated by multiplying the material-specific carbon content by the amount of material consumed or produced (see Table 4-55). The amount of coal tar produced was approximated using a production factor of 0.03 tons of coal tar per ton of coking coal consumed. The amount of coke breeze produced was approximated using a production factor of 0.075 tons of coke breeze per ton of coking coal consumed. Data on the consumption of carbonaceous materials (other than coking coal) as well as coke oven gas production were available for integrated steel mills only (i.e., steel mills with co-located coke plants). Therefore, carbonaceous material (other than coking coal) consumption and coke oven gas production were excluded from emission estimates for merchant coke plants. Carbon contained in coke oven gas used for coke-oven underfiring was not included in the deductions to avoid double-counting.

**Table 4-55: Material Carbon Contents for Metallurgical Coke Production**

Material	kg C/kg
Coal Tar	0.62
Coke	0.83
Coke Breeze	0.83
Coking Coal	0.73
Material	kg C/GJ
Coke Oven Gas	12.1
Blast Furnace Gas	70.8

Source: IPCC (2006), Table 4.3. Coke Oven Gas and Blast Furnace Gas, Table 1.3.

**Table 4-56: Production and Consumption Data for the Calculation of CO<sub>2</sub> and CH<sub>4</sub> Emissions from Metallurgical Coke Production (Thousand Metric Tons)**

Source/Activity Data	1990	1995	2000	2005	2006	2007	2008
<b>Metallurgical Coke Production</b>							
Coking Coal Consumption at Coke Plants	35,269	29,948	26,254	21,259	20,827	20,607	20,477
Coke Production at Coke Plants	25,054	21,545	18,877	15,167	14,882	14,698	14,194
Coke Breeze Production	1,879	1,616	1,416	1,138	1,116	1,102	1,065
Coal Tar Production	752	646	566	455	446	441	426

**Table 4-57: Production and Consumption Data for the Calculation of CO<sub>2</sub> Emissions from Metallurgical Coke Production (million ft<sup>3</sup>)**

Source/Activity Data	1990	1995	2000	2005	2006	2007	2008
<b>Metallurgical Coke Production</b>							
Coke Oven Gas Production <sup>a</sup>	250,767	166,750	149,477	114,213	114,386	109,912	103,191
Natural Gas Consumption	599	184	180	2,996	3,277	3,309	3,134
Blast Furnace Gas Consumption	24,602	29,423	26,075	4,460	5,505	5,144	4,829

<sup>a</sup> Includes coke oven gas used for purposes other than coke oven underfiring only.

The production processes for metallurgical coke production results in fugitive emissions of CH<sub>4</sub>, which are emitted via leaks in the production equipment rather than through the emission stacks or vents of the production plants. The fugitive emissions were calculated by applying Tier 1 emission factors (0.1 g CH<sub>4</sub> per metric ton) taken from the 2006 IPCC Guidelines for National Greenhouse Gas Inventories (IPCC 2006) for metallurgical coke production.

Data relating to the mass of coking coal consumed at metallurgical coke plants and the mass of metallurgical coke produced at coke plants were taken from the Energy Information Administration (EIA), *Quarterly Coal Report* October through December (EIA 1998 through 2004) and January through March (EIA 2006, 2007, 2008a, 2009) (see Table 4-56). Data on the volume of natural gas consumption, blast furnace gas consumption, and coke oven gas production for metallurgical coke production at integrated steel mills were obtained from the American Iron and Steel Institute (AISI), *Annual Statistical Report* (AISI 2004 through 2009) and through personal communications with AISI (2008b) (see Table 4-57). The factor for the quantity of coal tar produced per ton of coking coal consumed was provided by AISI (2008b). The factor for the quantity of coke breeze produced per ton of coking coal consumed was obtained through Table 2-1 of the report *Energy and Environmental Profile of the U.S. Iron and Steel Industry* (DOE 2000). Data on natural gas consumption and coke oven gas production at

merchant coke plants were not available and were excluded from the emission estimate. Carbon contents for coking coal, metallurgical coke, coal tar, coke oven gas, and blast furnace gas were provided by the 2006 IPCC Guidelines for National Greenhouse Gas Inventories (IPCC 2006). The C content for coke breeze was assumed to equal the C content of coke.

### Iron and Steel Production

Emissions of CO<sub>2</sub> from sinter production and direct reduced iron production were estimated by multiplying total national sinter production and the total national direct reduced iron production by Tier 1 CO<sub>2</sub> emission factors (see Table 4-58). Because estimates of sinter production and direct reduced iron production were not available, production was assumed to equal consumption.

To estimate emissions from pig iron production in the blast furnace, the amount of C contained in the produced pig iron and blast furnace gas were deducted from the amount of C contained in inputs (i.e., metallurgical coke, sinter, natural ore, pellets, natural gas, fuel oil, coke oven gas, direct coal injection). The C contained in the pig iron, blast furnace gas, and blast furnace inputs was estimated by multiplying the material-specific carbon content by each material type (see Table 4-59). Carbon in blast furnace gas used to pre-heat the blast furnace air is combusted to form CO<sub>2</sub> during this process.

**Table 4-58: CO<sub>2</sub> Emission Factors for Sinter Production and Direct Reduced Iron Production**

Material Produced	Metric Ton CO <sub>2</sub> /Metric Ton
Sinter	0.2
Direct Reduced Iron	0.7

Source: IPCC (2006), Table 4.1.

Emissions from steel production in EAFs were estimated by deducting the C contained in the steel produced from the carbon contained in the EAF anode, charge carbon, and scrap steel added to the EAF. Small amounts of C from direct reduced iron, pig iron, and flux additions to the EAFs were also included in the EAF calculation. For BOFs, estimates of C contained in BOF steel were deducted from carbon contained in inputs such as natural gas, coke oven gas, fluxes, and pig iron. In each case, the C was calculated by multiplying material-specific carbon contents by each material type (see Table 4-59). For EAFs, the amount of EAF anode consumed was approximated by multiplying total EAF steel production by the amount of EAF anode consumed per metric ton of steel produced (0.002 metric tons EAF anode per metric ton steel produced (AISI 2008b)). The amount of flux (e.g., limestone and dolomite) used during steel manufacture was deducted from the Limestone and Dolomite Use source category to avoid double-counting.

Carbon dioxide emissions from the consumption of blast furnace gas and coke oven gas for other activities occurring at the steel mill were estimated by multiplying the amount of these materials consumed for these purposes by the material-specific C content (see Table 4-59).

Carbon dioxide emissions associated with the sinter production, direct reduced iron production, pig iron production, steel production, and other steel mill activities were summed to calculate the total CO<sub>2</sub> emissions from iron and steel production (see Table 4-51 and Table 4-52).

The production processes for sinter and pig iron result in fugitive emissions of CH<sub>4</sub>, which are emitted via leaks in the production equipment rather than through the emission stacks or vents of the production plants. The fugitive emissions were calculated by applying Tier 1 emission factors taken from the 2006 IPCC Guidelines for *National Greenhouse Gas Inventories* (IPCC 2006) for sinter production and the 1995 IPCC Guidelines (IPCC/UNEP/OECD/IEA 1995) (see Table 4-60) for pig iron production. The production of direct

reduced iron also results in emissions of CH<sub>4</sub> through the consumption of fossil fuels (e.g., natural gas); however, these emissions estimates are excluded due to data limitations.

Sinter consumption and direct reduced iron consumption data were obtained from AISI's *Annual Statistical Report* (AISI 2004 through 2009) and through personal communications with AISI (2008b) (see Table 4-61). Data on direct reduced iron consumed in EAFs were not available for the years 1990, 1991, 1999, 2006, 2007 and 2008. EAF direct reduced iron consumption in 1990 and 1991 were assumed to equal consumption in 1992, and consumption in 1999 was assumed to equal the average of 1998 and 2000. EAF consumption in 2006, 2007, and 2008 were calculated by multiplying the total DRI consumption for all furnaces as provided in the 2008 AISI *Annual Statistical Report* by the EAF share of total DRI consumption in 2005 (the most recent year that data was available for EAF vs. BOF consumption of DRI). Data on direct reduced iron consumed in BOFs were not available for the years 1990 through 1994, 1999, 2006, 2007 and 2008. BOF direct reduced iron consumption in 1990 through 1994 was assumed to equal consumption in 1995, and consumption in 1999 was assumed to equal

**Table 4-59: Material Carbon Contents for Iron and Steel Production**

Material	kg C/kg
Coke	0.83
Direct Reduced Iron	0.02
Dolomite	0.13
EAF Carbon Electrodes	0.82
EAF Charge Carbon	0.83
Limestone	0.12
Pig Iron	0.04
Steel	0.01

Material	kg C/GJ
Coke Oven Gas	12.1
Blast Furnace Gas	70.8

Source: IPCC (2006), Table 4.3. Coke Oven Gas and Blast Furnace Gas, Table 1.3.

**Table 4-60: CH<sub>4</sub> Emission Factors for Sinter and Pig Iron Production**

Material Produced	Factor	Unit
Pig Iron	0.9	g CH <sub>4</sub> /kg
Sinter	0.07	kg CH <sub>4</sub> /metric ton

Source: Sinter (IPCC 2006, Table 4.2), Pig Iron (IPCC/UNEP/OECD/IEA 1995, Table 2.2).



the average of 1998 and 2000. BOF consumption in 2006, 2007, and 2008 were calculated by multiplying the total DRI consumption for all furnaces as provided in the 2008 *AISI Annual Statistical Report* by the BOF share of total DRI consumption in 2005 (the most recent year that data was available for EAF vs. BOF consumption of DRI). The Tier 1 CO<sub>2</sub> emission factors for sinter production and direct reduced iron production were obtained through the 2006 *IPCC Guidelines for National Greenhouse Gas Inventories* (IPCC 2006). Data for pig iron production, coke, natural gas, fuel oil, sinter, and pellets consumed in the blast furnace; pig iron production; and blast furnace gas produced at the iron and steel mill and used in the metallurgical coke ovens and other steel mill activities were obtained from *AISI's Annual Statistical Report* (AISI 2004 through 2009) and through personal communications with AISI (2008b) (see Table 4-62). Data for EAF steel production, flux, EAF charge carbon, direct reduced iron, pig iron, scrap steel, and natural gas consumption as well as EAF steel production were obtained from *AISI's Annual Statistical Report* (AISI 2004 through 2009) and through personal communications with AISI (2008b). The factor for the quantity of EAF anode consumed per ton of EAF steel produced was provided by AISI (AISI 2008b). Data for BOF steel production, flux,

direct reduced iron, pig iron, scrap steel, natural gas, natural ore, pellet sinter consumption as well as BOF steel production were obtained from *AISI's Annual Statistical Report* (AISI 2004 through 2009) and through personal communications with AISI (2008b). Because data on pig iron consumption and scrap steel consumption in BOFs and EAFs were not available for 2006, 2007, and 2008, values for these years were calculated by multiplying the total pig iron and scrap steel consumption for all furnaces as provided in the 2008 *AISI Annual Statistical Report* by the BOF and EAF shares of total pig iron and scrap consumption in 2005 (the most recent year that data was available for EAF vs. BOF consumption of pig iron and scrap steel). Because pig iron consumption in EAFs was also not available in 2003 and 2004, the average of 2002 and 2005 pig iron consumption data were used. Data on coke oven gas and blast furnace gas consumed at the iron and steel mill other than in the EAF, BOF, or blast furnace were obtained from *AISI's Annual Statistical Report* (AISI 2004 through 2009) and through personal communications with AISI (2008b). Data on blast furnace gas and coke oven gas sold for use as synthetic natural gas were obtained through EIA's *Natural Gas Annual 2007* (EIA 2008b). As 2008 data were not available, 2007 data were used. C contents for direct reduced iron, EAF carbon electrodes,

**Table 4-61: Production and Consumption Data for the Calculation of CO<sub>2</sub> and CH<sub>4</sub> Emissions from Iron and Steel Production (Thousand Metric Tons)**

Source/Activity Data	1990	1995	2000	2005	2006	2007	2008
<b>Sinter Production</b>							
Sinter Production	12,239	12,562	10,788	8,315	7,088	6,914	6,497
<b>Direct Reduced Iron Production</b>							
Direct Reduced Iron Production	936	989	1,914	1,633	1,497	2,087	1,769
<b>Pig Iron Production</b>							
Coke Consumption	24,946	22,198	19,215	13,832	14,684	15,039	14,251
Pig Iron Production	49,669	50,891	47,888	37,222	37,904	36,337	33,730
Direct Injection Coal Consumption	1,485	1,509	3,012	2,573	2,526	2,734	2,578
<b>EAF Steel Production</b>							
EAF Anode and Charge Carbon Consumption	67	77	96	1,127	1,245	1,214	1,109
Scrap Steel Consumption	35,743	39,010	43,001	37,558	38,033	40,845	38,414
Flux Consumption	319	267	654	695	671	567	680
EAF Steel Production	33,511	38,472	47,860	52,194	56,071	57,004	52,791
<b>BOF Steel Production</b>							
Pig Iron Consumption	46,564	49,896	46,993	32,115	32,638	33,773	29,322
Scrap Steel Consumption	14,548	15,967	14,969	11,612	11,759	12,628	11,877
Flux Consumption	576	1,259	978	582	610	408	431
BOF Steel Production	43,973	56,721	53,965	42,705	42,119	41,099	39,105
Blast Furnace Gas Production	1,439,380	1,559,795	1,524,891	1,299,980	1,236,526	1,173,588	1,104,674

**Table 4-62: Production and Consumption Data for the Calculation of CO<sub>2</sub> Emissions from Iron and Steel Production (million ft<sup>3</sup> unless otherwise specified)**

Source/Activity Data	1990	1995	2000	2005	2006	2007	2008
<b>Pig Iron Production</b>							
Natural Gas Consumption	56,273	106,514	91,798	59,844	58,344	56,112	53,349
Fuel Oil Consumption (thousand gallons)	163,397	108,196	120,921	16,170	87,702	84,498	55,552
Coke Oven Gas Consumption	22,033	10,097	13,702	16,557	16,649	16,239	15,336
Blast Furnace Gas Production	1,439,380	1,559,795	1,524,891	1,299,980	1,236,526	1,173,588	1,104,674
<b>EAF Steel Production</b>							
Natural Gas Consumption	9,604	11,026	13,717	14,959	16,070	16,337	15,130
<b>BOF Steel Production</b>							
Natural Gas Consumption	6,301	16,546	6,143	5,026	5,827	11,740	-4,304 <sup>b</sup>
Coke Oven Gas Consumption	3,851	1,284	640	524	559	525	528
<b>Other Activities</b>							
Coke Oven Gas Consumption	224,883	155,369	135,135	97,132	97,178	93,148	87,327
Blast Furnace Gas Consumption	1,414,778	1,530,372	1,498,816	1,295,520	1,231,021	1,168,444	1,099,845

<sup>a</sup> Includes blast furnace gas used for purposes other than in the blast furnace only.  
<sup>b</sup> EPA is continuing to investigate this value.

EAF charge carbon, limestone, dolomite, pig iron, and steel were provided by the *2006 IPCC Guidelines for National Greenhouse Gas Inventories* (IPCC 2006). The C contents for natural gas, fuel oil, and direct injection coal as well as the heat contents for the same fuels were provided by EIA (1992, 2008b, 2009). Heat contents for coke oven gas and blast furnace gas were provided in Table 2-2 of the report *Energy and Environmental Profile of the U.S. Iron and Steel Industry* (DOE 2000).

### Uncertainty and Time-Series Consistency

The estimates of CO<sub>2</sub> and CH<sub>4</sub> emissions from metallurgical coke production are based on material production and consumption data and average carbon contents. Uncertainty is associated with the total U.S. coking coal consumption, total U.S. coke production and materials consumed during this process. Data for coking coal consumption and metallurgical coke production are from different data sources (EIA) than data for other carbonaceous materials consumed at coke plants (AISI), which does not include data for merchant coke plants. There is uncertainty associated with the fact that coal tar and coke breeze production were estimated based on coke production because coal tar and coke breeze production data were not available. Since merchant coke plant data is not included in the estimate of other carbonaceous materials consumed at coke plants, the mass balance equation for CO<sub>2</sub> from metallurgical coke production cannot be reasonably completed. Therefore,

for the purpose of this analysis, uncertainty parameters are applied to primary data inputs to the calculation (i.e., coking coal consumption and metallurgical coke production) only.

The estimates of CO<sub>2</sub> emissions from iron and steel production are based on material production and consumption data and average carbon contents. There is uncertainty associated with the assumption that direct reduced iron and sinter consumption are equal to production. There is uncertainty associated with the assumption that all coal used for purposes other than coking coal is for direct injection coal. Some of this coal may be used for electricity generation. There is also uncertainty associated with the carbon contents for pellets, sinter, and natural ore, which are assumed to equal the carbon contents of direct reduced iron. For EAF steel production there is uncertainty associated with the amount of EAF anode and charge carbon consumed due to inconsistent data throughout the timeseries. Uncertainty is also associated with the use of process gases such as blast furnace gas and coke oven gas. Data are not available to differentiate between the use of these gases for processes at the steel mill versus for energy generation (e.g., electricity and steam generation); therefore, all consumption is attributed to iron and steel production. These data and carbon contents produce a relatively accurate estimate of CO<sub>2</sub> emissions. However, there are uncertainties associated with each.

**Table 4-63: Tier 2 Quantitative Uncertainty Estimates for CO<sub>2</sub> and CH<sub>4</sub> Emissions from Iron and Steel Production (Tg CO<sub>2</sub> Eq. and Percent)<sup>a</sup>**

Source	Gas	2008 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>b</sup>			
			(Tg CO <sub>2</sub> Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Metallurgical Coke Production	CO <sub>2</sub>	5.3	2.8	20.6	-47%	+289%
Metallurgical Coke Production	CH <sub>4</sub>	+	+	+	-21%	+23%
Iron and Steel Production	CO <sub>2</sub>	63.7	62.3	76.5	-2%	+20%
Iron and Steel Production	CH <sub>4</sub>	0.6	0.5	0.8	-21%	+22%

+ Does not exceed 0.05 Tg CO<sub>2</sub> Eq.  
<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

For the purposes of the CH<sub>4</sub> calculation from iron and steel production it is assumed that all of the CH<sub>4</sub> escapes as fugitive emissions and that none of the CH<sub>4</sub> is captured in stacks or vents. Additionally, the CO<sub>2</sub> emissions calculation is not corrected by subtracting the C content of the CH<sub>4</sub>, which means there may be a slight double counting of C as both CO<sub>2</sub> and CH<sub>4</sub>.

For both the CO<sub>2</sub> and CH<sub>4</sub> calculations for iron and steel production, it is assumed that the uncertainty associated with metallurgical coke production does not impact iron and steel production.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-63 for metallurgical coke production and iron and steel production. Metallurgical Coke Production CO<sub>2</sub> emissions were estimated to be between 1.3 and 9.3 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level. This indicates a range of approximately 47 percent below and 289 percent above the emission estimate of 5.3 Tg CO<sub>2</sub> Eq. Metallurgical Coke Production CH<sub>4</sub> emissions were estimated to be less than 0.05 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level. This indicates a range of approximately 21 percent below and 23 percent above the emission estimate of less than 0.05 Tg CO<sub>2</sub> Eq. Iron and Steel Production CO<sub>2</sub> emissions were estimated to be between 62.3 and 76.3 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level. This indicates a range of approximately 2 percent below and 20 percent above the emission estimate of 63.7 Tg CO<sub>2</sub> Eq. Iron and Steel Production CH<sub>4</sub> emissions were estimated to be between 0.5 Tg CO<sub>2</sub> Eq. and 0.8 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level. This indicates a range of approximately 21 percent below and 22 percent above the emission estimate of 0.6 Tg CO<sub>2</sub> Eq.

Methodological recalculations were applied to the entire time series to ensure time-series consistency from 1990 through 2008. Details on the emission trends through time are described in more detail in the Methodology section, above.

## Planned Improvements

Plans for improvements to the Iron and Steel Production source category include attributing emissions estimates for the production of metallurgical coke to the Energy chapter as well as identifying the amount of carbonaceous materials, other than coking coal, consumed at merchant coke plants. Additional improvements include identifying the amount of coal used for direct injection and the amount of coke breeze, coal tar, and light oil produced during coke production. Efforts will also be made to identify inputs for preparing Tier 2 estimates for sinter and direct reduced iron production, as well as identifying information to better characterize emissions from the use of process gases and fuels within the Energy and Industrial Processes chapters.

## Recalculations Discussion

In last year's Inventory, pig iron consumption for BOFs was being counted twice as a process input. This was the result of an incorrect interpretation of two tables in the AISI *Annual Statistical Yearbook*. This issue has been corrected and decreased the 1990 through 2007 emissions from iron and steel production by an average of 8 percent per year relative to the previous Inventory.

## 4.14. Ferroalloy Production (IPCC Source Category 2C2)

Carbon dioxide and CH<sub>4</sub> are emitted from the production of several ferroalloys. Ferroalloys are composites of iron and other elements such as silicon, manganese, and chromium. When incorporated in alloy steels, ferroalloys are used to alter the material properties of the steel. Estimates from two types of ferrosilicon (25 to 55 percent and 56 to 95 percent silicon), silicon metal (about 98 percent silicon), and miscellaneous alloys (36 to 65 percent silicon) have been calculated. Emissions from the production of ferrochromium and ferromanganese are not included here because of the small number of manufacturers of these materials in the United States. Subsequently, government information disclosure rules prevent the publication of production data for these production facilities.

Similar to emissions from the production of iron and steel, CO<sub>2</sub> is emitted when metallurgical coke is oxidized during a high-temperature reaction with iron and the selected alloying element. Due to the strong reducing environment, CO is initially produced, and eventually oxidized to CO<sub>2</sub>. A representative reaction equation for the production of 50 percent ferrosilicon is given below:



While most of the C contained in the process materials is released to the atmosphere as CO<sub>2</sub>, a percentage is also released as CH<sub>4</sub> and other volatiles. The amount of CH<sub>4</sub> that is released is dependent on furnace efficiency, operation technique, and control technology.

Emissions of CO<sub>2</sub> from ferroalloy production in 2008 were 1.6 Tg CO<sub>2</sub> Eq. (1,599 Gg) (see Table 4-64 and Table 4-65), which is a three percent increase from the previous year and a 26 percent reduction since 1990. Emissions of CH<sub>4</sub> from ferroalloy production in 2008 were 0.01 Tg CO<sub>2</sub> Eq. (0.465 Gg), which is a four percent increase from the previous year and a 32 percent decrease since 1990.

### Methodology

Emissions of CO<sub>2</sub> and CH<sub>4</sub> from ferroalloy production were calculated by multiplying annual ferroalloy production by material-specific emission factors. Emission factors taken from the *2006 IPCC Guidelines for National Greenhouse Gas Inventories* (IPCC 2006) were applied to ferroalloy production. For ferrosilicon alloys containing 25 to 55 percent silicon and miscellaneous alloys (including primarily magnesium-ferrosilicon, but also including other silicon alloys) containing 32 to 65 percent silicon, an emission factor for 45 percent silicon was applied for CO<sub>2</sub> (2.5 metric tons CO<sub>2</sub>/metric ton of alloy produced) and an emission factor for 65 percent silicon was applied for CH<sub>4</sub> (1 kg CH<sub>4</sub>/metric ton of alloy produced). Additionally, for ferrosilicon alloys containing 56 to 95 percent silicon, an emission factor for 75 percent silicon ferrosilicon was applied for both CO<sub>2</sub> and CH<sub>4</sub> (4 metric tons CO<sub>2</sub>/metric ton alloy produced and 1 kg CH<sub>4</sub>/metric ton of alloy produced, respectively). The emission factors for silicon metal equaled 5 metric tons CO<sub>2</sub>/metric ton metal produced and 1.2 kg CH<sub>4</sub>/metric ton metal produced. It was assumed that 100 percent of the ferroalloy production was produced using petroleum coke using an electric arc furnace process (IPCC 2006), although some

**Table 4-64: CO<sub>2</sub> and CH<sub>4</sub> Emissions from Ferroalloy Production (Tg CO<sub>2</sub> Eq.)**

Gas	1990	1995	2000	2005	2006	2007	2008
CO <sub>2</sub>	2.2	2.0	1.9	1.4	1.5	1.6	1.6
CH <sub>4</sub>	+	+	+	+	+	+	+
<b>Total</b>	<b>2.2</b>	<b>2.0</b>	<b>1.9</b>	<b>1.4</b>	<b>1.5</b>	<b>1.6</b>	<b>1.6</b>

+ Does not exceed 0.05 Tg CO<sub>2</sub> Eq.

Note: Totals may not sum due to independent rounding.

**Table 4-65: CO<sub>2</sub> and CH<sub>4</sub> Emissions from Ferroalloy Production (Gg)**

Gas	1990	1995	2000	2005	2006	2007	2008
CO <sub>2</sub>	2,152	2,036	1,893	1,392	1,505	1,552	1,599
CH <sub>4</sub>	1	1	1	+	+	+	+

+ Does not exceed 0.5 Gg.

ferroalloys may have been produced with coking coal, wood, other biomass, or graphite C inputs. The amount of petroleum coke consumed in ferroalloy production was calculated assuming that the petroleum coke used is 90 percent C and 10 percent inert material.

Ferroalloy production data for 1990 through 2008 (see Table 4-66) were obtained from the USGS through personal communications with the USGS Silicon Commodity Specialist (Corathers 2009) and through the *Minerals Yearbook: Silicon Annual Report* (USGS 1991 through 2009). Because USGS does not provide estimates of silicon metal production for 2006-2008, 2005 production data are used. Until 1999, the USGS reported production of ferrosilicon containing 25 to 55 percent silicon separately from production of miscellaneous alloys containing 32 to 65 percent silicon; beginning in 1999, the USGS reported these as a single category (see Table 4-66). The composition data for petroleum coke was obtained from Onder and Bagdoyan (1993).

## Uncertainty and Time-Series Consistency

Although some ferroalloys may be produced using wood or other biomass as a C source, information and data regarding these practices were not available. Emissions from ferroalloys produced with wood or other biomass would not be counted under this source because wood-based C is of biogenic origin.<sup>16</sup> Even though emissions from ferroalloys produced with coking coal or graphite inputs would be counted in national trends, they may be generated with varying amounts of CO<sub>2</sub> per unit of ferroalloy produced.

The most accurate method for these estimates would be to base calculations on the amount of reducing agent used in the process, rather than the amount of ferroalloys produced. These data, however, were not available.

Emissions of CH<sub>4</sub> from ferroalloy production will vary depending on furnace specifics, such as type, operation technique, and control technology. Higher heating temperatures and techniques such as sprinkle charging will reduce CH<sub>4</sub> emissions; however, specific furnace information was not available or included in the CH<sub>4</sub> emission estimates.

Also, annual ferroalloy production is now reported by the USGS in three broad categories: ferroalloys containing 25 to 55 percent silicon (including miscellaneous alloys), ferroalloys containing 56 to 95 percent silicon, and silicon metal. It was assumed that the IPCC emission factors apply to all of the ferroalloy production processes, including miscellaneous alloys. Finally, production data for silvery pig iron (alloys containing less than 25 percent silicon) are not reported by the USGS to avoid disclosing company proprietary data. Emissions from this production category, therefore, were not estimated.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-67. Ferroalloy production CO<sub>2</sub> emissions were estimated to be between 1.4 and 1.8 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level. This indicates a range of approximately 12 percent below and 13 percent above the emission estimate of 1.6 Tg CO<sub>2</sub> Eq. Ferroalloy production CH<sub>4</sub> emissions were estimated to be between a range of approximately 12 percent below and 13 percent above the emission estimate of 0.01 Tg CO<sub>2</sub> Eq.

**Table 4-66: Production of Ferroalloys (Metric Tons)**

Year	Ferrosilicon 25%–55%	Ferrosilicon 56%–95%	Silicon Metal	Misc. Alloys 32%–65%
1990	321,385	109,566	145,744	72,442
1995	184,000	128,000	163,000	99,500
2000	229,000	100,000	184,000	NA
2005	123,000	86,100	148,000	NA
2006	164,000	88,700	148,000	NA
2007	180,000	90,600	148,000	NA
2008	193,000	94,000	148,000	NA

NA (Not Available).

<sup>16</sup> Emissions and sinks of biogenic carbon are accounted for in the Land Use, Land-Use Change, and Forestry chapter.

**Table 4-67: Tier 2 Quantitative Uncertainty Estimates for CO<sub>2</sub> and CH<sub>4</sub> Emissions from Ferroalloy Production (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2008 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			Lower Bound	Upper Bound	Lower Bound (%)	Upper Bound (%)
Ferroalloy Production	CO <sub>2</sub>	1.6	1.4	1.8	-12%	+13%
Ferroalloy Production	CH <sub>4</sub>	+	+	+	-12%	+13%

+ Does not exceed 0.05 Tg CO<sub>2</sub> Eq.  
<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Methodological recalculations were applied to the entire time series to ensure time-series consistency from 1990 through 2008. Details on the emission trends through time are described in more detail in the Methodology section, above.

## Planned Improvements

Future improvements to the ferroalloy production source category include research into the data availability for ferroalloys other than ferrosilicon and silicon metal. If data are available, emissions will be estimated for those ferroalloys. Additionally, research will be conducted to determine whether data are available concerning raw material consumption (e.g., coal coke, limestone and dolomite flux, etc.) for inclusion in ferroalloy production emission estimates.

## 4.15. Aluminum Production (IPCC Source Category 2C3)

Aluminum is a light-weight, malleable, and corrosion-resistant metal that is used in many manufactured products, including aircraft, automobiles, bicycles, and kitchen utensils. As of last reporting, the United States was the fourth largest producer of primary aluminum, with approximately seven percent of the world total (USGS 2009). The United States was also a major importer of primary aluminum. The production of primary aluminum—in addition to consuming large quantities of electricity—results in process-related emissions of CO<sub>2</sub> and two perfluorocarbons (PFCs): perfluoromethane (CF<sub>4</sub>) and perfluoroethane (C<sub>2</sub>F<sub>6</sub>).

Carbon dioxide is emitted during the aluminum smelting process when alumina (aluminum oxide, Al<sub>2</sub>O<sub>3</sub>) is reduced to aluminum using the Hall-Heroult reduction process. The reduction of the alumina occurs through electrolysis in a

molten bath of natural or synthetic cryolite (Na<sub>3</sub>AlF<sub>6</sub>). The reduction cells contain a C lining that serves as the cathode. Carbon is also contained in the anode, which can be a C mass of paste, coke briquettes, or prebaked C blocks from petroleum coke. During reduction, most of this C is oxidized and released to the atmosphere as CO<sub>2</sub>.

Process emissions of CO<sub>2</sub> from aluminum production were estimated to be 4.5 Tg CO<sub>2</sub> Eq. (4,477 Gg) in 2008 (see Table 4-68). The C anodes consumed during aluminum production consist of petroleum coke and, to a minor extent, coal tar pitch. The petroleum coke portion of the total CO<sub>2</sub> process emissions from aluminum production is considered to be a non-energy use of petroleum coke, and is accounted for here and not under the CO<sub>2</sub> from Fossil Fuel Combustion source category of the Energy sector. Similarly, the coal tar pitch portion of these CO<sub>2</sub> process emissions is accounted for here rather than in the Iron and Steel source category of the Industrial Processes sector.

In addition to CO<sub>2</sub> emissions, the aluminum production industry is also a source of PFC emissions. During the smelting process, when the alumina ore content of the electrolytic bath falls below critical levels required for electrolysis, rapid voltage increases occur, which are termed “anode effects.” These anode effects cause carbon from the anode and fluorine from the dissociated molten cryolite bath to combine, thereby producing fugitive emissions of CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>. In general, the magnitude of emissions for a given smelter and level of production depends on the frequency and duration of these anode effects. As the frequency and duration of the anode effects increase, emissions increase.

Since 1990, emissions of CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> have declined by 86 percent and 82 percent, respectively, to 2.2 Tg CO<sub>2</sub> Eq. of CF<sub>4</sub> (0.34 Gg) and 0.49 Tg CO<sub>2</sub> Eq. of C<sub>2</sub>F<sub>6</sub> (0.054 Gg) in 2008, as shown in Table 4-69 and Table 4-70. This decline is due both to reductions in domestic aluminum production and

to actions taken by aluminum smelting companies to reduce the frequency and duration of anode effects. (Note, however, that production increased and the frequency and duration of anode effects decreased in 2008 compared to 2007. In 2007, higher emissions (and emission rate) were primarily due to increased anode effects at a relatively emissive smelter.) Since 1990, aluminum production has declined by 34 percent, while the combined CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> emission rate (per metric ton of aluminum produced) has been reduced by 78 percent.

In 2008, U.S. primary aluminum production totaled approximately 2.7 million metric tons, a 4 percent increase from 2007 production levels (USAA 2009). In 2008, six companies managed production at 14 operational primary aluminum smelters. Four smelters were temporarily idled and one smelter that was idle since 2000 was demolished (USGS 2009). During the first half of 2008, U.S. primary aluminum production increased (1.4 million metric tons during January–June as compared to 1.2 million metric tons for the same period in 2007; USGS 2008). However, in the second half of the year, Columbia Falls Aluminum Company shut two potlines and operated at 25 percent capacity from July (USGS 2008b). In October, production was curtailed at the Alcoa Inc. smelter in Rockdale, TX (Alcoa Inc. 2008) as a result of uncompetitive power supply to the smelter and overall market conditions. And in December, Century Aluminum Co. announced the immediate curtailment of one potline at its Ravenswood, WV smelter and possible future curtailment of 100 percent of plant operations as a result of the decline in aluminum prices leading to monthly losses (Century Aluminum Co. 2008).

For 2009, total production during January–June was 0.9 million metric tons compared to 1.4 million metric tons for the same period in 2008, a 33 percent decrease (USGS 2009b). Based on this decrease in production, process CO<sub>2</sub> and PFC emissions are likely to decrease over this period in 2009 given no significant changes in process controls at operational facilities.

## Methodology

Carbon dioxide emissions released during aluminum production were estimated using the combined application of process-specific emissions estimates modeling with individual partner reported data. These estimates are based on information gathered by EPA's Voluntary Aluminum Industrial Partnership (VAIP) program.

**Table 4-68: CO<sub>2</sub> Emissions from Aluminum Production (Tg CO<sub>2</sub> Eq. and Gg)**

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	6.8	6,831
1995	5.7	5,659
2000	6.1	6,086
2005	4.1	4,142
2006	3.8	3,801
2007	4.3	4,251
2008	4.5	4,477

**Table 4-69: PFC Emissions from Aluminum Production (Tg CO<sub>2</sub> Eq.)**

Year	CF <sub>4</sub>	C <sub>2</sub> F <sub>6</sub>	Total
1990	15.9	2.7	18.5
1995	10.2	1.7	11.8
2000	7.8	0.8	8.6
2005	2.5	0.4	3.0
2006	2.1	0.4	2.5
2007	3.2	0.6	3.8
2008	2.2	0.5	2.7

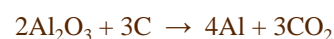
Note: Totals may not sum due to independent rounding.

**Table 4-70: PFC Emissions from Aluminum Production (Gg)**

Year	CF <sub>4</sub>	C <sub>2</sub> F <sub>6</sub>
1990	2.4	0.3
1995	1.6	0.2
2000	1.2	0.1
2005	0.4	+
2006	0.3	+
2007	0.5	0.1
2008	0.3	0.1

+ Does not exceed 0.05 Gg.

Most of the CO<sub>2</sub> emissions released during aluminum production occur during the electrolysis reaction of the C anode, as described by the following reaction:



For prebake smelter technologies, CO<sub>2</sub> is also emitted during the anode baking process. These emissions can account for approximately 10 percent of total process CO<sub>2</sub> emissions from prebake smelters.

Depending on the availability of smelter-specific data, the CO<sub>2</sub> emitted from electrolysis at each smelter was estimated from: (1) the smelter's annual anode consumption; (2) the smelter's annual aluminum production and rate of anode consumption (per ton of aluminum produced) for previous and /or following years; or (3) the smelter's annual aluminum production and IPCC default CO<sub>2</sub> emission factors. The first approach tracks the consumption and carbon content of the anode, assuming that all carbon in the anode is converted to CO<sub>2</sub>. Sulfur, ash, and other impurities in the anode are subtracted from the anode consumption to arrive at a carbon consumption figure. This approach corresponds to either the IPCC Tier 2 or Tier 3 method, depending on whether smelter-specific data on anode impurities are used. The second approach interpolates smelter-specific anode consumption rates to estimate emissions during years for which anode consumption data are not available. This avoids substantial errors and discontinuities that could be introduced by reverting to Tier 1 methods for those years. The last approach corresponds to the IPCC Tier 1 method (2006) and is used in the absence of present or historic anode consumption data.

The equations used to estimate CO<sub>2</sub> emissions in the Tier 2 and 3 methods vary depending on smelter type (IPCC 2006). For Prebake cells, the process formula accounts for various parameters, including net anode consumption, and the sulfur, ash, and impurity content of the baked anode. For anode baking emissions, the formula accounts for packing coke consumption, the sulfur and ash content of the packing coke, as well as the pitch content and weight of baked anodes produced. For Söderberg cells, the process formula accounts for the weight of paste consumed per metric ton of aluminum produced, and pitch properties, including sulfur, hydrogen, and ash content.

Through the VAIP, anode consumption (and some anode impurity) data have been reported for 1990, 2000, 2003, 2004, 2005, 2006, 2007, and 2008. Where available, smelter-specific process data reported under the VAIP were used; however, if the data were incomplete or unavailable, information was supplemented using industry average values recommended by IPCC (2006). Smelter-specific CO<sub>2</sub> process

data were provided by 18 of the 23 operating smelters in 1990 and 2000, by 14 out of 16 operating smelters in 2003 and 2004, 14 out of 15 operating smelters in 2005, 13 out of 14 operating smelters in 2006, and 5 out of 14 operating smelters in, 2007 and 2008. For years where CO<sub>2</sub> process data were not reported by these companies, estimates were developed through linear interpolation, and/or assuming industry default values.

In the absence of any previous smelter specific process data (i.e., 1 out of 14 smelters in 2006, 2007, and 2008, 1 out of 15 smelters in 2005, and 5 out of 23 smelters between 1990 and 2003), CO<sub>2</sub> emission estimates were estimated using Tier 1 Söderberg and/or Prebake emission factors (metric ton of CO<sub>2</sub> per metric ton of aluminum produced) from IPCC (2006).

Aluminum production data for 13 out of 14 operating smelters were reported under the VAIP in 2008. Between 1990 and 2007, production data were provided by 21 of the 23 U.S. smelters that operated during at least part of that period. For the non-reporting smelters, production was estimated based on the difference between reporting smelters and national aluminum production levels (USAA 2009), with allocation to specific smelters based on reported production capacities (USGS 2002, 2009c).

PFC emissions from aluminum production were estimated using a per-unit production emission factor that is expressed as a function of operating parameters (anode effect frequency and duration), as follows:

$$\text{PFC (CF}_4 \text{ or C}_2\text{F}_6\text{) kg/metric ton Al} = S \times \text{Anode Effect Minutes/Cell-Day}$$

where,

$$S = \frac{\text{Slope coefficient (kg PFC/metric ton Al)}}{\text{Anode Effect Minutes/Cell-Day}}$$

$$\text{Anode Effect Minutes/Cell-Day} = \text{Anode Effect Frequency/Cell-Day} \times \text{Anode Effect Duration (Minutes)}$$

This approach corresponds to either the Tier 3 or the Tier 2 approach in the 2006 IPCC Guidelines, depending upon whether the slope-coefficient is smelter-specific (Tier 3) or technology-specific (Tier 2). For 1990 through 2008, smelter-specific slope coefficients were available and were used for smelters representing between 30 and 94 percent of U.S. primary aluminum production. The percentage changed from year to year as some smelters closed or changed hands



and as the production at remaining smelters fluctuated. For smelters that did not report smelter-specific slope coefficients, IPCC technology-specific slope coefficients were applied (IPCC 2000, 2006). The slope coefficients were combined with smelter-specific anode effect data collected by aluminum companies and reported under the VAIP, to estimate emission factors over time. For 1990 through 2008, smelter-specific anode effect data were available for smelters representing between 80 and 100 percent of U.S. primary aluminum production. Where smelter-specific anode effect data were not available, industry averages were used.

For all smelters, emission factors were multiplied by annual production to estimate annual emissions at the smelter level. For 1990 through 2008, smelter-specific production data were available for smelters representing between 30 and 100 percent of U.S. primary aluminum production. (For the years after 2000, this percentage was near the high end of the range.) Production at non-reporting smelters was estimated by calculating the difference between the production reported under VAIP and the total U.S. production supplied by USGS or USAA and then allocating this difference to non-reporting smelters in proportion to their production capacity. Emissions were then aggregated across smelters to estimate national emissions.

National primary aluminum production data for 2008 were obtained via USAA (USAA 2009). For 1990 through 2001, and 2006 (see Table 4-71) data were obtained from USGS, *Mineral Industry Surveys: Aluminum Annual Report* (USGS 1995, 1998, 2000, 2001, 2002, 2007). For 2002 through 2005, and 2007 national aluminum production data were obtained from the United States Aluminum Association's *Primary Aluminum Statistics* (USAA 2004, 2005, 2006, 2008).

## Uncertainty and Time Series Consistency

The overall uncertainties associated with the 2008 CO<sub>2</sub>, CF<sub>4</sub>, and C<sub>2</sub>F<sub>6</sub> emission estimates were calculated using Approach 2, as defined by IPCC (2006). For CO<sub>2</sub>, uncertainty was assigned to each of the parameters used to estimate CO<sub>2</sub> emissions. Uncertainty surrounding reported production data was assumed to be 1 percent (IPCC 2006). For additional variables, such as net C consumption, and sulfur

**Table 4-71: Production of Primary Aluminum (Gg)**

Year	Gg
1990	4,048
1995	3,375
2000	3,668
2005	2,478
2006	2,284
2007	2,560
2008	2,659

and ash content in baked anodes, estimates for uncertainties associated with reported and default data were obtained from IPCC (2006). A Monte Carlo analysis was applied to estimate the overall uncertainty of the CO<sub>2</sub> emission estimate for the U.S. aluminum industry as a whole, and the results are provided below.

To estimate the uncertainty associated with emissions of CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>, the uncertainties associated with three variables were estimated for each smelter: (1) the quantity of aluminum produced; (2) the anode effect minutes per cell day (which may be reported directly or calculated as the product of anode effect frequency and anode effect duration); and, (3) the smelter- or technology-specific slope coefficient. A Monte Carlo analysis was then applied to estimate the overall uncertainty of the emission estimate for each smelter and for the U.S. aluminum industry as a whole.

The results of this quantitative uncertainty analysis are summarized in Table 4-72. Aluminum production-related CO<sub>2</sub> emissions were estimated to be between 4.3 and 4.6 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level. This indicates a range of approximately 4 percent below to 4 percent above the emission estimate of 4.5 Tg CO<sub>2</sub> Eq. Also, production-related CF<sub>4</sub> emissions were estimated to be between 2.0 and 2.4 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level. This indicates a range of approximately 9 percent below to 9 percent above the emission estimate of 2.2 Tg CO<sub>2</sub> Eq. Finally, aluminum production-related C<sub>2</sub>F<sub>6</sub> emissions were estimated to be between 0.4 and 0.5 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level. This indicates a range of approximately 11 percent below to 12 percent above the emission estimate of 0.5 Tg CO<sub>2</sub> Eq.

**Table 4-72: Tier 2 Quantitative Uncertainty Estimates for CO<sub>2</sub> and PFC Emissions from Aluminum Production (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2008 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			(Tg CO <sub>2</sub> Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Aluminum Production	CO <sub>2</sub>	4.5	4.3	4.6	-4%	+4%
Aluminum Production	CF <sub>4</sub>	2.2	2.0	2.4	-9%	+9%
Aluminum Production	C <sub>2</sub> F <sub>6</sub>	0.5	0.4	0.5	-11%	+12%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

The 2008 emission estimate was developed using either company-wide or site-specific PFC slope coefficients for all but 1 of the 14 operating smelters where default IPCC (2006) slope data was used. In some cases, where smelters are owned by one company, data have been reported on a company-wide basis as totals or weighted averages. Consequently, in the Monte Carlo analysis, uncertainties in anode effect minutes per cell day, slope coefficients, and aluminum production have been applied to the company as a whole and not to each smelter. This probably overestimates the uncertainty associated with the cumulative emissions from these smelters, because errors that were in fact independent were treated as if they were correlated. It is therefore likely that uncertainties calculated above for the total U.S. 2008 emission estimates for CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> are also overestimated.

Methodological recalculations were applied to the entire time series to ensure time-series consistency from 1990 through 2008. Details on the emission trends through time are described in more detail in the Methodology section, above.

## 4.16. Magnesium Production and Processing (IPCC Source Category 2C4)

The magnesium metal production and casting industry uses sulfur hexafluoride (SF<sub>6</sub>) as a cover gas to prevent the rapid oxidation of molten magnesium in the presence of air. Sulfur hexafluoride has been used in this application around the world for more than twenty-five years. A dilute gaseous mixture of SF<sub>6</sub> with dry air and/or CO<sub>2</sub> is blown over molten magnesium metal to induce and stabilize the formation of a protective crust. A small portion of the SF<sub>6</sub> reacts with

the magnesium to form a thin molecular film of mostly magnesium oxide and magnesium fluoride. The amount of SF<sub>6</sub> reacting in magnesium production and processing is considered to be negligible and thus all SF<sub>6</sub> used is assumed to be emitted into the atmosphere. Although alternative cover gases, such as AM-cover™ (containing HFC-134a), Novac™ 612 and dilute SO<sub>2</sub> systems can be used, most companies in the United States are still using traditional SF<sub>6</sub> cover gas systems.

The magnesium industry emitted 2.0 Tg CO<sub>2</sub> Eq. (0.1 Gg) of SF<sub>6</sub> in 2008, representing a decrease of approximately 23 percent from 2007 emissions (See Table 4-73). The decrease may be attributed to die casting facilities closing in the United States over the past year due to reduced demand from the American auto industry and other industrial sectors (USGS 2008a). Although the price of magnesium on the international level fell in 2008 because of weakening economies, the tight import market in the U.S. prevented domestic magnesium prices from declining on the same scale, which also lead to losses in the industry and expansion plan delays in the U.S. magnesium sector (USGS 2008a).

### Methodology

Emission estimates for the magnesium industry incorporate information provided by industry participants in EPA's SF<sub>6</sub> Emission Reduction Partnership for the Magnesium Industry. The Partnership started in 1999 and, currently, participating companies represent 100 percent of U.S. primary and secondary production and 90 percent of the casting sector production (i.e., die, sand, permanent mold, wrought, and anode casting). Absolute emissions for 1999 through 2008 from primary production, secondary production (i.e., recycling), and die casting were generally

**Table 4-73: SF<sub>6</sub> Emissions from Magnesium Production and Processing (Tg CO<sub>2</sub> Eq. and Gg)**

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	5.5	0.2
1995	5.6	0.2
2000	3.0	0.1
2005	2.9	0.1
2006	2.9	0.1
2007	2.6	0.1
2008	2.0	0.1

reported by Partnership participants. Partners reported their SF<sub>6</sub> consumption, which was assumed to be equivalent to emissions. When a Partner did not report emissions, they were estimated based on the metal processed and emission rate reported by that partner in previous and (if available) subsequent years. Where data for subsequent years was not available, metal production and emissions rates were extrapolated based on the trend shown by partners reporting in the current and previous years. When it was determined a Partner is no longer in production, their metal production and emissions rates were set to zero if no activity information was available; in one case a partner that closed mid-year was estimated to have produced 50 percent of the metal from the prior year.

Emission factors for 2002 to 2006 for sand casting activities were also acquired through the Partnership. For 2007 and 2008, the sand casting partner did not report and the reported emission factor from 2005 was utilized as being representative of the industry. The 1999 through 2008 emissions from casting operations (other than die) were estimated by multiplying emission factors (kg SF<sub>6</sub> per metric ton of Mg produced or processed) by the amount of metal produced or consumed. The emission factors for casting activities are provided below in Table 4-74. The emission factors for primary production, secondary production and sand casting are withheld to protect company-specific production information. However, the emission factor for primary production has not risen above the average 1995 partner value of 1.1 kg SF<sub>6</sub> per metric ton.

Die casting emissions for 1999 through 2008, which accounted for 17 to 52 percent of all SF<sub>6</sub> emissions from the U.S. magnesium industry during this period, were estimated

based on information supplied by industry partners. From 2000 to 2008, partners accounted for all U.S. die casting that was tracked by USGS. In 1999, partners did not account for all die casting tracked by USGS, and, therefore, it was necessary to estimate the emissions of die casters who were not partners. Die casters who were not partners were assumed to be similar to partners who cast small parts. Due to process requirements, these casters consume larger quantities of SF<sub>6</sub> per metric ton of processed magnesium than casters that process large parts. Consequently, emission estimates from this group of die casters were developed using an average emission factor of 5.2 kg SF<sub>6</sub> per metric ton of magnesium. The emission factors for the other industry sectors (i.e., permanent mold, wrought, and anode casting) were based on discussions with industry representatives.

Data used to develop SF<sub>6</sub> emission estimates were provided by the Magnesium Partnership participants and the USGS. U.S. magnesium metal production (primary and secondary) and consumption (casting) data from 1990 through 2008 were available from the USGS (USGS 2002, 2003, 2005, 2006, 2007, 2008b, 2009a). Emission factors from 1990 through 1998 were based on a number of sources. Emission factors for primary production were available from U.S. primary producers for 1994 and 1995, and an emission factor for die casting of 4.1 kg per metric ton was available for the mid-1990s from an international survey (Gjestland & Magers 1996).

To estimate emissions for 1990 through 1998, industry emission factors were multiplied by the corresponding metal

**Table 4-74: SF<sub>6</sub> Emission Factors (kg SF<sub>6</sub> per metric ton of Magnesium)**

Year	Die Casting	Permanent Mold	Wrought	Anodes
1999	2.14 <sup>a</sup>	2	1	1
2000	0.72	2	1	1
2001	0.72	2	1	1
2002	0.71	2	1	1
2003	0.81	2	1	1
2004	0.81	2	1	1
2005	0.79	2	1	1
2006	0.86	2	1	1
2007	0.67	2	1	1
2008	1.15	2	1	1

<sup>a</sup> Weighted average that includes an estimated emission factor of 5.2 kg SF<sub>6</sub> per metric ton of magnesium for die casters that do not participate in the Partnership.

production and consumption (casting) statistics from USGS. The primary production emission factors were 1.2 kg per metric ton for 1990 through 1993, and 1.1 kg per metric ton for 1994 through 1997. For die casting, an emission factor of 4.1 kg per metric ton was used for the period 1990 through 1996. For 1996 through 1998, the emission factors for primary production and die casting were assumed to decline linearly to the level estimated based on partner reports in 1999. This assumption is consistent with the trend in SF<sub>6</sub> sales to the magnesium sector that is reported in the RAND survey of major SF<sub>6</sub> manufacturers, which shows a decline of 70 percent from 1996 to 1999 (RAND 2002). Sand casting emission factors for 2002 through 2007 were provided by the Magnesium Partnership participants, and 1990 through 2001 emission factors for this process were assumed to have been the same as the 2002 emission factor. The emission factor for secondary production from 1990 through 1998 was assumed to be constant at the 1999 average partner value. The emission factors for the other processes (i.e., permanent mold, wrought, and anode casting), about which less is known, were assumed to remain constant at levels defined in Table 4-72.

## Uncertainty and Time Series Consistency

To estimate the uncertainty surrounding the estimated 2008 SF<sub>6</sub> emissions from magnesium production and processing, the uncertainties associated with three variables were estimated (1) emissions reported by magnesium producers and processors that participate in the SF<sub>6</sub> Emission Reduction Partnership; (2) emissions estimated for magnesium producers and processors that participate in the Partnership but did not report this year; and (3) emissions estimated for magnesium producers and processors that do not participate in the Partnership. An uncertainty of 5 percent was assigned to the data reported by each participant in the Partnership. If partners did not report emissions data during the current reporting year, SF<sub>6</sub> emissions data were estimated using available emission factor and production information reported in prior years; the extrapolation was based on the average trend for partners reporting in the current reporting year and the year prior. The uncertainty associated with the SF<sub>6</sub> usage estimate generated from the extrapolated emission factor and production information was estimated to be 30 percent for each year of extrapolation. The lone sand casting partner did not report in the past two reporting years and its

activity and emission factor were held constant at 2005 levels due to a reporting anomaly in 2006 because of malfunctions at the facility. The uncertainty associated with the SF<sub>6</sub> usage for the sand casting partner was 43 percent. For those industry processes that are not represented in Partnership, such as permanent mold and wrought casting, SF<sub>6</sub> emissions were estimated using production and consumption statistics reported by USGS and estimated process-specific emission factors (see Table 4-74). The uncertainties associated with the emission factors and USGS-reported statistics were assumed to be 75 percent and 25 percent, respectively. Emissions associated with sand casting activities utilized a partner-reported emission factor with an uncertainty of 75 percent. In general, where precise quantitative information was not available on the uncertainty of a parameter, a conservative (upper-bound) value was used.

Additional uncertainties exist in these estimates that are not addressed in this methodology, such as the basic assumption that SF<sub>6</sub> neither reacts nor decomposes during use. The melt surface reactions and high temperatures associated with molten magnesium could potentially cause some gas degradation. Recent measurement studies have identified SF<sub>6</sub> cover gas degradation in die casting applications on the order of 20 percent (Bartos et al. 2007). Sulfur hexafluoride may also be used as a cover gas for the casting of molten aluminum with high magnesium content; however, the extent to which this technique is used in the United States is unknown.

The results of this Tier 2 quantitative uncertainty analysis are summarized in Table 4-75. Sulfur hexafluoride emissions associated with magnesium production and processing were estimated to be between 1.9 and 2.1 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level. This indicates a range of approximately 6 percent below to 5 percent above the 2008 emission estimate of 2.0 Tg CO<sub>2</sub> Eq. The uncertainty estimates for 2008 are lower relative to the 2007 reporting year which is likely due to a significant decrease in reported sand casting activity.

Methodological recalculations were applied to the entire time series to ensure time-series consistency from 1990 through 2008. Details on the emission trends through time are described in more detail in the Methodology section, above.

**Table 4-75: Tier 2 Quantitative Uncertainty Estimates for SF<sub>6</sub> Emissions from Magnesium Production and Processing (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2008 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			(Tg CO <sub>2</sub> Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Magnesium Production	SF <sub>6</sub>	2.0	1.9	2.1	-6%	+5%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

## Recalculations Discussion

The USGS revised the volume of metal produced from the magnesium sand casting sector for the 2007 reporting year. This revision, which amounted to approximately 2,200 MT less metal produced from magnesium sand casting (USGS 2009a), is reflected in the current Inventory report. This revision resulted in an approximate decrease in 2007 emissions by 0.37 Tg CO<sub>2</sub> Eq. relative to the previous Inventory report.

## Planned Improvements

Cover gas research conducted by the EPA over the last decade has found that SF<sub>6</sub> used for magnesium melt protection can have degradation rates on the order of 20 percent in die casting applications (Bartos et al. 2007). Current emission estimates assume (per the 2006 IPCC Guidelines, IPCC 2006) that all SF<sub>6</sub> utilized is emitted to the atmosphere. Additional research may lead to a revision of IPCC Guidelines to reflect this phenomenon and until such time, developments in this sector will be monitored for possible application to the inventory methodology. Another issue that will be addressed in future inventories is the likely adoption of alternate cover gases by U.S. magnesium producers and processors. These cover gases, which include AM-cover™ (containing HFC-134a) and Novec™ 612, have lower GWPs than SF<sub>6</sub>, and tend to quickly decompose during their exposure to the molten metal. Magnesium producers and processors have already begun using these cover gases for 2006 through 2008 in a limited fashion; because the amounts being used by companies on the whole are low enough that they have a minor effect on the overall emissions from the industry, these emissions are only being monitored and recorded at this time.

## 4.17. Zinc Production (IPCC Source Category 2C5)

Zinc production in the United States consists of both primary and secondary processes. Primary production techniques used in the United States are the electrothermic and electrolytic process while secondary techniques used in the United States include a range of metallurgical, hydrometallurgical, and pyrometallurgical processes. Worldwide primary zinc production also employs a pyrometallurgical process using the Imperial Smelting Furnace process; however, this process is not used in the United States (Sjardin 2003). Of the primary and secondary processes used in the United States, the electrothermic process results in non-energy CO<sub>2</sub> emissions, as does the Waelz Kiln process—a technique used to produce secondary zinc from electric-arc furnace (EAF) dust (Viklund-White 2000).

During the electrothermic zinc production process, roasted zinc concentrate and, when available, secondary zinc products enter a sinter feed where they are burned to remove impurities before entering an electric retort furnace. Metallurgical coke added to the electric retort furnace reduces the zinc oxides and produces vaporized zinc, which is then captured in a vacuum condenser. This reduction process produces non-energy CO<sub>2</sub> emissions (Sjardin 2003). The electrolytic zinc production process does not produce non-energy CO<sub>2</sub> emissions.

In the Waelz Kiln process, EAF dust, which is captured during the recycling of galvanized steel, enters a kiln along with a reducing agent—often metallurgical coke. When kiln temperatures reach approximately 1100–1200°C, zinc fumes are produced, which are combusted with air entering the kiln. This combustion forms zinc oxide, which is collected in a baghouse or electrostatic precipitator, and is then leached to remove chloride and fluoride. Through this process,

**Table 4-76: CO<sub>2</sub> Emissions from Zinc Production (Tg CO<sub>2</sub> Eq. and Gg)**

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	0.9	929
1995	1.0	993
2000	1.1	1,115
2005	0.5	506
2006	0.5	513
2007	0.4	411
2008	0.4	402

approximately 0.33 ton of zinc is produced for every ton of EAF dust treated (Viklund-White 2000).

In 2008, U.S. primary and secondary zinc production totaled 440,000 metric tons (Nyrstar 2009, USGS 2009a). The resulting emissions of CO<sub>2</sub> from zinc production in 2008 were estimated to be 0.4 Tg CO<sub>2</sub> Eq. (402 Gg) (see Table 4-76). All 2008 CO<sub>2</sub> emissions result from secondary zinc production.

After a gradual increase in total emissions from 1990 to 2000, largely due to an increase in secondary zinc production, emissions have decreased in recent years due to the closing of an electrothermic-process zinc plant in Monaca, PA (USGS 2004). In 2008, emissions decreased 2 percent from 2007 and decreased by 57 percent since 1990.

## Methodology

Non-energy CO<sub>2</sub> emissions from zinc production result from those processes that use metallurgical coke or other C-based materials as reductants. Sjardin (2003) provides an emission factor of 0.43 metric tons CO<sub>2</sub>/ton zinc produced for emissive zinc production processes; however, this emission factor is based on the Imperial Smelting Furnace production process. Because the Imperial Smelting Furnace production process is not used in the United States, emission factors specific to those emissive zinc production processes used in the United States, which consist of the electro-thermic and Waelz Kiln processes, were needed. Due to the limited amount of information available for these electro-thermic processes, only Waelz Kiln process-specific emission factors were developed. These emission factors were applied to both the Waelz Kiln process and the electro-thermic zinc production processes. A Waelz Kiln emission factor based

on the amount of zinc produced was developed based on the amount of metallurgical coke consumed for non-energy purposes per ton of zinc produced, 1.19 metric tons coke/metric ton zinc produced (Viklund-White 2000), and the following equation:

The USGS disaggregates total U.S. primary zinc production capacity into zinc produced using the electrothermic process and zinc produced using the electrolytic process; however, the USGS does not report the amount of zinc produced using each process, only the total zinc production capacity of the zinc plants using each process. The total electro-thermic zinc production capacity is divided by total primary zinc production capacity to

$$EF_{\text{Waelz Kiln}} = 1.19 \frac{\text{metric tons coke}}{\text{metric tons zinc}} \times 0.85 \frac{\text{metric tons C}}{\text{metric tons coke}} \times 3.67 \frac{\text{metric tons CO}_2}{\text{metric tons C}} = 3.70 \frac{\text{metric tons CO}_2}{\text{metric tons zinc}}$$

estimate the percent of primary zinc produced using the electro-thermic process. This percent is then multiplied by total primary zinc production to estimate the amount of zinc produced using the electro-thermic process, and the resulting value is multiplied by the Waelz Kiln process emission factor to obtain total CO<sub>2</sub> emissions for primary zinc production. According to the USGS, the only remaining plant producing primary zinc using the electro-thermic process closed in 2003 (USGS 2004). Therefore, CO<sub>2</sub> emissions for primary zinc production are reported only for years 1990 through 2002.

In the United States, secondary zinc is produced through either the electro-thermic or Waelz Kiln process. In 1997, the Horsehead Corporation plant, located in Monaca, PA, produced 47,174 metric tons of secondary zinc using the electro-thermic process (Queneau et al. 1998). This is the only plant in the United States that uses the electro-thermic process to produce secondary zinc, which, in 1997, accounted for 12 percent of total secondary zinc production. This percentage was applied to all years within the time series up until the Monaca plant's closure in 2003 (USGS 2004) to estimate the total amount of secondary zinc produced using the electro-thermic process. This value is then multiplied by the Waelz Kiln process emission factor to obtain total CO<sub>2</sub>

emissions for secondary zinc produced using the electro-thermic process.

U.S. secondary zinc is also produced by processing recycled EAF dust in a Waelz Kiln furnace. Due to the complexities of recovering zinc from recycled EAF dust, an emission factor based on the amount of EAF dust consumed rather than the amount of secondary zinc produced is believed to represent actual CO<sub>2</sub> emissions from the process more accurately (Stuart 2005). An emission factor based on the amount of EAF dust consumed was developed based on the amount of metallurgical coke consumed per ton of EAF dust consumed, 0.4 metric tons coke/metric ton EAF dust consumed (Viklund-White 2000), and the following equation:

The Horsehead Corporation plant, located in Palmerton, PA, is the only large plant in the United States that produces secondary zinc by recycling EAF dust (Stuart 2005). In 2003, this plant consumed 408,240 metric tons of EAF dust, producing 137,169 metric tons of secondary zinc (Recycling Today 2005). This zinc production accounted for 34 percent of total secondary zinc produced in 2003. This percentage

$$\begin{aligned}
 EF_{\text{EAF Dust}} &= 0.4 \frac{\text{metric tons coke}}{\text{metric tons EAF dust}} \times \\
 &0.84 \frac{\text{metric tons C}}{\text{metric tons coke}} \times \\
 &3.67 \frac{\text{metric tons CO}_2}{\text{metric tons C}} = \\
 &1.23 \frac{\text{metric tons CO}_2}{\text{metric tons EAF dust}}
 \end{aligned}$$

was applied to the USGS data for total secondary zinc production for all years within the time series to estimate the total amount of secondary zinc produced by consuming recycled EAF dust in a Waelz Kiln furnace. This value is multiplied by the Waelz Kiln process emission factor for EAF dust to obtain total CO<sub>2</sub> emissions.

The 1990 through 2007 activity data for primary and secondary zinc production (see Table 4-77) were obtained through the *USGS Mineral Yearbook: Zinc* (USGS 1994 through 2009b). Preliminary data for 2008 primary production were obtained from the annual report for the company operating the only primary zinc refinery in the U.S. (Nyrstar 2009, Tolcin 2009). Preliminary data for 2008 production from scrap was obtained from the *USGS Mineral Commodity Summary for Zinc* (USGS 2009a). Because data for 2008 secondary zinc production were unavailable, 2007 data were used.

**Table 4-77: Zinc Production (Metric Tons)**

Year	Primary	Secondary
1990	262,704	341,400
1995	231,840	353,000
2000	227,800	440,000
2005	191,120	397,000
2006	113,000	402,000
2007	121,000	322,000
2008	125,000	315,000

## Uncertainty and Time-Series Consistency

The uncertainties contained in these estimates are two-fold, relating to activity data and emission factors used.

First, there are uncertainties associated with the percent of total zinc production, both primary and secondary, that is attributed to the electro-thermic and Waelz Kiln emissive zinc production processes. For primary zinc production, the amount of zinc produced annually using the electro-thermic process is estimated from the percent of primary-zinc production capacity that electro-thermic production capacity constitutes for each year of the time series. This assumes that each zinc plant is operating at the same percentage of total production capacity, which may not be the case and this calculation could either overestimate or underestimate the percentage of the total primary zinc production that is produced using the electro-thermic process. The amount of secondary zinc produced using the electro-thermic process is estimated from the percent of total secondary zinc production that this process accounted for during a single year, 2003. The amount of secondary zinc produced using the Waelz Kiln process is estimated from the percent of total secondary zinc production this process accounted for during a single year, 1997. This calculation could either overestimate or underestimate the percentage of the total secondary zinc production that is produced using the electro-thermic or Waelz Kiln processes. Therefore, there is uncertainty associated with the fact that percents of total production data estimated from production capacity, rather than actual production data, are used for emission estimates.

Second, there are uncertainties associated with the emission factors used to estimate CO<sub>2</sub> emissions from the primary and secondary production processes. Because the only published emission factors are based on the Imperial

**Table 4-78: Tier 2 Quantitative Uncertainty Estimates for CO<sub>2</sub> Emissions from Zinc Production (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2008 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Zinc Production	CO <sub>2</sub>	0.4	0.3	0.5	-22%	+24%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Smelting Furnace, which is not used in the United States, country-specific emission factors were developed for the Waelz Kiln zinc production process. Data limitations prevented the development of emission factors for the electro-thermic process. Therefore, emission factors for the Waelz Kiln process were applied to both electro-thermic and Waelz Kiln production processes. Furthermore, the Waelz Kiln emission factors are based on materials balances for metallurgical coke and EAF dust consumed during zinc production provided by Viklund-White (2000). Therefore, the accuracy of these emission factors depend upon the accuracy of these materials balances.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-78. Zinc production CO<sub>2</sub> emissions were estimated to be between 0.3 and 0.5 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level. This indicates a range of approximately 22 percent below and 24 percent above the emission estimate of 0.4 Tg CO<sub>2</sub> Eq.

Methodological recalculations were applied to the entire time series to ensure time-series consistency from 1990 through 2008. Details on the emission trends through time are described in more detail in the Methodology section, above.

## Recalculations Discussion

The data for secondary zinc production from 2003 through 2007 were revised in the 2007 *USGS Mineral Yearbook: Zinc*. As the revised production data were greater than the data used in the previous Inventory, this change resulted in increased emissions for these years. These revisions also affected emissions across the time series as the 2003 data are used to establish the “percent of total secondary zinc production” represented by secondary zinc production from EAF dust. As this percentage is applied to data in all years to complete the emission estimates, emissions for all years subsequently decreased, relative to the previous Inventory. The overall effect of the two revisions was to

increase average annual CO<sub>2</sub> emissions by 3.3% from 1990 to 2007.

## Planned Improvements

A future improvement will be to update the assumptions used to estimate the amount of secondary zinc production from EAF dust in the United States, which will affect the CO<sub>2</sub> emission estimates for zinc. Secondary zinc production from EAF dust is currently estimated by extrapolating a 2005 published production number by overall zinc production trends from USGS. However, there has been production information published in years since 2005 that can be used in place of the extrapolated estimates.

## 4.18. Lead Production (IPCC Source Category 2C5)

Lead production in the United States consists of both primary and secondary processes—both of which emit CO<sub>2</sub> (Sjardin 2003). Primary lead production, in the form of direct smelting, mostly occurs at plants located in Alaska and Missouri, though to a lesser extent in Idaho, Montana, and Washington. Secondary production largely involves the recycling of lead acid batteries at approximately 15 separate smelters located in 11 states (USGS 2010). Secondary lead production has increased in the United States over the past decade while primary lead production has decreased. In 2008, secondary lead production accounted for approximately 89 percent of total lead production (USGS 2010).

Primary production of lead through the direct smelting of lead concentrate produces CO<sub>2</sub> emissions as the lead concentrates are reduced in a furnace using metallurgical coke (Sjardin 2003). U.S. primary lead production increased by 10 percent from 2007 to 2008 and has decreased by 67 percent since 1990 (USGS 2010, USGS 1995).

Secondary lead production, primarily from the recycling of lead-acid batteries, accounted for approximately 89



**Table 4-79: CO<sub>2</sub> Emissions from Lead Production (Tg CO<sub>2</sub> Eq. and Gg)**

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	0.3	285
1995	0.3	298
2000	0.3	311
2005	0.3	266
2006	0.3	270
2007	0.3	267
2008	0.3	264

percent of total refined lead production in the United States in 2008 (USGS 2010). Similar to primary lead production, CO<sub>2</sub> emissions result when a reducing agent, usually metallurgical coke, is added to the smelter to aid in the reduction process (Sjardin 2003). U.S. secondary lead production decreased from 2007 to 2008 by 3 percent, and has increased by 25 percent since 1990 (USGS 2010, USGS 1995).

At last reporting, the United States was the third largest mine producer of lead in the world, behind China and Australia, accounting for 11 percent of world production in 2008 (USGS 2010). In 2008, U.S. primary and secondary lead production totaled 1,150,000 metric tons (USGS 2010). The resulting emissions of CO<sub>2</sub> from 2008 production were estimated to be 0.3 Tg CO<sub>2</sub> Eq. (264 Gg) (see Table 4-79). The majority of 2008 lead production is from secondary processes, which account for 87 percent of total 2008 CO<sub>2</sub> emissions.

After a gradual increase in total emissions from 1990 to 2000, total emissions have decreased by eight percent since 1990, largely due to a decrease in primary production (67 percent since 1990) and a transition within the United States from primary lead production to secondary lead production, which is less emissions intensive than primary production, although the sharp decrease leveled off in 2005 (USGS 2010, Smith 2007).

## Methodology

Non-energy CO<sub>2</sub> emissions from lead production result from primary and secondary production processes that use metallurgical coke or other C-based materials as reductants. For primary lead production using direct smelting, Sjardin (2003) and the IPCC (2006) provide an emission factor of 0.25 metric tons CO<sub>2</sub>/ton lead. For secondary lead

production, Sjardin (2003) and IPCC (2006) provide an emission factor of 0.2 metric tons CO<sub>2</sub>/ton lead produced. Both factors are multiplied by total U.S. primary and secondary lead production, respectively, to estimate CO<sub>2</sub> emissions.

The 1990 through 2008 activity data for primary and secondary lead production (see Table 4-80) were obtained through the *USGS Mineral Yearbook: Lead* (USGS 1994 through 2010) for 1990-2008.

**Table 4-80: Lead Production (Metric Tons)**

Year	Primary	Secondary
1990	386,000	922,000
1995	374,000	1,020,000
2000	341,000	1,130,000
2005	143,000	1,150,000
2006	153,000	1,160,000
2007	123,000	1,180,000
2008	135,000	1,150,000

## Uncertainty and Time-Series Consistency

Uncertainty associated with lead production relates to the emission factors and activity data used. The direct smelting emission factor used in primary production is taken from Sjardin (2003) who averages the values provided by three other studies (Dutrizac et al. 2000, Morris et al. 1983, Ullman 1997). For secondary production, Sjardin (2003) reduces this factor by 50 percent and adds a CO<sub>2</sub> emission factor associated with battery treatment. The applicability of these emission factors to plants in the United States is uncertain. There is also a smaller level of uncertainty associated with the accuracy of primary and secondary production data provided by the USGS.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-81. Lead production CO<sub>2</sub> emissions were estimated to be between 0.2 and 0.3 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level. This indicates a range of approximately 12 percent below and 22 percent above the emission estimate of 0.3 Tg CO<sub>2</sub> Eq.

Methodological recalculations were applied to the entire time series to ensure time-series consistency from 1990 through 2008. Details on the emission trends through time

**Table 4-81: Tier 2 Quantitative Uncertainty Estimates for CO<sub>2</sub> Emissions from Lead Production (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2008 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Lead Production	CO <sub>2</sub>	0.3	0.2	0.3	-12%	+22%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

are described in more detail in the Methodology section, above.

## 4.19. HCFC-22 Production (IPCC Source Category 2E1)

Trifluoromethane (HFC-23 or CHF<sub>3</sub>) is generated as a by-product during the manufacture of chlorodifluoromethane (HCFC-22), which is primarily employed in refrigeration and air conditioning systems and as a chemical feedstock for manufacturing synthetic polymers. Between 1990 and 2000, U.S. production of HCFC-22 increased significantly as HCFC-22 replaced chlorofluorocarbons (CFCs) in many applications. Since 2000, U.S. production has fluctuated but has generally remained above 1990 levels. Because HCFC-22 depletes stratospheric ozone, its production for non-feedstock uses is scheduled to be phased out by 2020 under the U.S. Clean Air Act.<sup>17</sup> Feedstock production, however, is permitted to continue indefinitely.

HCFC-22 is produced by the reaction of chloroform (CHCl<sub>3</sub>) and hydrogen fluoride (HF) in the presence of a catalyst, SbCl<sub>5</sub>. The reaction of the catalyst and HF produces SbCl<sub>x</sub>F<sub>y</sub>, (where x + y = 5), which reacts with chlorinated hydrocarbons to replace chlorine atoms with fluorine. The HF and chloroform are introduced by submerged piping into a continuous-flow reactor that contains the catalyst in a hydrocarbon mixture of chloroform and partially fluorinated intermediates. The vapors leaving the reactor contain HCFC-21 (CHCl<sub>2</sub>F), HCFC-22 (CHClF<sub>2</sub>), HFC-23 (CHF<sub>3</sub>), HCl, chloroform, and HF. The under-fluorinated intermediates (HCFC-21) and chloroform are then condensed and returned to the reactor, along with residual catalyst, to undergo further fluorination. The final vapors leaving the condenser are primarily HCFC-22, HFC-23, HCl and residual HF. The HCl

<sup>17</sup> As construed, interpreted, and applied in the terms and conditions of the *Montreal Protocol on Substances that Deplete the Ozone Layer* [42 U.S.C. §7671m(b), CAA §614].

is recovered as a useful byproduct, and the HF is removed. Once separated from HCFC-22, the HFC-23 may be released to the atmosphere, recaptured for use in a limited number of applications, or destroyed.

Emissions of HFC-23 in 2008 were estimated to be 13.6 Tg CO<sub>2</sub> Eq. (1.2 Gg) (Table 4-82). This quantity represents a 20 percent decrease from 2007 emissions and a 63 percent decline from 1990 emissions. The decrease from 2007 emissions was caused by a 22 percent decrease in HCFC-22 production and a 3 percent increase in the HFC-23 emission rate. The decline from 1990 emissions is due to a 59 percent decrease in the HFC-23 emission rate since 1990. The decrease is primarily attributable to four factors: (1) five plants that did not capture and destroy the HFC-23 generated have ceased production of HCFC-22 since 1990; (2) one plant that captures and destroys the HFC-23 generated began to produce HCFC-22; (3) one plant implemented and documented a process change that reduced the amount of HFC-23 generated; and (4) the same plant began recovering HFC-23, primarily for destruction and secondarily for sale. Three HCFC-22 production plants operated in the United States in 2006, two of which used thermal oxidation to significantly lower their HFC-23 emissions.

**Table 4-82: HFC-23 Emissions from HCFC-22 Production (Tg CO<sub>2</sub> Eq. and Gg)**

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	36.4	3
1995	33.0	3
2000	28.6	2
2005	15.8	1
2006	13.8	1
2007	17.0	1
2008	13.6	1

## Methodology

To estimate their emissions of HFC-23, five of the eight HCFC-22 plants that have operated in the U.S. since 1990 use (or, for those plants that have closed, used) methods comparable to the Tier 3 methods in the 2006 IPCC Guidelines (IPCC 2006). The other three plants, the last of which closed in 1993, used methods comparable to the Tier 1 method in the 2006 IPCC Guidelines. Emissions from these three plants have been recalculated using the recommended emission factor for unoptimized plants operating before 1995 (0.04 kg HCFC-23/kg HCFC-22 produced). (This recalculation was reflected in the 1990 through 2006 inventory submission.)

The five plants that have operated since 1994 measured concentrations of HFC-23 to estimate their emissions of HFC-23. Plants using thermal oxidation to abate their HFC-23 emissions monitor the performance of their oxidizers to verify that the HFC-23 is almost completely destroyed. Plants that release (or historically have released) some of their byproduct HFC-23 periodically measure HFC-23 concentrations in the output stream using gas chromatography. This information is combined with information on quantities of products (e.g., HCFC-22) to estimate HFC-23 emissions.

In most years, including 2009, an industry association aggregates and reports to EPA country-level estimates of HCFC-22 production and HFC-23 emissions (ARAP 1997, 1999, 2000, 2001, 2002, 2003, 2004, 2005, 2006, 2007, 2008, 2009). However, in 1997 and 2008, EPA (through a contractor) performed comprehensive reviews of plant-level estimates of HFC-23 emissions and HCFC-22 production (RTI 1997; RTI 2008). These reviews enabled EPA to review, update, and where necessary, correct U.S. totals, and also to perform plant-level uncertainty analyses (Monte-

Carlo simulations) for 1990, 1995, 2000, 2005, and 2006. Estimates of annual U.S. HCFC-22 production are presented in Table 4-83.

## Uncertainty and Time Series Consistency

The uncertainty analysis presented in this section was based on a plant-level Monte Carlo simulation for 2006. The Monte Carlo analysis used estimates of the uncertainties in the individual variables in each plant's estimating procedure. This analysis was based on the generation of 10,000 random samples of model inputs from the probability density functions for each input. A normal probability density function was assumed for all measurements and biases except the equipment leak estimates for one plant; a log-normal probability density function was used for this plant's equipment leak estimates. The simulation for 2006 yielded a 95-percent confidence interval for U.S. emissions of 6.8 percent below to 9.6 percent above the reported total.

Because EPA did not have access to plant-level emissions data for 2008, the relative errors yielded by the Monte Carlo simulation for 2006 were applied to the U.S. emission estimate for 2008. The resulting estimates of absolute uncertainty are likely to be accurate because (1) the methods used by the three plants to estimate their emissions are not believed to have changed significantly since 2006; (2) the distribution of emissions among the plants is not believed to have changed significantly since 2006 (one plant continues to dominate emissions); and (3) the country-level relative errors yielded by the Monte Carlo simulations for 2005 and 2006 were very similar, implying that these errors are not sensitive to small, year-to-year changes.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-84. HFC-23 emissions from HCFC-22 production were estimated to be between 12.7 and 14.9 Tg CO<sub>2</sub> Eq. at the 95-percent confidence level. This indicates a range of approximately 7 percent below and 10 percent above the emission estimate of 13.60 Tg CO<sub>2</sub> Eq.

Methodological recalculations were applied to the entire time series to ensure time-series consistency from 1990 through 2008. Details on the emission trends through time are described in more detail in the Methodology section, above.

**Table 4-83: HCFC-22 Production (Gg)**

Year	Gg
1990	139
1995	155
2000	186
2005	156
2006	154
2007	162
2008	126

**Table 4-84: Quantitative Uncertainty Estimates for HFC-23 Emissions from HCFC-22 Production (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2008 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
HCFC-22 Production	HFC-23	13.6	12.7	14.9	-7%	+10%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

## 4.20. Substitution of Ozone Depleting Substances (IPCC Source Category 2F)

HFCs and PFCs are used as alternatives to several classes of ODSs that are being phased out under the terms of the Montreal Protocol and the Clean Air Act Amendments of 1990.<sup>18</sup> Ozone depleting substances—chlorofluorocarbons (CFCs), halons, carbon tetrachloride, methyl chloroform, and hydrochlorofluorocarbons (HCFCs)—are used in a variety of industrial applications including refrigeration and air conditioning equipment, solvent cleaning, foam production, sterilization, fire extinguishing, and aerosols. Although HFCs and PFCs are not harmful to the stratospheric ozone layer, they are potent greenhouse gases. Emission estimates for HFCs and PFCs used as substitutes for ODSs are provided in Table 4-85 and Table 4-86.

In 1990 and 1991, the only significant emissions of HFCs and PFCs as substitutes to ODSs were relatively small amounts of HFC-152a—used as an aerosol propellant and also a component of the refrigerant blend R-500 used in chillers—and HFC-134a in refrigeration end-uses. Beginning in 1992, HFC-134a was used in growing amounts as a refrigerant in motor vehicle air-conditioners and in refrigerant blends such as R-404A.<sup>19</sup> In 1993, the use of HFCs in foam production began, and in 1994 these compounds also found applications as solvents. In 1995, ODS substitutes for halons entered widespread use in the United States as halon production was phased-out.

The use and subsequent emissions of HFCs and PFCs as ODS substitutes has been increasing from small amounts in 1990 to 113.0 Tg CO<sub>2</sub> Eq. in 2008. This increase was in large part the result of efforts to phase out CFCs and other

ODSs in the United States. In the short term, this trend is expected to continue, and will likely accelerate over the next decade as HCFCs, which are interim substitutes in many applications, are themselves phased-out under the provisions of the Copenhagen Amendments to the Montreal Protocol. Improvements in the technologies associated with the use of these gases and the introduction of alternative gases and technologies, however, may help to offset this anticipated increase in emissions.

Table 4-87 presents emissions of HFCs and PFCs as ODS substitutes by end-use sector for 1990 through 2008. The end-use sectors that contributed the most toward emissions of HFCs and PFCs as ODS substitutes in 2008 include refrigeration and air-conditioning (101.7 Tg CO<sub>2</sub> Eq., or approximately 90 percent), aerosols (6.4 Tg CO<sub>2</sub> Eq., or approximately 6 percent), and foams (2.8 Tg CO<sub>2</sub> Eq., or approximately 2 percent). Within the refrigeration and air-conditioning end-use sector, motor vehicle air-conditioning was the highest emitting end-use (50.7 Tg CO<sub>2</sub> Eq.), followed by refrigerated transport and retail food. Each of the end-use sectors is described in more detail below.

### Refrigeration/Air Conditioning

The refrigeration and air-conditioning sector includes a wide variety of equipment types that have historically used CFCs or HCFCs. End-uses within this sector include motor vehicle air-conditioning, retail food refrigeration, refrigerated transport (e.g., ship holds, truck trailers, railway freight cars), household refrigeration, residential and small commercial air-conditioning/heat pumps, chillers (large comfort cooling), cold storage facilities, and industrial process refrigeration (e.g., systems used in food processing, chemical, petrochemical, pharmaceutical, oil and gas, and metallurgical industries). As the ODS phaseout is

<sup>18</sup> [42 U.S.C § 7671, CAA § 601].

<sup>19</sup> R-404A contains HFC-125, HFC-143a, and HFC-134a.

**Table 4-85: Emissions of HFCs and PFCs from ODS Substitutes (Tg CO<sub>2</sub> Eq.)**

Gas	1990	1995	2000	2005	2006	2007	2008
HFC-23	+	+	+	+	+	+	+
HFC-32	+	+	+	0.4	0.6	0.9	1.2
HFC-125	+	0.8	5.2	10.3	12.3	14.7	17.7
HFC-134a	+	25.8	60.3	73.7	73.4	70.5	67.3
HFC-143a	+	0.5	4.1	12.2	14.4	16.7	19.2
HFC-236fa	+	0.2	0.5	0.8	0.8	0.9	0.9
CF <sub>4</sub>	+	+	+	+	+	+	+
Others <sup>a</sup>	0.3	1.6	4.0	5.9	6.2	6.5	6.8
<b>Total</b>	<b>0.3</b>	<b>29.0</b>	<b>74.3</b>	<b>103.2</b>	<b>107.7</b>	<b>110.1</b>	<b>113.0</b>

+ Does not exceed 0.05 Tg CO<sub>2</sub> Eq.  
<sup>a</sup> Others include HFC-152a, HFC-227ea, HFC-245fa, HFC-4310mee, and PFC/PFPEs, the latter being a proxy for a diverse collection of PFCs and perfluoropolyethers (PFPEs) employed for solvent applications. For estimating purposes, the GWP value used for PFC/PFPEs was based upon C<sub>6</sub>F<sub>14</sub>.  
Note: Totals may not sum due to independent rounding.

**Table 4-86: Emissions of HFCs and PFCs from ODS Substitution (Mg)**

Gas	1990	1995	2000	2005	2006	2007	2008
HFC-23	+	+	1	1	1	1	2
HFC-32	+	+	44	562	913	1,325	1,801
HFC-125	+	291	1,873	3,675	4,394	5,253	6,310
HFC-134a	+	19,875	46,379	56,675	56,484	54,210	51,750
HFC-143a	+	132	1,089	3,200	3,782	4,402	5,044
HFC-236fa	+	36	85	125	131	136	141
CF <sub>4</sub>	+	+	1	2	2	2	2
Others <sup>a</sup>	M	M	M	M	M	M	M

M (Mixture of Gases)  
+ Does not exceed 0.5 Mg.  
<sup>a</sup> Others include HFC-152a, HFC-227ea, HFC-245fa, HFC-4310mee, C<sub>4</sub>F<sub>10</sub>, and PFC/PFPEs, the latter being a proxy for a diverse collection of PFCs and perfluoropolyethers (PFPEs) employed for solvent applications.

**Table 4-87: Emissions of HFCs and PFCs from ODS Substitutes (Tg CO<sub>2</sub> Eq.) by Sector**

Sector	1990	1995	2000	2005	2006	2007	2008
Refrigeration/Air-conditioning	+	19.8	61.7	93.3	97.4	99.3	101.7
Aerosols	0.3	8.1	10.1	5.9	6.1	6.2	6.4
Foams	+	0.2	0.3	2.2	2.4	2.6	2.8
Solvents	+	0.9	2.1	1.3	1.3	1.3	1.3
Fire Protection	+	+	0.2	0.5	0.6	0.7	0.7
<b>Total</b>	<b>0.3</b>	<b>29.0</b>	<b>74.3</b>	<b>103.2</b>	<b>107.7</b>	<b>110.1</b>	<b>113.0</b>

+ Does not exceed 0.05 Tg CO<sub>2</sub> Eq.

taking effect, most equipment is being or will eventually be retrofitted or replaced to use HFC-based substitutes. Common HFCs in use today in refrigeration/air-conditioning

equipment are HFC-134a, R-410A,<sup>20</sup> R-404A, and R-507A.<sup>21</sup> These HFCs are emitted to the atmosphere during equipment

<sup>20</sup> R-410A contains HFC-32 and HFC-125.

<sup>21</sup> R-507 contains HFC-125 and HFC-143a.

manufacture and operation (as a result of component failure, leaks, and purges), as well as at servicing and disposal events.

### **Aerosols**

Aerosol propellants are used in metered dose inhalers (MDIs) and a variety of personal care products and technical/specialty products (e.g., duster sprays and safety horns). Many pharmaceutical companies that produce MDIs—a type of inhaled therapy used to treat asthma and chronic obstructive pulmonary disease—have committed to replace the use of CFCs with HFC-propellant alternatives. The earliest ozone-friendly MDIs were produced with HFC-134a, but eventually, the industry expects to use HFC-227ea as well. Conversely, since the use of CFC propellants was banned in 1978, most consumer aerosol products have not transitioned to HFCs, but to “not-in-kind” technologies, such as solid roll-on deodorants and finger-pump sprays. The transition away from ODS in specialty aerosol products has also led to the introduction of non-fluorocarbon alternatives (e.g., hydrocarbon propellants) in certain applications, in addition to HFC-134a or HFC-152a. These propellants are released into the atmosphere as the aerosol products are used.

### **Foams**

CFCs and HCFCs have traditionally been used as foam blowing agents to produce polyurethane (PU), polystyrene, polyolefin, and phenolic foams, which are used in a wide variety of products and applications. Since the Montreal Protocol, flexible PU foams as well as other types of foam, such as polystyrene sheet, polyolefin, and phenolic foam, have transitioned almost completely away from fluorocompounds, into alternatives such as CO<sub>2</sub>, methylene chloride, and hydrocarbons. The majority of rigid PU foams have transitioned to HFCs—primarily HFC-134a and HFC-245fa. Today, these HFCs are used to produce polyurethane appliance foam, PU commercial refrigeration, PU spray, and PU panel foams—used in refrigerators, vending machines, roofing, wall insulation, garage doors, and cold storage applications. In addition, HFC-152a is used to produce polystyrene sheet/board foam, which is used in food packaging and building insulation. Emissions of blowing agents occur when the foam is manufactured as well as during the foam lifetime and at foam disposal, depending on the particular foam type.

### **Solvents**

CFCs, methyl chloroform (1,1,1-trichloroethane or TCA), and to a lesser extent carbon tetrachloride (CCl<sub>4</sub>) were historically used as solvents in a wide range of cleaning applications, including precision, electronics, and metal cleaning. Since their phaseout, metal cleaning end-use applications have primarily transitioned to non-fluorocarbon solvents and not-in-kind processes. The precision and electronics cleaning end-uses have transitioned in part to high-GWP gases, due to their high reliability, excellent compatibility, good stability, low toxicity, and selective solvency. These applications rely on HFC-4310mee, HFC-365mfc, HFC-245fa, and to a lesser extent, PFCs. Electronics cleaning involves removing flux residue that remains after a soldering operation for printed circuit boards and other contamination-sensitive electronics applications. Precision cleaning may apply to either electronic components or to metal surfaces, and is characterized by products, such as disk drives, gyroscopes, and optical components, that require a high level of cleanliness and generally have complex shapes, small clearances, and other cleaning challenges. The use of solvents yields fugitive emissions of these HFCs and PFCs.

### **Fire Protection**

Fire protection applications include portable fire extinguishers (“streaming” applications) that originally used halon 1211, and total flooding applications that originally used halon 1301, as well as some halon 2402. Since the production and sale of halons were banned in the United States in 1994, the halon replacement agent of choice in the streaming sector has been dry chemical, although HFC-236ea is also used to a limited extent. In the total flooding sector, HFC-227ea has emerged as the primary replacement for halon 1301 in applications that require clean agents. Other HFCs, such as HFC-23, HFC-236fa, and HFC-125, are used in smaller amounts. The majority of HFC-227ea in total flooding systems is used to protect essential electronics, as well as in civil aviation, military mobile weapons systems, oil/gas/other process industries, and merchant shipping. As fire protection equipment is tested or deployed, emissions of these HFCs occur.

## Methodology

A detailed Vintaging Model of ODS-containing equipment and products was used to estimate the actual—versus potential—emissions of various ODS substitutes, including HFCs and PFCs. The name of the model refers to the fact that the model tracks the use and emissions of various compounds for the annual “vintages” of new equipment that enter service in each end-use. This Vintaging Model predicts ODS and ODS substitute use in the United States based on modeled estimates of the quantity of equipment or products sold each year containing these chemicals and the amount of the chemical required to manufacture and/or maintain equipment and products over time. Emissions for each end-use were estimated by applying annual leak rates and release profiles, which account for the lag in emissions from equipment as they leak over time. By aggregating the data for more than 50 different end-uses, the model produces estimates of annual use and emissions of each compound. Further information on the Vintaging Model is contained in Annex 3.8.

## Uncertainty and Time-Series Consistency

Given that emissions of ODS substitutes occur from thousands of different kinds of equipment and from millions of point and mobile sources throughout the United States, emission estimates must be made using analytical tools such as the Vintaging Model or the methods outlined in IPCC (2006). Though the model is more comprehensive than the IPCC default methodology, significant uncertainties still exist with regard to the levels of equipment sales, equipment characteristics, and end-use emissions profiles that were used to estimate annual emissions for the various compounds.

The Vintaging Model estimates emissions from over 50 end-uses. The uncertainty analysis, however, quantifies the level of uncertainty associated with the aggregate emissions

resulting from the top 17 end-uses, comprising over 95 percent of the total emissions, and 8 other end-uses. These 25 end-uses comprise 97 percent of the total emissions. In an effort to improve the uncertainty analysis, additional end-uses are added annually, with the intention that over time uncertainty for all emissions from the Vintaging Model will be fully characterized. This year, one new end-use was included in the uncertainty estimate—extruded polystyrene sheet foam. Any end-uses included in previous years’ uncertainty analysis were included in the current uncertainty analysis, whether or not those end-uses were included in the top 95 percent of emissions from ODS substitutes.

In order to calculate uncertainty, functional forms were developed to simplify some of the complex “vintaging” aspects of some end-use sectors, especially with respect to refrigeration and air-conditioning, and to a lesser degree, fire extinguishing. These sectors calculate emissions based on the entire lifetime of equipment, not just equipment put into commission in the current year, thereby necessitating simplifying equations. The functional forms used variables that included growth rates, emission factors, transition from ODSs, change in charge size as a result of the transition, disposal quantities, disposal emission rates, and either stock for the current year or original ODS consumption. Uncertainty was estimated around each variable within the functional forms based on expert judgment, and a Monte Carlo analysis was performed. The most significant sources of uncertainty for this source category include the emission factors for retail food equipment and refrigerated transport, as well as the percent of non-MDI aerosol propellant that is HFC-152a.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-88. Substitution of ozone depleting substances HFC and PFC emissions were estimated to be between 110.8 and 127.7 Tg CO<sub>2</sub> Eq. at the 95 percent

**Table 4-88: Tier 2 Quantitative Uncertainty Estimates for HFC and PFC Emissions from ODS Substitutes (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2008 Emission Estimate (Tg CO <sub>2</sub> Eq.) <sup>a</sup>	Uncertainty Range Relative to Emission Estimate <sup>b</sup>			
			Lower Bound	Upper Bound	Lower Bound (%)	Upper Bound (%)
Substitution of Ozone Depleting Substances	HFCs and PFCs	110.0	107.4	124.3	-2%	+13%

<sup>a</sup> 2008 Emission estimates and the uncertainty range presented in this table correspond to aerosols, foams, solvents, fire extinguishing agents, and refrigerants, but not for other remaining categories. Therefore, because the uncertainty associated with emissions from “other” ODS substitutes was not estimated, they were excluded in the estimates reported in this table.

<sup>b</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

confidence level. This indicates a range of approximately 2 percent below to 13 percent above the emission estimate of 113.0 Tg CO<sub>2</sub> Eq. These estimates exclude about 3 percent (or 3.0 Tg CO<sub>2</sub> Eq.) emissions from 37 end-uses within this source category, for which quantitative uncertainty estimates were not developed.

Methodological recalculations were applied to the entire time series to ensure time-series consistency from 1990 through 2008. Details on the emission trends through time are described in more detail in the Methodology section, above.

## Recalculations Discussion

An extensive review of growth rates and charge sizes for mobile air conditioning units resulted in updated assumptions for the Vintaging Model. These changes resulted in an average annual net increase of 1.7 Tg CO<sub>2</sub> Eq. (2.4 percent) in HFC and PFC emissions from the substitution of ozone depleting substances for the period 1990 through 2007 relative to the previous Inventory.

### 4.21. Semiconductor Manufacture (IPCC Source Category 2F6)

The semiconductor industry uses multiple long-lived fluorinated gases in plasma etching and plasma enhanced chemical vapor deposition (PECVD) processes to produce semiconductor products. The gases most commonly employed are trifluoromethane (HFC-23 or CHF<sub>3</sub>), perfluoromethane (CF<sub>4</sub>), perfluoroethane (C<sub>2</sub>F<sub>6</sub>), nitrogen trifluoride (NF<sub>3</sub>), and sulfur hexafluoride (SF<sub>6</sub>), although other compounds such as perfluoropropane (C<sub>3</sub>F<sub>8</sub>) and perfluorocyclobutane (c-C<sub>4</sub>F<sub>8</sub>) are also used. The exact combination of compounds is specific to the process employed.

A single 300 mm silicon wafer that yields between 400 to 500 semiconductor products (devices or chips) may require as many as 100 distinct fluorinated-gas-using process steps, principally to deposit and pattern dielectric films. Plasma etching (or patterning) of dielectric films, such as silicon dioxide and silicon nitride, is performed to provide pathways for conducting material to connect individual circuit components in each device. The patterning process uses plasma-generated fluorine atoms, which chemically react with exposed dielectric film to selectively remove the desired portions of the film. The material removed as well

as undissociated fluorinated gases flow into waste streams and, unless emission abatement systems are employed, into the atmosphere. PECVD chambers, used for depositing dielectric films, are cleaned periodically using fluorinated and other gases. During the cleaning cycle the gas is converted to fluorine atoms in plasma, which etches away residual material from chamber walls, electrodes, and chamber hardware. Undissociated fluorinated gases and other products pass from the chamber to waste streams and, unless abatement systems are employed, into the atmosphere. In addition to emissions of unreacted gases, some fluorinated compounds can also be transformed in the plasma processes into different fluorinated compounds which are then exhausted, unless abated, into the atmosphere. For example, when C<sub>2</sub>F<sub>6</sub> is used in cleaning or etching, CF<sub>4</sub> is generated and emitted as a process by-product. Besides dielectric film etching and PECVD chamber cleaning, much smaller quantities of fluorinated gases are used to etch polysilicon films and refractory metal films like tungsten.

For 2008, total weighted emissions of all fluorinated greenhouse gases by the U.S. semiconductor industry were estimated to be 5.4 Tg CO<sub>2</sub> Eq. Combined emissions of all fluorinated greenhouse gases are presented in Table 4-89 and Table 4-90 below for years 1990, 1995, 2000 and the period 2005 to 2008. The rapid growth of this industry and the increasing complexity (growing number of layers)<sup>22</sup> of semiconductor products led to an increase in emissions of 150 percent between 1990 and 1999, when emissions peaked at 7.2 Tg CO<sub>2</sub> Eq. The emissions growth rate began to slow after 1998, and emissions declined by 26 percent between 1999 and 2008. Together, industrial growth and adoption of emissions reduction technologies, including but not limited to abatement technologies, resulted in a net increase in emissions of 84 percent between 1990 and 2008.

## Methodology

Emissions are based on Partner reported emissions data received through the EPA's PFC Reduction/Climate Partnership and the EPA's PFC Emissions Vintage Model (PEVM), a model which estimates industry emissions in

<sup>22</sup> Complexity is a term denoting the circuit required to connect the active circuit elements (transistors) on a chip. Increasing miniaturization, for the same chip size, leads to increasing transistor density, which, in turn, requires more complex interconnections between those transistors. This increasing complexity is manifested by increasing the levels (i.e., layers) of wiring, with each wiring layer requiring fluorinated gas usage for its manufacture.



**Table 4-89: PFC, HFC, and SF<sub>6</sub> Emissions from Semiconductor Manufacture (Tg CO<sub>2</sub> Eq.)**

Gas	1990	1995	2000	2005	2006	2007	2008
CF <sub>4</sub>	0.7	1.3	1.8	1.1	1.2	1.3	1.3
C <sub>2</sub> F <sub>6</sub>	1.5	2.5	3.0	2.0	2.2	2.3	2.6
C <sub>3</sub> F <sub>8</sub>	0.0	0.0	0.1	0.0	0.0	0.0	0.0
c-C <sub>4</sub> F <sub>8</sub>	0.0	0.0	0.0	0.1	0.1	0.1	0.1
HFC-23	0.2	0.3	0.3	0.2	0.3	0.3	0.3
SF <sub>6</sub>	0.5	0.9	1.1	1.0	1.0	0.8	1.1
NF <sub>3</sub> <sup>a</sup>	0.0	0.1	0.2	0.4	0.7	0.5	0.4
<b>Total</b>	<b>2.9</b>	<b>4.9</b>	<b>6.2</b>	<b>4.4</b>	<b>4.7</b>	<b>4.7</b>	<b>5.4</b>

<sup>a</sup> NF<sub>3</sub> emissions are presented for informational purposes, using the AR4 GWP of 17,200, and are not included in totals.  
Note: Totals may not sum due to independent rounding.

**Table 4-90: PFC, HFC, and SF<sub>6</sub> Emissions from Semiconductor Manufacture (Mg)**

Gas	1990	1995	2000	2005	2006	2007	2008
CF <sub>4</sub>	115	193	281	168	181	195	199
C <sub>2</sub> F <sub>6</sub>	160	272	321	216	240	246	285
C <sub>3</sub> F <sub>8</sub>	0	0	18	5	5	6	4
c-C <sub>4</sub> F <sub>8</sub>	0	0	0	13	13	7	7
HFC-23	15	25	23	18	22	22	25
SF <sub>6</sub>	22	37	45	40	40	34	44
NF <sub>3</sub>	3	3	11	26	40	30	21

the absence of emission control strategies (Burton and Beizaie 2001).<sup>23</sup> The availability and applicability of Partner data differs across the 1990 through 2008 time series. Consequently, emissions from semiconductor manufacturing were estimated using four distinct methods, one each for the periods 1990 through 1994, 1995 through 1999, 2000 through 2006, and 2007 through 2008.

#### 1990 through 1994

From 1990 through 1994, Partnership data was unavailable and emissions were modeled using the PEVM (Burton and Beizaie 2001).<sup>24</sup> 1990 to 1994 emissions are

assumed to be uncontrolled, since reduction strategies such as chemical substitution and abatement were yet developed.

PEVM is based on the recognition that PFC emissions from semiconductor manufacturing vary with (1) the number of layers that comprise different kinds of semiconductor devices, including both silicon wafer and metal interconnect layers, and (2) silicon consumption (i.e., the area of semiconductors produced) for each kind of device. The product of these two quantities, Total Manufactured Layer Area (TMLA), constitutes the activity data for semiconductor manufacturing. PEVM also incorporates an emission factor that expresses emissions per unit of layer-area. Emissions are estimated by multiplying TMLA by this emission factor.

PEVM incorporates information on the two attributes of semiconductor devices that affect the number of layers: (1) linewidth technology (the smallest manufactured feature

<sup>23</sup> A Partner refers to a participant in the U.S. EPA PFC Reduction/Climate Partnership for the Semiconductor Industry. Through a Memorandum of Understanding (MoU) with the EPA, Partners voluntarily report their PFC emissions to the EPA by way of a third party, which aggregates the emissions.

<sup>24</sup> Various versions of the PEVM exist to reflect changing industrial practices. From 1990 to 1994 emissions estimates are from PEVM v1.0, completed in September 1998. The emission factor used to estimate 1990 to 1994 emissions is an average of the 1995 and 1996 emissions factors, which were derived from Partner reported data for those years.

size),<sup>25</sup> and (2) product type (discrete, memory or logic).<sup>26</sup> For each linewidth technology, a weighted average number of layers is estimated using VLSI product-specific worldwide silicon demand data in conjunction with complexity factors (i.e., the number of layers per Integrated Circuit (IC)) specific to product type (Burton and Beizaie 2001, ITRS 2007). PEVM derives historical consumption of silicon (i.e., square inches) by linewidth technology from published data on annual wafer starts and average wafer size (VLSI Research, Inc. 2009).

The emission factor in PEVM is the average of four historical emission factors, each derived by dividing the total annual emissions reported by the Partners for each of the four years between 1996 and 1999 by the total TMLA estimated for the Partners in each of those years. Over this period, the emission factors varied relatively little (i.e., the relative standard deviation for the average was 5 percent). Since Partners are believed not to have applied significant emission reduction measures before 2000, the resulting average emission factor reflects uncontrolled emissions. The emission factor is used to estimate world uncontrolled emissions using publicly available data on world silicon consumption.

#### **1995 through 1999**

For 1995 through 1999, total U.S. emissions were extrapolated from the total annual emissions reported by the Partners (1995 through 1999). Partner-reported emissions are considered more representative (e.g., in terms of capacity utilization in a given year) than PEVM estimated emissions, and are used to generate total U.S. emissions when applicable.

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<sup>25</sup> By decreasing features of IC components, more components can be manufactured per device, which increases its functionality. However, as those individual components shrink it requires more layers to interconnect them to achieve the functionality. For example, a microprocessor manufactured with the smallest feature sizes (65 nm) might contain as many as 1 billion transistors and require as many as 11 layers of component interconnects to achieve functionality while a device manufactured with 130 nm feature size might contain a few hundred million transistors and require 8 layers of component interconnects (ITRS 2007).

<sup>26</sup> Memory devices manufactured with the same feature sizes as microprocessors (a logic device) require approximately one-half the number of interconnect layers, whereas discrete devices require only a silicon base layer and no interconnect layers (ITRS 2007). Since discrete devices did not start using PFCs appreciably until 2004, they are only accounted for in the PEVM emissions estimates from 2004 onwards.

The emissions reported by the Partners were divided by the ratio of the total capacity of the plants operated by the Partners and the total capacity of all of the semiconductor plants in the United States; this ratio represents the share of capacity attributable to the Partnership. This method assumes that Partners and non-Partners have identical capacity utilizations and distributions of manufacturing technologies. Plant capacity data is contained in the *World Fab Forecast* (WFF) database and its predecessors, which is updated quarterly (Semiconductor Equipment and Materials Industry 2009).

#### **2000 through 2006**

The emission estimate for the years 2000 through 2006—the period during which Partners began the consequential application of PFC-reduction measures—was estimated using a combination of Partner reported emissions and PEVM modeled emissions. The emissions reported by Partners for each year were accepted as the quantity emitted from the share of the industry represented by those Partners. Remaining emissions, those from non-Partners, were estimated using PEVM and the method described above. This is because non-Partners are assumed not to have implemented any PFC-reduction measures, and PEVM models emissions without such measures. The portion of the U.S. total attributed to non-Partners is obtained by multiplying PEVM's total U.S. emissions figure by the non-Partner share of U. S. total silicon capacity for each year as described above.<sup>27,28</sup> Annual updates to PEVM reflect published figures for actual silicon consumption from VLSI Research, Inc., revisions and additions to the world population of semiconductor manufacturing plants, and changes in IC fabrication practices within the semiconductor

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<sup>27</sup> This approach assumes that the distribution of linewidth technologies is the same between Partners and non-Partners. As discussed in the description of the method used to estimate 2007 emissions, this is not always the case.

<sup>28</sup> Generally 5 percent or less of the fields needed to estimate TMLA shares are missing values in the World Fab Watch databases. In the 2007 *World Fab Watch* database used to generate the 2006 non-Partner TMLA capacity share, these missing values were replaced with the corresponding mean TMLA across fabs manufacturing similar classes of products. However, the impact of replacing missing values on the non-Partner TMLA capacity share was inconsequential.

industry (see, ITRS, 2007 and Semiconductor Equipment and Materials Industry 2009).<sup>29, 30, 31</sup>

### 2007 through 2008

For the years 2007 and 2008, emissions were also estimated using a combination of Partner reported emissions and PEVM modeled emissions; however, two improvements were made to the estimation method employed for the previous years in the time series. First, the 2007 and 2008 emission estimates account for the fact that Partners and non-Partners employ different distributions of manufacturing technologies, with the Partners using manufacturing technologies with greater transistor densities and therefore greater numbers of layers.<sup>32</sup> Second, the scope of the 2007 and 2008 estimates is expanded relative to the estimates for the years 2000 through 2006 to include emissions from Research and Development fabs. This was feasible through

<sup>29</sup> Special attention was given to the manufacturing capacity of plants that use wafers with 300 mm diameters because the actual capacity of these plants is ramped up to design capacity, typically over a 2-3 year period. To prevent overstating estimates of partner-capacity shares from plants using 300 mm wafers, design capacities contained in WFW were replaced with estimates of actual installed capacities for 2004 published by Citigroup Smith Barney (2005). Without this correction, the partner share of capacity would be overstated, by approximately 5 percentage points. For perspective, approximately 95 percent of all new capacity additions in 2004 used 300 mm wafers and by year-end those plants, on average, could operate at approximately 70 percent of the design capacity. For 2005, actual installed capacities were estimated using an entry in the *World Fab Watch* database (April 2006 Edition) called “wafers/month, 8-inch equivalent”, which denoted the actual installed capacity instead of the fully-ramped capacity. For 2006, actual installed capacities of new fabs were estimated using an average monthly ramp rate of 1100 wafer starts per month (wspm) derived from various sources such as semiconductor fabtech, industry analysts, and articles in the trade press. The monthly ramp rate was applied from the first-quarter of silicon volume (FQSV) to determine the average design capacity over the 2006 period.

<sup>30</sup> In 2006, the industry trend in co-ownership of manufacturing facilities continued. Several manufacturers, who are Partners, now operate fabs with other manufacturers, who in some cases are also Partners and in other cases not Partners. Special attention was given to this occurrence when estimating the Partner and non-Partner shares of U.S. manufacturing capacity.

<sup>31</sup> Two versions of PEVM are used to model non-Partner emissions during this period. For the years 2000 to 2003 PEVM v3.2.0506.0507 was used to estimate non-Partner emissions. During this time, discrete devices did not use PFCs during manufacturing and therefore only memory and logic devices were modeled in the PEVM v3.2.0506.0507. From 2004 onwards, discrete device fabrication started to use PFCs, hence PEVM v4.0.0701.0701, the first version of PEVM to account for PFC emissions from discrete devices, was used to estimate non-Partner emissions for this time period.

<sup>32</sup> EPA considered applying this change to years before 2007, but found that it would be difficult due to the large amount of data (i.e., technology-specific global and non-Partner TMLA) that would have to be examined and manipulated for each year. This effort did not appear to be justified given the relatively small impact of the improvement on the total estimate for 2007 and the fact that the impact of the improvement would likely be lower for earlier years because the estimated share of emissions accounted for by non-Partners is growing as Partners continue to implement emission-reduction efforts.

the use of more detailed data published in the World Fab Forecast. PEVM databases are updated annually as described above. The published world average capacity utilization for 2007 and 2008 was used for production fabs while in 2008 for R&D fabs a 20 percent figure was assumed (SIA 2009).

In addition, publicly available actual utilization data was used to account for differences in fab utilization for manufacturers of discrete and IC products for the emissions of 2008 for non-partner. PEVM estimates were adjusted using technology weighted capacity shares that reflect relative influence of different utilization.

### Gas-Specific Emissions

Two different approaches were also used to estimate the distribution of emissions of specific fluorinated gases. Before 1999, when there was no consequential adoption of fluorinated-gas-reducing measures, a fixed distribution of fluorinated-gas-use was assumed to apply to the entire U.S. industry. This distribution was based upon the average fluorinated-gas purchases by semiconductor manufacturers during this period and the application of IPCC default emission factors for each gas (Burton and Beizaie 2001). For the 2000 through 2008 period, the 1990 through 1999 distribution was assumed to apply to the non-Partners. Partners, however, began reporting gas-specific emissions during this period. Thus, gas-specific emissions for 2000 through 2008 were estimated by adding the emissions reported by the Partners to those estimated for the non-Partners.

### Data Sources

Partners estimate their emissions using a range of methods. For 2008, it is assumed that most Partners used a method at least as accurate as the IPCC’s Tier 2a Methodology, recommended in the *IPCC Guidelines for National Greenhouse Inventories* (2006). The Partners with relatively high emissions use leading-edge manufacturing technology, the newest process equipment. When purchased, this equipment is supplied with fluorinated-gas emission factors, measured using industry standard guidelines (International Sematech 2006). The larger emitting Partners likely use these process-specific emission factors instead of the somewhat less representative default emission factors provided in the IPCC guidelines. Data used to develop

emission estimates are attributed in part to estimates provided by the members of the Partnership, and in part from data obtained from PEVM estimates. Estimates of operating plant capacities and characteristics for Partners and non-Partners were derived from the *Semiconductor Equipment and Materials Industry (SEMI) World Fab Forecast* (formerly *World Fab Watch*) database (1996 through 2009). Actual world capacity utilizations for 2008 were obtained from *Semiconductor International Capacity Statistics* (SICAS). Estimates of silicon consumed by linewidth from 1990 through 2008 were derived from information from VLSI Research (2009), and the number of layers per linewidth was obtained from *International Technology Roadmap for Semiconductors: 2006 Update* (Burton and Beizaie 2001, ITRS 2007, ITRS 2008).

## Uncertainty and Time Series Consistency

A quantitative uncertainty analysis of this source category was performed using the IPCC-recommended Tier 2 uncertainty estimation methodology, the Monte Carlo Stochastic Simulation technique. The equation used to estimate uncertainty is:

$$\text{U.S. emissions} = \sum \text{Partnership gas-specific submittals} + [(\text{non-Partner share of world TMLA}) \times (\text{PEVM Emission Factor} \times \text{World TMLA})]$$

The Monte Carlo analysis results presented below relied on estimates of uncertainty attributed to the four quantities on the right side of the equation. Estimates of uncertainty for the four quantities were in turn developed using the estimated uncertainties associated with the individual inputs to each quantity, error propagation analysis, Monte Carlo simulation, and expert judgment. The relative uncertainty associated

with World TMLA estimate in 2008 is about  $\pm 10$  percent, based on the uncertainty estimate obtained from discussions with VLSI, Inc. For the share of World layer-weighted silicon capacity accounted for by non-Partners, a relative uncertainty of  $\pm 8$  percent was estimated based on a separate Monte Carlo simulation to account for the random occurrence of missing data in the World Fab Watch database. For the aggregate PFC emissions data supplied to the partnership, a relative uncertainty of  $\pm 50$  percent was estimated for each gas-specific PFC emissions value reported by an individual Partner, and error propagation techniques were used to estimate uncertainty for total Partnership gas-specific submittals.<sup>33</sup> A relative error of approximately 10 percent was estimated for the PEVM emission factor, based on the standard deviation of the 1996 to 1999 emission factors.<sup>34</sup> All estimates of uncertainties are given at 95-percent confidence intervals.

In developing estimates of uncertainty, consideration was also given to the nature and magnitude of the potential bias that World activity data (i.e., World TMLA) might have in its estimates of the number of layers associated with devices manufactured at each technology node. The result of a brief analysis indicated that U.S. TMLA overstates the average number of layers across all product categories and all manufacturing technologies for 2004 by 0.12 layers or 2.9 percent. The same upward bias is assumed for World TMLA, and is represented in the uncertainty analysis by deducting the absolute bias value from the World activity estimate when it is incorporated into the Monte Carlo analysis.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-91. The emissions estimate for total U.S. PFC emissions from semiconductor manufacturing

**Table 4-91: Tier 2 Quantitative Uncertainty Estimates for HFC, PFC, and SF<sub>6</sub> Emissions from Semiconductor Manufacture (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2008 Emission Estimate (Tg CO <sub>2</sub> Eq.) <sup>a</sup>	Uncertainty Range Relative to Emission Estimate <sup>b</sup> (Tg CO <sub>2</sub> Eq.)			
			Lower Bound <sup>c</sup>	Upper Bound <sup>c</sup>	Lower Bound	Upper Bound
Semiconductor Manufacture	HFC, PFC, and SF <sub>6</sub>	5.7	5.2	6.2	-9%	+9%

<sup>a</sup> Because the uncertainty analysis covered all emissions (including NF<sub>3</sub>), the emission estimate presented here does not match that shown in Table 4-90.  
<sup>b</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.  
<sup>c</sup> Absolute lower and upper bounds were calculated using the corresponding lower and upper bounds in percentages.

<sup>33</sup> Error propagation resulted in Partnership gas-specific uncertainties ranging from 17 to 27 percent.

<sup>34</sup> The average of 1996 to 1999 emission factor is used to derive the PEVM emission factor.

were estimated to be between 5.2 and 6.2 Tg CO<sub>2</sub> Eq. at a 95 percent confidence level. This range represents 9 percent below to 9 percent above the 2008 emission estimate of 5.7 Tg CO<sub>2</sub> Eq. This range and the associated percentages apply to the estimate of total emissions rather than those of individual gases. Uncertainties associated with individual gases will be somewhat higher than the aggregate, but were not explicitly modeled.

Methodological recalculations were applied to the entire time series to ensure time-series consistency from 1990 through 2008. Details on the emission trends through time are described in more detail in the Methodology section, above.

## Planned Improvements

With the exception of possible future updates to emission factors, the method to estimate non-Partner related emissions (i.e., PEVM) is not expected to change. Future improvements to the national emission estimates will primarily be associated with determining the portion of national emissions to attribute to Partner report totals (about 80 percent in recent years) and improvements in estimates of non-Partner totals. As the nature of the Partner reports change through time and industry-wide reduction efforts increase, consideration will be given to what emission reduction efforts—if any—are likely to be occurring at non-Partner facilities. Currently, none are assumed to occur.

Another point of consideration for future national emissions estimates is the inclusion of PFC emissions from heat transfer fluid (HTF) loss to the atmosphere and the production of photovoltaic cells (PVs). Heat transfer fluids, of which some are liquid perfluorinated compounds, are used during testing of semiconductor devices and, increasingly, are used to manage heat during the manufacture of semiconductor devices. Evaporation of these fluids is a source of emissions (EPA 2006). PFCs are also used during manufacture of PV cells that use silicon technology, specifically, crystalline, polycrystalline and amorphous silicon technologies. PV manufacture is growing in the United States, and therefore may be expected to constitute a growing share of U.S. PFC emissions from the electronics sector.

## 4.22. Electrical Transmission and Distribution (IPCC Source Category 2F7)

The largest use of SF<sub>6</sub>, both in the United States and internationally, is as an electrical insulator and interrupter in equipment that transmits and distributes electricity (RAND 2004). The gas has been employed by the electric power industry in the United States since the 1950s because of its dielectric strength and arc-quenching characteristics. It is used in gas-insulated substations, circuit breakers, and other switchgear. Sulfur hexafluoride has replaced flammable insulating oils in many applications and allows for more compact substations in dense urban areas.

Fugitive emissions of SF<sub>6</sub> can escape from gas-insulated substations and switchgear through seals, especially from older equipment. The gas can also be released during equipment manufacturing, installation, servicing, and disposal. Emissions of SF<sub>6</sub> from equipment manufacturing and from electrical transmission and distribution systems were estimated to be 13.1 Tg CO<sub>2</sub> Eq. (0.5 Gg) in 2008. This quantity represents a 51 percent decrease from the estimate for 1990 (see Table 4-92 and Table 4-93). This decrease is believed to have two causes: a sharp increase in the price of SF<sub>6</sub> during the 1990s and a growing awareness of the environmental impact of SF<sub>6</sub> emissions through programs such as EPA's SF<sub>6</sub> Emission Reduction Partnership for Electric Power Systems.

**Table 4-92: SF<sub>6</sub> Emissions from Electric Power Systems and Electrical Equipment Manufacturers (Tg CO<sub>2</sub> Eq.)**

Year	Electric Power Systems	Electrical Equipment Manufacturers	Total
1990	26.3	0.3	26.6
1995	20.9	0.5	21.4
2000	14.3	0.7	15.0
2005	13.1	0.8	14.0
2006	12.4	0.8	13.2
2007	12.0	0.7	12.7
2008	11.9	1.1	13.1

**Table 4-93: SF<sub>6</sub> Emissions from Electric Power Systems and Electrical Equipment Manufacturers (Gg)**

Year	Emissions
1990	1.1
1995	0.9
2000	0.6
2005	0.6
2006	0.6
2007	0.5
2008	0.5

## Methodology

The estimates of emissions from Electric Transmission and Distribution are comprised of emissions from electric power systems and emissions from the manufacture of electrical equipment. The methodologies for estimating both sets of emissions are described below.

### 1999 through 2008 Emissions from Electric Power Systems

Emissions from electric power systems from 1999 to 2008 were estimated based on: (1) reporting from utilities participating in EPA's SF<sub>6</sub> Emission Reduction Partnership for Electric Power Systems (Partners), which began in 1999; and, (2) the relationship between emissions and utilities' transmission miles as reported in the 2001, 2004 and 2007 Utility Data Institute (UDI) Directories of Electric Power Producers and Distributors (UDI 2001, 2004, 2007). (Transmission miles are defined as the miles of lines carrying voltages above 34.5 kV.) Over the period from 1999 to 2008, Partner utilities, which for inventory purposes are defined as utilities that either currently are or previously have been part of the Partnership, represented between 42 percent and 47 percent of total U.S. transmission miles. For each year, the emissions reported by or estimated for Partner utilities were added to the emissions estimated for utilities that have never participated in the Partnership (i.e., non-Partners).<sup>35</sup>

Partner utilities estimated their emissions using a Tier 3 utility-level mass balance approach (IPCC 2006). If a Partner utility did not provide data for a particular year, emissions were interpolated between years for which data were available or extrapolated based on Partner-specific

transmission mile growth rates. In 2008, non-reporting Partners accounted for approximately 9 percent of the total emissions attributed to Partner utilities.

Emissions from non-Partners in every year since 1999 were estimated using the results of a regression analysis that showed that the emissions from reporting utilities were most strongly correlated with their transmission miles. The results of this analysis are not surprising given that, in the United States, SF<sub>6</sub> is contained primarily in transmission equipment rated at or above 34.5 kV. The equations were developed based on the 1999 SF<sub>6</sub> emissions reported by 42 Partner utilities (representing approximately 23 percent of U.S. transmission miles) and 2000 transmission mileage data obtained from the 2001 *UDI Directory of Electric Power Producers and Distributors* (UDI 2001). Two equations were developed, one for small and one for large utilities (i.e., with fewer or more than 10,000 transmission miles, respectively). The distinction between utility sizes was made because the regression analysis showed that the relationship between emissions and transmission miles differed for small and large transmission networks. The same equations were used to estimate non-Partner emissions in 1999 and every year thereafter because non-Partners were assumed not to have implemented any changes that would have resulted in reduced emissions since 1999.

The regression equations are:

Non-Partner small utilities (less than 10,000 transmission miles, in kilograms):

$$\text{Emissions (kg)} = 0.89 \times \text{Transmission Miles}$$

Non-Partner large utilities (more than 10,000 transmission miles, in kilograms):

$$\text{Emissions (kg)} = 0.58 \times \text{Transmission Miles}$$

Data on transmission miles for each non-Partner utility for the years 2000, 2003, and 2006 were obtained from the 2001, 2004, and 2007 *UDI Directories of Electric Power Producers and Distributors*, respectively (UDI 2001, 2004, 2007). The U.S. transmission system grew by over 22,000 miles between 2000 and 2003 and by over 55,000 miles between 2003 and 2006. These periodic increases are assumed to have occurred gradually, therefore transmission mileage was assumed to increase at an annual rate of 1.2 percent between 2000 and 2003 and 2.8 percent between 2003 and 2006. Transmission miles in 2008 were then

<sup>35</sup> Partners in EPA's SF<sub>6</sub> Emission Reduction Partnership reduced their emissions by approximately 61% from 1999 to 2008.

extrapolated from 2006 based on the 2.8 percent annual growth rate.

As a final step, total electric power system emissions were determined for each year by summing the Partner reported and estimated emissions (reported data was available through the EPA's SF<sub>6</sub> Emission Reduction Partnership for Electric Power Systems) and the non-Partner emissions (determined using the 1999 regression equations).

### 1990 through 1998 Emissions from Electric Power Systems

Because most participating utilities reported emissions only for 1999 through 2008, modeling was used to estimate SF<sub>6</sub> emissions from electric power systems for the years 1990 through 1998. To perform this modeling, U.S. emissions were assumed to follow the same trajectory as global emissions from this source during the 1990 to 1999 period. To estimate global emissions, the RAND survey of global SF<sub>6</sub> sales were used, together with the following equation for estimating emissions, which is derived from the mass-balance equation for chemical emissions (Volume 3, Equation 7.3) in the *IPCC Guidelines for National Greenhouse Gas Inventories* (IPCC 2006).<sup>36</sup> (Although equation 7.3 of the IPCC Guidelines appears in the discussion of substitutes for ozone-depleting substances, it is applicable to emissions from any long-lived pressurized equipment that is periodically serviced during its lifetime.)

$$\text{Emissions (kilograms SF}_6\text{)} = \text{SF}_6 \text{ purchased to refill existing equipment (kilograms)} + \text{SF}_6 \text{ nameplate capacity of retiring equipment (kilograms)}^{37}$$

Note that the above equation holds whether the gas from retiring equipment is released or recaptured; if the gas is recaptured, it is used to refill existing equipment, thereby lowering the amount of SF<sub>6</sub> purchased by utilities for this purpose.

Gas purchases by utilities and equipment manufacturers from 1961 through 2003 are available from the RAND (2004) survey. To estimate the quantity of SF<sub>6</sub> released or recovered from retiring equipment, the nameplate capacity

of retiring equipment in a given year was assumed to equal 81.2 percent of the amount of gas purchased by electrical equipment manufacturers 40 years previous (e.g., in 2000, the nameplate capacity of retiring equipment was assumed to equal 81.2 percent of the gas purchased in 1960). The remaining 18.8 percent was assumed to have been emitted at the time of manufacture. The 18.8 percent emission factor is an average of IPCC default SF<sub>6</sub> emission rates for Europe and Japan for 1995 (IPCC 2006). The 40-year lifetime for electrical equipment is also based on IPCC (2006). The results of the two components of the above equation were then summed to yield estimates of global SF<sub>6</sub> emissions from 1990 through 1999.

U.S. emissions between 1990 and 1999 are assumed to follow the same trajectory as global emissions during this period. To estimate U.S. emissions, global emissions for each year from 1990 through 1998 were divided by the estimated global emissions from 1999. The result was a time series of factors that express each year's global emissions as a multiple of 1999 global emissions. Historical U.S. emissions were estimated by multiplying the factor for each respective year by the estimated U.S. emissions of SF<sub>6</sub> from electric power systems in 1999 (estimated to be 15.0 Tg CO<sub>2</sub> Eq.).

Two factors may affect the relationship between the RAND sales trends and actual global emission trends. One is utilities' inventories of SF<sub>6</sub> in storage containers. When SF<sub>6</sub> prices rise, utilities are likely to deplete internal inventories before purchasing new SF<sub>6</sub> at the higher price, in which case SF<sub>6</sub> sales will fall more quickly than emissions. On the other hand, when SF<sub>6</sub> prices fall, utilities are likely to purchase more SF<sub>6</sub> to rebuild inventories, in which case sales will rise more quickly than emissions. This effect was accounted for by applying 3-year smoothing to utility SF<sub>6</sub> sales data. The other factor that may affect the relationship between the RAND sales trends and actual global emissions is the level of imports from and exports to Russia and China. SF<sub>6</sub> production in these countries is not included in the RAND survey and is not accounted for in any another manner by RAND. However, atmospheric studies confirm that the downward trend in estimated global emissions between 1995 and 1998 was real (see the Uncertainty discussion below).

<sup>36</sup>Ideally, sales to utilities in the U.S. between 1990 and 1999 would be used as a model. However, this information was not available. There were only two U.S. manufacturers of SF<sub>6</sub> during this time period, so it would not have been possible to conceal sensitive sales information by aggregation.

<sup>37</sup>Nameplate capacity is defined as the amount of SF<sub>6</sub> within fully charged electrical equipment.

## 1990 through 2008 Emissions from Manufacture of Electrical Equipment

The 1990 to 2008 emission estimates for original equipment manufacturers (OEMs) were derived by assuming that manufacturing emissions equal 10 percent of the quantity of SF<sub>6</sub> provided with new equipment. The quantity of SF<sub>6</sub> provided with new equipment was estimated based on statistics compiled by the National Electrical Manufacturers Association (NEMA). These statistics were provided for 1990 to 2000; the quantities of SF<sub>6</sub> provided with new equipment for 2001 to 2008 were estimated using Partner reported data and the total industry SF<sub>6</sub> nameplate capacity estimate (136.3 Tg CO<sub>2</sub> Eq. in 2008). Specifically, the ratio of new nameplate capacity to total nameplate capacity of a subset of Partners for which new nameplate capacity data was available from 1999 to 2008 was calculated. This ratio was then multiplied by the total industry nameplate capacity estimate to derive the amount of SF<sub>6</sub> provided with new equipment for the entire industry. The 10 percent emission rate is the average of the “ideal” and “realistic” manufacturing emission rates (4 percent and 17 percent, respectively) identified in a paper prepared under the auspices of the International Council on Large Electric Systems (CIGRE) in February 2002 (O’Connell et al. 2002).

## Uncertainty and Time-Series Consistency

To estimate the uncertainty associated with emissions of SF<sub>6</sub> from Electric Transmission and Distribution, uncertainties associated with three quantities were estimated: (1) emissions from Partners; (2) emissions from non-Partners; and (3) emissions from manufacturers of electrical equipment. A Monte Carlo analysis was then applied to estimate the overall uncertainty of the emissions estimate.

Total emissions from the SF<sub>6</sub> Emission Reduction Partnership include emissions from both reporting and non-reporting Partners. For reporting Partners, individual Partner-reported SF<sub>6</sub> data was assumed to have an uncertainty of 10

percent. Based on a Monte Carlo analysis, the cumulative uncertainty of all Partner reported data was estimated to be 3.6 percent. The uncertainty associated with extrapolated or interpolated emissions from non-reporting Partners was assumed to be 20 percent.

There are two sources of uncertainty associated with the regression equations used to estimate emissions in 2008 from non-Partners: (1) uncertainty in the coefficients (as defined by the regression standard error estimate), and (2) the uncertainty in total transmission miles for non-Partners. In addition, there is uncertainty associated with the assumption that the emission factor used for non-Partner utilities (which accounted for approximately 58 percent of U.S. transmission miles in 2008) will remain at levels defined by Partners who reported in 1999. However, the last source of uncertainty was not modeled.

Uncertainties were also estimated regarding (1) the quantity of SF<sub>6</sub> supplied with equipment by equipment manufacturers, which is projected from Partner provided nameplate capacity data and industry SF<sub>6</sub> nameplate capacity estimates, and (2) the manufacturers’ SF<sub>6</sub> emissions rate.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-94. Electrical Transmission and Distribution SF<sub>6</sub> emissions were estimated to be between 10.1 and 16.2 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level. This indicates a range of approximately 23 percent below and 24 percent above the emission estimate of 13.1 Tg CO<sub>2</sub> Eq.

In addition to the uncertainty quantified above, there is uncertainty associated with using global SF<sub>6</sub> sales data to estimate U.S. emission trends from 1990 through 1999. However, the trend in global emissions implied by sales of SF<sub>6</sub> appears to reflect the trend in global emissions implied by changing SF<sub>6</sub> concentrations in the atmosphere. That is, emissions based on global sales declined by 29 percent between 1995 and 1998, and emissions based on atmospheric measurements declined by 27 percent over the same period.

**Table 4-94: Tier 2 Quantitative Uncertainty Estimates for SF<sub>6</sub> Emissions from Electrical Transmission and Distribution (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2008 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Electrical Transmission and Distribution	SF <sub>6</sub>	13.1	10.1	16.2	-23%	+24%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.



## Box 4-1: Potential Emission Estimates of HFCs, PFCs, and SF<sub>6</sub>

Emissions of HFCs, PFCs and SF<sub>6</sub> from industrial processes can be estimated in two ways, either as potential emissions or as actual emissions. Emission estimates in this chapter are “actual emissions,” which are defined by the Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories (IPCC/UNEP/OECD/IEA 1997) as estimates that take into account the time lag between consumption and emissions. In contrast, “potential emissions” are defined to be equal to the amount of a chemical consumed in a country, minus the amount of a chemical recovered for destruction or export in the year of consideration. Potential emissions will generally be greater for a given year than actual emissions, since some amount of chemical consumed will be stored in products or equipment and will not be emitted to the atmosphere until a later date, if ever. Although actual emissions are considered to be the more accurate estimation approach for a single year, estimates of potential emissions are provided for informational purposes.

Separate estimates of potential emissions were not made for industrial processes that fall into the following categories:

- **Byproduct emissions.** Some emissions do not result from the consumption or use of a chemical, but are the unintended byproducts of another process. For such emissions, which include emissions of CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> from aluminum production and of HFC-23 from HCFC-22 production, the distinction between potential and actual emissions is not relevant.
- **Potential emissions that equal actual emissions.** For some sources, such as magnesium production and processing, no delay between consumption and emission is assumed and, consequently, no destruction of the chemical takes place. In this case, actual emissions equal potential emissions.

Table 4-95 presents potential emission estimates for HFCs and PFCs from the substitution of ozone depleting substances, HFCs, PFCs, and SF<sub>6</sub> from semiconductor manufacture, and SF<sub>6</sub> from magnesium production and processing and electrical transmission and distribution.<sup>38</sup> Potential emissions associated with the substitution for ozone depleting substances were calculated using the EPA’s Vintaging Model. Estimates of HFCs, PFCs, and SF<sub>6</sub> consumed by semiconductor manufacture were developed by dividing chemical-by-chemical emissions by the appropriate chemical-specific emission factors from the *IPCC Good Practice Guidance (Tier 2c)*. Estimates of CF<sub>4</sub> consumption were adjusted to account for the conversion of other chemicals into CF<sub>4</sub> during the semiconductor manufacturing process, again using the default factors from the *IPCC Good Practice Guidance*. Potential SF<sub>6</sub> emissions estimates for electrical transmission and distribution were developed using U.S. utility purchases of SF<sub>6</sub> for electrical equipment. From 1999 through 2007, estimates were obtained from reports submitted by participants in EPA’s SF<sub>6</sub> Emission Reduction Partnership for Electric Power Systems. U.S. utility purchases of SF<sub>6</sub> for electrical equipment from 1990 through 1998 were backcasted based on world sales of SF<sub>6</sub> to utilities. Purchases of SF<sub>6</sub> by utilities were added to SF<sub>6</sub> purchases by electrical equipment manufacturers to obtain total SF<sub>6</sub> purchases by the electrical equipment sector.

**Table 4-95: 2008 Potential and Actual Emissions of HFCs, PFCs, and SF<sub>6</sub> from Selected Sources (Tg CO<sub>2</sub> Eq.)**

Source	Potential	Actual
Substitution of Ozone Depleting Substances	187.3	113.0
Aluminum Production	–	2.7
HCFC-22 Production	–	13.6
Semiconductor Manufacture	3.6	5.4
Magnesium Production and Processing	2.0	2.0
Electrical Transmission and Distribution	30.0	13.1

– Not applicable.

<sup>38</sup> See Annex 5 for a discussion of sources of SF<sub>6</sub> emissions excluded from the actual emissions estimates in this report.

Several pieces of evidence indicate that U.S. SF<sub>6</sub> emissions were reduced as global emissions were reduced. First, the decreases in sales and emissions coincided with a sharp increase in the price of SF<sub>6</sub> that occurred in the mid-1990s and that affected the United States as well as the rest of the world. A representative from DILO, a major manufacturer of SF<sub>6</sub> recycling equipment, stated that most

U.S. utilities began recycling rather than venting SF<sub>6</sub> within two years of the price rise. Finally, the emissions reported by the one U.S. utility that reported 1990 through 1999 emissions to EPA showed a downward trend beginning in the mid-1990s.

Methodological recalculations were applied to the entire time series to ensure time-series consistency from 1990

through 2008. Details on the emission trends through time are described in more detail in the Methodology section, above.

## Recalculations Discussion

Sulfur hexafluoride emission estimates for the period 1990 through 2007 were updated based on (1) new data from EPA's SF<sub>6</sub> Emission Reduction Partnership; (2) revisions to interpolated and extrapolated non-reported Partner data; and (3) a revised regression equation coefficient for non-Partner small utilities (fewer than 10,000 transmission miles). The new regression coefficient resulted from a revised 1999 emission estimate from a Partner of EPA's SF<sub>6</sub> Emission Reduction Partnership. This new emission estimate changed the regression coefficient slightly from 0.888 to 0.890 kg of emissions per transmission mile. Based on the revisions listed above, SF<sub>6</sub> emissions from electric transmission and distribution decreased between 0.04 to 0.73 percent for each year from 1990 through 2005 and increased by 0.10 and 0.15 percent for 2006 and 2007, respectively.

## 4.23. Industrial Sources of Indirect Greenhouse Gases

In addition to the main greenhouse gases addressed above, many industrial processes generate emissions of indirect greenhouse gases. Total emissions of nitrogen oxides (NO<sub>x</sub>), carbon monoxide (CO), and non-CH<sub>4</sub> volatile organic compounds (NMVOCs) from non-energy industrial processes from 1990 to 2008 are reported in Table 4-96.

### Methodology

These emission estimates were obtained from preliminary data (EPA 2009), and disaggregated based on EPA (2003), which, in its final iteration, will be published on the National Emission Inventory (NEI) Air Pollutant Emission Trends web site. Emissions were calculated either for individual categories or for many categories combined, using basic activity data (e.g., the amount of raw material processed) as an indicator of emissions. National activity data were collected for individual categories from various agencies.

**Table 4-96: NO<sub>x</sub>, CO, and NMVOC Emissions from Industrial Processes (Gg)**

Gas/Source	1990	1995	2000	2005	2006	2007	2008
<b>NO<sub>x</sub></b>	<b>591</b>	<b>607</b>	<b>626</b>	<b>569</b>	<b>553</b>	<b>537</b>	<b>520</b>
Other Industrial Processes	343	362	435	437	418	398	379
Chemical & Allied Product Manufacturing	152	143	95	55	57	59	61
Metals Processing	88	89	81	60	61	62	62
Storage and Transport	3	5	14	15	15	16	16
Miscellaneous <sup>a</sup>	5	8	2	2	2	2	2
<b>CO</b>	<b>4,125</b>	<b>3,959</b>	<b>2,216</b>	<b>1,555</b>	<b>1,597</b>	<b>1,640</b>	<b>1,682</b>
Metals Processing	2,395	2,159	1,175	752	788	824	859
Other Industrial Processes	487	566	537	484	474	464	454
Chemical & Allied Product Manufacturing	1,073	1,110	327	189	206	223	240
Storage and Transport	69	23	153	97	100	103	104
Miscellaneous <sup>a</sup>	101	102	23	32	30	27	25
<b>NMVOCs</b>	<b>2,422</b>	<b>2,642</b>	<b>1,773</b>	<b>1,997</b>	<b>1,933</b>	<b>1,869</b>	<b>1,804</b>
Storage and Transport	1,352	1,499	1,067	1,308	1,266	1,224	1,182
Other Industrial Processes	364	408	412	415	398	383	367
Chemical & Allied Product Manufacturing	575	599	230	213	211	210	207
Metals Processing	111	113	61	44	44	43	42
Miscellaneous <sup>a</sup>	20	23	3	17	14	10	7

<sup>a</sup> Miscellaneous includes the following categories: catastrophic/accidental release, other combustion, health services, cooling towers, and fugitive dust. It does not include agricultural fires or slash/prescribed burning, which are accounted for under the Field Burning of Agricultural Residues source. Note: Totals may not sum due to independent rounding.

Depending on the category, these basic activity data may include data on production, fuel deliveries, raw material processed, etc.

Activity data were used in conjunction with emission factors, which together relate the quantity of emissions to the activity. Emission factors are generally available from the *EPA's Compilation of Air Pollutant Emission Factors, AP-42* (EPA 1997). The EPA currently derives the overall emission control efficiency of a source category from a variety of information sources, including published reports, the *1985 National Acid Precipitation and Assessment Program Emissions Inventory*, and other EPA databases.

## **Uncertainty and Time-Series Consistency**

Uncertainties in these estimates are partly due to the accuracy of the emission factors used and accurate estimates of activity data. A quantitative uncertainty analysis was not performed.

Methodological recalculations were applied to the entire time series to ensure time-series consistency from 1990 through 2008. Details on the emission trends through time are described in more detail in the Methodology section, above.

## 5. Solvent and Other Product Use

Greenhouse gas emissions are produced as a by-product of various solvent and other product uses. In the United States, emissions from Nitrous Oxide (N<sub>2</sub>O) Product Usage, the only source of greenhouse gas emissions from this sector, accounted for less than 0.1 percent of total U.S. anthropogenic greenhouse gas emissions on a carbon equivalent basis in 2008 (see Table 5-1). Indirect greenhouse gas emissions also result from solvent and other product use, and are presented in Table 5-5 in gigagrams (Gg).

**Table 5-1: N<sub>2</sub>O Emissions from Solvent and Other Product Use (Tg CO<sub>2</sub> Eq. and Gg)**

Gas/Source	1990	1995	2000	2005	2006	2007	2008
N <sub>2</sub> O from Product Uses							
Tg CO <sub>2</sub> Eq.	4.4	4.6	4.9	4.4	4.4	4.4	4.4
Gg	14	15	16	14	14	14	14

### 5.1 Nitrous Oxide from Product Uses (IPCC Source Category 3D)

Nitrous oxide is a clear, colorless, oxidizing liquefied gas, with a slightly sweet odor. Two companies operate a total of five N<sub>2</sub>O production facilities in the United States (Airgas 2007, FTC 2001). Nitrous oxide is primarily used in carrier gases with oxygen to administer more potent inhalation anesthetics for general anesthesia and as an anesthetic in various dental and veterinary applications. As such, it is used to treat short-term pain, for sedation in minor elective surgeries, and as an induction anesthetic. The second main use of N<sub>2</sub>O is as a propellant in pressure and aerosol products, the largest application being pressure-packaged whipped cream. Small quantities of N<sub>2</sub>O also are used in the following applications:

- Oxidizing agent and etchant used in semiconductor manufacturing;
- Oxidizing agent used, with acetylene, in atomic absorption spectrometry;
- Production of sodium azide, which is used to inflate airbags;
- Fuel oxidant in auto racing; and
- Oxidizing agent in blowtorches used by jewelers and others (Heydorn 1997).

Production of N<sub>2</sub>O in 2008 was approximately 15 Gg (Table 5-2). Nitrous oxide emissions were 4.4 Tg CO<sub>2</sub> Eq. (14 Gg) in 2008 (Table 5-3). Production of N<sub>2</sub>O stabilized during the 1990s because medical markets had found other substitutes for anesthetics, and more medical procedures were being performed on an outpatient basis using local anesthetics that do not require N<sub>2</sub>O. The use of N<sub>2</sub>O as a propellant for whipped cream has also stabilized due to the increased popularity of cream products packaged in reusable plastic tubs (Heydorn 1997).

**Table 5-2: N<sub>2</sub>O Production (Gg)**

Year	Gg
1990	16
1995	17
2000	17
2005	15
2006	15
2007	15
2008	15

**Table 5-3: N<sub>2</sub>O Emissions from N<sub>2</sub>O Product Usage (Tg CO<sub>2</sub> Eq. and Gg)**

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	4.4	14
1995	4.6	15
2000	4.9	16
2005	4.4	14
2006	4.4	14
2007	4.4	14
2008	4.4	14

## Methodology

Emissions from N<sub>2</sub>O product usage were calculated by first multiplying the total amount of N<sub>2</sub>O produced in the United States by the share of the total quantity of N<sub>2</sub>O attributed to each end use. This value was then multiplied by the associated emission rate for each end use. After the emissions were calculated for each end use, they were added together to obtain a total estimate of N<sub>2</sub>O product usage emissions. Emissions were determined using the following equation:

$$\begin{aligned} \text{N}_2\text{O Product Usage Emissions} = & \\ & \sum_i [\text{Total U.S. Production of N}_2\text{O}] \times \\ & [\text{Share of Total Quantity of N}_2\text{O Usage by Sector } i] \times \\ & [\text{Emissions Rate for Sector } i] \end{aligned}$$

where,

i = Sector.

The share of total quantity of N<sub>2</sub>O usage by end use represents the share of national N<sub>2</sub>O produced that is used by the specific subcategory (i.e., anesthesia, food processing, etc.). In 2008, the medical/dental industry used an estimated 89.5 percent of total N<sub>2</sub>O produced, followed by food processing propellants at 6.5 percent. All other categories combined used the remainder of the N<sub>2</sub>O produced. This subcategory breakdown has changed only slightly over the past decade. For instance, the small share of N<sub>2</sub>O usage in the production of sodium azide has declined significantly during the decade of the 1990s. Due to the lack of information on the specific time period of the phase-out in this market subcategory, most of the N<sub>2</sub>O usage for sodium azide production is assumed to have ceased after 1996, with the majority of its small share of the market assigned to the larger medical/dental consumption subcategory (Heydorn 1997). The N<sub>2</sub>O was allocated across the following categories: medical applications, food processing propellant, and sodium azide production (pre-1996). A usage emissions rate was then applied for each sector to estimate the amount of N<sub>2</sub>O emitted.

Only the medical/dental and food propellant subcategories were estimated to release emissions into the atmosphere, and therefore these subcategories were the only usage subcategories with emission rates. For the medical/dental subcategory, due to the poor solubility of N<sub>2</sub>O in blood and other tissues, none of the N<sub>2</sub>O is assumed to be metabolized during anesthesia and quickly leaves the body in exhaled breath. Therefore, an emission factor of 100 percent was used for this subcategory (IPCC 2006). For N<sub>2</sub>O used as a propellant in pressurized and aerosol food products, none of the N<sub>2</sub>O is reacted during the process and all of the N<sub>2</sub>O is emitted to the atmosphere, resulting in an emission factor of 100 percent for this subcategory (IPCC 2006). For the remaining subcategories, all of the N<sub>2</sub>O is consumed/ reacted during the process, and therefore the emission rate was considered to be zero percent (Tupman 2002).

The 1990 through 1992 N<sub>2</sub>O production data were obtained from SRI Consulting's *Nitrous Oxide, North America* report (Heydorn 1997). N<sub>2</sub>O production data for 1993 through 1995 were not available. Production data for 1996 was specified as a range in two data sources (Heydorn 1997, Tupman 2002). In particular, for 1996, Heydorn (1997)

estimates N<sub>2</sub>O production to range between 13.6 and 18.1 thousand metric tons. Tupman (2003) provided a narrower range (i.e., 15.9 to 18.1 thousand metric tons) for 1996 that falls within the production bounds described by Heydorn (1997). Tupman (2003) data are considered more industry-specific and current. Therefore, the midpoint of the narrower production range was used to estimate N<sub>2</sub>O emissions for years 1993 through 2001 (Tupman 2003). The 2002 and 2003 N<sub>2</sub>O production data were obtained from the Compressed Gas Association *Nitrous Oxide Fact Sheet* and Nitrous Oxide Abuse Hotline (CGA 2002, 2003). These data were also provided as a range. For example, in 2003, CGA (2003) estimates N<sub>2</sub>O production to range between 13.6 and 15.9 thousand metric tons. Due to unavailable data, production for years 2004 through 2008 were held at the 2003 value.

The 1996 share of the total quantity of N<sub>2</sub>O used by each subcategory was obtained from SRI Consulting's *Nitrous Oxide, North America report* (Heydorn 1997). The 1990 through 1995 share of total quantity of N<sub>2</sub>O used by each subcategory was kept the same as the 1996 number provided by SRI Consulting. The 1997 through 2001 share of total quantity of N<sub>2</sub>O usage by sector was obtained from communication with a N<sub>2</sub>O industry expert (Tupman 2002). The 2002 and 2003 share of total quantity of N<sub>2</sub>O usage by sector was obtained from CGA (2002, 2003). Due to unavailable data, the share of total quantity of N<sub>2</sub>O usage data for years 2004 through 2008 was assumed to equal the 2003 value. The emissions rate for the food processing propellant industry was obtained from SRI Consulting's *Nitrous Oxide, North America report* (Heydorn 1997), and confirmed by a N<sub>2</sub>O industry expert (Tupman 2002). The emissions rate for all other subcategories was obtained from communication with a N<sub>2</sub>O industry expert (Tupman 2002). The emissions rate for the medical/dental subcategory was obtained from the 2006 IPCC Guidelines.

## Uncertainty and Time-Series Consistency

The overall uncertainty associated with the 2008 N<sub>2</sub>O emission estimate from N<sub>2</sub>O product usage was calculated using the *IPCC Guidelines for National Greenhouse Gas Inventories* (2006) Tier 2 methodology. Uncertainty associated with the parameters used to estimate N<sub>2</sub>O emissions included that of production data, total market share of each end use, and the emission factors applied to each end use, respectively.

The results of this Tier 2 quantitative uncertainty analysis are summarized in Table 5-4. Nitrous oxide emissions from N<sub>2</sub>O product usage were estimated to be between 4.3 and 4.5 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 2 percent below to 2 percent above the 2007 emissions estimate of 4.4 Tg CO<sub>2</sub> Eq.

Methodological recalculations were applied to the entire time series to ensure time-series consistency from 1990 through 2008. Details on the emission trends through time are described in more detail in the Methodology section, above.

## Planned Improvements

Planned improvements include a continued evaluation of alternative production statistics for cross verification and a reassessment of subcategory usage to accurately represent the latest trends in the product usage, and investigation of production and use cycles and the potential need to incorporate a time lag between production and ultimate product use and resulting release of N<sub>2</sub>O. Additionally, planned improvements include considering imports and exports of N<sub>2</sub>O for product uses.

**Table 5-4: Tier 2 Quantitative Uncertainty Estimates for N<sub>2</sub>O Emissions From N<sub>2</sub>O Product Usage (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2008 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			Lower Bound	Upper Bound	Lower Bound (%)	Upper Bound (%)
N <sub>2</sub> O Product Usage	N <sub>2</sub> O	4.4	4.3	4.5	-2%	+2%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

## 5.2 Indirect Greenhouse Gas Emissions from Solvent Use

The use of solvents and other chemical products can result in emissions of various ozone precursors (i.e., indirect greenhouse gases).<sup>1</sup> Non-methane volatile organic compounds (NMVOCs), commonly referred to as “hydrocarbons,” are the primary gases emitted from most processes employing organic or petroleum based solvents. As some of industrial applications also employ thermal incineration as a control technology, combustion by-products, such as carbon monoxide (CO) and nitrogen oxides (NO<sub>x</sub>),

are also reported with this source category. In the United States, emissions from solvents are primarily the result of solvent evaporation, whereby the lighter hydrocarbon molecules in the solvents escape into the atmosphere. The evaporation process varies depending on different solvent uses and solvent types. The major categories of solvent uses include: degreasing, graphic arts, surface coating, other industrial uses of solvents (i.e., electronics, etc.), dry cleaning, and non-industrial uses (i.e., uses of paint thinner, etc.).

Total emissions of NO<sub>x</sub>, NMVOCs, and CO from 1990 to 2008 are reported in Table 5-5.

**Table 5-5: Emissions of NO<sub>x</sub>, CO, and NMVOC from Solvent Use (Gg)**

Activity	1990	1995	2000	2005	2006	2007	2008
<b>NO<sub>x</sub></b>	<b>1</b>	<b>3</b>	<b>3</b>	<b>3</b>	<b>4</b>	<b>4</b>	<b>4</b>
Surface Coating	1	2	3	3	4	4	4
Graphic Arts	+	1	+	+	+	+	+
Degreasing	+	+	+	+	+	+	+
Dry Cleaning	+	+	+	+	+	+	+
Other Industrial Processes <sup>a</sup>	+	+	+	+	+	+	+
Non-Industrial Processes <sup>b</sup>	+	+	+	+	+	+	+
Other	NA	+	+	+	+	+	+
<b>CO</b>	<b>5</b>	<b>5</b>	<b>45</b>	<b>2</b>	<b>2</b>	<b>2</b>	<b>2</b>
Surface Coating	+	1	45	2	2	2	2
Other Industrial Processes <sup>a</sup>	4	3	+	+	+	+	+
Dry Cleaning	+	1	+	+	+	+	+
Degreasing	+	+	+	+	+	+	+
Graphic Arts	+	+	+	+	+	+	+
Non-Industrial Processes <sup>b</sup>	+	+	+	+	+	+	+
Other	NA	NA	+	+	+	+	+
<b>NMVOCs</b>	<b>5,216</b>	<b>5,609</b>	<b>4,384</b>	<b>3,851</b>	<b>3,846</b>	<b>3,839</b>	<b>3,834</b>
Surface Coating	2,289	2,432	1,766	1,578	1,575	1,573	1,571
Non-Industrial Processes <sup>b</sup>	1,724	1,858	1,676	1,446	1,444	1,441	1,439
Degreasing	675	716	316	280	280	280	279
Dry Cleaning	195	209	265	230	230	229	229
Graphic Arts	249	307	222	194	193	193	193
Other Industrial Processes <sup>a</sup>	85	87	98	88	88	87	87
Other	+	+	40	36	36	36	36

+ Does not exceed 0.5 Gg.  
<sup>a</sup> Includes rubber and plastics manufacturing, and other miscellaneous applications.  
<sup>b</sup> Includes cutback asphalt, pesticide application adhesives, consumer solvents, and other miscellaneous applications.  
 Note: Totals may not sum due to independent rounding.

<sup>1</sup> Solvent usage in the United States also results in the emission of small amounts of hydrofluorocarbons (HFCs) and hydrofluoroethers (HFEs), which are included under Substitution of Ozone Depleting Substances in the Industrial Processes chapter.

## Methodology

Emissions were calculated by aggregating solvent use data based on information relating to solvent uses from different applications such as degreasing, graphic arts, etc. Emission factors for each consumption category were then applied to the data to estimate emissions. For example, emissions from surface coatings were mostly due to solvent evaporation as the coatings solidify. By applying the appropriate solvent-specific emission factors to the amount of solvents used for surface coatings, an estimate of emissions was obtained. Emissions of CO and NO<sub>x</sub> result primarily from thermal and catalytic incineration of solvent-laden gas streams from painting booths, printing operations, and oven exhaust.

These emission estimates were obtained from preliminary data (EPA 2009), and disaggregated based on EPA (2003), which, in its final iteration, will be published on the National Emission Inventory (NEI) Air Pollutant Emission Trends web site. Emissions were calculated either for individual categories or for many categories combined, using basic activity data (e.g., the amount of solvent purchased) as an indicator of emissions. National activity data were collected for individual applications from various agencies.

Activity data were used in conjunction with emission factors, which together relate the quantity of emissions to the activity. Emission factors are generally available from the EPA's *Compilation of Air Pollutant Emission Factors, AP-42* (EPA 1997). The EPA currently derives the overall emission control efficiency of a source category from a variety of information sources, including published reports, the *1985 National Acid Precipitation and Assessment Program Emissions Inventory*, and other EPA databases.

## Uncertainty and Time-Series Consistency

Uncertainties in these estimates are partly due to the accuracy of the emission factors used and the reliability of correlations between activity data and actual emissions.

Methodological recalculations were applied to the entire time series to ensure time-series consistency from 1990 through 2008. Details on the emission trends through time are described in more detail in the Methodology section, above.

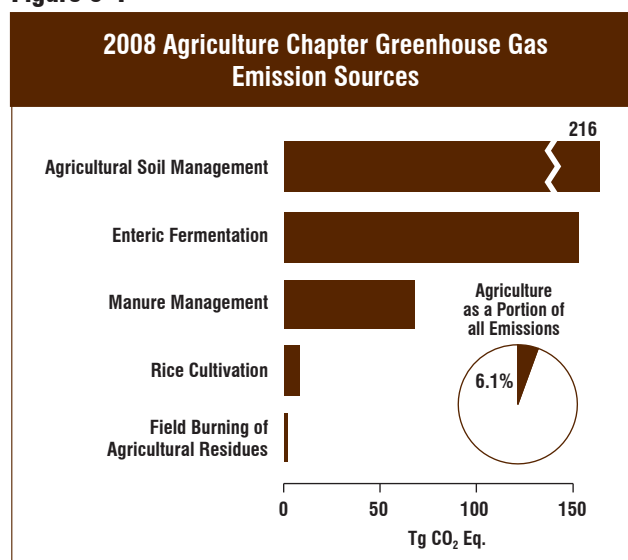


## 6. Agriculture

**A**gricultural activities contribute directly to emissions of greenhouse gases through a variety of processes. This chapter provides an assessment of non-carbon-dioxide emissions from the following source categories: enteric fermentation in domestic livestock, livestock manure management, rice cultivation, agricultural soil management, and field burning of agricultural residues (see Figure 6-1). Carbon dioxide (CO<sub>2</sub>) emissions and removals from agriculture-related land-use activities, such as conversion of grassland to cultivated land, are presented in the Land Use, Land-Use Change, and Forestry chapter. Carbon dioxide emissions from on-farm energy use are accounted for in the Energy chapter.

In 2008, the Agricultural sector was responsible for emissions of 427.5 teragrams of CO<sub>2</sub> equivalents (Tg CO<sub>2</sub> Eq.), or 6 percent of total U.S. greenhouse gas emissions. Methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O) were the primary greenhouse gases emitted by agricultural activities. Methane emissions from enteric fermentation and manure management represent about 25 percent and 8 percent of total CH<sub>4</sub> emissions from anthropogenic activities, respectively. Of all domestic animal types, beef and dairy cattle were by far the largest emitters of CH<sub>4</sub>. Rice cultivation and field burning of agricultural residues were minor sources of CH<sub>4</sub>. Agricultural soil management activities such as fertilizer application and

**Figure 6-1**



**Table 6-1: Emissions from Agriculture (Tg CO<sub>2</sub> Eq.)**

Gas/Source	1990	1995	2000	2005	2006	2007	2008
<b>CH<sub>4</sub></b>	<b>169.6</b>	<b>185.9</b>	<b>183.7</b>	<b>186.7</b>	<b>188.1</b>	<b>194.2</b>	<b>194.0</b>
Enteric Fermentation	132.4	143.7	136.8	136.7	139.0	141.2	140.8
Manure Management	29.3	33.9	38.6	42.2	42.3	45.9	45.0
Rice Cultivation	7.1	7.6	7.5	6.8	5.9	6.2	7.2
Field Burning of Agricultural Residues	0.8	0.7	0.9	0.9	0.9	1.0	1.0
<b>N<sub>2</sub>O</b>	<b>218.3</b>	<b>221.8</b>	<b>227.2</b>	<b>233.0</b>	<b>229.1</b>	<b>228.8</b>	<b>233.5</b>
Agricultural Soil Management	203.5	205.9	210.1	215.8	211.2	211.0	215.9
Manure Management	14.4	15.5	16.7	16.6	17.3	17.3	17.1
Field Burning of Agricultural Residues	0.4	0.4	0.5	0.5	0.5	0.5	0.5
<b>Total</b>	<b>387.8</b>	<b>407.7</b>	<b>410.9</b>	<b>419.7</b>	<b>417.2</b>	<b>423.0</b>	<b>427.5</b>

Note: Totals may not sum due to independent rounding.

**Table 6-2: Emissions from Agriculture (Gg)**

Gas/Source	1990	1995	2000	2005	2006	2007	2008
<b>CH<sub>4</sub></b>	<b>8,074</b>	<b>8,854</b>	<b>8,749</b>	<b>8,890</b>	<b>8,959</b>	<b>9,246</b>	<b>9,239</b>
Enteric Fermentation	6,303	6,844	6,513	6,509	6,619	6,723	6,707
Manure Management	1,395	1,612	1,837	2,011	2,015	2,183	2,144
Rice Cultivation	339	363	357	326	282	295	343
Field Burning of Agricultural Residues	36	35	42	44	43	46	46
<b>N<sub>2</sub>O</b>	<b>704</b>	<b>715</b>	<b>733</b>	<b>752</b>	<b>739</b>	<b>738</b>	<b>753</b>
Agricultural Soil Management	656	664	678	696	681	681	696
Manure Management	47	50	54	54	56	56	55
Field Burning of Agricultural Residues	1	1	2	2	2	2	2

Note: Totals may not sum due to independent rounding.

other cropping practices were the largest source of U.S. N<sub>2</sub>O emissions, accounting for 68 percent. Manure management and field burning of agricultural residues were also small sources of N<sub>2</sub>O emissions.

Table 6-1 and Table 6-2 present emission estimates for the Agriculture sector. Between 1990 and 2008, CH<sub>4</sub> emissions from agricultural activities increased by 14.4 percent, while N<sub>2</sub>O emissions fluctuated from year to year, but overall increased by 7.0 percent.

## 6.1. Enteric Fermentation (IPCC Source Category 4A)

Methane is produced as part of normal digestive processes in animals. During digestion, microbes resident in an animal's digestive system ferment food consumed by the animal. This microbial fermentation process, referred to as enteric fermentation, produces CH<sub>4</sub> as a byproduct, which can be exhaled or eructated by the animal. The amount of CH<sub>4</sub> produced and emitted by an individual animal depends primarily upon the animal's digestive system, and the amount and type of feed it consumes.

Ruminant animals (e.g., cattle, buffalo, sheep, goats, and camels) are the major emitters of CH<sub>4</sub> because of their unique digestive system. Ruminants possess a rumen, or large "fore-stomach," in which microbial fermentation breaks down the feed they consume into products that can be absorbed and metabolized. The microbial fermentation that occurs in the rumen enables them to digest coarse plant material that non-ruminant animals can not. Ruminant animals, consequently, have the highest CH<sub>4</sub> emissions among all animal types.

Non-ruminant animals (e.g., swine, horses, and mules) also produce CH<sub>4</sub> emissions through enteric fermentation, although this microbial fermentation occurs in the large intestine. These non-ruminants emit significantly less CH<sub>4</sub> on a per-animal basis than ruminants because the capacity of the large intestine to produce CH<sub>4</sub> is lower.

In addition to the type of digestive system, an animal's feed quality and feed intake also affects CH<sub>4</sub> emissions. In general, lower feed quality and/or higher feed intake leads to higher CH<sub>4</sub> emissions. Feed intake is positively correlated to animal size, growth rate, and production (e.g., milk production, wool growth, pregnancy, or work). Therefore, feed intake varies among animal types as well as among different management practices for individual animal types (e.g., animals in feedlots or grazing on pasture).

Methane emission estimates from enteric fermentation are provided in Table 6-3 and Table 6-4. Total livestock CH<sub>4</sub> emissions in 2008 were 140.8 Tg CO<sub>2</sub> Eq. (6,707 Gg). Beef cattle remain the largest contributor of CH<sub>4</sub> emissions from enteric fermentation, accounting for 72 percent in 2008. Emissions from dairy cattle in 2008 accounted for 23 percent, and the remaining emissions were from horses, sheep, swine, and goats.

From 1990 to 2008, emissions from enteric fermentation have increased by 6.4 percent. Generally, emissions decreased from 1996 to 2003, though with a slight increase in 2002. This trend was mainly due to decreasing populations of both beef and dairy cattle and increased digestibility of feed for feedlot cattle. Emissions increased from 2004 through 2007, as both dairy and beef populations have undergone increases and the literature for dairy cow diets indicated a trend toward

**Table 6-3: CH<sub>4</sub> Emissions from Enteric Fermentation (Tg CO<sub>2</sub> Eq.)**

Livestock Type	1990	1995	2000	2005	2006	2007	2008
Beef Cattle	94.5	107.7	100.6	99.3	100.9	101.6	100.8
Dairy Cattle	32.0	30.5	30.9	30.6	31.3	32.7	33.1
Horses	1.9	1.9	2.0	3.5	3.6	3.6	3.6
Sheep	1.9	1.5	1.2	1.0	1.0	1.0	1.0
Swine	1.7	1.9	1.9	1.9	1.9	2.1	2.1
Goats	0.3	0.2	0.3	0.3	0.3	0.3	0.3
<b>Total</b>	<b>132.4</b>	<b>143.7</b>	<b>136.8</b>	<b>136.7</b>	<b>139.0</b>	<b>141.2</b>	<b>140.8</b>

Note: Totals may not sum due to independent rounding.

**Table 6-4: CH<sub>4</sub> Emissions from Enteric Fermentation (Gg)**

Livestock Type	1990	1995	2000	2005	2006	2007	2008
Beef Cattle	4,502	5,128	4,790	4,731	4,803	4,837	4,799
Dairy Cattle	1,526	1,452	1,471	1,459	1,490	1,555	1,576
Horses	91	92	94	166	171	171	171
Sheep	91	72	56	49	50	49	48
Swine	81	88	88	92	93	98	101
Goats	13	12	12	13	13	13	13
<b>Total</b>	<b>6,303</b>	<b>6,844</b>	<b>6,513</b>	<b>6,509</b>	<b>6,619</b>	<b>6,723</b>	<b>6,707</b>

Note: Totals may not sum due to independent rounding.

a decrease in feed digestibility for those years. Emissions decreased again in 2008 as beef cattle populations decreased again. During the timeframe of this analysis, populations of sheep have decreased 48 percent since 1990 while horse populations have increased over 85 percent, mostly since 1999. Goat and swine populations have increased 1 percent and 25 percent, respectively, during this timeframe.

## Methodology

Livestock emission estimate methodologies fall into two categories: cattle and other domesticated animals. Cattle, due to their large population, large size, and particular digestive characteristics, account for the majority of CH<sub>4</sub> emissions from livestock in the United States. A more detailed methodology (i.e., IPCC Tier 2) was therefore applied to estimate emissions for all cattle except for bulls. Emission estimates for other domesticated animals (horses, sheep, swine, goats, and bulls) were handled using a less detailed approach (i.e., IPCC Tier 1).

While the large diversity of animal management practices cannot be precisely characterized and evaluated, significant scientific literature exists that provides the

necessary data to estimate cattle emissions using the IPCC Tier 2 approach. The Cattle Enteric Fermentation Model (CEFM), developed by EPA and used to estimate cattle CH<sub>4</sub> emissions from enteric fermentation, incorporates this information and other analyses of livestock population, feeding practices, and production characteristics.

National cattle population statistics were disaggregated into the following cattle sub-populations:

- Dairy Cattle
  - Calves
  - Heifer Replacements
  - Cows
- Beef Cattle
  - Calves
  - Heifer Replacements
  - Heifer and Steer Stockers
  - Animals in Feedlots (Heifers and Steers)
  - Cows
  - Bulls

Calf birth rates, end of year population statistics, detailed feedlot placement information, and slaughter weight data were used to create a transition matrix that models cohorts of individual animal types and their specific emission profiles. The key variables tracked for each of the cattle population categories are described in Annex 3.9. These variables include performance factors such as pregnancy and lactation as well as average weights and weight gain. Annual cattle population data were obtained from the U.S. Department of Agriculture's (USDA) National Agricultural Statistics Service Quick Stats database (USDA 2009).

Diet characteristics were estimated by region for U.S. dairy, beef, and feedlot cattle. These estimates were used to calculate Digestible Energy (DE) values (expressed as the percent of gross energy intake digested by the animal) and CH<sub>4</sub> conversion rates (Y<sub>m</sub>) (expressed as the fraction of gross energy converted to CH<sub>4</sub>) for each population category. The IPCC recommends Y<sub>m</sub> values of 3.0+/-1.0 percent for feedlot cattle and 6.5+/-1.0 percent for other well-fed cattle consuming temperate-climate feed types (IPCC 2006). Given the availability of detailed diet information for different regions and animal types in the United States, DE and Y<sub>m</sub> values unique to the United States were developed, rather than using the recommended IPCC values. The diet characterizations and estimation of DE and Y<sub>m</sub> values were based on information from state agricultural extension specialists, a review of published forage quality studies and scientific literature, expert opinion, and modeling of animal physiology. The diet characteristics for dairy cattle were based on Donovan (1999) and an extensive review of nearly 20 years of literature. Dairy replacement heifer diet assumptions were based on the observed relationship in the literature between dairy cow and dairy heifer diet characteristics. The diet assumptions for beef cattle were derived from NRC (2000). For feedlot animals, the DE and Y<sub>m</sub> values used for 1990 were recommended by Johnson (1999). Values for DE and Y<sub>m</sub> for 1991 through 1999 were linearly extrapolated based on the 1990 and 2000 data. DE and Y<sub>m</sub> values for 2000 onwards were based on survey data in Galyean and Gleghorn (2001) and Vasconcelos and Galyean (2007). For grazing beef cattle, DE values were based on

diet information in NRC (2000) and Y<sub>m</sub> values were based on Johnson (2002). Weight and weight gains for cattle were estimated from Enns (2008), Patton et al. (2008), Lippke et al. (2000), Pinchack et al., (2004), Platter et al. (2003), Skogerboe et al. (2000), and expert opinion. See Annex 3.9 for more details on the method used to characterize cattle diets and weights in the United States.

To estimate CH<sub>4</sub> emissions from all cattle types except bulls and calves younger than 7 months,<sup>1</sup> the population was divided into state, age, sub-type (i.e., dairy cows and replacements, beef cows and replacements, heifer and steer stockers, and heifer and steer in feedlots), and production (i.e., pregnant, lactating) groupings to more fully capture differences in CH<sub>4</sub> emissions from these animal types. The transition matrix was used to simulate the age and weight structure of each sub-type on a monthly basis, to more accurately reflect the fluctuations that occur throughout the year. Cattle diet characteristics were then used in conjunction with Tier 2 equations from IPCC (2006) to produce CH<sub>4</sub> emission factors for the following cattle types: dairy cows, beef cows, dairy replacements, beef replacements, steer stockers, heifer stockers, steer feedlot animals, and heifer feedlot animals. To estimate emissions from cattle, population data from the transition matrix were multiplied by the calculated emission factor for each cattle type. More details are provided in Annex 3.9.

Emission estimates for other animal types were based on average emission factors representative of entire populations of each animal type. Methane emissions from these animals accounted for a minor portion of total CH<sub>4</sub> emissions from livestock in the United States from 1990 through 2008. Also, the variability in emission factors for each of these other animal types (e.g., variability by age, production system, and feeding practice within each animal type) is less than that for cattle. Annual livestock population data for these other livestock types, except horses and goats, as well as feedlot placement information were obtained for all years from

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<sup>1</sup> Emissions from bulls are estimated using a Tier 1 approach because it is assumed there is minimal variation in population and diets; because calves younger than 7 months consume mainly milk and the IPCC recommends the use of methane conversion factor of zero for all juveniles consuming only milk, this results in no methane emissions from this subcategory of cattle.

the U.S. Department of Agriculture’s National Agricultural Statistics Service (USDA 2009). Horse population data were obtained from the FAOSTAT database (FAO 2009), because USDA does not estimate U.S. horse populations annually. Goat population data were obtained for 1992, 1997, and 2002 (USDA 2009); these data were interpolated and extrapolated to derive estimates for the other years. Methane emissions from sheep, goats, swine, and horses were estimated by using emission factors utilized in Crutzen et al. (1986, cited in IPCC 2006). These emission factors are representative of typical animal sizes, feed intakes, and feed characteristics in developed countries. The methodology is the same as that recommended by IPCC (2006).

See Annex 3.9 for more detailed information on the methodology and data used to calculate CH<sub>4</sub> emissions from enteric fermentation.

## Uncertainty and Time-Series Consistency

Quantitative uncertainty analysis for this source category was performed through the IPCC-recommended Tier 2 uncertainty estimation methodology, Monte Carlo Stochastic Simulation technique as described in ICF (2003). These uncertainty estimates were developed for the 1990 through 2001 Inventory report. No significant changes occurred in the method of data collection, data estimation methodology, or other factors that influence the uncertainty ranges around the 2008 activity data and emission factor input variables used in the current submission. Consequently, these uncertainty estimates were directly applied to the 2008 emission estimates.

A total of 185 primary input variables (177 for cattle and 8 for non-cattle) were identified as key input variables for the uncertainty analysis. A normal distribution was assumed for almost all activity- and emission factor-related input variables. Triangular distributions were assigned to three

input variables (specifically, cow-birth ratios for the three most recent years included in the 2001 model run) to capture the fact that these variables can not be negative. For some key input variables, the uncertainty ranges around their estimates (used for inventory estimation) were collected from published documents and other public sources; others were based on expert opinion and our best estimates. In addition, both endogenous and exogenous correlations between selected primary input variables were modeled. The exogenous correlation coefficients between the probability distributions of selected activity-related variables were developed through expert judgment.

The uncertainty ranges associated with the activity data-related input variables were plus or minus 10 percent or lower. However, for many emission factor-related input variables, the lower- and/or the upper-bound uncertainty estimates were over 20 percent. The results of the quantitative uncertainty analysis (Table 6-5) indicate that, on average, the emission estimate range of this source is approximately 125.3 to 166.2 Tg CO<sub>2</sub> Eq., calculated as 11 percent below and 18 percent above the actual 2008 emission estimate of 140.8 Tg CO<sub>2</sub> Eq. Among the individual cattle sub-source categories, beef cattle account for the largest amount of CH<sub>4</sub> emissions as well as the largest degree of uncertainty in the inventory emission estimates. Among non-cattle, horses account for the largest degree of uncertainty in the inventory emission estimates because there is a higher degree of uncertainty among the FAO population estimates used for horses than for the USDA population estimates used for swine, goats, and sheep.

Methodological recalculations were applied to the entire time series to ensure time series consistency from 1990 through 2008. Details on the emission trends through time are described in more detail in the Methodology section.

**Table 6-5: Tier 2 Quantitative Uncertainty Estimates for CH<sub>4</sub> Emissions from Enteric Fermentation (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2008 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a, b</sup>			
			(Tg CO <sub>2</sub> Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Enteric Fermentation	CH <sub>4</sub>	140.8	125.3	166.2	-11%	+18%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

<sup>b</sup> Note that the relative uncertainty range was estimated with respect to the 2001 emission estimates submitted in 2003 and applied to the 2008 estimates.

## QA/QC and Verification

In order to ensure the quality of the emission estimates from enteric fermentation, the IPCC Tier 1 and Tier 2 Quality Assurance/Quality Control (QA/QC) procedures were implemented consistent with the U.S. QA/QC plan. Tier 2 QA procedures included independent peer review of emission estimates. As described below, particular emphasis this year was placed on revising CEFM diet assumptions and additional modifications of the stocker population estimates in the transition matrix, which required further QA/QC to ensure consistency of estimates generated by the updated model.

## Recalculations Discussion

There were several modifications to the estimates relative to the previous Inventory that had an effect on emission estimates, including the following:

- Four models to predict CH<sub>4</sub> production from cattle (two mechanistic, and two empirical) were evaluated to determine appropriate Y<sub>m</sub> and DE values for use in the analysis. The results are described in Kebreab et al. (2008). In addition to the model evaluation, separate research was conducted to update the assumptions used for cattle diet components for feedlot and dairy cattle. An extensive literature review was performed on dairy diets and nearly 250 diets were analyzed to derive the current DE and Y<sub>m</sub> estimates for dairy. In addition, feedlot diets were updated based on current survey data from Galyean and Gleghorn (2001) and Vasconcelos and Galyean (2007).
- Further modifications were made to the feedlot placement methodology for reconciling the USDA placement data and the estimated populations of stockers available for placement. In cases where there are discrepancies between the USDA estimated placements by weight class and the calculated animals available by weight, the model pulls available stockers from one higher weight category if available. If there are still not enough animals to fulfill requirements, the model pulls animals from the next lower category. In the current time series, this method was able to ensure that total placement data matched USDA estimates, and no shortfalls have occurred. In the previous Inventory, additional animals were only added to the 700-800 lbs category.
- Bull populations are no longer averaged between January and July. It was determined that there is a greater degree of uncertainty in the July estimates; therefore they are no longer used, and bull populations are based solely on January estimates.
- The USDA published revised population estimates that affected historical emissions estimated for swine and sheep in 2007. The FAO published revised population estimates for horses for 2006 and 2007. In addition, some historical population estimates for certain beef and dairy populations were also updated as a result of changes in USDA inputs.

As a result of these changes, dairy cattle emissions decreased an average of 8.7 Gg (0.5 percent) per year and beef cattle emissions increased an average of 49 Gg (1.0 percent) per year over the entire time series relative to the previous Inventory. Historical emission estimates for 2007 increased by 0.6 percent for swine and decreased by 0.7 percent for sheep as a result of the USDA revisions described above. Horse emission estimates for 2006 and 2007 increased by approximately 3 percent from the revisions in the FAO data.

## Planned Improvements

Continued research and regular updates are necessary to maintain a current model of cattle diet characterization, feedlot placement data, rates of weight gain and calving, among other data inputs. Ongoing revisions could include some of the following options:

- Reviewing and updating the diet assumptions for foraging beef cattle;
- Estimating bull emissions using the IPCC Tier 2 approach;
- Updating input variables that are from older data sources, such as beef births by month and beef cow lactation rates;
- The possible breakout of other animal types (i.e., sheep, swine, goats, horses) from national estimates to state-level estimates; and
- Including bison in the estimates for other domesticated animals.

In addition, recent changes that have been implemented to the CEFM warrant an assessment of the current uncertainty analysis, therefore a revision of the quantitative uncertainty

surrounding emission estimates from this source category will be initiated.

## 6.2. Manure Management (IPCC Source Category 4B)

The management of livestock manure can produce anthropogenic CH<sub>4</sub> and N<sub>2</sub>O emissions. Methane is produced by the anaerobic decomposition of manure. Direct N<sub>2</sub>O emissions are produced as part of the N cycle through the nitrification and denitrification of the organic N in livestock manure and urine.<sup>2</sup> Indirect N<sub>2</sub>O emissions are produced as result of the volatilization of N as NH<sub>3</sub> and NO<sub>x</sub> and runoff and leaching of N during treatment, storage and transportation.

When livestock or poultry manure are stored or treated in systems that promote anaerobic conditions (e.g., as a liquid/slurry in lagoons, ponds, tanks, or pits), the decomposition of materials in the manure tends to produce CH<sub>4</sub>. When manure is handled as a solid (e.g., in stacks or drylots) or deposited on pasture, range, or paddock lands, it tends to decompose aerobically and produce little or no CH<sub>4</sub>. Ambient temperature, moisture, and manure storage or residency time affect the amount of CH<sub>4</sub> produced because they influence the growth of the bacteria responsible for CH<sub>4</sub> formation. For non-liquid-based manure systems, moist conditions (which are a function of rainfall and humidity) can promote CH<sub>4</sub> production. Manure composition, which varies by animal diet, growth rate, and type, including the animal's digestive system, also affects the amount of CH<sub>4</sub> produced. In general, the greater the energy content of the feed, the greater the potential for CH<sub>4</sub> emissions. However, some higher energy feeds also are more digestible than lower quality forages, which can result in less overall waste excreted from the animal.

The production of direct N<sub>2</sub>O emissions from livestock manure depends on the composition of the manure and urine, the type of bacteria involved in the process, and the amount of oxygen and liquid in the manure system. For direct N<sub>2</sub>O emissions to occur, the manure must first be handled

aerobically where ammonia (NH<sub>3</sub>) or organic N is converted to nitrates and nitrites (nitrification), and then handled anaerobically where the nitrates and nitrites are reduced to nitrogen gas (N<sub>2</sub>), with intermediate production of N<sub>2</sub>O and nitric oxide (NO) (denitrification) (Groffman et al. 2000). These emissions are most likely to occur in dry manure handling systems that have aerobic conditions, but that also contain pockets of anaerobic conditions due to saturation. A very small portion of the total N excreted is expected to convert to N<sub>2</sub>O in the waste management system (WMS). Indirect N<sub>2</sub>O emissions are produced when N is lost from the system through volatilization (as NH<sub>3</sub> or NO<sub>x</sub>) or through runoff and leaching. The vast majority of volatilization losses from these operations are NH<sub>3</sub>. Although there are also some small losses of NO<sub>x</sub>, there are no quantified estimates available for use, so losses due to volatilization are only based on NH<sub>3</sub> loss factors. Runoff losses would be expected from operations that house animals or store manure in a manner that is exposed to weather. Runoff losses are also specific to the type of animal housed on the operation due to differences in manure characteristics. Little information is known about leaching from manure management systems as most research focuses on leaching from land application systems. Since leaching losses are expected to be minimal, leaching losses are coupled with runoff losses and the runoff/leaching estimate does not include any leaching losses.

Estimates of CH<sub>4</sub> emissions in 2008 were 45 Tg CO<sub>2</sub> Eq. (2,144 Gg), 54 percent higher than in 1990. Emissions increased on average by 0.9 Tg CO<sub>2</sub> Eq. (2.5 percent) annually over this period. The majority of this increase was from swine and dairy cow manure, where emissions increased 50 and 91 percent, respectively. Although the majority of manure in the United States is handled as a solid, producing little CH<sub>4</sub>, the general trend in manure management, particularly for dairy and swine (which are both shifting towards larger facilities), is one of increasing use of liquid systems. Also, new regulations limiting the application of manure nutrients have shifted manure management practices at smaller dairies from daily spread to manure managed and stored on site. Although national dairy animal populations have been generally decreasing, some states have seen increases in their dairy populations as the industry becomes more concentrated in certain areas of the country. These areas of concentration, such as California, New Mexico, and Idaho, tend to utilize more liquid-based systems to manage

<sup>2</sup> Direct and indirect N<sub>2</sub>O emissions from manure and urine spread onto fields either directly as daily spread or after it is removed from manure management systems (e.g., lagoon, pit, etc.) and from livestock manure and urine deposited on pasture, range, or paddock lands are accounted for and discussed in the Agricultural Soil Management source category within the Agriculture sector.

**Table 6-6: CH<sub>4</sub> and N<sub>2</sub>O Emissions from Manure Management (Tg CO<sub>2</sub> Eq.)**

Gas/Animal Type	1990	1995	2000	2005	2006	2007	2008
<b>CH<sub>4</sub><sup>a</sup></b>	<b>29.3</b>	<b>33.9</b>	<b>38.6</b>	<b>42.2</b>	<b>42.3</b>	<b>45.9</b>	<b>45.0</b>
Dairy Cattle	10.2	11.8	15.3	17.3	17.5	19.5	19.4
Beef Cattle	2.6	2.8	2.6	2.5	2.6	2.6	2.5
Swine	13.1	16.0	17.5	18.9	18.5	20.1	19.6
Sheep	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Goats	+	+	+	+	+	+	+
Poultry	2.8	2.7	2.6	2.7	2.7	2.7	2.6
Horses	0.5	0.4	0.5	0.8	0.9	0.9	0.8
<b>N<sub>2</sub>O<sup>b</sup></b>	<b>14.4</b>	<b>15.5</b>	<b>16.7</b>	<b>16.6</b>	<b>17.3</b>	<b>17.3</b>	<b>17.1</b>
Dairy Cattle	5.0	5.2	5.3	5.4	5.6	5.6	5.5
Beef Cattle	6.3	6.8	7.7	7.2	7.7	7.6	7.4
Swine	1.2	1.4	1.4	1.5	1.5	1.6	1.7
Sheep	0.1	0.2	0.3	0.3	0.4	0.3	0.3
Goats	+	+	+	+	+	+	+
Poultry	1.5	1.6	1.7	1.7	1.8	1.8	1.8
Horses	0.2	0.2	0.2	0.4	0.4	0.4	0.4
<b>Total</b>	<b>43.7</b>	<b>49.4</b>	<b>55.3</b>	<b>58.8</b>	<b>59.6</b>	<b>63.2</b>	<b>62.1</b>

+ Less than 0.05 Tg CO<sub>2</sub> Eq.  
<sup>a</sup> Includes CH<sub>4</sub> emission reductions due to anaerobic digestion.  
<sup>b</sup> Includes both direct and indirect N<sub>2</sub>O emissions.  
Note: Totals may not sum due to independent rounding.

**Table 6-7: CH<sub>4</sub> and N<sub>2</sub>O Emissions from Manure Management (Gg)**

Gas/Animal Type	1990	1995	2000	2005	2006	2007	2008
<b>CH<sub>4</sub><sup>a</sup></b>	<b>1,395</b>	<b>1,612</b>	<b>1,837</b>	<b>2,011</b>	<b>2,015</b>	<b>2,183</b>	<b>2,144</b>
Dairy Cattle	485	561	727	822	835	929	925
Beef Cattle	126	133	125	120	125	122	117
Swine	624	764	832	899	882	957	932
Sheep	7	5	4	4	4	4	4
Goats	1	1	1	1	1	1	1
Poultry	131	128	126	127	128	131	125
Horses	22	21	22	39	41	41	39
<b>N<sub>2</sub>O<sup>b</sup></b>	<b>47</b>	<b>50</b>	<b>54</b>	<b>54</b>	<b>56</b>	<b>56</b>	<b>55</b>
Dairy Cattle	16	17	17	17	18	18	18
Beef Cattle	20	22	25	23	25	24	24
Swine	4	5	5	5	5	5	5
Sheep	+	1	1	1	1	1	1
Goats	+	+	+	+	+	+	+
Poultry	5	5	5	6	6	6	6
Horses	1	1	1	1	1	1	1

+ Less than 0.5 Gg.  
<sup>a</sup> Includes CH<sub>4</sub> emission reductions due to anaerobic digestion.  
<sup>b</sup> Includes both direct and indirect N<sub>2</sub>O emissions.  
Note: Totals may not sum due to independent rounding.

(flush or scrape) and store manure. Thus the shift toward larger facilities is translated into an increasing use of liquid manure management systems, which have higher potential CH<sub>4</sub> emissions than dry systems. This shift was accounted

for by incorporating state and WMS-specific CH<sub>4</sub> conversion factor (MCF) values in combination with the 1992, 1997, and 2002 farm-size distribution data reported in the *Census of Agriculture* (USDA 2005). Methane emissions from horses



have nearly doubled since 1990 (an 82 percent increase from 1990 to 2008); however, this is due to population increases rather than changes in manure management practices. Overall, horses contribute only 2 percent of CH<sub>4</sub> emissions from animal manure management. From 2007 to 2008, there was a 2 percent decrease in total CH<sub>4</sub> emissions, due to minor shifts in the animal populations and the resultant effects on manure management system allocations.

In 2008, total N<sub>2</sub>O emissions were estimated to be 17.11 Tg CO<sub>2</sub> Eq. (55 Gg); in 1990, emissions were 14.43 Tg CO<sub>2</sub> Eq. (47 Gg). These values include both direct and indirect N<sub>2</sub>O emissions from manure management. N<sub>2</sub>O emissions have remained fairly steady since 1990. Small changes in N<sub>2</sub>O emissions from individual animal groups exhibit the same trends as the animal group populations, with the overall net effect that N<sub>2</sub>O emissions showed a 19 percent increase from 1990 to 2008 and a 1 percent decrease from 2007 through 2008.

Table 6-6 and Table 6-7 provide estimates of CH<sub>4</sub> and N<sub>2</sub>O emissions from manure management by animal category.

## Methodology

The methodologies presented in IPCC (2006) form the basis of the CH<sub>4</sub> and N<sub>2</sub>O emission estimates for each animal type. This section presents a summary of the methodologies used to estimate CH<sub>4</sub> and N<sub>2</sub>O emissions from manure management for this Inventory. See Annex 3.10 for more detailed information on the methodology and data used to calculate CH<sub>4</sub> and N<sub>2</sub>O emissions from manure management.

### Methane Calculation Methods

The following inputs were used in the calculation of CH<sub>4</sub> emissions:

- Animal population data (by animal type and state);
- Typical animal mass (TAM) data (by animal type);
- Portion of manure managed in each waste management system (WMS), by state and animal type;
- Volatile solids (VS) production rate (by animal type and state or United States);
- Methane producing potential (B<sub>0</sub>) of the volatile solids (by animal type); and
- Methane conversion factors (MCF), the extent to which the CH<sub>4</sub> producing potential is realized for each type

of WMS (by state and manure management system, including the impacts of any biogas collection efforts).

Methane emissions were estimated by first determining activity data, including animal population, TAM, WMS usage, and waste characteristics. The activity data sources are described below:

- Annual animal population data for 1990 through 2008 for all livestock types, except horses and goats were obtained from the USDA National Agricultural Statistics Service (NASS). For cattle, the USDA populations were utilized in conjunction with birth rates, detailed feedlot placement information, and slaughter weight data to create the transition matrix in the Cattle Enteric Fermentation Model (CEFM) that models cohorts of individual animal types and their specific emission profiles. The key variables tracked for each of the cattle population categories are described in section 6.1, Enteric Fermentation and in more detail in Annex 3.9, Methodology for Estimating CH<sub>4</sub> Emissions from Enteric Fermentation. Horse population data were obtained from the Food and Agriculture Organization (FAO) FAOSTAT database (FAO 2009). Goat population data for 1992, 1997, and 2002 were obtained from the *Census of Agriculture* (USDA 2005).
- The TAM is an annual average weight which was obtained for each animal type from information in USDA's *Agricultural Waste Management Field Handbook* (USDA 1996a), the American Society of Agricultural Engineers, Standard D384.1 (ASAE 1999) and others (EPA 1992 and Safley 2000).
- WMS usage was estimated for swine and dairy cattle for different farm size categories using data from USDA (USDA 1996b, 1998b, 2000a) and EPA (ERG 2000a, EPA 2002a, 2002b). For beef cattle and poultry, manure management system usage data were not tied to farm size but were based on other data sources (ERG 2000a, USDA 2000b, UEP 1999). For other animal types, manure management system usage was based on previous estimates (EPA 1992).
- VS production rates for all cattle except for bulls and calves were calculated for each state and animal type in the Cattle Enteric Fermentation Model (CEFM), which is described in section 6.1, Enteric Fermentation and in more detail in Annex 3.9, Methodology for

Estimating CH<sub>4</sub> Emissions from Enteric Fermentation. VS production rates for all other animals were determined using data from USDA's *Agricultural Waste Management Field Handbook* (USDA 1996a) and data from the American Society of Agricultural Engineers, Standard D384.1 (ASAE 1999).

- The maximum CH<sub>4</sub> producing capacity of the VS (B<sub>0</sub>) was determined for each animal type based on literature values (Morris 1976, Bryant et al, 1976, Hashimoto 1981, Hashimoto 1984, EPA 1992, Hill 1982, and Hill 1984).
- MCFs for dry systems were set equal to default IPCC factors based on state climate for each year (IPCC 2006). MCFs for liquid/slurry, anaerobic lagoon, and deep pit systems were calculated based on the forecast performance of biological systems relative to temperature changes as predicted in the van't Hoff-Arrhenius equation which is consistent with IPCC 2006 Tier 2 methodology.
- Anaerobic digestion system data were obtained from the EPA AgSTAR Program, including information presented in the *AgSTAR Digest* (EPA 2000, 2003b, 2006). AD emissions were calculated based on estimated methane production and collection and destruction efficiency assumptions (ERG 2008).

To estimate CH<sub>4</sub> emissions, EPA first calculated the annual amount of VS (kg per year) from manure that is excreted in each WMS for each animal type, state, and year. This calculation multiplied the animal population (head) by the VS excretion rate (kg VS per 1,000 kg animal mass per day), the TAM (kg animal mass per head) divided by 1,000, the WMS distribution (percent), and the number of days per year.

The estimated amount of VS managed in each WMS was used to estimate the CH<sub>4</sub> emissions (kg CH<sub>4</sub> per year) from each WMS. The amount of VS (kg per year) were multiplied by the maximum CH<sub>4</sub> producing capacity of the VS (B<sub>0</sub>) (m<sup>3</sup> CH<sub>4</sub> per kg VS), the MCF for that WMS (percent), and the density of methane (kg CH<sub>4</sub> per m<sup>3</sup> CH<sub>4</sub>). The CH<sub>4</sub> emissions for each WMS, state, and animal type were summed to determine the total U.S. CH<sub>4</sub> emissions.

The following inputs were used in the calculation of direct and indirect N<sub>2</sub>O emissions:

- Animal population data (by animal type and state);
- TAM data (by animal type);
- Portion of manure managed in each WMS (by state and animal type);
- Total Kjeldahl N excretion rate (N<sub>ex</sub>);
- Direct N<sub>2</sub>O emission factor (EF<sub>WMS</sub>);
- Indirect N<sub>2</sub>O emission factor for volatilization (EF<sub>volatilization</sub>);
- Indirect N<sub>2</sub>O emission factor for runoff and leaching (EF<sub>runoff/leach</sub>);
- Fraction of N loss from volatilization of ammonia and NO<sub>x</sub> (Frac<sub>gas</sub>); and
- Fraction of N loss from runoff and leaching (Frac<sub>runoff/leach</sub>).

Nitrous oxide emissions were estimated by first determining activity data, including animal population, TAM, WMS usage, and waste characteristics. The activity data sources (except for population, TAM, and WMS, which were described above) are described below:

- Nex rates for all cattle except for bull and calves were calculated for each state and animal type in the Cattle Enteric Fermentation Model (CEFM), which is described in section 6.1, Enteric Fermentation and in more detail in Annex 3.9, Methodology for Estimating CH<sub>4</sub> Emissions from Enteric Fermentation. Nex rates for all other animals were determined using data from USDA's *Agricultural Waste Management Field Handbook* (USDA 1996a) and data from the American Society of Agricultural Engineers, Standard D384.1 (ASAE 1999).
- All N<sub>2</sub>O emissions factors (direct and indirect) were taken from IPCC (IPCC 2006).
- Country-specific estimates were developed for the fraction of N loss from volatilization (Frac<sub>gas</sub>) and runoff and leaching (Frac<sub>runoff/leach</sub>). Frac<sub>gas</sub> values were based on WMS-specific volatilization values as estimated from U.S. EPA's *National Emission Inventory - Ammonia Emissions from Animal Agriculture Operations* (EPA 2005). Frac<sub>runoff/leaching</sub> values were based on regional

## Nitrous Oxide Calculation Methods

cattle runoff data from EPA's Office of Water (EPA 2002b; see Table A-9 in Annex 3.1).

To estimate N<sub>2</sub>O emissions, first, the amount of N excreted (kg per year) in manure in each WMS for each animal type, state, and year was calculated. The population (head) for each state and animal was multiplied by TAM (kg animal mass per head) divided by 1,000, the N excretion rate (N<sub>ex</sub>, in kg N per 1000 kg animal mass per day), WMS distribution (percent), and the number of days per year.

Direct N<sub>2</sub>O emissions were calculated by multiplying the amount of N<sub>ex</sub> (kg per year) in each WMS by the N<sub>2</sub>O direct emission factor for that WMS (EF<sub>WMS</sub>, in kg N<sub>2</sub>O-N per kg N) and the conversion factor of N<sub>2</sub>O-N to N<sub>2</sub>O. These emissions were summed over state, animal and WMS to determine the total direct N<sub>2</sub>O emissions (kg of N<sub>2</sub>O per year).

Then, indirect N<sub>2</sub>O emissions from volatilization (kg N<sub>2</sub>O per year) were calculated by multiplying the amount of N excreted (kg per year) in each WMS by the fraction of N lost through volatilization (Frac<sub>gas</sub>) divided by 100, and the emission factor for volatilization (EF<sub>volatilization</sub> in kg N<sub>2</sub>O per kg N), and the conversion factor of N<sub>2</sub>O-N to N<sub>2</sub>O. Next, indirect N<sub>2</sub>O emissions from runoff and leaching (kg N<sub>2</sub>O per year) were calculated by multiplying the amount of N excreted (kg per year) in each WMS by the fraction of N lost through runoff and leaching (Frac<sub>runoff/leach</sub>) divided by 100, and the emission factor for runoff and leaching (EF<sub>runoff/leach</sub> in kg N<sub>2</sub>O per kg N), and the conversion factor of N<sub>2</sub>O-N to N<sub>2</sub>O. The indirect N<sub>2</sub>O emissions from volatilization and runoff and leaching were summed to determine the total indirect N<sub>2</sub>O emissions.

The direct and indirect N<sub>2</sub>O emissions were summed to determine total N<sub>2</sub>O emissions (kg N<sub>2</sub>O per year).

## Uncertainty and Time-Series Consistency

An analysis was conducted for the manure management emission estimates presented in this Inventory to determine the uncertainty associated with estimating CH<sub>4</sub> and N<sub>2</sub>O emissions from livestock manure management. The quantitative uncertainty analysis for this source category was first performed in 2002 through the IPCC-recommended Tier 2 uncertainty estimation methodology, the Monte Carlo Stochastic Simulation technique. The uncertainty analysis was developed based on the methods used to estimate CH<sub>4</sub> and N<sub>2</sub>O emissions from manure management systems. A normal probability distribution was assumed for each source data category. The series of equations used were condensed into a single equation for each animal type and state. The equations for each animal group contained four to five variables around which the uncertainty analysis was performed for each state.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 6-8. Manure management CH<sub>4</sub> emissions in 2008 were estimated to be between 36.9 and 54.0 Tg CO<sub>2</sub> Eq. at a 95 percent confidence level, which indicates a range of 18 percent below to 20 percent above the actual 2008 emission estimate of 45.0 Tg CO<sub>2</sub> Eq. At the 95 percent confidence level, N<sub>2</sub>O emissions were estimated to be between 14.4 and 21.2 Tg CO<sub>2</sub> Eq. (or approximately 16 percent below and 24 percent above the actual 2008 emission estimate of 17.1 Tg CO<sub>2</sub> Eq.).

Methodological recalculations were applied to the entire time series to ensure time-series consistency from 1990 through 2008. Details on the emission trends through time are described in more detail in the Methodology section, above.

**Table 6-8: Tier 2 Quantitative Uncertainty Estimates for CH<sub>4</sub> and N<sub>2</sub>O (Direct and Indirect) Emissions from Manure Management (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2008 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a, b</sup>			
			(Tg CO <sub>2</sub> Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Manure Management	CH <sub>4</sub>	45.0	36.9	54.0	-18%	+20%
Manure Management	N <sub>2</sub> O	17.1	14.4	21.2	-16%	+24%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

<sup>b</sup> Note that the relative uncertainty range was estimated with respect to the 2001 emission estimates submitted in 2003 and applied to the 2008 estimates.

## QA/QC and Verification

Tier 1 and Tier 2 QA/QC activities were conducted consistent with the U.S. QA/QC plan. Tier 2 activities focused on comparing estimates for the previous and current inventories for N<sub>2</sub>O emissions from managed systems and CH<sub>4</sub> emissions from livestock manure. All errors identified were corrected. Order of magnitude checks were also conducted, and corrections made where needed. Manure N data were checked by comparing state-level data with bottom up estimates derived at the county level and summed to the state level. Similarly, a comparison was made by animal and WMS type for the full time series, between national level estimates for N excreted and the sum of county estimates for the full time series.

## Recalculations Discussion

The Cattle Enteric Fermentation Model (CEFM) produces volatile solids data for cattle that are used in the manure management inventory. The CEFM team implemented changes to the estimated diet characteristics for feedlot and dairy cattle, as well as other minor data updates, which created changes in VS data and changes in the amount of CH<sub>4</sub> estimated for manure management. These updates decreased historical emissions through 1995, after which emissions increased (except for 2003); total emissions for the time series remained approximately the same (within 0.5 Tg CO<sub>2</sub> Eq.) (See section 6.1, Enteric Fermentation).

For the current Inventory, cattle population data from the CEFM were incorporated. The incorporation of these data and updated VS data changed the estimated CH<sub>4</sub> emissions from manure management for cattle relative to the previous report. With these changes, CH<sub>4</sub> emission estimates from manure management systems are slightly higher than reported in the previous Inventory for beef and lower for dairy cattle. Over the inventory years of 1990 through 2007, the annual CH<sub>4</sub> emission estimates differ from those of the previous Inventory report by less than 5 percent.

For the current Inventory, Nex data from the CEFM was incorporated. Due to the population and Nex changes, N<sub>2</sub>O emission estimates from manure management systems have increased for all years in the current Inventory as compared to the previous Inventory report. Overall the total emission estimates from manure management for the current Inventory increased by an average of 18 percent, as compared to the previous report.

## Planned Improvements

In future Inventories, the manure management inventory will be updated to reflect changes in the Cattle Enteric Fermentation Model (CEFM). Additional steps will be taken to complete the harmonization of animal populations and characteristics between the manure management and enteric fermentation source categories. Specifically, the TAM estimates will be evaluated and updated so that total VS and N excretion estimates from the CEFM can be utilized.

The manure management emission estimates will be updated to ensure that the dairy heifer WMS distribution is consistent between the CH<sub>4</sub> and N<sub>2</sub>O inventories.

An updated version of the USDA *Agricultural Waste Management Field Handbook* is expected to be available in the next year. This reference will be reviewed to determine if updates should be made to any of the activity data.

The emission estimates only take into account anaerobic digestion systems for dairy and swine operations. Data from the AgSTAR Program will be reviewed and anaerobic digestions systems that exist for other animals types will be incorporated.

An examination of new research on B<sub>0</sub> values for dairy and swine will be undertaken and applied to future emission estimates.

The uncertainty analysis will be updated in the future to more accurately assess uncertainty of emission calculations. This update is necessary due to the extensive changes in emission calculation methodology which began with the 1990 through 2006 Inventory, including estimation of emissions at the WMS level and the use of new calculations and variables for indirect N<sub>2</sub>O emissions.

## 6.3. Rice Cultivation (IPCC Source Category 4C)

Most of the world's rice, and all rice in the United States, is grown on flooded fields. When fields are flooded, aerobic decomposition of organic material gradually depletes most of the oxygen present in the soil, causing anaerobic soil conditions. Once the environment becomes anaerobic, CH<sub>4</sub> is produced through anaerobic decomposition of soil organic matter by methanogenic bacteria. As much as 60 to 90 percent of the CH<sub>4</sub> produced is oxidized by aerobic methanotrophic bacteria in the soil (some oxygen remains

at the interfaces of soil and water, and soil and root system) (Holzapfel-Pschorn et al. 1985, Sass et al. 1990). Some of the CH<sub>4</sub> is also leached away as dissolved CH<sub>4</sub> in floodwater that percolates from the field. The remaining un-oxidized CH<sub>4</sub> is transported from the submerged soil to the atmosphere primarily by diffusive transport through the rice plants. Minor amounts of CH<sub>4</sub> also escape from the soil via diffusion and bubbling through floodwaters.

The water management system under which rice is grown is one of the most important factors affecting CH<sub>4</sub> emissions. Upland rice fields are not flooded, and therefore are not believed to produce CH<sub>4</sub>. In deepwater rice fields (i.e., fields with flooding depths greater than one meter), the lower stems and roots of the rice plants are dead, so the primary CH<sub>4</sub> transport pathway to the atmosphere is blocked. The quantities of CH<sub>4</sub> released from deepwater fields, therefore, are believed to be significantly less than the quantities released from areas with shallower flooding depths. Some flooded fields are drained periodically during the growing season, either intentionally or accidentally. If water is drained and soils are allowed to dry sufficiently, CH<sub>4</sub> emissions decrease or stop entirely. This is due to soil aeration, which not only causes existing soil CH<sub>4</sub> to oxidize but also inhibits further CH<sub>4</sub> production in soils. All rice in the United States is grown under continuously flooded conditions; none is grown under deepwater conditions. Mid-season drainage does not occur except by accident (e.g., due to levee breach).

Other factors that influence CH<sub>4</sub> emissions from flooded rice fields include fertilization practices (especially the use of organic fertilizers), soil temperature, soil type, rice variety, and cultivation practices (e.g., tillage, seeding, and weeding practices). The factors that determine the amount of organic material available to decompose (i.e., organic fertilizer use, soil type, rice variety,<sup>3</sup> and cultivation practices) are the most important variables influencing the amount of CH<sub>4</sub> emitted over the growing season; the total amount of CH<sub>4</sub> released depends primarily on the amount of organic substrate available. Soil temperature is known to be an important factor regulating the activity of methanogenic bacteria, and therefore the rate of CH<sub>4</sub> production. However, although temperature controls the amount of time it takes to convert

a given amount of organic material to CH<sub>4</sub>, that time is short relative to a growing season, so the dependence of total emissions over an entire growing season on soil temperature is weak. The application of synthetic fertilizers has also been found to influence CH<sub>4</sub> emissions; in particular, both nitrate and sulfate fertilizers (e.g., ammonium nitrate and ammonium sulfate) appear to inhibit CH<sub>4</sub> formation.

Rice is cultivated in eight states: Arkansas, California, Florida, Louisiana, Mississippi, Missouri, Oklahoma, and Texas.<sup>4</sup> Soil types, rice varieties, and cultivation practices for rice vary from state to state, and even from farm to farm. However, most rice farmers apply organic fertilizers in the form of residue from the previous rice crop, which is left standing, disked, or rolled into the fields. Most farmers also apply synthetic fertilizer to their fields, usually urea. Nitrate and sulfate fertilizers are not commonly used in rice cultivation in the United States. In addition, the climatic conditions of southwest Louisiana, Texas, and Florida often allow for a second, or ratoon, rice crop. Ratoon crops are much less common or non-existent in Arkansas, California, Mississippi, Missouri, Oklahoma, and northern areas of Louisiana. Methane emissions from ratoon crops have been found to be considerably higher than those from the primary crop. This second rice crop is produced from regrowth of the stubble after the first crop has been harvested. Because the first crop's stubble is left behind in ratooned fields, and there is no time delay between cropping seasons (which would allow the stubble to decay aerobically), the amount of organic material that is available for anaerobic decomposition is considerably higher than with the first (i.e., primary) crop.

Rice cultivation is a small source of CH<sub>4</sub> in the United States (Table 6-9 and Table 6-10). In 2008, CH<sub>4</sub> emissions from rice cultivation were 7.2 Tg CO<sub>2</sub> Eq. (343 Gg). Although annual emissions fluctuated unevenly between the years 1990 and 2008, ranging from an annual decrease of 14 percent to an annual increase of 17 percent, there was an overall decrease of 14 percent between 1990 and 2007, due to an overall decrease in primary crop area.<sup>5</sup> However, emissions levels increased by 16 percent in 2008 due to an increase in rice crop area in all states except Florida and

<sup>3</sup> The roots of rice plants shed organic material, which is referred to as "root exudate." The amount of root exudate produced by a rice plant over a growing season varies among rice varieties.

<sup>4</sup> A very small amount of rice is grown on about 20 acres in South Carolina; however, this amount was determined to be too insignificant to warrant inclusion in national emission estimates.

<sup>5</sup> The 14 percent decrease occurred between 2005 and 2006; the 17 percent increase happened between 1993 and 1994.

**Table 6-9: CH<sub>4</sub> Emissions from Rice Cultivation (Tg CO<sub>2</sub> Eq.)**

State	1990	1995	2000	2005	2006	2007	2008
<b>Primary</b>	<b>5.1</b>	<b>5.6</b>	<b>5.5</b>	<b>6.0</b>	<b>5.1</b>	<b>4.9</b>	<b>5.3</b>
Arkansas	2.1	2.4	2.5	2.9	2.5	2.4	2.5
California	0.7	0.8	1.0	0.9	0.9	1.0	0.9
Florida	+	+	+	+	+	+	+
Louisiana	1.0	1.0	0.9	0.9	0.6	0.7	0.8
Mississippi	0.4	0.5	0.4	0.5	0.3	0.3	0.4
Missouri	0.1	0.2	0.3	0.4	0.4	0.3	0.4
Oklahoma	+	+	+	+	+	0.0	+
Texas	0.6	0.6	0.4	0.4	0.3	0.3	0.3
<b>Ratoon</b>	<b>2.1</b>	<b>2.1</b>	<b>2.0</b>	<b>0.8</b>	<b>0.9</b>	<b>1.3</b>	<b>1.9</b>
Arkansas	+	+	+	+	+	+	+
Florida	+	0.1	0.1	+	+	+	+
Louisiana	1.1	1.1	1.3	0.5	0.5	0.9	1.2
Texas	0.9	0.8	0.7	0.4	0.4	0.3	0.6
<b>Total</b>	<b>7.1</b>	<b>7.6</b>	<b>7.5</b>	<b>6.8</b>	<b>5.9</b>	<b>6.2</b>	<b>7.2</b>

+ Less than 0.05 Tg CO<sub>2</sub> Eq.  
Note: Totals may not sum due to independent rounding.

**Table 6-10: CH<sub>4</sub> Emissions from Rice Cultivation (Gg)**

State	1990	1995	2000	2005	2006	2007	2008
<b>Primary</b>	<b>241</b>	<b>265</b>	<b>260</b>	<b>287</b>	<b>241</b>	<b>235</b>	<b>254</b>
Arkansas	102	114	120	139	119	113	119
California	34	40	47	45	44	45	44
Florida	1	2	2	1	1	1	1
Louisiana	46	48	41	45	29	32	39
Mississippi	21	24	19	22	16	16	19
Missouri	7	10	14	18	18	15	17
Oklahoma	+	+	+	+	+	0	+
Texas	30	27	18	17	13	12	15
<b>Ratoon</b>	<b>98</b>	<b>98</b>	<b>97</b>	<b>39</b>	<b>41</b>	<b>60</b>	<b>89</b>
Arkansas	+	+	+	1	+	+	+
Florida	2	4	2	+	1	1	1
Louisiana	52	54	61	22	22	42	59
Texas	45	40	34	17	18	16	29
<b>Total</b>	<b>339</b>	<b>363</b>	<b>357</b>	<b>326</b>	<b>282</b>	<b>295</b>	<b>343</b>

+ Less than 0.5 Gg  
Note: Totals may not sum due to independent rounding.

California, and especially due to an increase in the ratoon crop in Louisiana and Texas. The factors that affect the rice acreage in any year vary from state to state, although the price of rice relative to competing crops is the primary controlling variable in most states.

## Methodology

IPCC (2006) recommends using harvested rice areas, area-based daily emission factors (i.e., amount of CH<sub>4</sub> emitted per day per unit harvested area), and length of growing season to estimate annual CH<sub>4</sub> emissions from rice cultivation. This Inventory uses the recommended methodology and employs Tier 2 U.S.-specific emission factors derived from rice field measurements. State-specific and daily emission factors were

**Table 6-11: Rice Areas Harvested (Hectares)**

State/Crop	1990	1995	2000	2005	2006	2007	2008
Arkansas							
Primary	485,633	542,291	570,619	661,675	566,572	536,220	564,549
Ratoon <sup>a</sup>	0	0	0	662	6	5	6
California	159,854	188,183	221,773	212,869	211,655	215,702	209,227
Florida							
Primary	4,978	9,713	7,801	4,565	4,575	6,242	5,463
Ratoon	2,489	4,856	3,193	0	1,295	1,873	1,639
Louisiana							
Primary	220,558	230,676	194,253	212,465	139,620	152,975	187,778
Ratoon	66,168	69,203	77,701	27,620	27,924	53,541	75,111
Mississippi	101,174	116,552	88,223	106,435	76,487	76,487	92,675
Missouri	32,376	45,326	68,393	86,605	86,605	72,036	80,534
Oklahoma	617	364	283	271	17	0	77
Texas							
Primary	142,857	128,693	86,605	81,344	60,704	58,681	69,607
Ratoon	57,143	51,477	43,302	21,963	23,675	21,125	36,892
<b>Total Primary</b>	<b>1,148,047</b>	<b>1,261,796</b>	<b>1,237,951</b>	<b>1,366,228</b>	<b>1,146,235</b>	<b>1,118,343</b>	<b>1,209,911</b>
<b>Total Ratoon</b>	<b>125,799</b>	<b>125,536</b>	<b>124,197</b>	<b>50,245</b>	<b>52,899</b>	<b>76,544</b>	<b>113,648</b>
<b>Total</b>	<b>1,273,847</b>	<b>1,387,333</b>	<b>1,362,148</b>	<b>1,416,473</b>	<b>1,199,135</b>	<b>1,194,887</b>	<b>1,323,559</b>

<sup>a</sup> Arkansas ratooning occurred only in 1998, 1999, and 2005 through 2008.  
Note: Totals may not sum due to independent rounding.

**Table 6-12: Ratooned Area as Percent of Primary Growth Area**

State	1990	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008
Arkansas	0%		+	+			0%			0.1%	+	+	+
Florida		50%		65%	41%	60%	54%	100%	77%	0%	28%	30%	30%
Louisiana		30%			40%	30%	15%	35%	30%	13%	20%	35%	40%
Texas		40%			50%	40%	37%	38%	35%	27%	39%	36%	53%

+ Indicates ratooning rate less than 0.1 percent.

not available, however, so average U.S. seasonal emission factors were used. Seasonal emissions have been found to be much higher for ratooned crops than for primary crops, so emissions from ratooned and primary areas are estimated separately using emission factors that are representative of the particular growing season. This approach is consistent with IPCC (2006).

The harvested rice areas for the primary and ratoon crops in each state are presented in Table 6-11, and the area of ratoon crop area as a percent of primary crop area is shown in Table 6-12. Primary crop areas for 1990 through 2008 for all states except Florida and Oklahoma were taken from U.S. Department of Agriculture's Field Crops Final Estimates 1987–1992 (USDA 1994), Field Crops Final Estimates 1992–1997 (USDA 1998), Field Crops Final Estimates

1997–2002 (USDA 2003), and Crop Production Summary (USDA 2005 through 2009). Source data for non-USDA sources of primary and ratoon harvest areas are shown in Table 6-13. California, Mississippi, Missouri, and Oklahoma have not ratooned rice over the period 1990 through 2008 (Guethle 1999, 2000, 2001a, 2002 through 2008; Lee 2003 through 2007; Mutters 2002 through 2005; Street 1999 through 2003; Walker 2005, 2007, 2008).

To determine what CH<sub>4</sub> emission factors should be used for the primary and ratoon crops, CH<sub>4</sub> flux information from rice field measurements in the United States was collected. Experiments that involved atypical or nonrepresentative management practices (e.g., the application of nitrate or sulfate fertilizers, or other substances believed to suppress CH<sub>4</sub> formation), as well as experiments in which

**Table 6-13: Non-USDA Data Sources for Rice Harvest Information**

State/Crop	1990	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008
<b>Arkansas</b>											
Ratoon	Wilson (2002–2009)										
<b>Florida</b>											
Primary	Scheuneman (1999b, 1999c, 2000, 2001a)			Deren (2002)		Kirstein (2003, 2006)			Gonzales (2006–2009)		
Ratoon	Scheuneman (1999a)			Deren (2002)		Kirstein (2003–2004)	Cantens (2005)		Gonzales (2006–2009)		
<b>Louisiana</b>											
Ratoon	Bollich (2000)		Linscombe (1999, 2001a, 2002 through 2009)								
<b>Oklahoma</b>											
Primary	Lee (2003–2007)									Anderson (2008–2009)	
<b>Texas</b>											
Ratoon		Klosterboer (1999–2003)					Stansel (2004–2005)	Texas Ag Experiment Station (2006–2009)			

measurements were not made over an entire flooding season or floodwaters were drained mid-season, were excluded from the analysis. The remaining experimental results<sup>6</sup> were then sorted by season (i.e., primary and ratoon) and type of fertilizer amendment (i.e., no fertilizer added, organic fertilizer added, and synthetic and organic fertilizer added). The experimental results from primary crops with added synthetic and organic fertilizer (Bossio et al. 1999; Cicerone et al. 1992; Sass et al. 1991a, 1991b) were averaged to derive an emission factor for the primary crop, and the experimental results from ratoon crops with added synthetic fertilizer (Lindau and Bollich 1993, Lindau et al. 1995) were averaged to derive an emission factor for the ratoon crop. The resultant emission factor for the primary crop is 210 kg CH<sub>4</sub>/hectare-season, and the resultant emission factor for the ratoon crop is 780 kg CH<sub>4</sub>/hectare-season.

### Uncertainty and Time-Series Consistency

The largest uncertainty in the calculation of CH<sub>4</sub> emissions from rice cultivation is associated with the emission factors. Seasonal emissions, derived from field measurements in the United States, vary by more than one order of magnitude. This inherent variability is due to differences in cultivation practices, particularly fertilizer type,

amount, and mode of application; differences in cultivar type; and differences in soil and climatic conditions. A portion of this variability is accounted for by separating primary from ratooned areas. However, even within a cropping season or a given management regime, measured emissions may vary significantly. Of the experiments used to derive the emission factors applied here, primary emissions ranged from 22 to 479 kg CH<sub>4</sub>/hectare-season and ratoon emissions ranged from 481 to 1,490 kg CH<sub>4</sub>/hectare-season. The uncertainty distributions around the primary and ratoon emission factors were derived using the distributions of the relevant primary or ratoon emission factors available in the literature and described above. Variability about the rice emission factor means was not normally distributed for either primary or ratooned crops, but rather skewed, with a tail trailing to the right of the mean. A lognormal statistical distribution was, therefore, applied in the Tier 2 Monte Carlo analysis.

Other sources of uncertainty include the primary rice-cropped area for each state, percent of rice-cropped area that is ratooned, and the extent to which flooding outside of the normal rice season is practiced. Expert judgment was used to estimate the uncertainty associated with primary rice-cropped area for each state at 1 to 5 percent, and a normal distribution was assumed. Uncertainties were applied to ratooned area by state, based on the level of reporting performed by the state. No uncertainties were calculated for the practice of flooding outside of the normal rice season because CH<sub>4</sub> flux measurements have not been undertaken over a sufficient geographic range or under a broad enough

<sup>6</sup> In some of these remaining experiments, measurements from individual plots were excluded from the analysis because of the aforementioned reasons. In addition, one measurement from the ratooned fields (i.e., the flux of 1,490 kg CH<sub>4</sub>/hectare-season in Lindau and Bollich 1993) was excluded, because this emission rate is unusually high compared to other flux measurements in the United States, as well as IPCC (2006) default emission factors.



**Table 6-14: Tier 2 Quantitative Uncertainty Estimates for CH<sub>4</sub> Emissions from Rice Cultivation Manure Management (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2008 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			(Tg CO <sub>2</sub> Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Rice Cultivation	CH <sub>4</sub>	7.2	2.6	17.5	-64%	+143%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

range of representative conditions to account for this source in the emission estimates or its associated uncertainty.

To quantify the uncertainties for emissions from rice cultivation, a Monte Carlo (Tier 2) uncertainty analysis was performed using the information provided above. The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 6-14. Rice cultivation CH<sub>4</sub> emissions in 2008 were estimated to be between 2.6 and 17.5 Tg CO<sub>2</sub> Eq. at a 95 percent confidence level, which indicates a range of 64 percent below to 143 percent above the actual 2008 emission estimate of 7.2 Tg CO<sub>2</sub> Eq.

Methodological recalculations were applied to the entire time series to ensure time-series consistency from 1990 through 2008. Details on the emission trends through time are described in more detail in the Methodology section, above.

## QA/QC and Verification

A source-specific QA/QC plan for rice cultivation was developed and implemented. This effort included a Tier 1 analysis, as well as portions of a Tier 2 analysis. The Tier 2 procedures focused on comparing trends across years, states, and cropping seasons to attempt to identify any outliers or inconsistencies. No problems were found.

## Planned Improvements

A possible future improvement is to create region-specific emission factors for rice cultivation. The current methodology uses a nationwide average emission factor, derived from several studies done in a number of states. The prospective improvement would take the same studies and average them by region, presumably resulting in more spatially-specific emission factors.

## 6.4. Agricultural Soil Management (IPCC Source Category 4D)

Nitrous oxide is produced naturally in soils through the microbial processes of nitrification and denitrification.<sup>7</sup> A number of agricultural activities increase mineral nitrogen (N) availability in soils, thereby increasing the amount available for nitrification and denitrification, and ultimately the amount of N<sub>2</sub>O emitted. These activities increase soil mineral N either directly or indirectly (see Figure 6-2). Direct increases occur through a variety of management practices that add or lead to greater release of mineral N to the soil, including fertilization; application of managed livestock manure and other organic materials such as sewage sludge; deposition of manure on soils by domesticated animals in pastures, rangelands, and paddocks (PRP) (i.e., by grazing animals and other animals whose manure is not managed); production of N-fixing crops and forages; retention of crop residues; and drainage and cultivation of organic cropland soils (i.e., soils with a high organic matter content, otherwise known as histosols).<sup>8</sup> Other agricultural soil management activities, including irrigation, drainage, tillage practices, and fallowing of land, can influence N mineralization in soils and thereby affect direct emissions. Mineral N is also made available in soils through decomposition of soil organic matter and plant litter, as well as asymbiotic fixation of N from the atmosphere,<sup>9</sup> which are influenced by agricultural management through impacts on moisture

<sup>7</sup> Nitrification and denitrification are driven by the activity of microorganisms in soils. Nitrification is the aerobic microbial oxidation of ammonium (NH<sub>4</sub><sup>+</sup>) to nitrate (NO<sub>3</sub><sup>-</sup>), and denitrification is the anaerobic microbial reduction of nitrate to N<sub>2</sub>. Nitrous oxide is a gaseous intermediate product in the reaction sequence of denitrification, which leaks from microbial cells into the soil and then into the atmosphere. Nitrous oxide is also produced during nitrification, although by a less well-understood mechanism (Nevison 2000).

<sup>8</sup> Drainage and cultivation of organic soils in former wetlands enhances mineralization of N-rich organic matter, thereby increasing N<sub>2</sub>O emissions from these soils.

<sup>9</sup> Asymbiotic N fixation is the fixation of atmospheric N<sub>2</sub> by bacteria living in soils that do not have a direct relationship with plants.

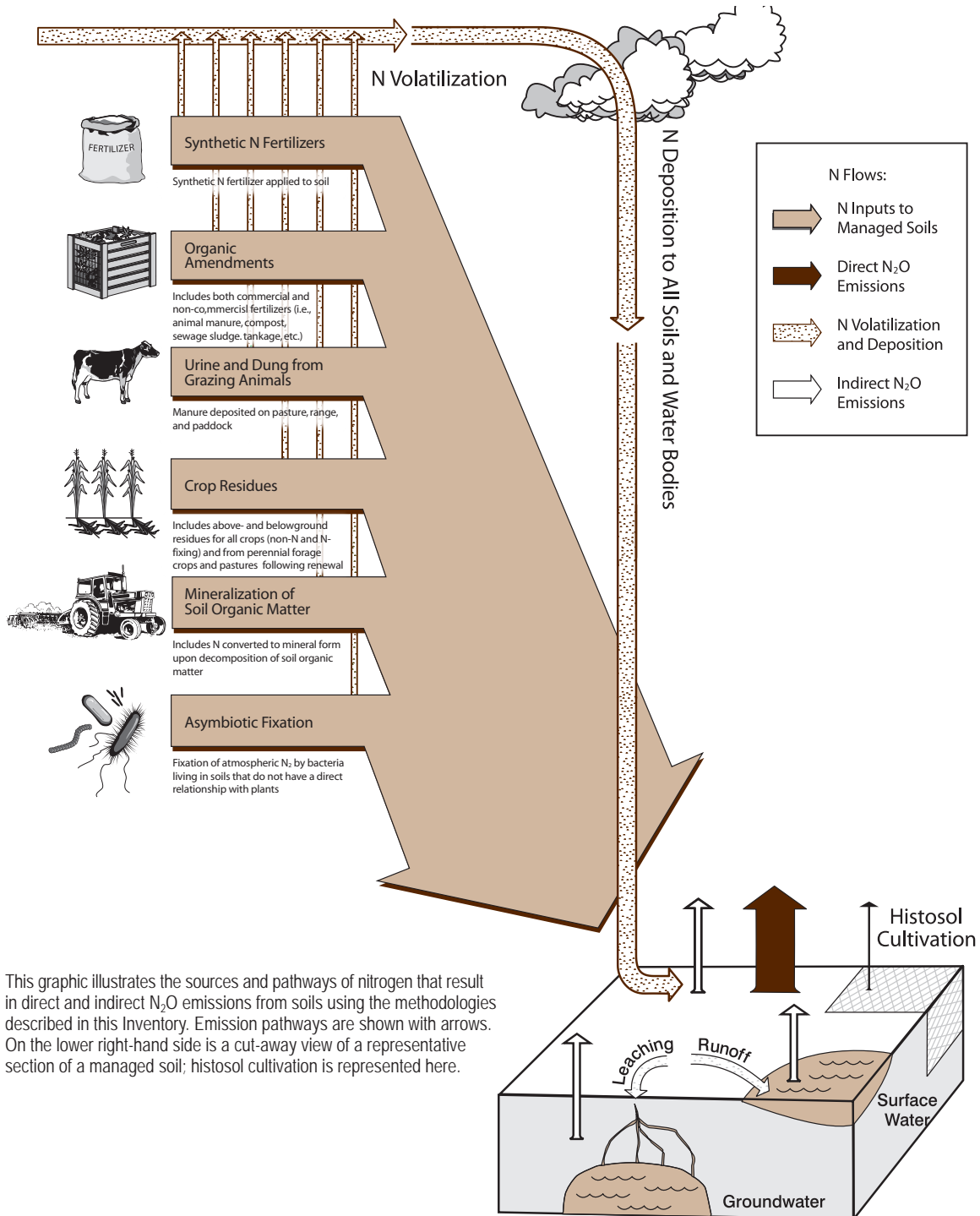
and temperature regimes in soils. These additional sources of mineral N are included at the recommendation of IPCC (2006) for complete accounting of management impacts on greenhouse gas emissions, as discussed in the Methodology section. Indirect emissions of N<sub>2</sub>O occur through two pathways: (1) volatilization and subsequent atmospheric deposition of applied/mineralized N,<sup>10</sup> and (2) surface runoff and leaching of applied/mineralized N into groundwater and surface water. Direct emissions from agricultural lands (i.e., croplands and grasslands) are included in this section, while direct emissions from forest lands and settlements are presented in the Land Use, Land-Use Change, and Forestry chapter. However, indirect N<sub>2</sub>O emissions from all land-use types (cropland, grassland, forest lands, and settlements) are reported in this section.

Agricultural soils produce the majority of N<sub>2</sub>O emissions in the United States. Estimated emissions from this source in 2008 were 215.9 Tg CO<sub>2</sub> Eq. (696 Gg N<sub>2</sub>O) (see Table 6-15 and Table 6-16). Annual N<sub>2</sub>O emissions from agricultural soils fluctuated between 1990 and 2008, although overall emissions were 6 percent higher in 2008 than in 1990. Year-to-year fluctuations are largely a reflection of annual variation in weather patterns, synthetic fertilizer use, and crop production. On average, cropland accounted for approximately 69 percent of total direct emissions, while grassland accounted for approximately 31 percent. These percentages are about the same for indirect emissions since forest lands and settlements account for such a small percentage of total indirect emissions. Estimated direct and indirect N<sub>2</sub>O emissions by sub-source category are shown in Table 6-17 and Table 6-18.

<sup>10</sup> These processes entail volatilization of applied or mineralized N as NH<sub>3</sub> and NO<sub>x</sub>, transformation of these gases within the atmosphere (or upon deposition), and deposition of the N primarily in the form of particulate NH<sub>4</sub><sup>+</sup>, nitric acid (HNO<sub>3</sub>), and NO<sub>x</sub>.

Figure 6-2

Sources and Pathways of N that Result in N<sub>2</sub>O Emissions from Agricultural Soil Management



This graphic illustrates the sources and pathways of nitrogen that result in direct and indirect N<sub>2</sub>O emissions from soils using the methodologies described in this Inventory. Emission pathways are shown with arrows. On the lower right-hand side is a cut-away view of a representative section of a managed soil; histosol cultivation is represented here.

**Table 6-15: N<sub>2</sub>O Emissions from Agricultural Soils (Tg CO<sub>2</sub> Eq.)**

Activity	1990	1995	2000	2005	2006	2007	2008
<b>Direct</b>	<b>156.7</b>	<b>161.8</b>	<b>165.8</b>	<b>170.5</b>	<b>166.0</b>	<b>167.2</b>	<b>170.4</b>
Cropland	103.0	109.8	115.6	117.9	114.7	116.7	118.3
Grassland	53.7	51.9	50.2	52.6	51.3	50.5	52.1
<b>Indirect (All Land-Use Types)</b>	<b>46.7</b>	<b>44.2</b>	<b>44.3</b>	<b>45.4</b>	<b>45.2</b>	<b>43.8</b>	<b>45.5</b>
Cropland	36.0	33.9	35.7	35.4	35.3	34.1	35.1
Grassland	10.4	9.7	8.0	9.3	9.2	9.0	9.6
Forest Land	+	0.1	0.1	0.1	0.1	0.1	0.1
Settlements	0.3	0.5	0.5	0.6	0.6	0.6	0.6
<b>Total</b>	<b>203.5</b>	<b>205.9</b>	<b>210.1</b>	<b>215.8</b>	<b>211.2</b>	<b>211.0</b>	<b>215.9</b>

+ Less than 0.05 Tg CO<sub>2</sub> Eq.

**Table 6-16: N<sub>2</sub>O Emissions from Agricultural Soils (Gg)**

Activity	1990	1995	2000	2005	2006	2007	2008
<b>Direct</b>	<b>506</b>	<b>522</b>	<b>535</b>	<b>550</b>	<b>535</b>	<b>539</b>	<b>550</b>
Cropland	332	354	373	380	370	376	382
Grassland	173	168	162	170	165	163	168
<b>Indirect (All Land-Use Types)</b>	<b>151</b>	<b>143</b>	<b>143</b>	<b>146</b>	<b>146</b>	<b>141</b>	<b>147</b>
Cropland	116	109	115	114	114	110	113
Grassland	33	31	26	30	30	29	31
Forest Land	0	+	+	+	+	+	+
Settlements	1	2	1	2	2	2	2
<b>Total</b>	<b>656</b>	<b>664</b>	<b>678</b>	<b>696</b>	<b>681</b>	<b>681</b>	<b>696</b>

+ Less than 0.5 Gg N<sub>2</sub>O

**Table 6-17: Direct N<sub>2</sub>O Emissions from Agricultural Soils by Land Use Type and N Input Type (Tg CO<sub>2</sub> Eq.)**

Activity	1990	1995	2000	2005	2006	2007	2008
<b>Cropland</b>	<b>103.0</b>	<b>109.8</b>	<b>115.6</b>	<b>117.9</b>	<b>114.7</b>	<b>116.7</b>	<b>118.3</b>
<b>Mineral Soils</b>	<b>100.2</b>	<b>106.9</b>	<b>112.7</b>	<b>115.0</b>	<b>111.8</b>	<b>113.8</b>	<b>115.4</b>
Synthetic Fertilizer	35.1	39.8	39.0	41.4	39.4	40.3	40.8
Organic Amendments <sup>a</sup>	10.0	10.9	11.2	11.4	11.6	11.8	11.7
Residue N <sup>b</sup>	7.0	7.7	7.8	7.5	7.5	7.5	7.8
Mineralization and Asymbiotic Fixation	48.1	48.6	54.7	54.7	53.3	54.2	55.1
<b>Organic Soils</b>	<b>2.9</b>	<b>2.9</b>	<b>2.9</b>	<b>2.9</b>	<b>2.9</b>	<b>2.9</b>	<b>2.9</b>
<b>Grassland</b>	<b>53.7</b>	<b>51.9</b>	<b>50.2</b>	<b>52.6</b>	<b>51.3</b>	<b>50.5</b>	<b>52.1</b>
Synthetic Fertilizer	3.9	4.1	3.8	4.0	4.0	3.9	4.0
PRP Manure	10.3	10.8	10.3	10.5	10.4	10.3	10.4
Managed Manure <sup>c</sup>	0.7	0.7	0.7	0.8	0.8	0.8	0.8
Sewage Sludge	0.3	0.3	0.4	0.5	0.5	0.5	0.5
Residue N <sup>d</sup>	11.6	11.1	10.4	11.1	10.8	10.7	11.0
Mineralization and Asymbiotic Fixation	26.9	24.8	24.6	25.6	24.8	24.4	25.4
<b>Total</b>	<b>156.7</b>	<b>161.8</b>	<b>165.8</b>	<b>170.5</b>	<b>166.0</b>	<b>167.2</b>	<b>170.4</b>

<sup>a</sup> Organic amendment inputs include managed manure amendments, daily spread manure amendments, and commercial organic fertilizers (i.e., dried blood, dried manure, tankage, compost, and other).

<sup>b</sup> Cropland residue N inputs include N in unharvested legumes as well as crop residue N.

<sup>c</sup> Accounts for managed manure and daily spread manure amendments that are applied to grassland soils.

<sup>d</sup> Grassland residue N inputs include N in ungrazed legumes as well as ungrazed grass residue N.

**Table 6-18: Indirect N<sub>2</sub>O Emissions from all Land-Use Types (Tg CO<sub>2</sub> Eq.)**

Activity	1990	1995	2000	2005	2006	2007	2008
<b>Cropland</b>	<b>36.0</b>	<b>33.9</b>	<b>35.7</b>	<b>35.4</b>	<b>35.3</b>	<b>34.1</b>	<b>35.1</b>
Volatilization & Atm. Deposition	10.5	11.7	11.9	11.7	12.9	11.3	12.0
Surface Leaching & Run-Off	25.6	22.2	23.8	23.6	22.4	22.7	23.1
<b>Grassland</b>	<b>10.4</b>	<b>9.7</b>	<b>8.0</b>	<b>9.3</b>	<b>9.2</b>	<b>9.0</b>	<b>9.6</b>
Volatilization & Atm. Deposition	5.6	5.6	5.1	5.3	5.3	5.2	5.2
Surface Leaching & Run-Off	4.8	4.1	2.9	4.0	3.9	3.8	4.4
<b>Forest Land</b>	<b>+</b>	<b>0.1</b>	<b>0.1</b>	<b>0.1</b>	<b>0.1</b>	<b>0.1</b>	<b>0.1</b>
Volatilization & Atm. Deposition	+	+	+	+	+	+	+
Surface Leaching & Run-Off	+	+	0.1	0.1	0.1	0.1	0.1
<b>Settlements</b>	<b>0.3</b>	<b>0.5</b>	<b>0.5</b>	<b>0.6</b>	<b>0.6</b>	<b>0.6</b>	<b>0.6</b>
Volatilization & Atm. Deposition	0.1	0.2	0.2	0.2	0.2	0.2	0.2
Surface Leaching & Run-Off	0.2	0.3	0.3	0.4	0.4	0.4	0.4
<b>Total</b>	<b>46.7</b>	<b>44.2</b>	<b>44.3</b>	<b>45.4</b>	<b>45.2</b>	<b>43.8</b>	<b>45.5</b>

+ Less than 0.05 Tg CO<sub>2</sub> Eq.

Figure 6-3 through Figure 6-6 show regional patterns in direct N<sub>2</sub>O emissions, and also show N losses from volatilization, leaching, and runoff that lead to indirect N<sub>2</sub>O emissions. Average annual emissions and N losses from croplands that produce major crops and from grasslands are shown for each state. Direct N<sub>2</sub>O emissions from croplands tend to be high in the Corn Belt (Illinois, Iowa, Indiana, Ohio, southern Minnesota, southern Wisconsin, and eastern Nebraska), where a large portion of the land is used for growing highly fertilized corn and N-fixing soybean crops. Direct emissions are also high in Missouri, Kansas, and Texas, primarily from irrigated cropping in western Texas, dryland wheat in Kansas, and hay cropping in eastern Texas and Missouri. Direct emissions are low in many parts of the eastern United States because a small portion of land is cultivated, and also low in many western states where rainfall and access to irrigation water are limited.

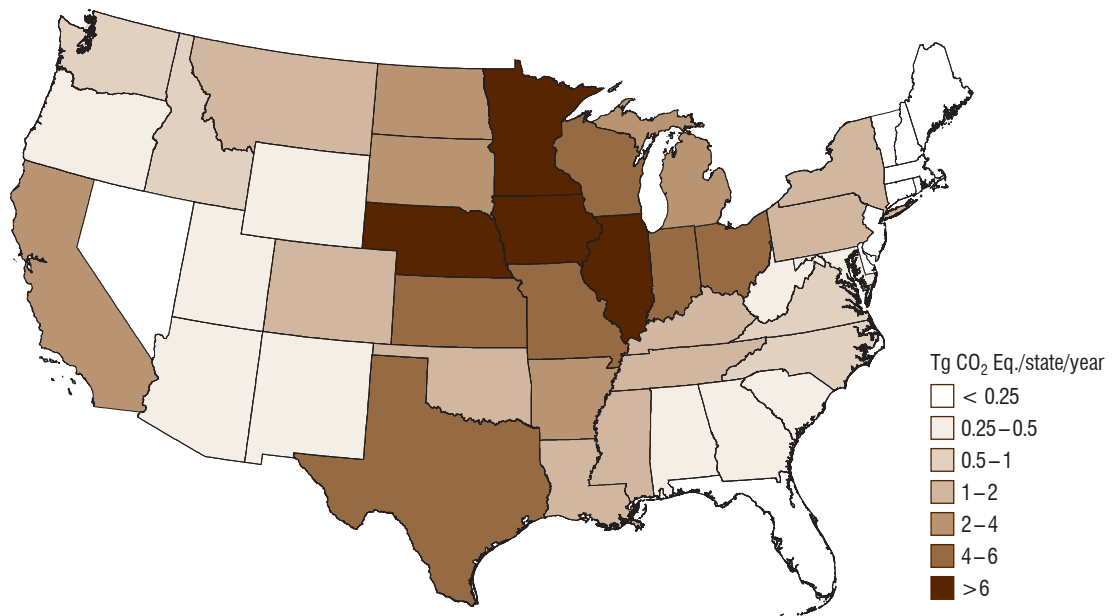
Direct emissions (Tg CO<sub>2</sub>Eq./state/year) from grasslands are highest in the central and western United States (Figure

6-4) where a high proportion of the land is used for cattle grazing. Some areas in the Great Lake states, the Northeast, and Southeast have moderate to low emissions even though emissions from these areas tend to be high on a per unit area basis, because the total amount of grazed land is much lower than states in the central and western United States.

Indirect emissions from croplands and grasslands (Figure 6-5 and Figure 6-6) show patterns similar to direct emissions, because the factors that control direct emissions (N inputs, weather, soil type) also influence indirect emissions. However, there are some exceptions, because the processes that contribute to indirect emissions (NO<sub>3</sub><sup>-</sup> leaching, N volatilization) do not respond in exactly the same manner as the processes that control direct emissions (nitrification and denitrification). For example, coarser-textured soils facilitate relatively high indirect emissions in Florida grasslands due to high rates of N volatilization and NO<sub>3</sub><sup>-</sup> leaching, even though they have only moderate rates of direct N<sub>2</sub>O emissions.

**Figure 6-3**

**Major Crops, Average Annual Direct N<sub>2</sub>O Emissions Estimated Using the DAYCENT Model, 1990–2008 (Tg CO<sub>2</sub> Eq./year)**



**Figure 6-4**

**Grasslands, Average Annual Direct N<sub>2</sub>O Emissions Estimated Using the DAYCENT Model, 1990–2008 (Tg CO<sub>2</sub> Eq./year)**

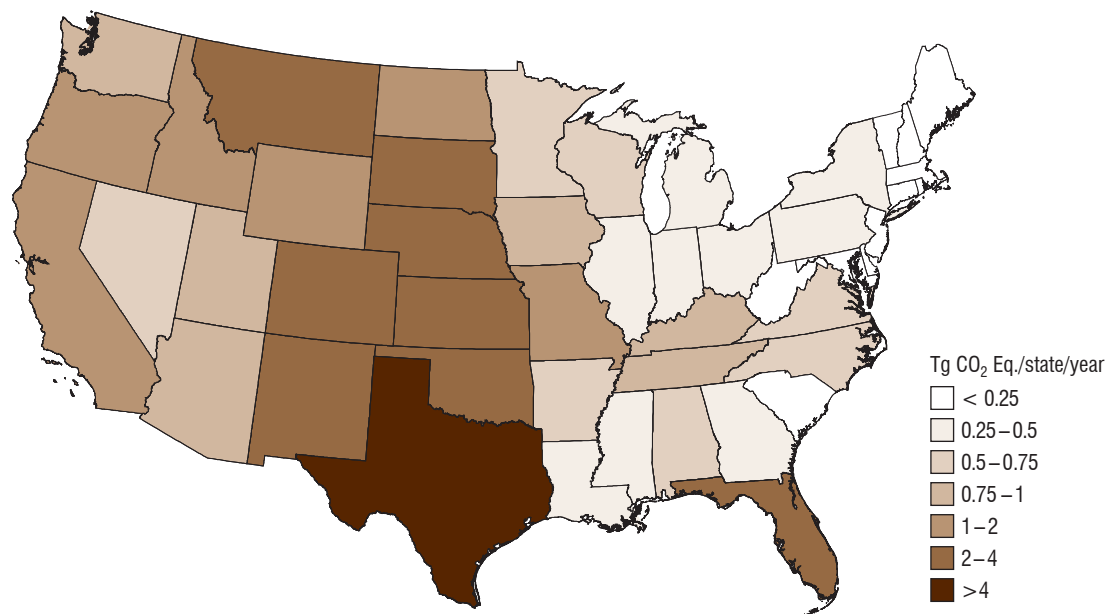


Figure 6-5

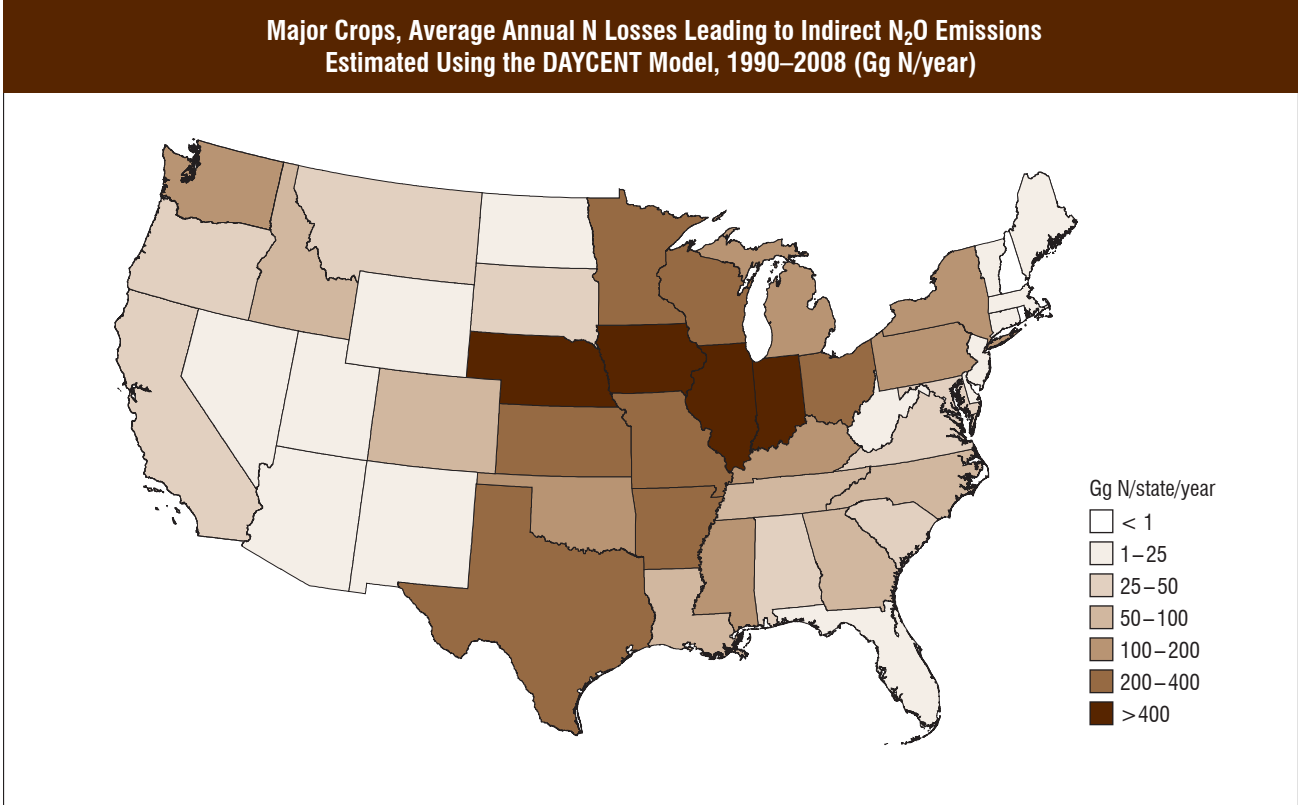
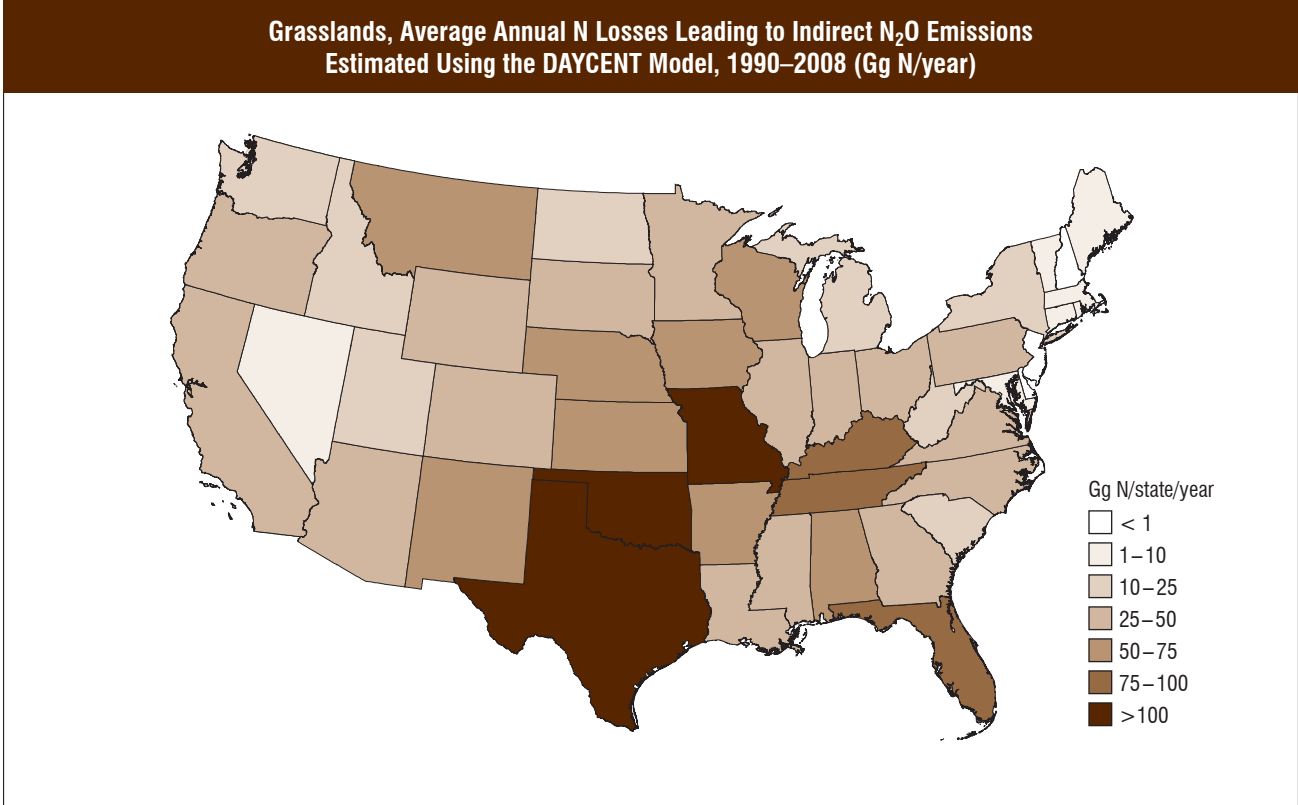


Figure 6-6



## Methodology

The 2006 IPCC Guidelines (IPCC 2006) divide the Agricultural Soil Management source category into four components: (1) direct emissions due to N additions to cropland and grassland mineral soils, including synthetic fertilizers, sewage sludge applications, crop residues, organic amendments, and biological N fixation associated with planting of legumes on cropland and grassland soils; (2) direct emissions from drainage and cultivation of organic cropland soils; (3) direct emissions from soils due to the deposition of manure by livestock on PRP grasslands; and (4) indirect emissions from soils and water due to N additions and manure deposition to soils that lead to volatilization, leaching, or runoff of N and subsequent conversion to N<sub>2</sub>O.

The United States has adopted recommendations from IPCC (2006) on methods for agricultural soil management. These recommendations include (1) estimating the contribution of N from crop residues to indirect soil N<sub>2</sub>O emissions; (2) adopting a revised emission factor for direct N<sub>2</sub>O emissions to the extent that Tier 1 methods are used in the Inventory (described later in this section); (3) removing double counting of emissions from N-fixing crops associated with the biological N fixation and crop residue N input categories; (4) using revised crop residue statistics to compute N inputs to soils based on harvest yield data to the extent that Tier 1 methods are used in the Inventory; (5) accounting for

indirect as well as direct emissions from N made available via mineralization of soil organic matter and litter, in addition to asymbiotic fixation<sup>11</sup> (i.e., computing total emissions from managed land); and (6) reporting all emissions from managed lands, largely because management affects all processes leading to soil N<sub>2</sub>O emissions. One recommendation from IPCC (2006) has not been adopted: accounting for emissions from pasture renewal, which involves occasional plowing to improve forage production. This practice is not common in the United States, and is not estimated.

The methodology used to estimate emissions from agricultural soil management in the United States is based on a combination of IPCC Tier 1 and 3 approaches. A Tier 3, process-based model (DAYCENT) was used to estimate direct emissions from major crops on mineral (i.e., non-organic) soils; as well as most of the direct emissions from grasslands. The Tier 3 approach has been specifically designed and tested to estimate N<sub>2</sub>O emissions in the United States, accounting for more of the environmental and management influences on soil N<sub>2</sub>O emissions than the IPCC Tier 1 method (see Box 6-1 for further elaboration). The Tier 1 IPCC (2006) methodology was used to estimate (1) direct emissions from non-major crops on mineral soils (e.g., barley, oats, vegetables, and other crops); (2) the portion of the grassland direct emissions that were not estimated with the Tier 3 DAYCENT model (i.e., federal grasslands); and

### Box 6-1: Tier 1 vs. Tier 3 Approach for Estimating N<sub>2</sub>O Emissions

The IPCC (2006) Tier 1 approach is based on multiplying activity data on different N inputs (e.g., synthetic fertilizer, manure, N fixation, etc.) by the appropriate default IPCC emission factors to estimate N<sub>2</sub>O emissions on an input-by-input basis. The Tier 1 approach requires a minimal amount of activity data, readily available in most countries (e.g., total N applied to crops); calculations are simple; and the methodology is highly transparent. In contrast, the Tier 3 approach developed for this Inventory employs a process-based model (i.e., DAYCENT) that represents the interaction of N inputs and the environmental conditions at specific locations. Consequently, the Tier 3 approach is likely to produce more accurate estimates; it accounts more comprehensively for land-use and management impacts and their interaction with environmental factors (i.e., weather patterns and soil characteristics), which may enhance or dampen anthropogenic influences. However, the Tier 3 approach requires more refined activity data (e.g., crop-specific N amendment rates), additional data inputs (e.g., daily weather, soil types, etc.), and considerable computational resources and programming expertise. The Tier 3 methodology is less transparent, and thus it is critical to evaluate the output of Tier 3 methods against measured data in order to demonstrate the adequacy of the method for estimating emissions (IPCC 2006). Another important difference between the Tier 1 and Tier 3 approaches relates to assumptions regarding N cycling. Tier 1 assumes that N added to a system is subject to N<sub>2</sub>O emissions only during that year and cannot be stored in soils and contribute to N<sub>2</sub>O emissions in subsequent years. This is a simplifying assumption that is likely to create bias in estimated N<sub>2</sub>O emissions for a specific year. In contrast, the process-based model used in the Tier 3 approach includes such legacy effects when N added to soils is re-mineralized from soil organic matter and emitted as N<sub>2</sub>O during subsequent years.

<sup>11</sup> N inputs from asymbiotic N fixation are not directly addressed in 2006 IPCC Guidelines, but are a component of the total emissions from managed lands and are included in the Tier 3 approach developed for this source.



(3) direct emissions from drainage and cultivation of organic cropland soils. Indirect emissions were also estimated with a combination of DAYCENT and the IPCC Tier 1 method.

In past Inventories, attempts were made to subtract “background” emissions that would presumably occur if the lands were not managed. However, this approach is likely to be inaccurate for estimating the anthropogenic influence on soil N<sub>2</sub>O emissions. Moreover, if background emissions could be measured or modeled based on processes unaffected by anthropogenic activity, they would be a very small portion of the total emissions, due to the high inputs of N to agricultural soils from fertilization and legume cropping. Given the recommendation from IPCC (2006) and the influence of management on all processes leading to N<sub>2</sub>O emissions from soils in agricultural systems, the decision was made to report total emissions from managed lands for this source category. Annex 3.11 provides more detailed information on the methodologies and data used to calculate N<sub>2</sub>O emissions from each component.

### **Direct N<sub>2</sub>O Emissions from Cropland Soils**

#### ***Major Crop Types on Mineral Cropland Soils***

The DAYCENT ecosystem model (Del Grosso et al. 2001, Parton et al. 1998) was used to estimate direct N<sub>2</sub>O emissions from mineral cropland soils that are managed for production of major crops—specifically corn, soybeans, wheat, alfalfa hay, other hay, sorghum, and cotton—representing approximately 90 percent of total croplands in the United States. For these croplands, DAYCENT was used to simulate crop growth, soil organic matter decomposition, greenhouse gas fluxes, and key biogeochemical processes affecting N<sub>2</sub>O emissions, and the simulations were driven by model input data generated from daily weather records (Thornton et al. 1997, 2000; Thornton and Running 1999), land management surveys (see citations below), and soil physical properties determined from national soil surveys (Soil Survey Staff 2005). Note that the influence of land-use change on soil N<sub>2</sub>O emissions was not addressed in this analysis, but is a planned improvement.

DAYCENT simulations were conducted for each major crop at the county scale in the United States. Simulating N<sub>2</sub>O emissions at the county scale was facilitated by soil and weather data that were available for every county with more than 100 acres of agricultural land, and by land management

data (e.g., timing of planting, harvesting, intensity of cultivation) that were available at the agricultural-region level as defined by the Agricultural Sector Model (McCarl et al. 1993). ASM has 63 agricultural regions in the contiguous United States. Most regions correspond to one state, except for those states with greater heterogeneity in agricultural practices; in such cases, more than one region is assigned to a state. While cropping systems were simulated for each county, the results best represent emissions at regional (i.e., state) and national levels due to the regional scale of management data, which include model parameters that determined the influence of management activities on soil N<sub>2</sub>O emissions (e.g., when crops were planted/harvested).

Nitrous oxide emissions from managed agricultural lands are the result of interactions among anthropogenic activities (e.g., N fertilization, manure application, tillage) and other driving variables, such as weather and soil characteristics. These factors influence key processes associated with N dynamics in the soil profile, including immobilization of N by soil microbial organisms, decomposition of organic matter, plant uptake, leaching, runoff, and volatilization, as well as the processes leading to N<sub>2</sub>O production (nitrification and denitrification). It is not possible to partition N<sub>2</sub>O emissions into each anthropogenic activity directly from model outputs due to the complexity of the interactions (e.g., N<sub>2</sub>O emissions from synthetic fertilizer applications cannot be distinguished from those resulting from manure applications). To approximate emissions by activity, the amount of mineral N added to the soil for each of these sources was determined and then divided by the total amount of mineral N that was made available in the soil according to the DAYCENT model. The percentages were then multiplied by the total of direct N<sub>2</sub>O emissions in order to approximate the portion attributed to key practices. This approach is only an approximation because it assumes that all N made available in soil has an equal probability of being released as N<sub>2</sub>O, regardless of its source, which is unlikely to be the case (Delgado et al., 2009). However, this approach allows for further disaggregation of emissions by source of N, which is valuable for reporting purposes and is analogous to the reporting associated with the IPCC (2006) Tier 1 method, in that it associates portions of the total soil N<sub>2</sub>O emissions with individual sources of N.

DAYCENT was used to estimate direct N<sub>2</sub>O emissions due to mineral N available from: (1) the application of

synthetic fertilizers; (2) the application of livestock manure; (3) the retention of crop residues (i.e., leaving residues in the field after harvest instead of burning or collecting residues); and (4) mineralization of soil organic matter and litter, in addition to asymbiotic fixation. Note that commercial organic fertilizers are addressed with the Tier 1 method because county-level application data would be needed to simulate applications in the DAYCENT, and currently data are only available at the national scale. The third and fourth sources are generated internally by the DAYCENT model. For the first two practices, annual changes in soil mineral N due to anthropogenic activity were obtained or derived from the following sources:

- Crop-specific N-fertilization rates: Data sources for fertilization rates include Alexander and Smith (1990), Anonymous (1924), Battaglin and Goolsby (1994), Engle and Makela (1947), ERS (1994, 2003), Fraps and Asbury (1931), Ibach and Adams (1967), Ibach et al. (1964), NFA (1946), NRIAI (2003), Ross and Mehring (1938), Skinner (1931), Smalley et al. (1939), Taylor (1994), USDA (1966, 1957, 1954, 1946). Information on fertilizer use and rates by crop type for different regions of the United States were obtained primarily from the USDA *Economic Research Service Cropping Practices Survey* (ERS 1997) with additional data from other sources, including the National Agricultural Statistics Service (NASS 1992, 1999, 2004).
- Managed manure production and application to croplands and grasslands: Manure N amendments and daily spread manure N amendments applied to croplands and grasslands (not including PRP manure) were determined using USDA Manure N Management Databases for 1997 (Kellogg et al. 2000; Edmonds et al. 2003). Amendment data for 1997 were scaled to estimate values for other years based on the availability of managed manure N for application to soils in 1997 relative to other years. The amount of available N from managed manure for each livestock type was calculated as described in the Manure Management section (Section 6.2) and Annex 3.10.
- Retention of crop residue, N mineralization from soil organic matter, and asymbiotic N fixation from the atmosphere: The IPCC approach considers crop residue N and N mineralized from soil organic matter as activity data. However, they are not treated as activity data in

DAYCENT simulations because residue production, N fixation, mineralization of N from soil organic matter, and asymbiotic fixation are internally generated by the model. In other words, DAYCENT accounts for the influence of N fixation, mineralization of N from soil organic matter, and retention of crop residue on N<sub>2</sub>O emissions, but these are not model inputs.

- Historical and modern crop rotation and management information (e.g., timing and type of cultivation, timing of planting/harvest, etc.): These activity data were derived from Hurd (1930, 1929), Latta (1938), Iowa State College Staff Members (1946), Bogue (1963), Hurt (1994), USDA (2000a) as extracted by Eve (2001) and revised by Ogle (2002), CTIC (1998), Piper et al. (1924), Hardies and Hume (1927), Holmes (1902, 1929), Spillman (1902, 1905, 1907, 1908), Chilcott (1910), Smith (1911), Kezer (ca. 1917), Hargreaves (1993), ERS (2002), Warren (1911), Langston et al. (1922), Russell et al. (1922), Elliott and Tapp (1928), Elliott (1933), Ellsworth (1929), Garey (1929), Hodges et al. (1930), Bonnen and Elliott (1931), Brenner et al. (2002, 2001), and Smith et al. (2002). Approximately 3 percent of the crop residues were assumed to be burned based on state inventory data (ILENR 1993, Oregon Department of Energy 1995, Noller 1996, Wisconsin Department of Natural Resources 1993, and Cibrowski 1996), and therefore did not contribute to soil N<sub>2</sub>O emissions.

DAYCENT simulations produced per-area estimates of N<sub>2</sub>O emissions (g N<sub>2</sub>O-N/m<sup>2</sup>) for major crops in each county, which were multiplied by the cropland areas in each county to obtain county-scale emission estimates. Cropland area data were from NASS (USDA 2009a,b). The emission estimates by reported crop areas in the county were scaled to the regions, and the national estimate was calculated by summing results across all regions. DAYCENT is sensitive to interannual variability in weather patterns and other controlling variables, so emissions associated with individual activities vary through time even if the management practices remain the same (e.g., if N fertilization remains the same for two years). In contrast, Tier 1 methods do not capture this variability and rather have a linear, monotonic response that depends solely on management practices. DAYCENT's ability to capture these interactions between management and environmental conditions produces more accurate estimates of N<sub>2</sub>O emissions than the Tier 1 method.

### **Non-Major Crop Types on Mineral Cropland Soils**

The IPCC (2006) Tier 1 methodology was used to estimate direct N<sub>2</sub>O emissions for mineral cropland soils that are managed for production of non-major crop types, including barley, oats, tobacco, sugarcane, sugar beets, sunflowers, millet, rice, peanuts, and other crops that were not included in the DAYCENT simulations. Estimates of direct N<sub>2</sub>O emissions from N applications to non-major crop types were based on mineral soil N that was made available from the following practices: (1) the application of synthetic commercial fertilizers; (2) application of managed manure and non-manure commercial organic fertilizers;<sup>12</sup> and (3) the retention of above- and below-ground crop residues in agricultural fields (i.e., crop biomass that is not harvested). Non-manure organic amendments were not included in the DAYCENT simulations because county-level data were not available. Consequently, non-manure organic amendments, as well as manure amendments not included in the DAYCENT simulations, were included in the Tier 1 analysis. The influence of land-use change on soil N<sub>2</sub>O emissions from non-major crops has not been addressed in this analysis, but is a planned improvement. The following sources were used to derive activity data:

- A process-of-elimination approach was used to estimate synthetic N fertilizer additions for non-major crops, because little information exists on their fertilizer application rates. The total amount of fertilizer used on farms has been estimated by the USGS from sales records (Ruddy et al. 2006), and these data were aggregated to obtain state-level N additions to farms. After subtracting the portion of fertilizer applied to major crops and grasslands (see sections on Major Crops and Grasslands for information on data sources), the remainder of the total fertilizer used on farms was assumed to be applied to non-major crops.
- A process-of-elimination approach was used to estimate manure N additions for non-major crops, because little information exists on application rates for these crops. The amount of manure N applied to major crops and grasslands was subtracted from total manure N available

<sup>12</sup> Commercial organic fertilizers include dried blood, tankage, compost, and other; dried manure and sewage sludge that are used as commercial fertilizer have been excluded to avoid double counting. The dried manure N is counted with the non-commercial manure applications, and sewage sludge is assumed to be applied only to grasslands.

for land application (see sections on Major Crops and Grasslands for information on data sources), and this difference was assumed to be applied to non-major crops.

- Non-manure, non-sewage-sludge commercial organic fertilizer additions were based on organic fertilizer consumption statistics, which were converted to units of N using average organic fertilizer N content (TVA 1991 through 1994; AAPFCO 1995 through 2008). Manure and sewage sludge components were subtracted from total commercial organic fertilizers to avoid double counting.
- Crop residue N was derived by combining amounts of above- and below-ground biomass, which were determined based on crop production yield statistics (USDA 1994, 1998, 2003, 2005, 2006, 2008, 2009a), dry matter fractions (IPCC 2006), linear equations to estimate above-ground biomass given dry matter crop yields from harvest (IPCC 2006), ratios of below-to-above-ground biomass (IPCC 2006), and N contents of the residues (IPCC 2006). Approximately 3 percent of the crop residues were burned and therefore did not contribute to soil N<sub>2</sub>O emissions, based on state inventory data (ILENR 1993, Oregon Department of Energy 1995, Noller 1996, Wisconsin Department of Natural Resources 1993, and Cibrowski 1996).

The total increase in soil mineral N from applied fertilizers and crop residues was multiplied by the IPCC (2006) default emission factor to derive an estimate of direct N<sub>2</sub>O emissions from non-major crop types.

### **Drainage and Cultivation of Organic Cropland Soils**

The IPCC (2006) Tier 1 methods were used to estimate direct N<sub>2</sub>O emissions due to drainage and cultivation of organic soils at a state scale. State-scale estimates of the total area of drained and cultivated organic soils were obtained from the *National Resources Inventory* (NRI) (USDA 2000a, as extracted by Eve 2001 and amended by Ogle 2002). Temperature data from Daly et al. (1994, 1998) were used to subdivide areas into temperate and tropical climates using the climate classification from IPCC (2006). Data were available for 1982, 1992 and 1997. To estimate annual emissions, the total temperate area was multiplied by the IPCC default emission factor for temperate regions, and the total sub-tropical area was multiplied by the average of

the IPCC default emission factors for temperate and tropical regions (IPCC 2006).

### **Direct N<sub>2</sub>O Emissions from Grassland Soils**

As with N<sub>2</sub>O from croplands, the Tier 3 process-based DAYCENT model and Tier 1 method described in IPCC (2006) were combined to estimate emissions from grasslands. Grasslands include pastures and rangelands used for grass forage production, where the primary use is livestock grazing. Rangelands are typically extensive areas of native grasslands that are not intensively managed, while pastures are often seeded grasslands, possibly following tree removal, which may or may not be improved with practices such as irrigation and interseeding legumes.

DAYCENT was used to simulate county-scale N<sub>2</sub>O emissions from non-federal grasslands resulting from manure deposited by livestock directly onto pastures and rangelands (i.e., PRP manure), N fixation from legume seeding, managed manure amendments (i.e., manure other than PRP manure), and synthetic fertilizer application. Other N inputs were simulated within the DAYCENT framework, including N input from mineralization due to decomposition of soil organic matter and N inputs from senesced grass litter, as well as asymbiotic fixation of N from the atmosphere. The simulations used the same weather, soil, and synthetic N fertilizer data as discussed under the section for Major Crop Types on Mineral Cropland Soils. Managed manure N amendments to grasslands were estimated from Edmonds et al. (2003) and adjusted for annual variation using data on the availability of managed manure N for application to soils, according to methods described in the Manure Management section (Section 6.2) and Annex 3.10. Biological N fixation is simulated within DAYCENT and therefore was not an input to the model.

Manure N deposition from grazing animals (i.e., PRP manure) was an input to the DAYCENT model (see Annex 3.10), and included approximately 91 percent of total PRP manure. The remainder of the PRP manure N excretions in each county was assumed to be excreted on federal grasslands (i.e., DAYCENT simulations were only conducted for non-federal grasslands), and the N<sub>2</sub>O emissions were estimated using the IPCC (2006) Tier 1 method with IPCC default emission factors. The amounts of PRP manure N applied on non-federal and federal grasslands in each county were based on the proportion of non-federal grassland area according

to data from the NRI (USDA 2000a), relative to the area of federal grasslands from the National Land Cover Dataset (Vogelman et al. 2001).

Sewage sludge was assumed to be applied on grasslands because of the heavy metal content and other pollutants in human waste that limit its use as an amendment to croplands. Sewage sludge application was estimated from data compiled by EPA (1993, 1999, 2003), McFarland (2001), and NEBRA (2007). Sewage sludge data on soil amendments on agricultural lands were only available at the national scale, and it was not possible to associate application with specific soil conditions and weather at the county scale. Therefore, DAYCENT could not be used to simulate the influence of sewage sludge amendments on N<sub>2</sub>O emissions from grassland soils, and consequently, emissions from sewage sludge were estimated using the IPCC (2006) Tier 1 method.

DAYCENT simulations produced per-area estimates of N<sub>2</sub>O emissions (g N<sub>2</sub>O-N/m<sup>2</sup>) for pasture and rangelands, which were multiplied by the reported pasture and rangeland areas in each county. Grassland area data were obtained from the NRI (USDA 2000a). The 1997 NRI area data for pastures and rangeland were aggregated to the county level to estimate the grassland areas for 1995 to 2007, and the 1992 NRI pasture and rangeland data were aggregated to the county level to estimate areas from 1990 to 1994. The county estimates were scaled to the 63 agricultural regions, and the national estimate was calculated by summing results across all regions. Tier 1 estimates of N<sub>2</sub>O emissions for the PRP manure N deposited on non-federal lands and applied sewage sludge N were produced by multiplying the N input by the appropriate emission factor.

### **Total Direct N<sub>2</sub>O Emissions from Cropland and Grassland Soils**

Annual direct emissions from major and non-major crops on mineral cropland soils, from drainage and cultivation of organic cropland soils, and from grassland soils were summed to obtain the total direct N<sub>2</sub>O emissions from agricultural soil management (see Table 6-15 and Table 6-16).

### **Indirect N<sub>2</sub>O Emissions from Managed Soils of all Land-Use Types**

This section describes the methods used for estimating indirect soil N<sub>2</sub>O emissions from all land-use types (i.e., croplands, grasslands, forest lands, and settlements). Indirect N<sub>2</sub>O emissions occur when mineral N made available through

anthropogenic activity is transported from the soil either in gaseous or aqueous forms and later converted into N<sub>2</sub>O. There are two pathways leading to indirect emissions. The first pathway results from volatilization of N as NO<sub>x</sub> and NH<sub>3</sub> following application of synthetic fertilizer, organic amendments (e.g., manure, sewage sludge), and deposition of PRP manure. N made available from mineralization of soil organic matter and asymbiotic fixation also contributes to volatilized N emissions. Volatilized N can be returned to soils through atmospheric deposition, and a portion of the deposited N is emitted to the atmosphere as N<sub>2</sub>O. The second pathway occurs via leaching and runoff of soil N (primarily in the form of NO<sub>3</sub><sup>-</sup>) that was made available through anthropogenic activity on managed lands, mineralization of soil organic matter, and asymbiotic fixation. The nitrate is subject to denitrification in water bodies, which leads to N<sub>2</sub>O emissions. Regardless of the eventual location of the indirect N<sub>2</sub>O emissions, the emissions are assigned to the original source of the N for reporting purposes, which here includes croplands, grasslands, forest lands, and settlements.

#### ***Indirect N<sub>2</sub>O Emissions from Atmospheric Deposition of Volatilized N from Managed Soils***

As in the direct emissions calculation, the Tier 3 DAYCENT model and IPCC (2006) Tier 1 methods were combined to estimate the amount of N that was transported from croplands, grasslands, forest lands, and settlements through volatilization and eventually emitted as N<sub>2</sub>O. DAYCENT was used to estimate N volatilization for land areas whose direct emissions were simulated with DAYCENT (i.e., major croplands and most grasslands). The N inputs included are the same as described for direct N<sub>2</sub>O emissions in the sections on major crops and grasslands. N volatilization for all other areas was estimated using the Tier 1 method and default IPCC fractions for N subject to volatilization (i.e., N inputs on non-major croplands, PRP manure N excretion on federal grasslands, sewage sludge application on grasslands). The Tier 1 method and default fractions were also used to estimate N subject to volatilization from N inputs on settlements and forest lands (see the Land Use, Land-Use Change, and Forestry chapter). With both the DAYCENT and Tier 1 approaches, the IPCC (2006) default emission factor was used to estimate indirect N<sub>2</sub>O emissions associated with the amount of volatilized N (Table 6-18).

#### ***Indirect N<sub>2</sub>O Emissions from Leaching/Runoff***

As with the calculations of indirect emissions from volatilized N, the Tier 3 DAYCENT model and IPCC (2006) Tier 1 method were combined to estimate the amount of N that was transported from croplands, grasslands, forest lands, and settlements through leaching and surface runoff into water bodies, and eventually emitted as N<sub>2</sub>O. DAYCENT was used to simulate the amount of N transported from lands used to produce major crops and most grasslands. N transport from all other areas was estimated using the Tier 1 method and the IPCC (2006) default factor for the proportion of N subject to leaching and runoff. This N transport estimate includes N applications on croplands that produce non-major crops, sewage sludge amendments on grasslands, PRP manure N excreted on federal grasslands, and N inputs on settlements and forest lands. For both the DAYCENT and IPCC (2006) Tier 1 methods, nitrate leaching was assumed to be an insignificant source of indirect N<sub>2</sub>O in cropland and grassland systems in arid regions as discussed in IPCC (2006). In the United States, the threshold for significant nitrate leaching is based on the potential evapotranspiration (PET) and rainfall amount, similar to IPCC (2006), and is assumed to be negligible in regions where the amount of precipitation plus irrigation does not exceed 80 percent of PET. With both the DAYCENT and Tier 1 approaches, the IPCC (2006) default emission factor was used to estimate indirect N<sub>2</sub>O emissions associated with N losses through leaching and runoff (Table 6-18).

### **Uncertainty and Time-Series Consistency**

Uncertainty was estimated for each of the following five components of N<sub>2</sub>O emissions from agricultural soil management: (1) direct emissions calculated by DAYCENT; (2) the components of indirect emissions (N volatilized and leached or runoff) calculated by DAYCENT; (3) direct emissions calculated with the IPCC (2006) Tier 1 method; (4) the components of indirect emissions (N volatilized and leached or runoff) calculated with the IPCC (2006) Tier 1 method; and (5) indirect emissions calculated with the IPCC (2006) Tier 1 method. Uncertainty in direct emissions, which account for the majority of N<sub>2</sub>O emissions from agricultural management, as well as the components of indirect emissions calculated by DAYCENT were estimated with a Monte Carlo Analysis, addressing uncertainties in model inputs and

**Table 6-19: Quantitative Uncertainty Estimates of N<sub>2</sub>O Emissions from Agricultural Soil Management in 2008 (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2008 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate (Tg CO <sub>2</sub> Eq.)			
			Lower Bound	Upper Bound	Lower Bound (%)	Upper Bound (%)
Direct Soil N <sub>2</sub> O Emissions	N <sub>2</sub> O	170.4	129.7	278.4	-24%	+63%
Indirect Soil N <sub>2</sub> O Emissions	N <sub>2</sub> O	45.5	23.8	110.2	-48%	+142%

Note: Due to lack of data, uncertainties in areas for major crops, managed manure N production, PRP manure N production, other organic fertilizer amendments, indirect losses of N in the DAYCENT simulations, and sewage sludge amendments to soils are currently treated as certain; these sources of uncertainty will be included in future inventories.

structure (i.e., algorithms and parameterization) (Del Grosso et al., 2009). Uncertainties in direct emissions calculated with the IPCC (2006) Tier 1 method, the proportion of volatilization and leaching or runoff estimated with the IPCC (2006) Tier 1 method, and indirect N<sub>2</sub>O emissions were estimated with a simple error propagation approach (IPCC 2006). Additional details on the uncertainty methods are provided in Annex 3.11.

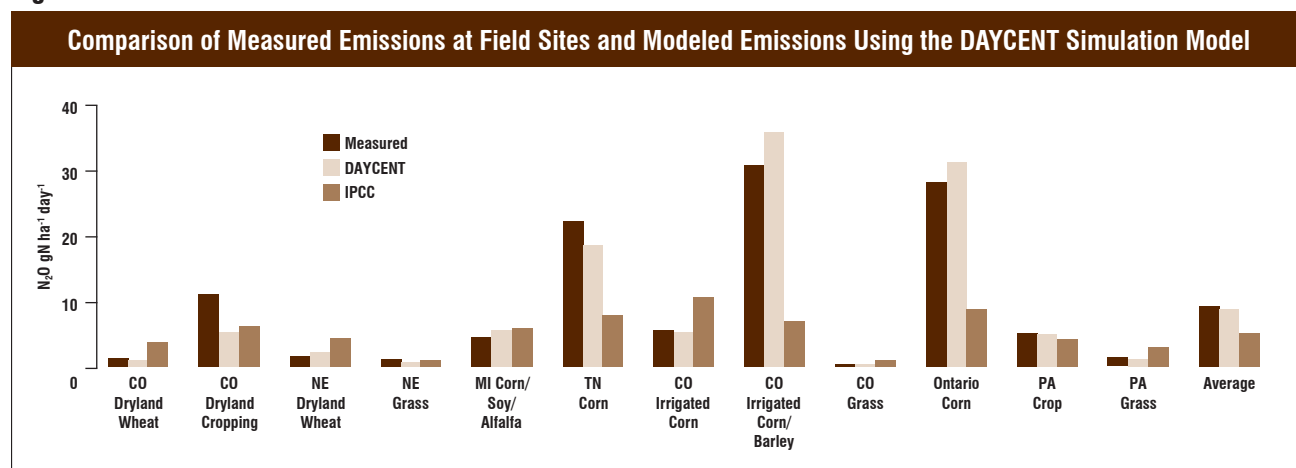
Uncertainties from the Tier 1 and Tier 3 (i.e., DAYCENT) estimates were combined using simple error propagation (IPCC 2006), and the results are summarized in Table 6-19. Agricultural direct soil N<sub>2</sub>O emissions in 2008 were estimated to be between 129.7 and 278.4 Tg CO<sub>2</sub> Eq. at a 95 percent confidence level. This indicates a range of 24 percent below and 63 percent above the 2008 emission estimate of 170.4 Tg CO<sub>2</sub> Eq. The indirect soil N<sub>2</sub>O emissions in 2008 were estimated to range from 23.6 to 110.4 Tg CO<sub>2</sub> Eq. at a 95 percent confidence level, indicating an uncertainty of 48 percent below and 142 percent above the 2008 emission estimate of 45.5 Tg CO<sub>2</sub> Eq.

Methodological recalculations were applied to the entire time series to ensure time-series consistency from 1990 through 2008. Details on the emission trends through time are described in more detail in the Methodology section, above.

### QA/QC and Verification

For quality control, DAYCENT results for N<sub>2</sub>O emissions and NO<sub>3</sub><sup>-</sup> leaching were compared with field data representing various cropped/grazed systems, soil types, and climate patterns (Del Grosso et al. 2005, Del Grosso et al. 2008), and further evaluated by comparing to emission estimates produced using the IPCC (2006) Tier 1 method for the same sites. Nitrous oxide measurement data were available for 11 sites in the United States and one in Canada, representing 30 different combinations of fertilizer treatments and cultivation practices. DAYCENT estimates of N<sub>2</sub>O emissions were closer to measured values at all sites except for Colorado dryland cropping (Figure 6-7). In general, IPCC Tier 1 methodology tends to over-estimate emissions when observed values are low and under-estimate emissions when

**Figure 6-7**



observed values are high, while DAYCENT estimates are less biased. This is not surprising because DAYCENT accounts for site-level factors (weather, soil type) that influence N<sub>2</sub>O emissions. Nitrate leaching data were available for three sites in the United States representing nine different combinations of fertilizer amendments. Linear regressions of simulated vs. observed emission and leaching data yielded correlation coefficients of 0.89 and 0.94 for annual N<sub>2</sub>O emissions and NO<sub>3</sub><sup>-</sup> leaching, respectively. This comparison demonstrates that DAYCENT provides relatively high predictive capability for N<sub>2</sub>O emissions and NO<sub>3</sub><sup>-</sup> leaching, and is an improvement over the IPCC Tier 1 method (see additional information in Annex 3.11).

Spreadsheets containing input data and probability distribution functions required for DAYCENT simulations of major croplands and grasslands and unit conversion factors were checked, as were the program scripts that were used to run the Monte Carlo uncertainty analysis. Several errors were identified following re-organization of the calculation spreadsheets, and corrective actions have been taken. In particular, some of the links between spreadsheets were missing or needed to be modified. Spreadsheets containing input data, emission factors, and calculations required for the Tier 1 approach were checked and no errors were found.

## Recalculations Discussion

Several revisions were made in the Agricultural Soil Management Section for the current Inventory.

First, NO<sub>3</sub><sup>-</sup> leaching to groundwater and flow into streams does not occur in more arid regions according to the IPCC (2006). In the previous Inventory, it was assumed that NO<sub>3</sub><sup>-</sup> leaching was not significant in soils with precipitation input that did not exceed potential evapotranspiration, except in soils that were irrigated. Quality control measures revealed that NO<sub>3</sub><sup>-</sup> leaching was under-estimated using this criterion; for example, a large portion of Iowa and some counties in other parts of the central and eastern United States were assumed to have no leaching during some years with this criterion. Several studies have shown that significant NO<sub>3</sub><sup>-</sup> leaching occurs annually in these regions (Jaynes et al., 2001; David et al., 2009) so the threshold was revised to better reflect U.S. conditions. Specifically, the criterion was modified so that NO<sub>3</sub><sup>-</sup> leaching would be estimated and lead to indirect N<sub>2</sub>O emissions for soils with a precipitation input that was equal to or greater than 80 percent of the potential

evapotranspiration, in addition to irrigated soils. Second, in the previous Inventory, the leaching criterion was not applied for lands estimated using Tier 1 methodology. For this year's Inventory, NO<sub>3</sub><sup>-</sup> leaching was assumed to occur in states where the area weighted mean precipitation plus irrigation input was equal to or greater than 80 percent of the potential evapotranspiration.

Third, the N<sub>2</sub>O emission factor for PRP manure associated with horses, sheep and goats was revised to 0.01 in accordance with guidance from IPCC (2006). Previously the emission factor of 0.02, which is for manure from cattle, swine, and poultry, had been used for all livestock. Fourth, the methodology to calculate livestock manure N was changed such that total manure N added to soils increased by approximately 5 percent (see Chapter 6, Section 6.2 "Manure Management" for details).

The recalculations increased emissions from agricultural soil management by about 2 percent on average over the time series relative to the previous Inventory.

## Planned Improvements

A key improvement is underway for Agricultural Soil Management to incorporate more land-use survey data from the NRI (USDA 2000a) into the DAYCENT simulation analysis, beyond the area estimates for rangeland and pasture that are currently used to estimate emissions from grasslands. NRI has a record of land-use activities since 1979 for all U.S. agricultural land, which is estimated at about 386 Mha. NASS is used as the basis for land-use records in the current Inventory, and there are three major disadvantages to this. First, most crops are grown in rotation with other crops (e.g., corn-soybean), but NASS data provide no information regarding rotation histories. In contrast, NRI is designed to track rotation histories, which is important because emissions from any particular year can be influenced by the crop that was grown the previous year. Second, NASS does not conduct a complete survey of cropland area each year, leading to gaps in the land base. NRI provides a complete history of cropland areas for four out of every five years from 1979 to 1997, and then every year after 1998. Third, the current Inventory based on NASS does not quantify the influence of land-use change on emissions, which can be addressed using the NRI survey records. NRI also provides additional information on pasture land management that can be incorporated into the analysis (particularly the use of irrigation). Using NRI data

will also make the Agricultural Soil Management methods more consistent with the methods used to estimate C stock changes for agricultural soils. The structure of model input files that contain land management data will need to be extensively revised to facilitate use of the annualized NRI data. This improvement is planned to take place over the next several years.

Other planned improvements are minor but will lead to more accurate estimates, including updating DAYMET weather data for more recent years following the release of new data and using a rice-crop-specific emission factor for N amendments to rice areas.

## 6.5. Field Burning of Agricultural Residues (IPCC Source Category 4F)

Farming activities produce large quantities of agricultural crop residues, and farmers use or dispose of these residues in a variety of ways. For example, agricultural residues can be left on or plowed into the field; composted and then applied to soils; landfilled; or burned in the field. Alternatively, they

can be collected and used as fuel, animal bedding material, supplemental animal feed, or construction material. Field burning of crop residues is not considered a net source of CO<sub>2</sub>, because the C released to the atmosphere as CO<sub>2</sub> during burning is assumed to be reabsorbed during the next growing season. Crop residue burning is, however, a net source of CH<sub>4</sub>, N<sub>2</sub>O, CO, and NO<sub>x</sub>, which are released during combustion.

Field burning is not a common method of agricultural residue disposal in the United States. The primary crop types whose residues are typically burned in the United States are wheat, rice, sugarcane, corn, barley, soybeans, and peanuts. It is assumed that 3 percent of the residue for each of these crops is burned each year, except for rice and sugarcane.<sup>13</sup> In 2008, CH<sub>4</sub> and N<sub>2</sub>O emissions from field burning were 1.0 Tg CO<sub>2</sub> Eq. (46 Gg) and 0.5 Tg CO<sub>2</sub> Eq. (2 Gg), respectively. Annual emissions from this source over the period 1990 to 2008 have remained relatively constant, averaging approximately 0.9 Tg CO<sub>2</sub> Eq. (41 Gg) of CH<sub>4</sub> and 0.5 Tg CO<sub>2</sub> Eq. (1 Gg) of N<sub>2</sub>O (see Table 6-20 and Table 6-21).

**Table 6-20: CH<sub>4</sub> and N<sub>2</sub>O Emissions from Field Burning of Agricultural Residues (Tg CO<sub>2</sub> Eq.)**

Gas/Crop Type	1990	1995	2000	2005	2006	2007	2008
<b>CH<sub>4</sub></b>	<b>0.8</b>	<b>0.7</b>	<b>0.9</b>	<b>0.9</b>	<b>0.9</b>	<b>1.0</b>	<b>1.0</b>
Wheat	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Rice	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Sugarcane	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Corn	0.3	0.3	0.4	0.4	0.4	0.5	0.4
Barley	+	+	+	+	+	+	+
Soybeans	0.1	0.2	0.2	0.2	0.2	0.2	0.2
Peanuts	+	+	+	+	+	+	+
<b>N<sub>2</sub>O</b>	<b>0.4</b>	<b>0.4</b>	<b>0.5</b>	<b>0.5</b>	<b>0.5</b>	<b>0.5</b>	<b>0.5</b>
Wheat	+	+	+	+	+	+	+
Rice	+	+	+	+	+	+	+
Sugarcane	+	+	+	+	+	+	+
Corn	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Barley	+	+	+	+	+	+	+
Soybeans	0.2	0.2	0.3	0.3	0.3	0.3	0.3
Peanuts	+	+	+	+	+	+	+
<b>Total</b>	<b>1.2</b>	<b>1.1</b>	<b>1.4</b>	<b>1.5</b>	<b>1.4</b>	<b>1.5</b>	<b>1.5</b>

+ Less than 0.05 Tg CO<sub>2</sub> Eq.  
Note: Totals may not sum due to independent rounding.

<sup>13</sup> The fractions of rice straw and sugarcane residue burned each year are significantly higher than those for other crops (see “Methodology” discussion below).



**Table 6-21: CH<sub>4</sub>, N<sub>2</sub>O, CO, and NO<sub>x</sub> Emissions from Field Burning of Agricultural Residues (Gg)**

Gas/Crop Type	1990	1995	2000	2005	2006	2007	2008
<b>CH<sub>4</sub></b>	<b>36</b>	<b>35</b>	<b>42</b>	<b>44</b>	<b>43</b>	<b>46</b>	<b>46</b>
Wheat	7	5	5	5	4	5	6
Rice	4	4	4	5	4	4	3
Sugarcane	4	5	6	4	5	5	5
Corn	13	13	17	19	18	22	21
Barley	1	1	1	+	+	+	+
Soybeans	7	8	10	11	12	10	11
Peanuts	+	+	+	+	+	+	+
<b>N<sub>2</sub>O</b>	<b>1</b>	<b>1</b>	<b>2</b>	<b>2</b>	<b>2</b>	<b>2</b>	<b>2</b>
Wheat	+	+	+	+	+	+	+
Rice	+	+	+	+	+	+	+
Sugarcane	+	+	+	+	+	+	+
Corn	+	+	+	+	+	+	+
Barley	+	+	+	+	+	+	+
Soybeans	1	1	1	1	1	1	1
Peanuts	+	+	+	+	+	+	+
<b>CO</b>	<b>766</b>	<b>745</b>	<b>888</b>	<b>930</b>	<b>905</b>	<b>960</b>	<b>970</b>
<b>NO<sub>x</sub></b>	<b>30</b>	<b>30</b>	<b>37</b>	<b>40</b>	<b>40</b>	<b>38</b>	<b>40</b>

+ Less than 0.5 Gg  
 Note: Totals may not sum due to independent rounding.

## Methodology

The Tier 2 methodology used for estimating greenhouse gas emissions from field burning of agricultural residues in the United States is consistent with IPCC (2006) (for more details, see Box 6-2). In order to estimate the amounts of C and nitrogen (N) released during burning, the following equation was used:<sup>14</sup>

$$\begin{aligned} \text{C or N released} &= \Sigma \text{ over all crop types} \\ &(\text{Crop Production} \times \text{Residue/Crop Ratio} \times \\ &\text{Dry Matter Fraction} \times \text{Fraction of Residue Burned} \times \\ &\text{Burning Efficiency} \times \text{Combustion Efficiency} \times \\ &\text{Fraction of C or N}) \end{aligned}$$

where,

Crop Production	=	Annual production of crop in Gg
Residue/Crop Ratio	=	Amount of residue produced per unit of crop production
Fraction of Residue Burned	=	Amount of residue that is burned per unit of total residue

Dry Matter Fraction	=	Amount of dry matter per unit of biomass
Fraction of C or N	=	Amount of C or N per unit of dry matter
Burning Efficiency	=	The proportion of prefire fuel biomass consumed <sup>15</sup>
Combustion Efficiency	=	The proportion of C or N released with respect to the total amount of C or N available in the burned material, respectively <sup>15</sup>

The amount C or N released was used in the following equation to determine the CH<sub>4</sub>, CO, N<sub>2</sub>O and NO<sub>x</sub> emissions from the field burning of agricultural residues:

$$\begin{aligned} \text{CH}_4 \text{ and CO, or N}_2\text{O and NO}_x \text{ Emissions from Field} \\ \text{Burning of Agricultural Residues} &= (\text{C or N Released}) \times \\ &(\text{Emissions Ratio for C or N}) \times (\text{Conversion Factor}) \end{aligned}$$

where,

Emissions Ratio	=	g CH <sub>4</sub> -C or CO-C/g C released, or g N <sub>2</sub> O-N or NO <sub>x</sub> -N/g N released
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<sup>14</sup>As is explained later in this section, the fraction of rice residues burned varies among states, so these equations were applied at the state level for rice. These equations were applied at the national level for all other crop types.

<sup>15</sup>In IPCC/UNEP/OECD/IEA (1997), the equation for C or N released contains the variable 'fraction oxidized in burning.' This variable is equivalent to (burning efficiency × combustion efficiency).

Conversion Factor = conversion, by molecular weight ratio, of CH<sub>4</sub>-C to C (16/12), or CO-C to C (28/12), or N<sub>2</sub>O-N to N (44/28), or NO<sub>x</sub>-N to N (30/14)

The types of crop residues burned in the United States were determined from various state-level greenhouse gas emission inventories (ILENR 1993, Oregon Department of Energy 1995, Wisconsin Department of Natural Resources 1993) and publications on agricultural burning in the United States (Jenkins et al. 1992, Turn et al. 1997, EPA 1992).

Crop production data for all crops except rice in Florida and Oklahoma were taken from the USDA's Field Crops, Final Estimates 1987–1992, 1992–1997, 1997–2002 (USDA 1994, 1998, 2003), and Crop Production Summary (USDA 2005 through 2009). Rice production data for Florida and Oklahoma, which are not collected by USDA, were estimated separately. Average primary and ratoon crop yields for Florida (Schueneman and Deren 2002) were applied to Florida acreages (Schueneman 1999b, 2001; Deren 2002; Kirstein 2003, 2004; Cantens 2004, 2005; Gonzalez 2007a, 2008, 2009), and crop yields for Arkansas (USDA 1994, 1998, 2003, 2005 through 2009) were applied to Oklahoma acreages<sup>16</sup> (Lee 2003 through 2006; Anderson 2008, 2009). The production data for the crop types whose residues are burned are presented in Table 6-22.

The percentage of crop residue burned was assumed to be 3 percent for all crops in all years, except rice and sugarcane, based on state inventory data (ILENR 1993, Oregon Department of Energy 1995, Noller 1996, Wisconsin Department of Natural Resources 1993, and Cibrowski 1996). Estimates of the percentage of rice residue burned were derived from state-level estimates of the percentage of rice area burned each year, which were multiplied by state-level annual rice production statistics. The annual percentages of rice area burned in each state were obtained from agricultural extension agents in each state and reports of the California Air Resources Board (Anonymous 2006; Bollich 2000; Buehring 2009; California Air Resources Board 1999, 2001; Cantens 2005; Deren 2002; Fife 1999; Guethle 2007, 2008, 2009; Klosterboer 1999a, 1999b, 2000 through 2003; Lancero 2006 through 2009; Lee 2005 through

<sup>16</sup> Rice production yield data are not available for Oklahoma, so the Arkansas values are used as a proxy.

## Box 6-2: Comparison of Tier 2 U.S. Inventory Approach and IPCC (2006) Default Approach

This Inventory calculates emissions from Burning of Agricultural Residues using a Tier 2 methodology that is based on IPCC/UNEP/OECD/IEA (1997) and incorporates crop- and country-specific emission factors and variables. The equation used in this Inventory varies slightly in form from the one presented in the IPCC (2006) guidelines, but both equations rely on the same underlying variables. The IPCC (2006) equation was developed to be broadly applicable to all types of biomass burning, and, thus, is not specific to agricultural residues. IPCC (2006) default factors are provided only for four crops (wheat, corn, rice, and sugarcane), while this Inventory analyzes emissions from seven crops. A comparison of the methods and factors used in (1) the current Inventory and (2) the default IPCC (2006) approach was undertaken to determine the magnitude of the difference in overall estimates resulting from the two approaches. Since the default IPCC (2006) approach calls for area burned data that are currently unavailable for the United States, estimates of area burned were developed using USDA data on area harvested for each crop multiplied by the estimated fraction of residue burned for that crop (see Table 6-24).

The IPCC (2006) default approach resulted in 20 percent higher emissions of CH<sub>4</sub> and 42 percent higher emissions of N<sub>2</sub>O than the current estimates in this Inventory. It is reasonable to maintain the current methodology, since the IPCC (2006) defaults are only available for four crops and are worldwide average estimates, while current inventory estimates are based on U.S.-specific, crop-specific, published data.

2007; Lindberg 2002 through 2005; Linscombe 1999a, 1999b, 2001 through 2009; Najita 2000, 2001; Sacramento Valley Basinwide Air Pollution Control Council 2005, 2007; Schueneman 1999a, 1999b, 2001; Stansel 2004, 2005; Street 2001 through 2003; Texas Agricultural Experiment Station 2006 through 2009; Walker 2004 through 2008; Wilson 2003 through 2007, 2009) (see Table 6-23). The estimates provided for Florida remained constant over the entire 1990 through 2008 period. While the estimates for all other states varied over the time series, estimates for Missouri remained constant through 2005, dropped in 2006, and remained constant near the 2006 value in 2007 and 2008. For California, the annual percentages of rice area burned in the Sacramento Valley are assumed to be representative of burning in the entire state, because the Sacramento Valley accounts for over 95 percent of the rice acreage in California (Fife 1999). These values generally declined between 1990 and 2008 because of a legislated reduction in rice straw burning (Lindberg 2002),

**Table 6-22: Agricultural Crop Production (Gg of Product)**

Crop	1990	1995	2000	2005	2006	2007	2008
Wheat	74,292	59,404	60,641	57,280	49,316	55,821	68,026
Rice	7,114	7,947	8,705	10,150	8,813	9,033	9,272
Sugarcane	25,525	27,922	32,762	24,137	26,820	27,187	27,842
Corn <sup>a</sup>	201,534	187,970	251,854	282,311	267,598	331,177	307,386
Barley	9,192	7,824	6,919	4,613	3,923	4,575	5,214
Soybeans	52,416	59,174	75,055	83,368	86,770	72,859	80,536
Peanuts	1,635	1,570	1,481	2,209	1,571	1,666	2,335

<sup>a</sup> Corn for grain (i.e., excludes corn for silage).

**Table 6-23: Percent of Rice Area Burned by State**

State	1990	1995	2000	2005	2006	2007	2008
Arkansas	13%	13%	13%	22%	27%	20%	20%
California	75%	59%	27%	16%	10%	16%	11%
Florida <sup>a</sup>	0%	0%	0%	0%	0%	0%	0%
Louisiana	6%	6%	5%	3%	5%	5%	5%
Mississippi	10%	10%	40%	23%	25%	24%	25%
Missouri	18%	18%	18%	18%	3%	3%	3%
Oklahoma	90%	90%	90%	94%	0%	0%	91%
Texas	1%	1%	0%	0%	0%	0%	0%

<sup>a</sup> Although rice is cultivated in Florida, crop residue burning is illegal.

**Table 6-24: Key Assumptions for Estimating Emissions from Field Burning of Agricultural Residues**

Crop	Residue/ Crop Ratio	Fraction of Residue Burned	Dry Matter Fraction	C Fraction	N Fraction	Burning Efficiency	Combustion Efficiency
Wheat	1.3	0.03	0.93	0.4428	0.0062	0.93	0.88
Rice	1.4	Variable	0.91	0.3806	0.0072	0.93	0.88
Sugarcane	0.2	0.95	0.62	0.4235	0.0040	0.81	0.68
Corn	1.0	0.03	0.91	0.4478	0.0058	0.93	0.88
Barley	1.2	0.03	0.93	0.4485	0.0077	0.93	0.88
Soybeans	2.1	0.03	0.87	0.4500	0.0230	0.93	0.88
Peanuts	1.0	0.03	0.86	0.4500	0.0106	0.93	0.88

although there was a slight increase from 2004 to 2005 and from 2006 to 2007 (see Table 6-23). Estimates for percent of sugarcane burned were obtained from Ashman (2008).

All residue/crop product mass ratios except sugarcane were obtained from Strehler and Stützle (1987). The datum for sugarcane is from Kinoshita (1988). Residue dry matter contents for all crops except soybeans, peanuts were obtained from Turn et al. (1997). Soybean dry matter content was obtained from Strehler and Stützle (1987). Peanut dry matter content was obtained through personal communications with Jen Ketzis (1999), who accessed Cornell University's Department of Animal Science's computer model, Cornell

Net Carbohydrate and Protein System. The residue C contents and N contents for all crops except soybeans and peanuts are from Turn et al. (1997). The residue C content for soybeans and peanuts is the IPCC default (IPCC/UNEP/OECD/IEA 1997). The N content of soybeans is from Barnard and Kristoferson (1985). The N content of peanuts is from Ketzis (1999). These data are listed in Table 6-24. The burning efficiency was assumed to be 93 percent, and the combustion efficiency was assumed to be 88 percent, for all crop types, except sugarcane (EPA 1994). For sugarcane, the burning efficiency was assumed to be 81 percent (Kinoshita

**Table 6-25: Greenhouse Gas Emission Ratios and Conversion Factors**

Gas	Emission Ratio	Conversion Factor
CH <sub>4</sub> :C	0.005 <sup>a</sup>	16/12
CO:C	0.060 <sup>a</sup>	28/12
N <sub>2</sub> O:N	0.007 <sup>b</sup>	44/28
NO <sub>x</sub> :N	0.121 <sup>b</sup>	30/14

<sup>a</sup> Mass of C compound released (units of C) relative to mass of total C released from burning (units of C).  
<sup>b</sup> Mass of N compound released (units of N) relative to mass of total N released from burning (units of N).

1988) and the combustion efficiency was assumed to be 68 percent (Turn et al. 1997). Emission ratios and conversion factors for all gases (see Table 6-25) were taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997).

### Uncertainty and Time-Series Consistency

A significant source of uncertainty in the calculation of non-CO<sub>2</sub> emissions from field burning of agricultural residues is in the estimates of the fraction of residue of each crop type burned each year. Data on the fraction burned, as well as the gross amount of residue burned each year, are not collected at either the national or state level. In addition, burning practices are highly variable among crops and among states. The fractions of residue burned used in these calculations were based upon information collected by state agencies and in published literature. Based on expert judgment, uncertainty in the fraction of crop residue burned ranged from zero to 100 percent, depending on the state and crop type.

The results of the Tier 2 Monte Carlo uncertainty analysis are summarized in Table 6-26. CH<sub>4</sub> emissions from field burning of agricultural residues in 2008 were

estimated to be between 0.3 and 1.8 Tg CO<sub>2</sub> Eq. at a 95 percent confidence level. This indicates a range of 68 percent below and 88 percent above the 2008 emission estimate of 1.0 Tg CO<sub>2</sub> Eq. Also at the 95 percent confidence level, N<sub>2</sub>O emissions were estimated to be between 0.2 and 1.0 Tg CO<sub>2</sub> Eq. (or approximately 71 percent below and 83 percent above the 2008 emission estimate of 0.5 Tg CO<sub>2</sub> Eq.).

Methodological recalculations were applied to the entire time series to ensure time-series consistency from 1990 through 2008. Details on the emission trends through time are described in more detail in the Methodology section, above.

### QA/WC and Verification

A source-specific QA/QC plan for field burning of agricultural residues was implemented. This effort included a Tier 1 analysis, as well as portions of a Tier 2 analysis. The Tier 2 procedures focused on comparing trends across years, states, and crops to attempt to identify any outliers or inconsistencies. No problems were found.

### Recalculation Discussion

The crop production data for 2007 were updated using data from USDA (2009). In addition, sugarcane-specific information for residue/crop ratio, fraction residue burned, dry matter fraction, burning efficiency, and combustion efficiency were obtained. Although some of these factors are specific to Hawaii, it was felt that they better represented the common practice in the United States than the factors previously in use. These changes resulted in an average increase in the CH<sub>4</sub> emission estimates of 11 percent across the time series, and an average increase in the N<sub>2</sub>O emission estimate of 4 percent across the time series, relative to the previous Inventory.

**Table 6-26: Tier 2 Quantitative Uncertainty Estimates for CH<sub>4</sub> and N<sub>2</sub>O Emissions from Field Burning of Agricultural Residues (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2008 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup> (Tg CO <sub>2</sub> Eq.) (%)			
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Field Burning of Agricultural Residues	CH <sub>4</sub>	1.0	0.3	1.8	-68%	+88%
Field Burning of Agricultural Residues	N <sub>2</sub> O	0.5	0.2	1.0	-71%	+83%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

## **Planned Improvements**

The estimated 3 percent of crop residue burned for all crops, except rice and sugarcane, is based on data gathered from several state greenhouse gas inventories. This fraction is the most statistically significant input to the emissions equation, and an important area for future improvement. More crop- and state-specific information on the fraction burned will be investigated by literature review and/or by contacting state departments of agriculture.

Preliminary research on agricultural burning in the United States indicates that residues from several additional crop types (e.g., grass for seed, blueberries, and fruit and nut trees) are burned. Whether sufficient information exists for inclusion of these additional crop types in future Inventories is being investigated. The extent of recent state crop-burning regulations is also being investigated.