

4. Industrial Processes

Greenhouse 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 (CO₂), methane (CH₄), and nitrous oxide (N₂O). 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, CO₂ 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).

Figure 4-1: 2009 Industrial Processes Chapter Greenhouse Gas Sources

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 (SF₆). 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; SF₆ is the most potent greenhouse gas the Intergovernmental Panel on Climate Change (IPCC) has evaluated. Usage of HFCs is growing rapidly since 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, and SF₆ 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.

In 2009, industrial processes generated emissions of 282.9 teragrams of CO₂ equivalent (Tg CO₂ Eq.), or 4 percent of total U.S. greenhouse gas emissions. CO₂ emissions from all industrial processes were 119.0 Tg CO₂ Eq. (119,010 Gg) in 2009, or 2 percent of total U.S. CO₂ emissions. CH₄ emissions from industrial processes resulted in emissions of approximately 1.2 Tg CO₂ Eq. (58 Gg) in 2009, which was less than 1 percent of U.S. CH₄ emissions. N₂O emissions from adipic acid and nitric acid production were 16.5 Tg CO₂ Eq. (53 Gg) in 2009, or 6 percent of total U.S. N₂O emissions. In 2009 combined emissions of HFCs, PFCs and SF₆ totaled 146.1 Tg CO₂ Eq. Despite the significant increase in HFC emissions associated with increased usage of ODSs, total emissions from industrial processes in 2009 were less than 1990 for the first time since 1994. This decrease is primarily due to significant reductions in emissions from iron and steel production, metallurgical coke production, ammonia production and urea consumption, adipic acid production, HCFC-22 production, aluminum production and cement production.

Table 4-1 summarizes emissions for the Industrial Processes chapter in Tg CO₂ 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 SF₆.

Table 4-1: Emissions from Industrial Processes (Tg CO₂ Eq.)

Gas/Source	1990	2000	2005	2006	2007	2008	2009
CO₂	188.4	184.9	165.4	169.9	172.6	159.5	119.0
Iron and Steel Production and Metallurgical Coke Production	99.5	85.9	65.9	68.8	71.0	66.0	41.9
<i>Iron and Steel Production</i>	97.1	83.7	63.9	66.9	69.0	63.7	40.9
<i>Metallurgical Coke Production</i>	2.5	2.2	2.0	1.9	2.1	2.3	1.0
Cement Production	33.3	40.4	45.2	45.8	44.5	40.5	29.0
Ammonia Production & Urea Consumption	16.8	16.4	12.8	12.3	14.0	11.9	11.8

Lime Production	11.5	14.1	14.4	15.1	14.6	14.3	11.2
Limestone and Dolomite Use	5.1	5.1	6.8	8.0	7.7	6.3	7.6
Soda Ash Production and Consumption	4.1	4.2	4.2	4.2	4.1	4.1	4.3
Aluminum Production	6.8	6.1	4.1	3.8	4.3	4.5	3.0
Petrochemical Production	3.3	4.5	4.2	3.8	3.9	3.4	2.7
Carbon Dioxide Consumption	1.4	1.4	1.3	1.7	1.9	1.8	1.8
Titanium Dioxide Production	1.2	1.8	1.8	1.8	1.9	1.8	1.5
Ferroalloy Production	2.2	1.9	1.4	1.5	1.6	1.6	1.5
Phosphoric Acid Production	1.5	1.4	1.4	1.2	1.2	1.2	1.0
Zinc Production	0.7	1.0	1.1	1.1	1.1	1.2	1.0
Lead Production	0.5	0.6	0.6	0.6	0.6	0.6	0.5
Silicon Carbide Production and Consumption	0.4	0.2	0.2	0.2	0.2	0.2	0.1
CH₄	1.9	2.2	1.8	1.7	1.7	1.6	1.2
Petrochemical Production	0.9	1.2	1.1	1.0	1.0	0.9	0.8
Iron and Steel Production and Metallurgical Coke Production	1.0	0.9	0.7	0.7	0.7	0.6	0.4
<i>Iron and Steel Production</i>	<i>1.0</i>	<i>0.9</i>	<i>0.7</i>	<i>0.7</i>	<i>0.7</i>	<i>0.6</i>	<i>0.4</i>
<i>Metallurgical Coke Production</i>	+	+	+	+	+	+	+
Ferroalloy Production	+	+	+	+	+	+	+
Silicon Carbide Production and Consumption	+	+	+	+	+	+	+
N₂O	33.5	24.9	21.5	20.5	22.9	18.5	16.5
Nitric Acid Production	17.7	19.4	16.5	16.2	19.2	16.4	14.6
Adipic Acid Production	15.8	5.5	5.0	4.3	3.7	2.0	1.9
HFCs	36.9	103.2	120.2	123.5	129.5	129.4	125.7
Substitution of Ozone Depleting Substances ^a	0.3	74.3	104.2	109.4	112.3	115.5	120.0
HCFC-22 Production	36.4	28.6	15.8	13.8	17.0	13.6	5.4
Semiconductor Manufacturing HFCs	0.2	0.3	0.2	0.3	0.3	0.3	0.3
PFCs	20.8	13.5	6.2	6.0	7.5	6.7	5.6
Aluminum Production	18.5	8.6	3.0	2.5	3.8	2.7	1.6
Semiconductor Manufacturing PFCs	2.2	4.9	3.2	3.5	3.7	4.0	4.0
SF₆	34.4	20.1	19.0	17.9	16.7	16.1	14.8
Electrical Transmission and Distribution	28.4	16.0	15.1	14.1	13.2	13.3	12.8
Semiconductor Manufacturing SF ₆	0.5	1.1	1.0	1.0	0.8	0.9	1.0
Magnesium Production and Processing	5.4	3.0	2.9	2.9	2.6	1.9	1.1
Total	315.8	348.8	334.1	339.4	350.9	331.7	282.9

+ Does not exceed 0.05 Tg CO₂ Eq.

Note: Totals may not sum due to independent rounding.

^a Small amounts of PFC emissions also result from this source.

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

Gas/Source	1990	2000	2005	2006	2007	2008	2009
CO₂	188,431	184,919	165,384	169,870	172,592	159,470	119,010
Iron and Steel Production and Metallurgical Coke Production	99,528	85,935	65,925	68,772	71,045	66,015	41,871

<i>Iron and Steel</i>								
<i>Production</i>	97,058	83,740	63,882	66,852	68,991	63,682	40,914	
<i>Metallurgical Coke</i>								
<i>Production</i>	2,470	2,195	2,043	1,919	2,054	2,334	956	
Cement Production	33,278	40,405	45,197	45,792	44,538	40,531	29,018	
Ammonia Production & Urea Consumption	16,831	16,402	12,849	12,300	14,038	11,949	11,797	
Lime Production	11,533	14,088	14,379	15,100	14,595	14,330	11,223	
Limestone and Dolomite Use	5,127	5,056	6,768	8,035	7,702	6,276	7,649	
Soda Ash Production and Consumption	4,141	4,181	4,228	4,162	4,140	4,111	4,265	
Aluminum Production	6,831	6,086	4,142	3,801	4,251	4,477	3,009	
Petrochemical Production	3,311	4,479	4,181	3,837	3,931	3,449	2,735	
Carbon Dioxide Consumption	1,416	1,421	1,321	1,709	1,867	1,780	1,763	
Titanium Dioxide Production	1,195	1,752	1,755	1,836	1,930	1,809	1,541	
Ferroalloy Production	2,152	1,893	1,392	1,505	1,552	1,599	1,469	
Phosphoric Acid Production	1,529	1,382	1,386	1,167	1,166	1,187	1,035	
Zinc Production	667	997	1,088	1,088	1,081	1,230	966	
Lead Production	516	594	553	560	562	551	525	
Silicon Carbide Production and Consumption	375	248	219	207	196	175	145	
CH₄	88	104	86	83	82	75	58	
Petrochemical Production	41	59	51	48	48	43	40	
Iron and Steel Production and Metallurgical Coke Production	46	44	34	35	33	31	17	
<i>Iron and Steel</i>								
<i>Production</i>	46	44	34	35	33	31	17	
<i>Metallurgical Coke</i>								
<i>Production</i>	+	+	+	+	+	+	+	
Ferroalloy Production	1	1	+	+	+	+	+	
Silicon Carbide Production and Consumption	1	1	+	+	+	+	+	
N₂O	108	80	69	66	74	60	53	
Nitric Acid Production	57	63	53	52	62	53	47	
Adipic Acid Production	51	18	16	14	12	7	6	
HFCs	M	M	M	M	M	M	M	
Substitution of Ozone Depleting Substances ^a	M	M	M	M	M	M	M	
HCFC-22 Production	3	2	1	1	1	1	+	
Semiconductor Manufacturing HFCs	+	+	+	+	+	+	+	
PFCs	M	M	M	M	M	M	M	
Aluminum Production Semiconductor Manufacturing PFCs	M	M	M	M	M	M	M	
SF₆	1	1	1	1	1	1	1	
Electrical Transmission and Distribution Semiconductor	1	1	1	1	1	1	1	
	+	+	+	+	+	+	+	

Manufacturing SF ₆ Magnesium Production and Processing	+	+	+	+	+	+	+
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+ Does not exceed 0.5 Gg

M (Mixture of gases)

Note: Totals may not sum due to independent rounding.

^a Small amounts of PFC emissions also result from this source.

Methodological recalculations were applied to the entire time-series to ensure time-series consistency from 1990 through 2009. 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 CO₂ and CH₄ emissions, a detailed plan was developed and implemented. This plan was based on the overall 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 process sources. Examples of these procedures include 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 CO₂ 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 2009 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 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. 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 CO₂ from both

the energy consumed in making the cement and the chemical process itself.¹⁰² Cement is produced in 36 states and Puerto Rico. CO₂ emitted from the chemical process of cement production is the second largest source of industrial CO₂ emissions in the United States.

During the cement production process, calcium carbonate (CaCO₃) 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 CO₂ in a process known as calcination or calcining. A very small amount of carbonates other than CaCO₃ and non-carbonates are also present in the raw material; however, for calculation purposes all of the raw material is assumed to be CaCO₃. Next, the lime is combined with silica-containing materials to produce clinker (an intermediate product), with the earlier by-product CO₂ 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.¹⁰³

In 2009, U.S. clinker production—including Puerto Rico—totaled 56,116 thousand metric tons (USGS 2011). The resulting CO₂ emissions were estimated to be 29.0 Tg CO₂ Eq. (29,018 Gg) (see Table 4-3).

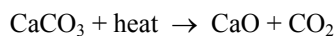
Table 4-3: CO₂ Emissions from Cement Production (Tg CO₂ Eq. and Gg)

Year	Tg CO ₂ Eq.	Gg
1990	33.3	33,278
2000	40.4	40,405
2005	45.2	45,197
2006	45.8	45,792
2007	44.5	44,538
2008	40.5	40,531
2009	29.0	29,018

Greenhouse gas emissions from cement production grew every year from 1991 through 2006, but have decreased since. Emissions since 1990 have decreased by 13 percent. Emissions decreased significantly between 2008 and 2009, due to the economic recession and associated decrease in demand for construction materials. Cement continues to be a critical component of the construction industry; therefore, the availability of public construction funding, as well as overall economic conditions, have considerable influence on cement production.

Methodology

CO₂ 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 CO₂ and lime with the CO₂ released to the atmosphere. The quantity of CO₂ emitted during cement production is directly proportional to the lime content of the clinker. During calcination, each mole of CaCO₃ (i.e., limestone) heated in the clinker kiln forms one mole of lime (CaO) and one mole of CO₂:



CO₂ emissions were estimated by applying an emission factor, in tons of CO₂ 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 and a constant reflecting the mass of CO₂ released per unit of lime (van Oss 2008). This calculation yields an emission factor of 0.51 tons of CO₂ per ton of clinker produced, which was determined as follows:

¹⁰² The CO₂ emissions related to the consumption of energy for cement manufacture are accounted for under CO₂ from Fossil Fuel Combustion in the Energy chapter.

¹⁰³ Approximately three percent of total clinker production is used to produce masonry cement, which is produced using plasticizers (e.g., ground limestone, lime) and portland cement (USGS 2011). CO₂ emissions that result from the production of lime used to create masonry cement are included in the Lime Manufacture source category.

$$EF_{\text{Clinker}} = 0.6460 \text{ CaO} \times \left[\frac{44.01 \text{ g/mole CO}_2}{56.08 \text{ g/mole CaO}} \right] = 0.5070 \text{ tons CO}_2/\text{ton clinker}$$

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 CO₂ emissions should be estimated as two percent of the CO₂ emissions calculated from clinker production.¹⁰⁴ Total cement production emissions were calculated by adding the emissions from clinker production to the emissions assigned to CKD (IPCC 2006).¹⁰⁵

The 1990 through 2009 activity data for clinker production (see Table 4-4) were obtained from USGS (US Bureau of Mines 1990 through 1993, USGS 1995 through 2011). The data were compiled by USGS through questionnaires sent to domestic clinker and cement manufacturing plants.

Table 4-4: Clinker Production (Gg)

Year	Clinker
1990	64,355
2000	78,138
2005	87,405
2006	88,555
2007	86,130
2008	78,382
2009	56,116

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 CaCO₃, 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; 65 percent is used as a representative value (van Oss 2008). CKD loss can range from 1.5 to 8 percent depending upon plant specifications. Additionally, some amount of CO₂ 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 CO₂ 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 CO₂ 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. 2009 CO₂ emissions from cement production were estimated to be between 25.3 and 33.0 Tg CO₂ Eq. at the 95 percent confidence level. This confidence level indicates a range of approximately 13 percent below and 14 percent above the emission estimate of 29.0 Tg CO₂ Eq.

Table 4-5: Tier 2 Quantitative Uncertainty Estimates for CO₂ Emissions from Cement Production (Tg CO₂ Eq. and Percent)

Source	Gas	2009 Emission Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to Emission Estimate ^a			
			Lower	Upper	Lower	Upper

¹⁰⁴ Default IPCC clinker and CKD emission factors were verified through expert consultation with the Portland Cement Association (PCA 2008) and van Oss (2008).

¹⁰⁵ The two percent CO₂ 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 (CaCO₃) 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 2008).

			Bound	Bound	Bound	Bound
Cement Production	CO ₂	29.0	25.3	33.0	-13%	+14%

^a Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Recalculations Discussion

Activity data for the time series was revised for the current Inventory. Specifically, clinker production data for 1995 through 2008 (excluding 2001) were revised to reflect published USGS data. In a given Inventory year, advance clinker data is typically used. This data is typically finalized several years later by USGS. The published time series was reviewed to ensure time series consistency. Published data generally differed from advance data by approximately 1,000 metric tons, or 1 percent of the total. 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 evaluating facility level greenhouse gas emissions data as a basis for improving emissions calculations from cement production. Beginning in 2010, all U.S. cement production facilities are required to monitor, calculate and report their greenhouse gas emissions to EPA through its Greenhouse Gas Reporting Program. Under the program, EPA will obtain data for 2010 emissions from facilities based on use of higher tier methods and in particular assess how this data could be used to improve the overall method for calculating emissions from the U.S. cement industry, including also improving emission factors for clinker production and CKD.

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 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)₂), or hydrated lime; dolomitic quicklime ([CaO•MgO]); and dolomitic hydrate ([Ca(OH)₂•MgO] or [Ca(OH)₂•Mg(OH)₂]).

Lime production involves three main processes: stone preparation, calcination, and hydration. CO₂ is generated during the calcination stage, when limestone—mostly calcium carbonate (CaCO₃)—is roasted at high temperatures in a kiln to produce CaO and CO₂. The CO₂ is given off as a gas and is normally emitted to the atmosphere. Some of the CO₂ generated during the production process, however, is recovered at some facilities for use in sugar refining and precipitated calcium carbonate (PCC) production.¹⁰⁶ In certain additional applications, lime reabsorbs CO₂ during use.

Lime production in the United States—including Puerto Rico—was reported to be 15,781 thousand metric tons in 2009 (USGS 2010). This production resulted in estimated CO₂ emissions of 11.2 Tg CO₂ Eq. (11,223 Gg) (see Table 4-6 and Table 4-7).

Table 4-6: CO₂ Emissions from Lime Production (Tg CO₂ Eq. and Gg)

Year	Tg CO₂ Eq.	Gg
1990	11.5	11,533
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
2009	11.2	11,223

¹⁰⁶ PCC is obtained from the reaction of CO₂ with calcium hydroxide. It is used as a filler and/or coating in the paper, food, and plastic industries.

Table 4-7: Potential, Recovered, and Net CO₂ Emissions from Lime Production (Gg)

Year	Potential	Recovered*	Net Emissions
1990	12,004	471	11,533
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
2009	11,913	690	11,223

* For sugar refining and PCC production.

Note: Totals may not sum due to rounding

Lime production in 2009 decreased by 21 percent compared to 2008, owing mostly to a significant downturn in major markets such as construction and steel. Because of this significant downturn, overall lime production in 2009 was approximately equal to production in 1990. The contemporary lime market is approximately distributed across five end-use categories as follows: environmental uses, 34 percent; metallurgical uses, 31 percent; chemical and industrial uses, 25 percent; construction uses, 9 percent; and refractory dolomite, 1 percent. In the construction sector, lime is used to improve durability in plaster, stucco, and mortars, as well as to stabilize soils. Consumption for metallurgical uses accounted for 57 percent of the overall decrease in lime consumption (USGS 2010).

Methodology

During the calcination stage of lime production, CO₂ 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 CO₂ 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:

$$[(44.01 \text{ g/mole CO}_2) \div (56.08 \text{ g/mole CaO})] \times (0.9500 \text{ CaO/lime}) = 0.7455 \text{ g CO}_2/\text{g lime}$$

For dolomitic lime:

$$[(88.02 \text{ g/mole CO}_2) \div (96.39 \text{ g/mole CaO})] \times (0.9500 \text{ CaO/lime}) = 0.8675 \text{ g CO}_2/\text{g lime}$$

Production was adjusted to remove the mass of chemically combined water found in hydrated lime, determined according to the molecular weight ratios of H₂O to (Ca(OH)₂ and [Ca(OH)₂•Mg(OH)₂]) (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 CO₂ emitted by lime production facilities for use as an input into production or refining processes. For CO₂ recovery by sugar refineries, lime consumption estimates from USGS were multiplied by a CO₂ recovery factor to determine the total amount of CO₂ recovered from lime production facilities. According to industry surveys, sugar refineries use captured CO₂ for 100 percent of their CO₂ input (Lutter 2009). CO₂ recovery by PCC producers was determined by multiplying estimates for the percentage CO₂ of production weight for PCC production at lime plants by a CO₂ recovery factor based on the amount of purchased CO₂ by PCC manufacturers (Prillaman 2008 through 2010). As data were only available starting in 2007, CO₂ 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 1992 through 2008).

Lime production data (high-calcium- and dolomitic-quicklime, high-calcium- and dolomitic-hydrated, and dead-burned dolomite) for 1990 through 2009 (see Table 4-8) were obtained from USGS (1992 through 2010). Natural

hydraulic lime, which is produced from CaO and hydraulic calcium silicates, is not produced in the United States (USGS 2009). 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, and is presented in Table 4-9 (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.

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
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
2009	11,800	1,830	1,690	261	200

Table 4-9: Adjusted Lime Production^a (Gg)

Year	High-Calcium	Dolomitic
1990	12,514	2,809
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
2009	13,079	2,220

^a 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 CO₂ 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, CO₂ reacts with the lime to create calcium carbonate (e.g., water softening). CO₂ reabsorption rates vary, however, depending on the application. For example, 100 percent of the lime used to produce precipitated calcium carbonate reacts with CO₂; 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 CO₂ that is reabsorbed.¹⁰⁷

In some cases, lime is generated from calcium carbonate by-products at pulp mills and water treatment plants.¹⁰⁸

¹⁰⁷ Representatives of the National Lime Association estimate that CO₂ reabsorption that occurs from the use of lime may offset as much as a quarter of the CO₂ emissions from calcination (Males 2003).

¹⁰⁸ Some carbide producers may also regenerate lime from their calcium hydroxide by-products, which does not result in

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 CO₂—for reuse in the pulping process. Although this re-generation of lime could be considered a lime manufacturing process, the CO₂ emitted during this process is mostly biogenic in origin, and therefore is not included in the industrial processes totals (Miner and Upton 2002). In accordance with IPCC methodological guidelines, any such emissions are calculated by accounting for net carbon (C) fluxes from changes in biogenic C reservoirs in wooded or crop lands (see Chapter 7).

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 CO₂ from lime plants (Lutter 2010). This analysis assumes that all sugar refineries located on-site at lime plants also use 100 percent recovered CO₂. The recovery rate for PCC producers located on-site at lime plants is based on the 2009 value for PCC manufactured at commercial lime plants, given by the National Lime Association (Prillaman 2010).

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-10. Lime CO₂ emissions were estimated to be between 10.4 and 12.3 Tg CO₂ Eq. at the 95 percent confidence level. This confidence level indicates a range of approximately 7 percent below and 10 percent above the emission estimate of 11.2 Tg CO₂ Eq.

Table 4-10: Tier 2 Quantitative Uncertainty Estimates for CO₂ Emissions from Lime Production (Tg CO₂ Eq. and Percent)

Source	Gas	2009 Emission Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to Emission Estimate ^a			
			(Tg CO ₂ Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Lime Production	CO ₂	11.2	10.4	12.3	-7%	+10%

^a Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

No methodological or activity data changes to the time series were made to this source for the current Inventory. Details on the emission trends through time are described in more detail in the Methodology section, above.

Planned Improvements

Future improvements to the lime source category involve evaluating facility level greenhouse gas emissions data as a basis for improving emissions calculations from lime production. Beginning in 2010, all U.S. lime production facilities are required to monitor, calculate and report their greenhouse gas emissions to EPA through its Greenhouse Gas Reporting Program. Under the program, EPA will obtain data for 2010 emissions from facilities based on use of higher tier methods and in particular assess how this data could be used to improve the overall method for calculating emissions from the U.S. lime industry, including improving emission factors for various lime types and LKD.

Future improvements to the lime source category will also involve continued research into CO₂ 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 CO₂ produced in lime kilns located on the same site as the sugar refinery (Lutter 2010). Data on CO₂ production by these lime facilities is unavailable. Future work will

emissions of CO₂. 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) [CaC₂ + 2H₂O → C₂H₂ + Ca(OH)₂], not calcium carbonate [CaCO₃]. Thus, the calcium hydroxide is heated in the kiln to simply expel the water [Ca(OH)₂ + heat → CaO + H₂O] and no CO₂ is released.

include research to determine the number of sugar refineries that employ the carbonation technique, the percentage of these that use captured CO₂ from lime production facilities, and the amount of CO₂ recovered per unit of lime production. Future research will also aim to improve estimates of CO₂ recovered as part of the PCC production process using estimates of PCC production and CO₂ inputs rather than lime consumption by PCC facilities.

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

Limestone (CaCO₃) and dolomite (CaCO₃MgCO₃)¹⁰⁹ 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 heated sufficiently enough to calcine the material and generate CO₂ as a by-product. Examples of such applications include limestone used as a flux or purifier in metallurgical furnaces, as a sorbent in flue gas desulfurization (FGD) systems for utility and industrial plants, or as a raw material in glass manufacturing and magnesium production.

In 2009, approximately 14,928 thousand metric tons of limestone and 3,020 thousand metric tons of dolomite were consumed for these emissive applications. Overall, usage of limestone and dolomite resulted in aggregate CO₂ emissions of 7.6 Tg CO₂ Eq. (7,649 Gg) (see Table 4-11 and Table 4-12). Overall, emissions have increased 49 percent from 1990 through 2009.

Table 4-11: CO₂ Emissions from Limestone & Dolomite Use (Tg CO₂ Eq.)

Year	Flux Stone	Glass Making	FGD	Magnesium Production	Other Miscellaneous Uses	Total
1990	2.6	0.2	1.4	0.1	0.8	5.1
2000	2.1	0.4	1.8	0.1	0.7	5.1
2005	2.7	0.4	3.0	0.0	0.7	6.8
2006	4.5	0.7	2.1	0.0	0.7	8.0
2007	2.0	0.3	3.2	0.0	2.2	7.7
2008	1.0	0.4	3.8	0.0	1.1	6.3
2009	1.8	0.1	5.4	0.0	0.4	7.6

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.

Table 4-12: CO₂ Emissions from Limestone & Dolomite Use (Gg)

Year	Flux Stone	Glass Making	FGD	Magnesium Production	Other Miscellaneous Uses	Total
1990	2,593	217	1,433	64	819	5,127
2000	2,104	371	1,787	73	722	5,056
2005	2,650	425	2,975	0	718	6,768
2006	4,492	747	2,061	0	735	8,035
2007	1,959	333	3,179	0	2,231	7,702
2008	974	387	3,801	0	1,114	6,276
2009	1,785	61	5,406	0	396	7,649

Methodology

CO₂ emissions were calculated by multiplying the quantity of limestone or dolomite consumed by the average C

¹⁰⁹ Limestone and dolomite are collectively referred to as limestone by the industry, and intermediate varieties are seldom distinguished.

content, 12.0 percent for limestone and 13.0 percent for dolomite (based on stoichiometry), and converting this value to CO₂. 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 CO₂ 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 CO₂ 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 CO₂ emissions, while the other plant produced magnesium from magnesium chloride using a CO₂-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 2010a) and the U.S. Bureau of Mines (1991 & 1993a). Consumption data for 2009 were obtained from personal communication with the USGS crushed stone commodity specialist (Willett 2010). The production capacity data for 1990 through 2009 of dolomitic magnesium metal also came from the USGS (1995 through 2010b) 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 *Minerals Yearbook: Magnesium*; therefore, it is assumed that this process continues to be non-existent in the United States (USGS 2010b). 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.¹¹⁰

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

Activity	1990	2000	2005	2006	2007	2008	2009
Flux Stone	6,737	6,283	7,022	11,030	5,305	3,253	4,623
Limestone	5,804	4,151	3,165	5,208	3,477	1,970	1,631
Dolomite	933	2,132	3,857	5,822	1,827	1,283	2,992
Glass Making	489	843	962	1,693	757	879	139
Limestone	430	843	920	1,629	757	879	139
Dolomite	59	0	43	64	0	0	0
FGD	3,258	4,061	6,761	4,683	7,225	8,639	12,288
Other Miscellaneous Uses	1,835	1,640	1,632	1,671	5,057	2,531	898
Total	12,319	12,826	16,377	19,078	18,344	15,302	17,948

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.

¹¹⁰This approach was recommended by USGS.

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 4-14. Limestone and Dolomite Use CO₂ emissions were estimated to be between 6.6 and 9.1 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 13 percent below and 19 percent above the emission estimate of 7.6 Tg CO₂ Eq.

Table 4-14: Tier 2 Quantitative Uncertainty Estimates for CO₂ Emissions from Limestone and Dolomite Use (Tg CO₂ Eq. and Percent)

Source	Gas	2009 Emission Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to Emission Estimate ^a (%)			
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Limestone and Dolomite Use	CO ₂	7.6	6.6	9.1	-13%	+19%

^a 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 2009. Details on the emission trends through time are described in more detail in the Methodology section, above.

Planned Improvements

Future improvements to the limestone and dolomite source category involve research into the availability of limestone and dolomite end-use data, including from EPA’s new Greenhouse Gas Reporting Program. 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, Na₂CO₃) 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 CO₂

from Wyoming were calculated due to specifics regarding the production processes employed in the state.¹¹¹ During the production process used in Wyoming, trona ore is calcined to produce crude soda ash. CO₂ is generated as a by-product of this reaction, and is eventually emitted into the atmosphere. In addition, CO₂ may also be released when soda ash is consumed.

In 2009, CO₂ emissions from the production of soda ash from trona were approximately 1.7 Tg CO₂ Eq. (1,733 Gg). Soda ash consumption in the United States generated 2.5 Tg CO₂ Eq. (2,532 Gg) in 2009. Total emissions from soda ash production and consumption in 2009 were 4.3 Tg CO₂ Eq. (4,265 Gg) (see Table 4-15 and Table 4-16). 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 from the production of soda ash from trona in 2009 are currently proxied to emissions in 2008, due to lack of available data at time of publication. Emissions in 2009 increased by approximately 4 percent from emissions in 2008, and have also increased overall by 3 percent since 1990.

Table 4-15: CO₂ Emissions from Soda Ash Production and Consumption (Tg CO₂ Eq.)

Year	Production	Consumption	Total
1990	1.4	2.7	4.1
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
2009	1.7	2.5	4.3

Note: Totals may not sum due to independent rounding.

Table 4-16: CO₂ Emissions from Soda Ash Production and Consumption (Gg)

Year	Production	Consumption	Total
1990	1,431	2,710	4,141
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
2009	1,733	2,532	4,265

Note: Totals may not sum due to independent rounding.

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). The same distribution by end-use is currently assumed for 2009, due to lack of available data at time of publication.

¹¹¹ 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 CO₂ 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 CO₂ is generated as a by-product, the CO₂ 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, NaHCO₃ 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 4-18: Tier 2 Quantitative Uncertainty Estimates for CO₂ Emissions from Soda Ash Production and Consumption (Tg CO₂ Eq. and Percent)

Source	Gas	2009 Emission Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to Emission Estimate ^a			
			Lower Bound	Upper Bound	Lower Bound (%)	Upper Bound (%)
Soda Ash Production and Consumption	CO ₂	4.3	4.0	4.6	-7%	+7%

^a 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 2009. 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.

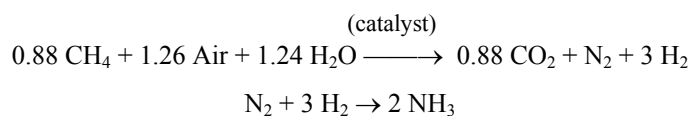
In addition, future improvements to the soda ash production category involve evaluating facility level greenhouse gas emissions data as a basis for improving emissions calculations from soda ash production. Beginning in 2010, all U.S. soda ash production facilities are required to monitor, calculate and report their greenhouse gas emissions to EPA through its Greenhouse Gas Reporting Program. Under the program, EPA will obtain data for 2010 emissions from facilities based on use of higher tier methods and in particular assess how this data could be used to improve the overall method for calculating emissions from the U.S. soda ash production industry, including also improving emission factors associated with trona consumption.

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

Emissions of CO₂ 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 CO₂ and hydrogen (H₂), 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 CO₂ produced is captured and used to produce urea. The brine electrolysis process for production of ammonia does not lead to process-based CO₂ emissions.

There are five principal process steps in synthetic ammonia production from natural gas feedstock. The primary reforming step converts CH₄ to CO₂, carbon monoxide (CO), and H₂ in the presence of a catalyst. Only 30 to 40 percent of the CH₄ feedstock to the primary reformer is converted to CO and CO₂. The secondary reforming step converts the remaining CH₄ feedstock to CO and CO₂. The CO in the process gas from the secondary reforming step (representing approximately 15 percent of the process gas) is converted to CO₂ in the presence of a catalyst, water, and air in the shift conversion step. CO₂ is removed from the process gas by the shift conversion process, and the hydrogen gas is combined with the nitrogen (N₂) gas in the process gas during the ammonia synthesis step to produce ammonia. The CO₂ is included in a waste gas stream with other process impurities and is absorbed by a scrubber solution. In regenerating the scrubber solution, CO₂ is released.

The conversion process for conventional steam reforming of CH₄, 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 CO₂ and H₂. These gases are separated, and the H₂ is used as a feedstock to the ammonia production process, where it is reacted with N₂ to form ammonia.

Not all of the CO₂ produced in the production of ammonia is emitted directly to the atmosphere. Both ammonia and CO₂ are used as raw materials in the production of urea [CO(NH₂)₂], 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 CO₂ during use. Therefore, the CO₂ produced by ammonia production that is subsequently used in the production of urea is still emitted during urea consumption. The majority of CO₂ 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. CO₂ emissions associated with other uses of urea are accounted for in this chapter. Net emissions of CO₂ from ammonia production in 2009 were 11.8 Tg CO₂ Eq. (11,797 Gg), and are summarized in Table 4-19 and Table 4-20. Emissions of CO₂ from urea consumed for non-fertilizer purposes in 2009 totaled 3.9 Tg CO₂ Eq. (3,942 Gg), and are summarized in Table 4-19 and Table 4-20. 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 4-19: CO₂ Emissions from Ammonia Production and Urea Consumption (Tg CO₂ Eq.)

Source	1990	2000	2005	2006	2007	2008	2009
Ammonia Production	13.0	12.2	9.2	8.8	9.1	7.9	7.9
Urea Consumption ^a	3.8	4.2	3.7	3.5	5.0	4.1	3.9
Total	16.8	16.4	12.8	12.3	14.0	11.9	11.8

Note: Totals may not sum due to independent rounding.

^a 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.

Table 4-20: CO₂ Emissions from Ammonia Production and Urea Consumption (Gg)

Source	1990	2000	2005	2006	2007	2008	2009
Ammonia							
Production	13,047	12,172	9,196	8,781	9,074	7,883	7,855
Urea Consumption ^a	3,784	4,231	3,653	3,519	4,963	4,066	3,942
Total	16,831	16,402	12,849	12,300	14,038	11,949	11,797

^a 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.

Methodology

The calculation methodology for non-combustion CO₂ emissions from production of nitrogenous fertilizers from natural gas feedstock is based on a CO₂ 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 United States. The CO₂ emission factor (1.2 metric tons CO₂/metric ton NH₃) 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 CO₂ from ammonia production are then adjusted to account for the use of some of the CO₂ 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 CO₂ are consumed and 6.8 of every 12 tons of ammonia are consumed (IPCC 2006, EFMA 2000). The CO₂ emissions reported for ammonia production are therefore reduced by a factor of 0.73 multiplied by total annual domestic urea production. Total CO₂ emissions resulting from nitrogenous fertilizer production do not change as a result of this calculation, but some of the CO₂ emissions are attributed to ammonia production and some of the CO₂ emissions are attributed to urea consumption. Those CO₂ 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 4-21, 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. CO₂ emissions associated with urea that is used for non-fertilizer purposes are estimated using a factor of 0.73 tons of CO₂ 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 CO₂ 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 CO₂ (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 CO₂ emission factor (3.57 metric tons CO₂/metric ton NH₃) is applied to the percent of total annual domestic ammonia production from petroleum coke feedstock.

The emission factor of 1.2 metric ton CO₂/metric ton NH₃ 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 CO₂/metric ton NH₃, with 1.2 metric ton CO₂/metric ton NH₃ 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 indicates that more than 99 percent of the CH₄ feedstock to the catalytic reforming process is ultimately converted to CO₂. The emission factor of 3.57 metric ton CO₂/metric ton NH₃ 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 4-21) was obtained from Coffeyville Resources (Coffeyville 2005, 2006, 2007a, 2007b, 2009, 2010) and the Census Bureau of the U.S. Department of Commerce (U.S. Census Bureau 1991 through 1994, 1998 through 2010) 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, 2010). Urea production data for 1990 through 2008 were obtained from the Minerals Yearbook: Nitrogen (USGS 1994 through 2009). Urea production data for 2009 was obtained from the U.S. Bureau of the Census (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 2009 (U.S. Census Bureau 1998 through 2010), 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 4-21). Urea export data for 1990 through 2009 were taken from U.S. Fertilizer Import/Exports from USDA Economic Research Service Data Sets (U.S. Department of Agriculture 2010).

Table 4-21: 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
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	5,097	6,546	271
2008	9,570	5,240	4,925	5,459	230
2009	9,372	5,084	4,295	5,505	289

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 CO₂ emissions depending upon the end use to which the recovered CO₂ is applied. Further research is required to determine whether byproduct CO₂ 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 4-22. Ammonia Production and Urea Consumption CO₂ emissions were estimated to be between 10.9 and 12.7 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 7 percent below and 8 percent above the emission estimate of 11.8 Tg CO₂ Eq.

Table 4-22: Tier 2 Quantitative Uncertainty Estimates for CO₂ Emissions from Ammonia Production and Urea Consumption (Tg CO₂ Eq. and Percent)

Source	Gas	2009 Emission Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to Emission Estimate ^a			
			Uncertainty Range Relative to Emission Estimate ^a		Uncertainty Range Relative to Emission Estimate ^a	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Ammonia Production and Urea Consumption	CO ₂	11.8	10.9	12.7	-7%	+8%

^a 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 2009. Details on the emission trends through time are described in more detail in the Methodology section, above.

Recalculations Discussion

The uncertainty range (-7 percent/+8 percent) has decreased by 7 percent compared to the uncertainty range in the previous Inventory (±11 percent), due to two stoichiometric variables being removed from the uncertainty analysis.

Planned Improvements

Future improvements to the ammonia production and urea consumption category involve evaluating facility level greenhouse gas emissions data as a basis for improving emissions calculations from ammonia production. Beginning in 2010, all U.S. ammonia production facilities are required to monitor, calculate and report their greenhouse gas emissions to EPA through its Greenhouse Gas Reporting Program. Under the program, EPA will obtain data for 2010 emissions from facilities based on use of higher tier methods and in particular assess how this data could be used to improve the overall method for calculating emissions from U.S. ammonia production. Specifically, the planned improvements include assessing data to update the emission factors to include both fuel and feedstock CO₂ emissions and incorporate CO₂ 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.

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

Nitric acid (HNO₃) 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, N₂O 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 NO₂ (i.e., NO_x). As such, the industry in the US uses a combination of non-selective catalytic reduction (NSCR) and selective catalytic reduction (SCR) technologies. In the process of destroying NO_x, NSCR systems are also very effective at destroying N₂O. 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 25 percent of nitric acid plants use NSCR and they represent 15.3 percent of estimated national production (EPA 2010a). The remaining 84.7 percent of production occurs using SCR or extended absorption, neither of which is known to reduce N₂O emissions.

N₂O emissions from this source were estimated to be 14.6 Tg CO₂ Eq. (47 Gg) in 2009 (see Table 4-23). Emissions from nitric acid production have decreased by 18 percent since 1990, with the trend in the time series closely tracking the changes in production. Emissions decreased 11.4 percent between 2008 and 2009. Emissions have decreased by 30.8 percent since 1997, the highest year of production in the time series.

Table 4-23: N₂O Emissions from Nitric Acid Production (Tg CO₂ Eq. and Gg)

Year	Tg CO₂ Eq.	Gg
1990	17.7	57
2000	19.4	63
2005	16.5	53
2006	16.2	52
2007	19.2	62
2008	16.4	53
2009	14.6	47

Methodology

N₂O emissions were calculated by multiplying nitric acid production by the amount of N₂O emitted per unit of nitric acid produced. The emission factor was determined as a weighted average of two known emission factors: 2 kg N₂O/metric ton HNO₃ produced at plants using non-selective catalytic reduction (NSCR) systems and 9 kg N₂O/metric ton HNO₃ produced at plants not equipped with NSCR (IPCC 2006). In the process of destroying NO_x, NSCR systems destroy 80 to 90 percent of the N₂O, which is accounted for in the emission factor of 2 kg N₂O/metric ton HNO₃. Approximately 25 percent of HNO₃ plants in the United States are equipped with NSCR representing 15.3 percent of estimated national production (EPA 2010a). Hence, the emission factor is equal to $(9 \times 0.847) + (2 \times 0.153) = 7.9$ kg N₂O per metric ton HNO₃.

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 2009 were obtained from the U.S. Census Bureau, Current Industrial Reports (2010) (see Table 4-24).

Table 4-24: Nitric Acid Production (Gg)

Year	Gg
1990	7,195
2000	7,900
2005	6,711
2006	6,572
2007	7,827
2008	6,686
2009	5,924

Uncertainty and Time-Series Consistency

The overall uncertainty associated with the 2009 N₂O emissions estimate from nitric acid production was calculated using the 2006 IPCC Guidelines for National Greenhouse Gas Inventories (IPCC 2006) Tier 2 methodology.

Uncertainty associated with the parameters used to estimate N₂O emissions included that of production data, the share of U.S. nitric acid production attributable to each emission abatement technology over the time series, and the emission factors applied to each abatement technology type.

The results of this Tier 2 quantitative uncertainty analysis are summarized in Table 4-25. N₂O emissions from nitric acid production were estimated to be between 8.8 and 20.7 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 40 percent below to 42 percent above the 2009 emissions estimate of 14.6 Tg CO₂ Eq.

Table 4-25: Tier 2 Quantitative Uncertainty Estimates for N₂O Emissions from Nitric Acid Production (Tg CO₂ Eq. and Percent)

Source	Gas	2009 Emission Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to Emission Estimate ^a			
			(Tg CO ₂ Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Nitric Acid Production	N ₂ O	14.6	8.8	20.7	-40%	+42%

^a 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 2009. Details on the emission trends through time are described in more detail in the Methodology section, above.

Planned Improvements

Future improvements to the nitric acid production category involve evaluating facility level greenhouse gas emissions data as a basis for improving emissions calculations from nitric acid production. Beginning in 2010, all U.S. nitric acid production facilities are required to monitor, calculate and report their greenhouse gas emissions to EPA through its Greenhouse Gas Reporting Program. Under the program, EPA will obtain data for 2010 emissions from facilities based on use of higher tier methods and in particular assess how this data could be used to improve the overall method for calculating emissions from U.S. nitric acid production. Specifically, the planned improvements include assessing data to update the N₂O emission factors, abatement utilization and destruction factors, and the current share of nitric acid production attributable to various abatement technologies.

Recalculations Discussion

Historical estimates for N₂O emissions from nitric acid production have been revised relative to the previous Inventory based on updated information from EPA (2010) on abatement technologies in use and based on revised production data published by the U.S. Census Bureau (2010). The previous Inventory assumed that approximately 17 percent of facilities accounting for less than 8 percent of national production were equipped with NSCR systems (EPA 2010b). The current Inventory assumes that approximately 25 percent of facilities, accounting for roughly 15 percent of national production, were equipped with NSCR systems (EPA 2010a). This change resulted in a decrease in the weighted average emission factor of 0.6 kg N₂O/metric ton HNO₃ (6.3 percent). Additionally, national nitric acid production values for 1991, 1993-1995, 1997-1999, 2002, and 2008 have been updated relative to the previous Inventory (US Census Bureau 2009, 2010). Revised production in 2008 contributed to an overall decrease in emissions of 2.6 Tg CO₂ Eq. (13.6 percent) in that year; revised production in the other historical years had a negligible impact on emissions. Overall, changes relative to the previous Inventory resulted in an average annual decrease in emissions of 1.3 Tg CO₂ Eq. (6.7 percent) for the period 1990 through 2008.

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

Adipic acid production is an anthropogenic source of N₂O emissions. Worldwide, few adipic acid plants exist. The United States and Europe are the major producers. In 2009, the United States had two companies with a total of three adipic acid processes, two of which were operational (CW 2007; Desai 2010; VA DEQ 2009). The United States accounts for the largest share of global adipic acid production capacity (30 percent), followed by the European Union (29 percent) and China (22 percent) (SEI 2010). 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 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 N₂O 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. N₂O 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 N₂O abatement technologies in place and, as of 1998, the three major adipic acid production facilities had control systems in place (Reimer et al. 1999). One small plant, which last operated in April 2006 and represented approximately two percent of production, did not control for N₂O (VA DEQ 2009; ICIS 2007; VA DEQ 2006).

N₂O emissions from adipic acid production were estimated to be 1.9 Tg CO₂ Eq. (6 Gg) in 2009 (see Table 4-26). National adipic acid production has increased by approximately 11 percent over the period of 1990 through 2009, to roughly 820,000 metric tons. Over the same period, emissions have been reduced by 88 percent due to both the widespread installation of pollution control measures in the late 1990s and plant idling in the late 2000s. In April 2006, the smallest of the four facilities ceased production of adipic acid (VA DEQ 2009); furthermore, one of the major adipic acid production facilities was not operational in 2009 (Desai 2010).

Table 4-26: N₂O Emissions from Adipic Acid Production (Tg CO₂ Eq. and Gg)

Year	Tg CO ₂ Eq.	Gg
1990	15.8	51
2000	5.5	18
2005	5.0	16
2006	4.3	14
2007	3.7	12
2008	2.0	7
2009	1.9	6

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 2009 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. In 2009, no Adipic acid production occurred at Plant 1. For Plants 3 and 4, N₂O emissions were calculated by multiplying adipic acid production by an emission factor (i.e., N₂O emitted per unit of adipic acid produced) and adjusting for the percentage of N₂O released as a result of plant-specific emission controls. On the basis of experiments, the overall reaction stoichiometry for N₂O production in the preparation of adipic acid was estimated at approximately 0.3 metric tons of N₂O per metric ton of product (IPCC 2006). Emissions are estimated using the following equation:

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

The “N₂O destruction factor” represents the percentage of N₂O 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 N₂O abatement equipment (Plant 4). For Plant 3, which uses thermal destruction and for which no reported plant-specific emissions are available, the N₂O 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).

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 for 2007 through 2009; therefore, production values for 2007 through 2009 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 time series from 1990 through 2008 (VA DEQ 2010). Since the plant has not operated since 2006, production in 2009 is assumed to be equal to the 2008 estimate, which was zero. The plant-specific production data were then used for calculating emissions as described above.

National adipic acid production data (see Table 4-27) from 1990 through 2009 were obtained from the American Chemistry Council (ACC 2010).

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 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 2009, 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).

Table 4-27: Adipic Acid Production (Gg)

Year	Gg
1990	735
2000	925
2005	903
2006	964
2007	930
2008	869
2009	819

Uncertainty and Time-Series Consistency

The overall uncertainty associated with the 2009 N₂O emission estimate from adipic acid production was calculated using the 2006 IPCC Guidelines for National Greenhouse Gas Inventories (IPCC 2006) Tier 2 methodology. Uncertainty associated with the parameters used to estimate N₂O emissions included that of company specific production data, emission factors for abated and unabated emissions, and company-specific historical emission estimates.

The results of this Tier 2 quantitative uncertainty analysis are summarized in Table 4-28. N₂O emissions from adipic acid production were estimated to be between 1.2 and 2.8 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 40 percent below to 42 percent above the 2009 emission estimate of 1.9 Tg CO₂ Eq.

Table 4-28: Tier 2 Quantitative Uncertainty Estimates for N₂O Emissions from Adipic Acid Production (Tg CO₂ Eq. and Percent)

Source	Gas	2009 Emission	
		Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to Emission Estimate^a (Tg CO ₂ Eq.) (%)

			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Adipic Acid Production	N ₂ O	1.9	1.2	2.8	-40%	+42%

^a 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 2009. Details on the emission trends through time are described in more detail in the Methodology section, above.

Recalculations

The current Inventory uses national production data from the ACC (2010) across the full time series. Previous Inventories relied upon a variety of sources and linear interpolation for missing intervening years in the national production time series. This change resulted in an average annual decrease in the national production estimate of approximately 2 percent for the period 1990 through 2008 relative to the previous Inventory. Emissions decreased by less than 0.1 percent over the same time period relative to the previous Inventory.

Planned Improvements

Future improvements to the adipic acid production category involve evaluating facility level greenhouse gas emissions data as a basis for improving emissions calculations from adipic acid production. Beginning in 2010, all U.S. adipic acid production facilities are required to monitor, calculate and report their greenhouse gas emissions to EPA through its Greenhouse Gas Reporting Program. Under the program, EPA will obtain data for 2010 emissions from facilities based on use of higher tier methods and in particular assess how this data could be used to improve the overall method for calculating emissions from U.S. adipic acid production. Specifically, the planned improvements include assessing data to update the N₂O emission factors and update abatement utility and destruction factors based on actual performance of the latest catalytic and thermal abatement equipment at plants with continuous process and emission monitoring equipment.

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

CO₂ and CH₄ are emitted from the production¹¹² of silicon carbide (SiC), a material used as an industrial abrasive. To make SiC, quartz (SiO₂) 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 CO₂, CH₄, or CO.

CO₂ 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).

CO₂ from SiC production and consumption in 2009 were 0.1 Tg CO₂ Eq. (145 Gg) (USGS 2009). Approximately 63 percent of these emissions resulted from SiC production while the remainder results from SiC consumption. CH₄ emissions from SiC production in 2009 were 0.01 Tg CO₂ Eq. CH₄ (0.4 Gg) (see Table 4-29 and Table 4-30).

Table 4-29: CO₂ and CH₄ Emissions from Silicon Carbide Production and Consumption (Tg CO₂ Eq.)

Year	1990	2000	2005	2006	2007	2008	2009
CO ₂	0.4	0.2	0.2	0.2	0.2	0.2	0.1
CH ₄	+	+	+	+	+	+	+
Total	0.4	0.3	0.2	0.2	0.2	0.2	0.2

+ Does not exceed 0.05 Tg CO₂ Eq.

Note: Totals may not sum due to independent rounding.

Table 4-30: CO₂ and CH₄ Emissions from Silicon Carbide Production and Consumption (Gg)

Year	1990	2000	2005	2006	2007	2008	2009
-------------	-------------	-------------	-------------	-------------	-------------	-------------	-------------

¹¹² Silicon carbide is produced for both abrasive and metallurgical applications in the United States. Production for metallurgical applications is not available and therefore both CH₄ and CO₂ estimates are based solely upon production estimates of silicon carbide for abrasive applications.

CO ₂	375	248	219	207	196	175	145
CH ₄	1	1	+	+	+	+	+

+ Does not exceed 0.5 Gg.

Methodology

Emissions of CO₂ and CH₄ from the production of SiC were calculated by multiplying annual SiC production by the emission factors (2.62 metric tons CO₂/metric ton SiC for CO₂ and 11.6 kg CH₄/metric ton SiC for CH₄) provided by the 2006 IPCC Guidelines for National Greenhouse Gas Inventories (IPCC 2006).

Emissions of CO₂ 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 2009). 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 2009). Production data for 2009 was taken from the Minerals Commodity Summary: Abrasives (Manufactured) (USGS 2010). Silicon carbide consumption by major end use was obtained from the Minerals Yearbook: Silicon (USGS 1991b through 2005b) (see Table 4-31) 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 2009 is proxied using 2008 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 2010).

Table 4-31: Production and Consumption of Silicon Carbide (Metric Tons)

Year	Production	Consumption
1990	105,000	172,465
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
2009	35,000	92,280

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 CH₄, 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.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-32. Silicon carbide production and consumption CO₂ emissions were estimated to be between 9 percent below and 9 percent above the emission estimate of 0.2 Tg CO₂ Eq. at the 95 percent confidence level. Silicon carbide production CH₄ emissions were estimated to be between 9 percent below and 9 percent above the emission estimate of 0.01 Tg CO₂ Eq. at the 95 percent confidence level.

Table 4-32: Tier 2 Quantitative Uncertainty Estimates for CH₄ and CO₂ Emissions from Silicon Carbide Production and Consumption (Tg CO₂ Eq. and Percent)

Source	Gas	2009 Emission Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to Emission Estimate ^a			
			(Tg CO ₂ Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Silicon Carbide Production	CO ₂	0.2	0.13	0.16	-9%	+9%

and Consumption								
Silicon Carbide Production	CH ₄	+	+	+			-9%	+9%

^a Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

+ Does not exceed 0.05 Tg CO₂ Eq. or 0.5 Gg.

Methodological recalculations were applied to the entire time-series to ensure time-series consistency from 1990 through 2009. Details on the emission trends through time are described in more detail in the Methodology section, above.

Planned Improvements

Future improvements to the silicon carbide production source category include evaluating facility level greenhouse gas emissions data as a basis for improving emissions calculations from silicon carbide production. Beginning in 2010, all U.S. silicon carbide production facilities are required to monitor, calculate and report their greenhouse gas emissions to EPA through its Greenhouse Gas Reporting Program. Under the program, EPA will obtain data for 2010 emissions from facilities based on use of higher tier methods and in particular assess how this data could be used to improve the overall method for calculating emissions from the U.S. silicon carbide production industry. In addition, improvements will involve 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. Additionally, as future improvement to the silicon carbide uncertainty analysis, USGS Mineral Commodity Specialists will be contacted to verify the uncertainty range associated with silicon carbide emissive utilization.

4.9. Petrochemical Production (IPCC Source Category 2B5)

The production of some petrochemicals results in the release of small amounts of CH₄ and CO₂ emissions. Petrochemicals are chemicals isolated or derived from petroleum or natural gas. CH₄ emissions are presented here from the production of carbon black, ethylene, ethylene dichloride, and methanol, while CO₂ emissions are presented here for only carbon black production. The CO₂ 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 CO₂ from carbon black production is included here to allow for the direct reporting of CO₂ 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 CO₂ and CH₄ from petrochemical production in 2009 were 2.7 Tg CO₂ Eq. (2,735 Gg) and 0.8 Tg CO₂ Eq. (40 Gg), respectively (see Table 4-33 and Table 4-34), totaling 3.6 Tg CO₂ Eq. There has been an overall decrease in CO₂ emissions from carbon black production of 17 percent since 1990. CH₄ emissions from petrochemical production decreased by approximately two percent since 1990.

Table 4-33: CO₂ and CH₄ Emissions from Petrochemical Production (Tg CO₂ Eq.)

Year	1990	2000	2005	2006	2007	2008	2009
CO ₂	3.3	4.5	4.2	3.8	3.9	3.4	2.7
CH ₄	0.9	1.2	1.1	1.0	1.0	0.9	0.8
Total	4.2	5.7	5.3	4.8	4.9	4.4	3.6

Note: Totals may not sum due to independent rounding.

Table 4-34: CO₂ and CH₄ Emissions from Petrochemical Production (Gg)

Year	1990	2000	2005	2006	2007	2008	2009
------	------	------	------	------	------	------	------

CO ₂	3,311	4,479	4,181	3,837	3,931	3,449	2,735
CH ₄	41	59	51	48	48	43	40

Methodology

Emissions of CH₄ were calculated by multiplying annual estimates of chemical production by the appropriate emission factor, as follows: 11 kg CH₄/metric ton carbon black, 1 kg CH₄/metric ton ethylene, 0.4 kg CH₄/metric ton ethylene dichloride,¹¹³ and 2 kg CH₄/metric ton methanol. Although the production of other chemicals may also result in CH₄ emissions, insufficient data were available to estimate their emissions.

Emission factors were taken from the Revised 1996 IPCC Guidelines (IPCC/UNEP/OECD/IEA 1997). Annual production data (see Table 4-35) were obtained from the American Chemistry Council's Guide to the Business of Chemistry (ACC 2002, 2003, 2005 through 2010) and the International Carbon Black Association (Johnson 2003, 2005 through 2010). Note that 2009 production data for Methanol was not available at time of publication, as such, 2008 methanol production is used as a proxy for 2009.

Table 4-35: Production of Selected Petrochemicals (Thousand Metric Tons)

Chemical	1990	2000	2005	2006	2007	2008	2009
Carbon Black	1,307	1,769	1,651	1,515	1,552	1,362	1,080
Ethylene	16,541	24,970	23,954	25,000	25,392	22,539	22,596
Ethylene Dichloride	6,282	9,866	11,260	9,736	9,566	8,981	8,131
Methanol	3,785	5,221	2,336	1,123	1,068	1,136	1,136

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 CO₂, carbon monoxide, sulfur compounds, CH₄, and non-CH₄ 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 CO₂ 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 CH₄ or CO₂. The C content of the CH₄ emissions, estimated as described above, is subtracted from the total C lost in the process to calculate the amount of C emitted as CO₂. The total amount of primary and secondary carbon black feedstock consumed in the process (see Table 4-36) 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

¹¹³ The emission factor obtained from IPCC/UNEP/OECD/IEA (1997), page 2.23 is assumed to have a misprint; the chemical identified should be ethylene dichloride (C₂H₄Cl₂) rather than dichloroethylene (C₂H₂Cl₂).

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).

Table 4-36: Carbon Black Feedstock (Primary Feedstock) and Natural Gas Feedstock (Secondary Feedstock) Consumption (Thousand Metric Tons)

Activity	1990	2000	2005	2006	2007	2008	2009
Primary Feedstock	2,213	2,993	2,794	2,564	2,627	2,305	1,828
Secondary Feedstock	284	384	359	329	337	296	235

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 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 CH₄ 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 CH₄ arising from petrochemical production activities that have not been included in these estimates.

The results of the quantitative uncertainty analysis for the CO₂ 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 CO₂ 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 4-37. Petrochemical production CO₂ emissions were estimated to be between 2.0 and 3.6 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 27 percent below to 31 percent above the emission estimate of 2.7 Tg CO₂ Eq. Petrochemical production CH₄ emissions were estimated to be between 0.6 and 1.1 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 26 percent below to 27 percent above the emission estimate of 0.8 Tg CO₂ Eq.

Table 4-37: Tier 2 Quantitative Uncertainty Estimates for CH₄ Emissions from Petrochemical Production and CO₂ Emissions from Carbon Black Production (Tg CO₂ Eq. and Percent)

Source	Gas	2009 Emission		Uncertainty Range Relative to Emission Estimate ^a			
		Estimate (Tg CO ₂ Eq.)	Relative to Emission Estimate ^a				
			Lower Bound	Upper Bound	Lower Bound	Upper Bound	
Petrochemical Production	CO ₂	2.7	2.0	3.6	-27%	+31%	
Petrochemical Production	CH ₄	0.8	0.6	1.1	-26%	+27%	

^a 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 2009. Details on the emission trends through time are described in more detail in the Methodology section, above.

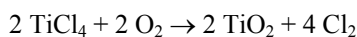
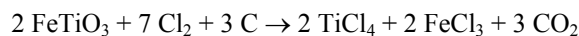
Planned Improvements

Future improvements to the petrochemicals source category involve updating the methodology to use CH₄ emission factors for petrochemical production from the IPCC 2006 guidelines rather than the IPCC 1996 guidelines. Further future improvements involve evaluating facility level greenhouse gas emissions data as a basis for improving emissions calculations from petrochemical production. Beginning in 2010, all U.S. petrochemical production facilities are required to monitor, calculate and report their greenhouse gas emissions to EPA through its Greenhouse Gas Reporting Program. Under the program, EPA will obtain data for 2010 emissions from facilities based on use of higher tier methods and in particular assess how this data could be used to improve the overall method for calculating emissions from the U.S. petrochemical production industry, for example using a Tier 2 methodology to calculate emissions from the production of methanol, ethylene, propylene, ethylene dichloride, and ethylene oxide. In addition, the planned improvements include assessing the data EPA obtains to update data sources for acrylonitrile production in the United States.

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

Titanium dioxide (TiO₂) 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 TiO₂: the chloride process and the sulfate process. The chloride process uses petroleum coke and chlorine as raw materials and emits process-related CO₂. The sulfate process does not use petroleum coke or other forms of C as a raw material and does not emit CO₂.

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 FeTiO₃ (the Ti-containing ore) to form CO₂. The majority of U.S. TiO₂ was produced in the United States through the chloride process, and a special grade of “calcined” petroleum coke is manufactured specifically for this purpose.

Emissions of CO₂ in 2009 were 1.5 Tg CO₂ Eq. (1,541 Gg), which represents an increase of 29 percent since 1990 (see Table 4-38).

Table 4-38: CO₂ Emissions from Titanium Dioxide (Tg CO₂ Eq. and Gg)

Year	Tg CO ₂ Eq.	Gg
1990	1.2	1,195
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
2009	1.5	1,541

Methodology

Emissions of CO₂ from TiO₂ production were calculated by multiplying annual TiO₂ production by chloride-process-specific emission factors.

Data were obtained for the total amount of TiO₂ produced each year. For years previous to 2004, it was assumed that TiO₂ 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 TiO₂ was applied to the estimated chloride-process production. It was assumed that all TiO₂ produced using the chloride process was produced using petroleum coke, although some TiO₂ may have been produced with graphite or other C inputs. The amount of petroleum coke consumed annually in TiO₂ 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 TiO₂ 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 TiO₂ production capacity that is chloride process for 1990 through 2008 (see Table 4-39) were obtained through the Minerals Yearbook: Titanium Annual Report (USGS 1991 through 2008). Production data in 2009 was obtained from the Minerals Commodity Summary: Titanium and Titanium Dioxide (USGS 2010). Due to lack of available 2009 capacity data at the time of publication, the 2008 capacity estimate is used as a proxy for 2009. 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).

Table 4-39: Titanium Dioxide Production (Gg)

Year	Gg
1990	979
2000	1,400
2005	1,310
2006	1,370
2007	1,440
2008	1,350
2009	1,150

Uncertainty and Time-Series Consistency

Although some TiO₂ 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 CO₂ per unit of TiO₂ 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 TiO₂ produced, sufficient data were not available to do so.

Also, annual TiO₂ 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 TiO₂ production capacity that was attributed to the chloride process was multiplied by total TiO₂ production to estimate the amount of TiO₂ 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 TiO₂ production, literature data were used for petroleum coke composition. Certain grades of petroleum coke are manufactured specifically for use in the TiO₂ chloride process; however, this composition information was not available.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-40. Titanium dioxide consumption CO₂ emissions were estimated to be between 1.4 and 1.7 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 13 percent below and 13 percent above the emission estimate of 1.5 Tg CO₂ Eq.

Table 4-40: Tier 2 Quantitative Uncertainty Estimates for CO₂ Emissions from Titanium Dioxide Production (Tg CO₂ Eq. and Percent)

Source	Gas	2009 Emission	Uncertainty Range Relative to Emission Estimate ^a			
		Estimate	(Tg CO ₂ Eq.)		(%)	
		(Tg CO ₂ Eq.)	Lower Bound	Upper Bound	Lower Bound	Upper Bound
Titanium Dioxide Production	CO ₂	1.5	1.3	1.7	-13%	+13%

^a 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 2009. Details on the emission trends through time are described in more detail in the Methodology section, above.

Planned Improvements

Future improvements to the titanium dioxide production category involve evaluating facility level greenhouse gas emissions data as a basis for improving emissions calculations from titanium dioxide production. Beginning in 2010, all U.S. titanium dioxide production facilities using the chloride production process are required to monitor, calculate and report their greenhouse gas emissions to EPA through its Greenhouse Gas Reporting Program. Under the program, EPA will obtain data for 2010 emissions from facilities based on use of higher tier methods and in particular assess how this data could be used to improve the overall method for calculating emissions from the U.S. titanium dioxide production industry, including improving the emission factors. In addition, the planned improvements 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.

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

CO₂ 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). CO₂ 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, CO₂ used in non-EOR applications will eventually be released to the atmosphere, and for the purposes of this analysis CO₂ used in commercial applications other than EOR is assumed to be emitted to the atmosphere. CO₂ 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.

CO₂ is produced from naturally occurring CO₂ 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 CO₂ as a component. Only CO₂ produced from naturally occurring CO₂ reservoirs and used in industrial applications other than EOR is included in this analysis. Neither by-product CO₂ generated from energy nor industrial production processes nor CO₂ separated from crude oil and natural gas are included in this analysis for a number of reasons. CO₂ captured from biogenic sources (e.g., ethanol production plants) is not included in the inventory. CO₂ captured from crude oil and gas production is used in EOR applications and is therefore reported in the Energy Chapter. Any CO₂ 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 CO₂ emissions from such capture and use are

therefore accounted for under Ammonia Production, Fossil Fuel Combustion, or other appropriate source category.¹¹⁴

CO₂ is produced as a by-product of crude oil and natural gas production. This CO₂ 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 CO₂ used in EOR is described in the Energy Chapter under the text box titled “Carbon Dioxide Transport, Injection, and Geological Storage.” The only CO₂ consumption that is accounted for in this analysis is CO₂ produced from naturally-occurring CO₂ reservoirs that is used in commercial applications other than EOR.

There are currently two facilities, one in Mississippi and one in New Mexico, producing CO₂ from naturally occurring CO₂ reservoirs for use in both EOR and in other commercial applications (e.g., chemical manufacturing, food production). There are other naturally occurring CO₂ reservoirs, mostly located in the western United States. Facilities are producing CO₂ from these natural reservoirs, but they are only producing CO₂ for EOR applications, not for other commercial applications (Allis et al. 2000). CO₂ production from these facilities is discussed in the Energy Chapter.

In 2009, the amount of CO₂ produced by the Mississippi and New Mexico facilities for commercial applications and subsequently emitted to the atmosphere was 1.8 Tg CO₂ Eq. (1,763 Gg) (see Table 4-41). This amount represents a decrease of one percent from the previous year and an increase of 24 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 4-41: CO₂ Emissions from CO₂ Consumption (Tg CO₂ Eq. and Gg)

Year	Tg CO₂ Eq.	Gg
1990	1.4	1,416
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
2009	1.8	1,763

Methodology

CO₂ emission estimates for 1990 through 2009 were based on production data for the two facilities currently producing CO₂ from naturally-occurring CO₂ reservoirs for use in non-EOR applications. Some of the CO₂ 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 CO₂ production used in commercial applications other than EOR is eventually released into the atmosphere.

CO₂ 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 2010) for 2001 to 2009 (see Table 4-42). Denbury Resources reported the average CO₂ production in units of MMCF CO₂ per day for 2001 through 2009 and reported the percentage of the total average annual production that was used for EOR. CO₂ production data for the Bravo Dome, New Mexico facility were obtained from the Advanced Resources International, Inc. (ARI 1990 through 2010). 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).

Table 4-42: CO₂ Production (Gg CO₂) and the Percent Used for Non-EOR Applications for Jackson Dome and

¹¹⁴ There are currently four known electric power plants operating in the U.S. that capture CO₂ for use as food-grade CO₂ or other industrial processes; however, insufficient data prevents estimating emissions from these activities as part of Carbon Dioxide Consumption.

Bravo Dome

Year	Jackson Dome CO ₂ Production (Gg)	Jackson Dome % Used for Non-EOR	Bravo Dome CO ₂ Production (Gg)	Bravo Dome % Used for Non-EOR
1990	1,353	100%	6,301	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%
2009	13,201	13%	4,639	1%

Uncertainty and Time-Series Consistency

Uncertainty is associated with the number of facilities that are currently producing CO₂ from naturally occurring CO₂ reservoirs for commercial uses other than EOR, and for which the CO₂ 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 CO₂ 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 CO₂ emissions from that sector depending upon the end use to which the recovered CO₂ is applied. Further research is required to determine whether CO₂ 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 4-43. CO₂ consumption CO₂ emissions were estimated to be between 1.3 and 2.3 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 26 percent below to 30 percent above the emission estimate of 1.8 Tg CO₂ Eq.

Table 4-43: Tier 2 Quantitative Uncertainty Estimates for CO₂ Emissions from CO₂ Consumption (Tg CO₂ Eq. and Percent)

Source	Gas	2009 Emission Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to Emission Estimate ^a (%)			
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
CO ₂ Consumption	CO ₂	1.8	1.3	2.3	-26%	+30%

^a 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 2009. Details on the emission trends through time are described in more detail in the Methodology section, above.

Planned Improvements

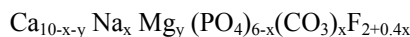
Future improvements to the Carbon Dioxide Consumption source category involve evaluating facility level greenhouse gas emissions data as a basis for improving emissions calculations from carbon dioxide consumption. Beginning in 2010, all U.S. CO₂ producers are required to monitor, calculate and report the quantity of CO₂ supplied to EPA through its Greenhouse Gas Reporting Program. Under the program, EPA will obtain data for 2010 on CO₂ supplied from facilities based on use of higher tier methods and in particular assess how this data could be used to improve the overall method for calculating emissions from consumption of CO₂.

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

Phosphoric acid (H₃PO₄) 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 (CaSO₄·2H₂O), referred to as phosphogypsum.

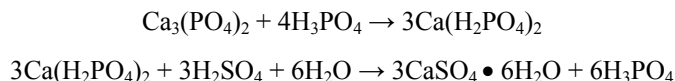
The composition of natural phosphate rock varies depending upon the location where it is mined. Natural phosphate

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:

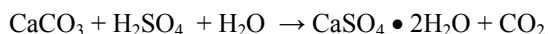


The calcium carbonate component of the phosphate rock is integral to the phosphate rock chemistry. Phosphate rock can also contain organic C that is physically incorporated into the mined rock but is not an integral component of the phosphate rock chemistry. Phosphoric acid production from natural phosphate rock is a source of CO₂ 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 (Ca₃(PO₄)₂) component of the phosphate rock with sulfuric acid (H₂SO₄) and recirculated phosphoric acid (H₃PO₄) (EFMA 2000). The primary chemical reactions for the production of phosphoric acid from phosphate rock are:



The limestone (CaCO₃) component of the phosphate rock reacts with the sulfuric acid in the phosphoric acid production process to produce calcium sulfate (phosphogypsum) and CO₂. The chemical reaction for the limestone-sulfuric acid reaction is:



Total marketable phosphate rock production in 2009 was 27.2 million metric tons (USGS 2010). 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. Total imports of phosphate rock in 2009 were 1.8 million metric tons (USGS 2010). 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, decreased by 13.6 percent between 2008 and 2009. Over the 1990 to 2009 period, production has decreased by 34 percent. Total CO₂ emissions from phosphoric acid production were 1.0 Tg CO₂ Eq. (1,035 Gg) in 2009 (see Table 4-44). According to USGS 2010, the weak market conditions of phosphate rock in the U.S. in 2009 were a result of the global economic crisis that started in late 2008 and carried into 2009.

Table 4-44: CO₂ Emissions from Phosphoric Acid Production (Tg CO₂ Eq. and Gg)

Year	Tg CO ₂ Eq.	Gg
1990	1.5	1,529
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
2009	1.0	1,035

Methodology

CO₂ 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 CO₂ emissions calculation methodology is based on the assumption that all of the inorganic C (calcium carbonate) content of the phosphate rock reacts to CO₂ 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 CO₂ 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 4-45). 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 2008 were obtained from *USGS Minerals Yearbook: Phosphate Rock* (USGS 1994 through 2010). 2009 data were obtained from *USGS Minerals Commodity Summary: Phosphate Rock* (USGS 2010). From 2004 through 2009, the USGS reported no exports of phosphate rock from U.S. producers (USGS 2005 through 2010).

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 4-46).

Carbonate content data for phosphate rock mined in Florida are used to calculate the CO₂ 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 CO₂ emissions from consumption of imported phosphate rock. The CO₂ 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 content data for calcined phosphate rock mined in Idaho.

Table 4-45: Phosphate Rock Domestic Production, Exports, and Imports (Gg)

Location/Year	1990	2000	2005	2006	2007	2008	2009
U.S. Production ^a	49,800	37,370	36,100	30,100	29,700	30,200	27,200
FL & NC	42,494	31,900	31,227	26,037	25,691	26,123	23,528
ID & UT	7,306	5,470	4,874	4,064	4,010	4,077	3,672
Exports—FL & NC	6,240	299	-	-	-	-	-
Imports—Morocco	451	1,930	2,630	2,420	2,670	2,754	1,800
Total U.S. Consumption	44,011	39,001	38,730	32,520	32,370	32,954	29,000

^a 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.

- Assumed equal to zero.

Table 4-46: Chemical Composition of Phosphate Rock (percent by weight)

Composition	Central Florida		North Carolina		Morocco
	Florida	North Florida	(calcined)	Idaho (calcined)	
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 ₂)	3.67	3.43	1.50	1.00	5.00

Source: FIPR 2003

- Assumed equal to zero.

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 2009. For previous years in the time series, USGS provided the data disaggregated regionally; however, beginning in 2006 only total U.S. phosphate rock production were reported. Regional production for 2008 was estimated based on regional production data from previous years and multiplied by regionally-specific emission factors. There is uncertainty associated with the degree to which the estimated 2008 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 CO₂ 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 CO₂ 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 CO₂. 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 CO₂ in the elemental phosphorus production process. The calculation for CO₂ emissions is based on the assumption that phosphate rock consumption, for purposes other than phosphoric acid production, results in CO₂ 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 4-47. Phosphoric acid production CO₂ emissions were estimated to be between 0.9 and 1.2 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 18 percent below and 19 percent above the emission estimate of 1.0 Tg CO₂ Eq.

Table 4-47: Tier 2 Quantitative Uncertainty Estimates for CO₂ Emissions from Phosphoric Acid Production (Tg CO₂ Eq. and Percent)

Source	Gas	2009 Emission Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to Emission Estimate ^a			
			(Tg CO ₂ Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Phosphoric Acid Production	CO ₂	1.0	0.9	1.2	-18%	+19%

^a 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 2009. Details on the emission trends through time are described in more detail in the Methodology section, above.

Planned Improvements

Future improvements to the phosphoric acid production source category involve evaluating facility level greenhouse gas emissions data as a basis for improving emissions calculations from phosphoric acid production. Beginning in 2010, all U.S. phosphoric acid producers are required to monitor, calculate and report their greenhouse gas emissions to EPA through its Greenhouse Gas Reporting Program. Under the program, EPA will obtain data for 2010 from facilities based on use of higher tier methods and assess how this data could be used to improve the method for calculating emissions from the U.S. phosphoric acid production industry. 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. Additionally, as future improvement to the phosphoric acid uncertainty analysis, USGS Mineral Commodity Specialists will be contacted to verify uncertainty ranges associated with phosphate rock

imports and exports.

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

The production of iron and steel is an energy-intensive activity that also generates process-related emissions of CO₂ and CH₄. Process emissions occur at each step of steel production from the production of raw materials to the refinement of iron to the making of crude steel. In the United States, steel is produced through both primary and secondary processes. Historically, primary production—using a basic oxygen furnace (BOF) with pig iron as the primary feedstock—has been the dominant method. But secondary production through the use scrap steel and electric arc furnaces (EAFs) has increased significantly in recent years due to the economic advantages of steel recycling, which has been driven by the increased availability of scrap steel. Total production of crude steel in the United States in the time period between 2001 and 2008 ranged from a low of 99,321,000 tons to a high of 109,879,000 tons (2001 and 2004, respectively). But due to the decrease in demand caused by the global economic downturn, crude steel production in the United States decreased to 65,460,000 tons in 2009 (AISI 2010).

Metallurgical coke is an important input in the production of iron and steel. Coke is used to produce iron or pig iron feedstock from raw iron ore. 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 CO₂ emissions and fugitive CH₄ emissions.

Iron is produced by first reducing iron oxide (iron ore) with metallurgical coke in a blast furnace. Iron can be introduced into the blast furnace in the form of raw iron ore, taconite pellets (9-16mm iron-containing spheres), briquettes, or sinter. In addition to metallurgical coke and iron, other 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 CO₂. The CO is then converted and emitted as CO₂ when combusted to either pre-heat the blast air used in the blast furnace or for other purposes at the steel mill. This pig iron or crude iron that is produced from this process contains about 3 to 5 percent carbon by weight. The pig iron production process in a blast furnace produces CO₂ emissions and fugitive CH₄ 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 CO₂ and emissions of CH₄ 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 CO₂ and fugitive CH₄ 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. CO₂ emissions occur in BOFs through the reduction process. In EAFs, CO₂ 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, CO₂ 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. 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).

The majority of CO₂ 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 lesser amounts emitted 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, CO₂ 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 the use of conventional fuels (e.g., natural gas and fuel oil) for electricity generation, heating and annealing, or other miscellaneous purposes downstream of the iron and steelmaking furnaces are reported in the Energy chapter.

Metallurgical Coke Production

Emissions of CO₂ and CH₄ from metallurgical coke production in 2009 were 1.0 Tg CO₂ Eq. (956 Gg) and less than 0.002 Tg CO₂ Eq. (less than 0.00003 Gg), respectively (see Table 4-48 and Table 4-49), totaling 1.0 Tg CO₂ Eq. Emissions decreased in 2009, and have decreased overall since 1990. In 2009, domestic coke production decreased by 29 percent and has decreased overall since 1990. Coke production in 2009 was 46 percent lower than in 2000 and 60 percent below 1990. Overall, emissions from metallurgical coke production have declined by 61 percent (1.5 Tg CO₂ Eq.) from 1990 to 2009.

Table 4-48: CO₂ and CH₄ Emissions from Metallurgical Coke Production (Tg CO₂ Eq.)

Year	1990	2000	2005	2006	2007	2008	2009
CO ₂	2.5	2.2	2.0	1.9	2.1	2.3	1.0
CH ₄	+	+	+	+	+	+	+
Total	2.5	2.2	2.0	1.9	2.1	2.3	1.0

+ Does not exceed 0.05 Tg CO₂ Eq.

Table 4-49: CO₂ and CH₄ Emissions from Metallurgical Coke Production (Gg)

Year	1990	2000	2005	2006	2007	2008	2009
CO ₂	2,470	2,195	2,043	1,919	2,054	2,334	956
CH ₄	+	+	+	+	+	+	+

+ Does not exceed 0.5 Gg

Iron and Steel Production

Emissions of CO₂ and CH₄ from iron and steel production in 2009 were 40.9 Tg CO₂ Eq. (40,914 Gg) and 0.4 Tg CO₂ Eq. (17.4 Gg), respectively (see Table 4-50 through Table 4-53), totaling approximately 41 Tg CO₂ Eq. Emissions decreased in 2009—largely due to decreased steel production associated with the global economic downturn—and have decreased overall since 1990 due to restructuring of the industry, technological improvements, and increased scrap steel utilization. CO₂ 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 2009, domestic production of pig iron decreased by 44 percent. Overall, domestic pig iron production has declined since the 1990s. Pig iron production in 2009 was 60 percent lower than in 2000 and 62 percent below 1990. CO₂ emissions from steel production have declined by 15 percent (1.1 Tg CO₂ Eq.) since 1990, while overall CO₂ emissions from iron and steel production have declined by 58 percent (56.1 Tg CO₂ Eq.) from 1990 to 2009.

Table 4-50: CO₂ Emissions from Iron and Steel Production (Tg CO₂ Eq.)

Year	1990	2000	2005	2006	2007	2008	2009
Sinter Production	2.4	2.2	1.7	1.4	1.4	1.3	0.8
Iron Production	47.9	33.8	19.6	23.9	27.3	25.7	15.9
Steel Production	7.5	7.9	8.5	8.9	9.4	7.5	6.4
Other Activities ^a	39.3	39.9	34.2	32.6	31.0	29.1	17.8
Total	97.1	83.7	63.9	66.9	69.0	63.7	40.9

Note: Totals may not sum due to independent rounding.

^a 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.

Table 4-51: CO₂ Emissions from Iron and Steel Production (Gg)

Year	1990	2000	2005	2006	2007	2008	2009
Sinter Production	2,448	2,158	1,663	1,418	1,383	1,299	763
Iron Production	47,880	33,818	19,570	23,928	27,262	25,696	15,948
Steel Production	7,475	7,887	8,489	8,924	9,382	7,541	6,389
Other Activities ^a	39,256	39,877	34,160	32,583	30,964	29,146	17,815
Total	97,058	83,740	63,882	66,852	68,991	63,682	40,914

Note: Totals may not sum due to independent rounding.

^a 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.

Table 4-52: CH₄ Emissions from Iron and Steel Production (Tg CO₂ Eq.)

Year	1990	2000	2005	2006	2007	2008	2009
Sinter Production	+	+	+	+	+	+	+
Iron Production	0.9	0.9	0.7	0.7	0.7	0.6	0.4
Total	1.0	0.9	0.7	0.7	0.7	0.6	0.4

+ Does not exceed 0.05 Tg CO₂ Eq.

Note: Totals may not sum due to independent rounding.

Table 4-53: CH₄ Emissions from Iron and Steel Production (Gg)

Year	1990	2000	2005	2006	2007	2008	2009
Sinter Production	0.9	0.7	0.6	0.5	0.5	0.4	0.3
Iron Production	44.7	43.1	33.5	34.1	32.7	30.4	17.1
Total	45.6	43.8	34.1	34.6	33.2	30.8	17.4

Note: Totals may not sum due to independent rounding.

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 4-54). 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 4-54: 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.

The production processes for metallurgical coke production results in fugitive emissions of CH₄, 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 CH₄ 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 2010a) (see Table 4-55). 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 20010) and through personal communications with AISI (2008b) (see Table 4-56). 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.

Table 4-55: Production and Consumption Data for the Calculation of CO₂ and CH₄ Emissions from Metallurgical Coke Production (Thousand Metric Tons)

Source/Activity Data	1990	2000	2005	2006	2007	2008	2009
Metallurgical Coke Production							
Coking Coal Consumption at Coke Plants	35,269	26,254	21,259	20,827	20,607	20,022	13,904
Coke Production at Coke Plants	25,054	18,877	15,167	14,882	14,698	14,194	10,109
Coal Breeze Production	2,645	1,969	1,594	1,562	1,546	1,502	1,043
Coal Tar Production	1,058	788	638	625	618	601	417

Table 4-56: Production and Consumption Data for the Calculation of CO₂ Emissions from Metallurgical Coke Production (million ft³)

Source/Activity Data	1990	2000	2005	2006	2007	2008	2009
Metallurgical Coke Production							
Coke Oven Gas Production ^a	250,767	149,477	114,213	114,386	109,912	103,191	66,155
Natural Gas Consumption	599	180	2,996	3,277	3,309	3,134	2,121
Blast Furnace Gas Consumption	24,602	26,075	4,460	5,505	5,144	4,829	2,435

^a Includes coke oven gas used for purposes other than coke oven underfiring only.

Iron and Steel Production

Emissions of CO₂ 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 CO₂ emission factors (see Table 4-57). Because estimates of sinter production and direct reduced iron production were not available, production was assumed to equal consumption.

Table 4-57: CO₂ Emission Factors for Sinter Production and Direct Reduced Iron Production

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

Source: IPCC 2006, Table 4.1.

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 4-58). Carbon in blast furnace gas used to pre-heat the blast furnace air is combusted to form CO₂ during this process.

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 4-58). 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.

CO₂ 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 4-58).

CO₂ 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 CO₂ emissions from iron and steel production (see Table 4-50 and Table 4-51).

Table 4-58: 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.

The production processes for sinter and pig iron result in fugitive emissions of CH₄, 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 4-59) for pig iron production. The production of direct reduced iron also results in emissions of CH₄ through the consumption of fossil fuels (e.g., natural gas); however, these emissions estimates are excluded due to data limitations.

Table 4-59: CH₄ Emission Factors for Sinter and Pig Iron Production

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

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

Sinter consumption and direct reduced iron consumption data were obtained from AISI's Annual Statistical Report (AISI 2004 through 2010) and through personal communications with AISI (2008b) (see Table 4-60). Data on direct reduced iron consumed in EAFs were not available for the years 1990, 1991, 1999, 2006, 2007, 2008, and 2009. 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, 2008, and 2009 were calculated by multiplying the total DRI consumption for all furnaces as provided in the 2009 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, 2008, and 2009. BOF direct reduced iron consumption in 1990 through 1994 was assumed to equal consumption in 1995, and consumption in 1999 was assumed to equal 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 2009 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 CO₂ 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 2010) and through personal communications with AISI (2008b) (see Table 4-61). 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 2010) and through personal communications with AISI (2011). 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 2010) 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 2009, values for these years were calculated by multiplying the total pig iron and scrap steel consumption for all furnaces as provided in the 2009 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 2010) 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 2009* (EIA 2010b). C contents for direct reduced iron, EAF carbon electrodes, 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, 2010c). 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).

Table 4-60: Production and Consumption Data for the Calculation of CO₂ and CH₄ Emissions from Iron and Steel Production (Thousand Metric Tons)

Source/Activity Data	1990	2000	2005	2006	2007	2008	2009
Sinter Production							
Sinter Production	12,239	10,788	8,315	7,088	6,914	6,497	3,814
Direct Reduced Iron Production							
Direct Reduced Iron Production	936	1,914	1,633	1,497	2,087	1,769	1,243
Pig Iron Production							
Coke Consumption	24,946	19,215	13,832	14,684	15,039	14,251	8,572
Pig Iron Production	49,669	47,888	37,222	37,904	36,337	33,730	19,019
Direct Injection Coal Consumption	1,485	3,012	2,573	2,526	2,734	2,578	1,674
EAF Steel Production							
EAF Anode and Charge Carbon Consumption	67	96	1,127	1,245	1,214	1,109	845
Scrap Steel Consumption	35,743	43,001	37,558	38,033	40,845	40,824	35,472
Flux Consumption	319	654	695	671	567	680	476
EAF Steel Production	33,511	47,860	52,194	56,071	57,004	52,791	36,700
BOF Steel Production							
Pig Iron Consumption	46,564	46,993	32,115	32,638	33,773	29,322	23,134
Scrap Steel Consumption	14,548	14,969	11,612	11,759	12,628	8,029	6,641
Flux Consumption	576	978	582	610	408	431	318
BOF Steel Production	43,973	53,965	42,705	42,119	41,099	39,105	22,659

Table 4-61: Production and Consumption Data for the Calculation of CO₂ Emissions from Iron and Steel Production (million ft³ unless otherwise specified)

Source/Activity Data	1990	2000	2005	2006	2007	2008	2009
Pig Iron Production							
Natural Gas Consumption	56,273	91,798	59,844	58,344	56,112	53,349	35,933
Fuel Oil Consumption (thousand gallons)	163,397	120,921	16,170	87,702	84,498	55,552	23,179
Coke Oven Gas Consumption	22,033	13,702	16,557	16,649	16,239	15,336	9,951
Blast Furnace Gas Production	1,439,380	1,524,891	1,299,980	1,236,526	1,173,588	1,104,674	672,486
EAF Steel Production							
Natural Gas Consumption	9,604	13,717	14,959	16,070	16,337	15,130	10,518
BOF Steel Production							
Natural Gas Consumption	6,301	6,143	5,026	5,827	11,740	-4,304 ^a	-2,670 ^a
Coke Oven Gas Consumption	3,851	640	524	559	525	528	373
Other Activities							
Coke Oven Gas Consumption	224,883	135,135	97,132	97,178	93,148	87,327	55,831
Blast Furnace Gas Consumption	1,414,778	1,498,816	1,295,520	1,231,021	1,168,444	1,099,845	670,051

^a EPA is continuing to work with AISI to investigate why this value is negative.

Uncertainty and Time-Series Consistency

The estimates of CO₂ and CH₄ 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 CO₂ 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 CO₂ emissions from iron and steel production are based on material production and consumption data and average C 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 C contents for pellets, sinter, and natural ore, which are assumed to equal the C contents of direct reduced iron. For EAF steel production there is uncertainty associated with the amount of EAF anode and charge C consumed due to inconsistent data throughout the time series. 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 C contents produce a relatively accurate estimate of CO₂ emissions. However, there are uncertainties associated with each.

For the purposes of the CH₄ calculation from iron and steel production it is assumed that all of the CH₄ escapes as fugitive emissions and that none of the CH₄ is captured in stacks or vents. Additionally, the CO₂ emissions calculation is not corrected by subtracting the C content of the CH₄, which means there may be a slight double counting of C as both CO₂ and CH₄.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-62 for metallurgical coke production and iron and steel production. Total CO₂ emissions from metallurgical coke production and iron and steel production were estimated to be between 35.2 and 48.4 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 16 percent below and 16 percent above the emission estimate of 41.9 Tg CO₂ Eq. Total CH₄ emissions from metallurgical coke production and iron and steel production were estimated to be 0.4 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 21 percent below and 23 percent above the emission estimate of 0.4 Tg CO₂ Eq.

Table 4-62: Tier 2 Quantitative Uncertainty Estimates for CO₂ and CH₄ Emissions from Iron and Steel Production and Metallurgical Coke Production (Tg. CO₂ Eq. and Percent)

Source	Gas	2009 Emission Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to Emission Estimate ^a			
			Lower Bound (Tg CO ₂ Eq.)	Upper Bound	Lower Bound (%)	Upper Bound
Metallurgical Coke & Iron and Steel Production	CO ₂	41.9	35.2	48.4	-16%	+16%
Metallurgical Coke & Iron and Steel Production	CH ₄	0.4	0.3	0.4	-21%	+23%

^a 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 2009. Details on the emission trends through time are described in more detail in the Methodology section, above.

Planned Improvements

Future improvements to the Iron and Steel production source category involve evaluating facility level greenhouse gas emissions data as a basis for improving emissions calculations from iron and steel production. Beginning in 2010, all U.S. iron and steel producing facilities that emit over 25,000 tons of greenhouse gases (CO₂ Eq.) are required to monitor, calculate and report their greenhouse gas emissions to EPA through its Greenhouse Gas Reporting Program. Under the program, EPA will obtain data for 2010 from these facilities based on use of higher tier methods and assess how this data could be used to improve the method for calculating emissions from the U.S. iron and steel industry. Specifically, plans 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.

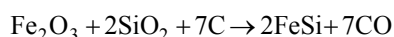
Recalculations Discussion

In the previous Inventory, coal tar production and coke breeze production were incorrectly estimated by multiplying the respective production factors by U.S. coke production at coke plants rather than U.S. coking coal consumption at coke plants (to which the coal tar and coke breeze production factors should be applied). This issue has been corrected and decreased the 1990 through 2008 emissions from metallurgical coke production by an average of 53 percent per year relative to the previous Inventory. The total 1990 through 2008 emissions for metallurgical coke and iron and steel production decreased by an average of 3 percent per year relative to the previous Inventory.

4.14. Ferroalloy Production (IPCC Source Category 2C2)

CO₂ and CH₄ 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, CO₂ 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 CO₂. 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 CO₂, a percentage is also released as CH₄ and other volatiles. The amount of CH₄ that is released is dependent on furnace efficiency, operation technique, and control technology.

Emissions of CO₂ from ferroalloy production in 2009 were 1.5 Tg CO₂ Eq. (1,469 Gg) (see Table 4-63 and Table 4-64), which is a 32 percent reduction since 1990. Emissions of CH₄ from ferroalloy production in 2009 were 0.01 Tg CO₂ Eq. (0.406 Gg), which is a 40 percent decrease since 1990.

Table 4-63: CO₂ and CH₄ Emissions from Ferroalloy Production (Tg CO₂ Eq.)

Year	1990	2000	2005	2006	2007	2008	2009
CO ₂	2.2	1.9	1.4	1.5	1.6	1.6	1.5
CH ₄	+	+	+	+	+	+	+
Total	2.2	1.9	1.4	1.5	1.6	1.6	1.6

+ Does not exceed 0.05 Tg CO₂ Eq.

Note: Totals may not sum due to independent rounding.

Table 4-64: CO₂ and CH₄ Emissions from Ferroalloy Production (Gg)

Year	1990	2000	2005	2006	2007	2008	2009
CO ₂	2,152	1,893	1,392	1,505	1,552	1,599	1,469
CH ₄	1	1	+	+	+	+	+

Methodology

Emissions of CO₂ and CH₄ 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 CO₂ (2.5 metric tons CO₂/metric ton of alloy produced) and an emission factor for 65 percent silicon was applied for CH₄ (1 kg CH₄/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 CO₂ and CH₄ (4 metric tons CO₂/metric ton alloy produced and 1 kg CH₄/metric ton of alloy produced, respectively). The emission factors for silicon metal equaled 5 metric tons CO₂/metric ton metal produced and 1.2 kg CH₄/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 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 2009 (see Table 4-65) were obtained from the USGS through personal communications with the USGS Silicon Commodity Specialist (Corathers 2011) and through the *Minerals Yearbook: Silicon Annual Report* (USGS 1991 through 2010). Because USGS does not provide estimates of silicon metal production for 2006-2009, 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 4-65). The composition data for petroleum coke was obtained from Onder and Bagdoyan (1993).

Table 4-65: 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
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
2009	123,932	104,855	148,000	NA

NA (Not Available)

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.¹¹⁵ 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 CO₂ 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.

¹¹⁵ Emissions and sinks of biogenic carbon are accounted for in the Land Use, Land-Use Change, and Forestry chapter.

Emissions of CH₄ 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 CH₄ emissions; however, specific furnace information was not available or included in the CH₄ 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 4-66. Ferroalloy production CO₂ emissions were estimated to be between 1.3 and 1.7 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 12 percent below and 13 percent above the emission estimate of 1.5 Tg CO₂ Eq. Ferroalloy production CH₄ emissions were estimated to be between a range of approximately 12 percent below and 12 percent above the emission estimate of 0.01 Tg CO₂ Eq.

Table 4-66: Tier 2 Quantitative Uncertainty Estimates for CO₂ Emissions from Ferroalloy Production (Tg CO₂ Eq. and Percent)

Source	Gas	2009 Emission		Uncertainty Range Relative to Emission Estimate ^a		
		Estimate (Tg CO ₂ Eq.)	Range Relative to Emission Estimate ^a (%)			
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Ferroalloy Production	CO ₂	1.5	1.3	1.7	-12%	+13%
Ferroalloy Production	CH ₄	+	+	+	-12%	+12%

^a Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

+ Does not exceed 0.05 Tg CO₂ Eq.

Methodological recalculations were applied to the entire time-series to ensure time-series consistency from 1990 through 2009. 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 involve evaluating facility level greenhouse gas emissions data as a basis for improving emissions calculations from ferroalloy production. Beginning in 2010, all U.S. ferroalloy producing facilities that emit over 25,000 tons of greenhouse gases (CO₂ Eq.) are required to monitor, calculate and report their greenhouse gas emissions to EPA through its Greenhouse Gas Reporting Program. Under the program, EPA will obtain data for 2010 from these facilities based on use of higher tier methods and assess how this data could be used to improve the methodology and emissions factors for calculating emissions from the U.S. ferroalloy industry, in particular, including emission estimates from production of 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 2009a). 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 CO₂ and two perfluorocarbons (PFCs): perfluoromethane (CF₄) and perfluoroethane (C₂F₆).

CO₂ is emitted during the aluminum smelting process when alumina (aluminum oxide, Al₂O₃) 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_3AlF_6). The reduction cells contain a carbon lining that serves as the cathode. Carbon is also contained in the anode, which can be a carbon mass of paste, coke briquettes, or prebaked carbon blocks from petroleum coke. During reduction, most of this carbon is oxidized and released to the atmosphere as CO_2 .

Process emissions of CO_2 from aluminum production were estimated to be 3.0 Tg CO_2 Eq. (3,009 Gg) in 2009 (see Table 4-67). The carbon 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_2 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_2 from Fossil Fuel Combustion source category of the Energy sector. Similarly, the coal tar pitch portion of these CO_2 process emissions is accounted for here.

Table 4-67: CO_2 Emissions from Aluminum Production (Tg CO_2 Eq. and Gg)

Year	Tg CO_2 Eq.	Gg
1990	6.8	6,831
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
2009	3.0	3,009

In addition to CO_2 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_4 and C_2F_6 . 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_4 and C_2F_6 have declined by 92 percent and 89 percent, respectively, to 1.3 Tg CO_2 Eq. of CF_4 (0.20 Gg) and 0.30 Tg CO_2 Eq. of C_2F_6 (0.032 Gg) in 2009, as shown in Table 4-68 and Table 4-69. 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. Since 1990, aluminum production has declined by 57 percent, while the combined CF_4 and C_2F_6 emission rate (per metric ton of aluminum produced) has been reduced by 80 percent.

Table 4-68: PFC Emissions from Aluminum Production (Tg CO_2 Eq.)

Year	CF_4	C_2F_6	Total
1990	15.9	2.7	18.5
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
2009	1.3	0.3	1.6

Note: Totals may not sum due to independent rounding.

Table 4-69: PFC Emissions from Aluminum Production (Gg)

Year	CF_4	C_2F_6
1990	2.4	0.3
2000	1.2	0.1
2005	0.4	+

2006	0.3	+
2007	0.5	0.1
2008	0.3	0.1
2009	0.2	+

+ Does not exceed 0.05 Gg.

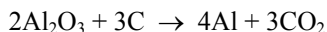
In 2009, U.S. primary aluminum production totaled approximately 1.7 million metric tons, a 35 percent decrease from 2008 production levels (USAA 2010). In 2009, six companies managed production at 13 operational primary aluminum smelters. Four smelters were closed the entire year, and demolition of one smelter that had been idle since 2000 was completed in 2009. Of the operating smelters, three were temporarily idled during some fraction of 2009, and parts of four others were temporarily closed in 2009 (USGS 2010a). During 2009, U.S. primary aluminum production was less for every month when compared to the corresponding month in 2008 (USGS 2009b, USGS 2010b).

For 2010, total production during January through September was approximately 1.28 million metric tons, compared to 1.32 million metric tons for the same period in 2009, only a 3 percent decrease (USGS 2010c). Based on the similarity in production, process CO₂ and PFC emissions are likely to be similar over this period in 2009 given no significant changes in process controls at operational facilities.

Methodology

CO₂ emissions released during aluminum production were estimated by combining individual partner reported data with process-specific emissions modeling. These estimates are based on information gathered by EPA's Voluntary Aluminum Industrial Partnership (VAIP) program.

Most of the CO₂ emissions released during aluminum production occur during the electrolysis reaction of the carbon anode, as described by the following reaction:



For prebake smelter technologies, CO₂ is also emitted during the anode baking process. These emissions can account for approximately 10 percent of total process CO₂ emissions from prebake smelters.

Depending on the availability of smelter-specific data, the CO₂ 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 CO₂ emission factors. The first approach tracks the consumption and C content of the anode, assuming that all C in the anode is converted to CO₂. Sulfur, ash, and other impurities in the anode are subtracted from the anode consumption to arrive at total C consumption. 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 CO₂ 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, 2008, and 2009. 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 CO₂ 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, 5 out of 14 operating smelters in, 2007 and 2008, and 3 out of 13 operating smelters in 2009. For years where CO₂ 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 13 smelters in 2009, 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), CO₂ emission estimates were estimated using Tier 1 Söderberg and/or Prebake emission factors (metric ton of CO₂ per metric ton of aluminum produced) from IPCC (2006).

Aluminum production data for 10 out of 13 operating smelters were reported under the VAIP in 2009. Between 1990 and 2008, 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 2010), with allocation to specific smelters based on reported production capacities (USGS 2009a).

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,

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

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

This approach corresponds to either the Tier 3 or the Tier 2 approach in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories (IPCC 2006), depending upon whether the slope-coefficient is smelter-specific (Tier 3) or technology-specific (Tier 2). For 1990 through 2009, 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 2009, 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 2009, 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 2009 were obtained via the United States Aluminum Association (USAA 2010). For 1990 through 2001, and 2006 (see Table 4-70) data were obtained from USGS, Mineral Industry Surveys: Aluminum Annual Report (USGS 1995, 1998, 2000, 2001, 2002, 2007). For 2002 through 2005, and 2007 through 2008 national aluminum production data were obtained from the USAA's Primary Aluminum Statistics (USAA 2004, 2005, 2006, 2008, 2009).

Table 4-70: Production of Primary Aluminum (Gg)

Year	Gg
1990	4,048
2000	3,668
2005	2,478
2006	2,284
2007	2,560
2008	2,659
2009	1,727

Uncertainty and Time Series Consistency

The overall uncertainties associated with the 2009 CO₂, CF₄, and C₂F₆ emission estimates were calculated using Approach 2, as defined by IPCC (2006). For CO₂, uncertainty was assigned to each of the parameters used to estimate CO₂ emissions. Uncertainty surrounding reported production data was assumed to be 1 percent (IPCC 2006). For additional variables, such as net C consumption, and sulfur 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 CO₂ 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 CF₄ and C₂F₆, 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 4-71. Aluminum production-related CO₂ emissions were estimated to be between 2.90 and 3.12 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 4 percent below to 4 percent above the emission estimate of 3.01 Tg CO₂ Eq. Also, production-related CF₄ emissions were estimated to be between 1.14 and 1.44 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 12 percent below to 12 percent above the emission estimate of 1.29 Tg CO₂ Eq. Finally, aluminum production-related C₂F₆ emissions were estimated to be between 0.25 and 0.35 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 17 percent below to 19 percent above the emission estimate of 0.30 Tg CO₂ Eq.

Table 4-71: Tier 2 Quantitative Uncertainty Estimates for CO₂ and PFC Emissions from Aluminum Production (Tg CO₂ Eq. and Percent)

Source	Gas	2009 Emission Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to 2009 Emission Estimate ^a			
			(Tg CO ₂ Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Aluminum Production	CO ₂	3.0	2.9	3.1	-4%	+4%
Aluminum Production	CF ₄	1.3	1.1	1.4	-12%	+12%
Aluminum Production	C ₂ F ₆	0.3	0.2	0.4	-17%	+19%

^a Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

The 2009 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 the uncertainties calculated above for the total U.S. 2009 emission estimates for CF₄ and C₂F₆ are also overestimated.

Methodological recalculations were applied to the entire time-series to ensure time-series consistency from 1990 through 2009. Details on the emission trends through time are described in more detail in the Methodology section, above.

Planned Improvements

Beginning in 2010, all primary U.S. aluminum producing facilities are required to monitor, calculate and report their greenhouse gas emissions to EPA through its Greenhouse Gas Reporting Program. Under the program, EPA will obtain data for 2010 from these facilities based on use of higher tier methods and assess how this data could be used to improve the methodology and emissions factors for calculating emissions from the U.S. primary aluminum production industry.

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

The magnesium metal production and casting industry uses sulfur hexafluoride (SF₆) 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 SF₆ with dry air and/or CO₂ is blown over molten magnesium metal to induce and stabilize the formation of a protective crust. A small portion of the SF₆ reacts with the magnesium to form a thin molecular film of mostly magnesium oxide and magnesium fluoride. The amount of SF₆ reacting in magnesium production and processing is considered to be negligible, and thus all SF₆ used is assumed to be emitted into the atmosphere. Although alternative cover gases, such as AM-cover™ (containing HFC-134a), Novec™ 612 and dilute SO₂ systems can be used, many facilities in the United States are still using traditional SF₆ cover gas systems.

The magnesium industry emitted 1.1 Tg CO₂ Eq. (0.04 Gg) of SF₆ in 2009, representing a decrease of approximately 45 percent from 2008 emissions (See Table 4-72). The decrease can be attributed to die casting facilities in the United States closing or halting production due to reduced demand from the American auto industry and other industrial sectors (USGS 2010a). Production associated with primary and secondary facilities also dropped in 2009. The significant reduction in emissions can also be attributed to industry efforts to switch to cover gas alternatives, such as sulfur dioxide, as part of the EPA's SF₆ Emission Reduction Partnership for the Magnesium Industry.

Table 4-72: SF₆ Emissions from Magnesium Production and Processing (Tg CO₂ Eq. and Gg)

Year	Tg CO ₂ Eq.	Gg
1990	5.4	0.2
2000	3.0	0.1
2005	2.9	0.1
2006	2.9	0.1
2007	2.6	0.1
2008	1.9	0.1
2009	1.1	0.04

Methodology

Emission estimates for the magnesium industry incorporate information provided by industry participants in EPA's SF₆ 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 2009 from primary production, secondary production (i.e., recycling), and die casting were generally reported by Partnership participants. Partners reported their SF₆ 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, 2008 and 2009, 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 2009 emissions from casting operations (other than die) were estimated by multiplying emission factors (kg SF₆ per metric ton of metal produced or processed) by the amount of metal produced or consumed. The emission factors for casting activities are provided below in Table 4-73. 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 SF₆ per metric ton. The emission factors for the other industry sectors (i.e., permanent mold, wrought, and anode casting) were based on discussions with industry representatives. U.S. magnesium consumption (casting) data from 1990 through 2009 were available from the USGS (USGS 2002, 2003, 2005, 2006, 2007, 2008, 2010).

Table 4-73: SF₆ Emission Factors (kg SF₆ per metric ton of magnesium)

Year	Die Casting	Permanent Mold	Wrought	Anodes
1999	2.14 ^a	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 ^b	2	1	1
2009	1.77 ^b	2	1	1

^a This is a weighted average that includes an estimated emission factor of 5.2 kg SF₆ per metric ton of magnesium for die casters that did not participate in the Partnership in 1999. These die casters were assumed to be similar to partners that cast small parts. Due to process requirements, these casters consume larger quantities of SF₆ per metric ton of processed magnesium than casters that process large parts. In later years, die casters participating in the Partnership accounted for all U.S. die casting tracked by USGS.

^b The emission factor for die casting increased significantly between 2007 and 2008, and again between 2008 and 2009. These increases occurred for two reasons. First, one of the die casters with a significant share of U.S. production that had used SF₆ as a cover gas and that had maintained a relatively low emission rate began using an alternative cover gas in 2008. Since the SF₆ emission factor provided here is based only on die casting operations that use SF₆ as a cover gas, the removal of the low-emitting die caster from the SF₆-using group increased the weighted average emission rate of that group. Second, one SF₆-using die caster experienced a significant leak in its cover gas distribution system in 2009 that resulted in an abnormally high SF₆ emission rate.

To estimate emissions for 1990 through 1998, industry emission factors were multiplied by the corresponding metal 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. These factors were based on information provided by U.S. primary producers. For die casting, an emission factor of 4.1 kg per metric ton was used for the period 1990 through 1996. This factor was drawn from an international survey of die casters (Gjestland & Magers 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 SF₆ sales to the magnesium sector that is reported in the RAND survey of major SF₆ manufacturers, which shows a decline of 70 percent from 1996 to 1999 (RAND 2002). Sand casting emission factors for 2002 through 2009 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 4-73.

Uncertainty

To estimate the uncertainty surrounding the estimated 2009 SF₆ 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 Magnesium 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, SF₆ 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 SF₆ 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 SF₆ usage for the sand casting partner was 52 percent. For those industry processes that are not represented in Partnership, such as permanent mold and wrought casting, SF₆ emissions were estimated using production and consumption statistics reported by USGS and estimated process-

specific emission factors (see Table 4-73). 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 SF₆ 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 SF₆ 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 4-74. SF₆ emissions associated with magnesium production and processing were estimated to be between 1.01 and 1.10 Tg CO₂ 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 1.05 Tg CO₂ Eq.

Table 4-74: Tier 2 Quantitative Uncertainty Estimates for SF₆ Emissions from Magnesium Production and Processing (Tg CO₂ Eq. and Percent)

Source	Gas	2009 Emission		Uncertainty Range Relative to Emission Estimate ^a		
		Estimate (Tg CO ₂ Eq.)	Range		Relative to Emission Estimate ^a (%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Magnesium Production	SF ₆	1.05	1.01	1.10	-4%	+4%

^a Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Recalculations Discussion

The uncertainty estimates for 2009 are lower relative to the previous inventory uncertainty estimate for 2008 emissions, which is likely due to the fact that emission estimates for 2009 are based more on actual reported data than emission estimates for 2008 were in the 1990-2008 inventory, with two emission sources using projected (highly uncertain) estimates.

Planned Improvements

Cover gas research conducted by the EPA over the last decade has found that SF₆ 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 for National Greenhouse Gas Inventories (IPCC 2006)) that all SF₆ 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 SF₆, and tend to quickly degrade during their exposure to the molten metal. Magnesium producers and processors have already begun using these cover gases for 2006 through 2009 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 in the United States is conducted through the electrolytic process while secondary techniques used in the United States include the electrothermic and Waelz kiln processes as well as a range of other 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, only the electrothermic and Waelz kiln secondary

processes result in non-energy CO₂ emissions (Viklund-White 2000).

During the electrothermic zinc production process, roasted zinc concentrate and 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 CO₂ emissions (Sjardin 2003).

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

In 2009, U.S. primary and secondary zinc production was estimated to total 286,000 metric tons (USGS 2010). Since reported activity data for 2009 were not available for all necessary inputs in time for this publication, production values in 2009 were assumed to equal 2008 values in some cases. The resulting emissions of CO₂ from zinc production in 2009 were estimated to be 0.97 Tg CO₂ Eq. (966 Gg) (see Table 4-75). All 2009 CO₂ emissions resulted from secondary zinc production.

Table 4-75: CO₂ Emissions from Zinc Production (Tg CO₂ Eq. and Gg)

Year	Tg CO ₂ Eq.	Gg
1990	0.7	667
2000	1.0	997
2005	1.1	1088
2006	1.1	1088
2007	1.1	1081
2008	1.2	1230
2009	1.0	966

Emissions from zinc production in the U.S. have increased overall due to a gradual shift from non-emissive primary production to emissive secondary production. In 2009, emissions were estimated to be 45 percent higher than they were in 1990.

Methodology

Non-energy CO₂ emissions from zinc production result from the electrothermic and Waelz kiln secondary production processes, which both use metallurgical coke or other C-based materials as reductants. Sjardin (2003) provides an emission factor of 0.43 metric tons CO₂/metric 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 electrothermic and Waelz kiln processes were needed. Due to the limited amount of information available for these electrothermic processes, only Waelz kiln process-specific emission factors were developed. These emission factors were applied to both the Waelz kiln and electrothermic secondary 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:

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

In addition, a Waelz kiln 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:¹¹⁶

$$EF_{\text{EAF Dust}} = \frac{0.4 \text{ metric tons coke}}{\text{metric tons EAF dust}} \times \frac{0.85 \text{ metric tons C}}{\text{metric tons coke}} \times \frac{3.67 \text{ metric tons CO}_2}{\text{metric tons C}} = \frac{1.24 \text{ metric tons CO}_2}{\text{metric tons EAF Dust}}$$

The only companies in the United States that use emissive technology to produce secondary zinc products are Horsehead Corp and Steel Dust Recycling. For Horsehead Corp, EAF dust is recycled in Waelz kilns at their Beaumont, TX; Calumet, IL; Palmerton, PA; and Rockwood, TN facilities (and soon to be performed at their new South Carolina facility). These Waelz kiln facilities produce intermediate zinc products (crude zinc oxide or calcine), most of which is transported to their Monaca, PA facility where the products are smelted into refined zinc using electrothermic technology. Some of Horsehead's intermediate zinc products that are not smelted at Monaca are instead exported to other countries around the world (Horsehead Corp 2010). Steel Dust Recycling recycles EAF dust into intermediate zinc products using Waelz kilns, and then sells the intermediate products to companies who smelt it into refined products.

The total amount of EAF dust consumed by Horsehead Corp at their Waelz kilns was available from Horsehead financial reports for years 2006 through 2009 (Horsehead 2010). Consumption levels for 1990 through 2005 were extrapolated using the percentage change in annual refined zinc production at secondary smelters in the United States as provided by USGS Minerals Yearbook: Zinc (USGS 1994 through 2010). The EAF dust consumption values for each year were then multiplied by the 1.24 metric tons CO₂/metric ton EAF dust consumed emission factor to develop CO₂ emission estimates for Horsehead's Waelz kiln facilities.

The amount of EAF dust consumed by the Steel Dust Recycling facility for 2008 and 2009 (the only two years it has been in operation) was not publically available. Therefore, these consumption values were estimated by calculating the 2008 and 2009 capacity utilization of Horsehead's Waelz kilns and multiplying this utilization ratio by the capacity of Steel Dust Recycling's facility, which were available from the company (Steel Dust Recycling LLC 2010). The 1.24 metric tons CO₂/metric ton EAF dust consumed emission factor was then applied to Steel Dust Recycling's estimated EAF dust consumption to develop CO₂ emission estimates for its Waelz kiln facility.

Refined zinc production levels for Horsehead's Monaca, PA facility (utilizing electrothermic technology) were available from the company for years 2005 through 2009 (Horsehead Corp 2010, Horsehead Corp 2008). Production levels for 1990 through 2004 were extrapolated using the percentage changes in annual refined zinc production at secondary smelters in the United States as provided by USGS Minerals Yearbook: Zinc (USGS 1994 through 2010). The 3.70 metric tons CO₂/metric ton zinc emission factor was then applied to the Monaca facility's production levels to estimate CO₂ emissions for the facility. The Waelz kiln production emission factor was applied in this case rather than the EAF dust consumption emission factor since Horsehead's Monaca facility did not consume EAF dust.

Table 4-76: Zinc Production (Metric Tons)

Year	Primary	Secondary
1990	262,704	95,708
2000	227,800	143,000
2005	191,120	156,000
2006	113,000	156,000
2007	121,000	157,000
2008	125,000	161,000
2009	125,000	161,000

¹¹⁶ For Waelz kiln based secondary zinc production, IPCC recommends the use of emission factors based on EAF dust consumption rather than the amount of zinc produced since the amount of reduction materials used is more directly dependent on the amount of EAF dust consumed (IPCC 2006).

Uncertainty and Time-Series Consistency

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

First, there is uncertainty associated with the amount of EAF dust consumed in the United States to produce secondary zinc using emission-intensive Waelz kilns. The estimate for the total amount of EAF dust consumed in Waelz kilns is based on (1) an EAF dust consumption value reported annually by Horsehead Corporation as part of its financial reporting to the Securities and Exchange Commission (SEC), and (2) an estimate of the amount of EAF dust consumed at a Waelz kiln facility operated in Alabama by Steel Dust Recycling LLC. Since actual EAF dust consumption information is not available for the Steel Dust Recycling LLC facility, the amount is estimated by multiplying the EAF dust recycling capacity of the facility (available from the company's Web site) by the capacity utilization factor for Horsehead Corporation (which is available from Horsehead's financial reports). Therefore, there is uncertainty associated with the assumption that the capacity utilization of Steel Dust Recycling LLC's Waelz kiln facility is equal to the capacity utilization of Horsehead's Waelz kiln facility. Second, there are uncertainties associated with the emission factors used to estimate CO₂ emissions from secondary zinc production processes. The Waelz kiln emission factors are based on materials balances for metallurgical coke and EAF dust consumed as provided by Viklund-White (2000). Therefore, the accuracy of these emission factors depend upon the accuracy of these materials balances. Data limitations prevented the development of emission factors for the electrothermic process. Therefore, emission factors for the Waelz kiln process were applied to both electrothermic and Waelz kiln production processes. The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-77. Zinc production CO₂ emissions were estimated to be between 0.8 and 1.1 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 17 percent below and 18 percent above the emission estimate of 1.0 Tg CO₂ Eq.

Table 4-77: Tier 2 Quantitative Uncertainty Estimates for CO₂ Emissions from Zinc Production (Tg CO₂ Eq. and Percent)

Source	Gas	2009 Emission Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to Emission Estimate ^a			
			(Tg CO ₂ Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Zinc Production	CO ₂	1.0	0.8	1.1	-17%	+18%

^a 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 2009. Details on the emission trends through time are described in more detail in the Methodology section, above.

Planned Improvements

Future improvements to the zinc production source category involve evaluating facility level greenhouse gas emissions data as a basis for improving emissions calculations from zinc production. Beginning in 2010, all U.S. zinc producing facilities (both primary and secondary) that emit over 25,000 tons of greenhouse gases (CO₂ Eq.) are required to monitor, calculate and report their greenhouse gas emissions to EPA through its Greenhouse Gas Reporting Program. Under the program, EPA will obtain data for 2010 from these facilities based on use of higher tier methods and assess how this data could be used to improve the methodology and emissions factors for calculating emissions from the U.S. zinc production industry.

Recalculations Discussion

The methodology for estimating CO₂ emissions from zinc production was revised for the current Inventory based on the availability of new data regarding secondary zinc production in the United States. The previous Inventory methodology assumed that two facilities had produced zinc in the United States using emissive processes since 1990: Horsehead Corporation's Monaca, PA facility (electrothermic) and Horsehead Corporation's Palmerton, PA facility (Waelz kiln). The 3.70 metric tons CO₂/metric ton zinc emission factor was applied to the estimated refined zinc production at the Monaca, PA electrothermic facility, and the 1.24 metric tons CO₂/metric ton EAF dust consumed emission factor was applied to the estimated EAF dust consumption at the Palmerton, PA Waelz kiln facility. The annual zinc production (for the Monaca facility) and EAF dust consumption (for the Palmerton

facility) were estimated using historic values that were published in articles for select years (extrapolation techniques were used for years in which published data was not available). The Monaca, PA facility was assumed to have closed in 2003 and not operated since.

New data for the industry showed that there were emissive zinc-producing facilities not being captured by the previous Inventory methodology. The facilities that were not captured included three Horsehead Corp Waelz kiln facilities in Beaumont, TX; Calumet, IL; and Rockwood, TN as well as a Waelz kiln facility commissioned in 2008 in Millport, AL by Steel Dust Recycling LLC. Also, research showed that the Monaca, PA facility only closed temporarily in 2003 and has been operating every year since (the Monaca, PA facility produces refined zinc from intermediary zinc products produced at Horsehead’s other facilities). The updated methodology utilizes EAF dust consumption values and secondary zinc production values released annually by the main secondary zinc producer in the United States (Horsehead Corp.), and also includes the previously overlooked secondary zinc producing facilities in the emission estimates.

As a result of the revised methodology, historical emission estimates decreased by an average of 11 percent between 1990 and 2002, while emission estimates increased by an average of 140 percent between 2003 and 2009. The significant changes in emission estimates for years 2005 through 2008 were largely driven by Horsehead Corp’s Monaca, PA facility being captured in the emission calculations for these years.

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 CO₂ (Sjardin 2003). Primary lead production, in the form of direct smelting, occurs at a just a single plant in Missouri. Secondary production largely involves the recycling of lead acid batteries at approximately 21 separate smelters in the United States. Fifteen of those secondary smelters have annual capacities of 15,000 tons or more and were collectively responsible for 99 percent of secondary lead production in 2009 (USGS 2010). Secondary lead production has increased in the United States over the past decade while primary lead production has decreased. In 2009, secondary lead production accounted for approximately 92 percent of total lead production (USGS 2011).

Primary production of lead through the direct smelting of lead concentrate produces CO₂ emissions as the lead concentrates are reduced in a furnace using metallurgical coke (Sjardin 2003). U.S. primary lead production decreased by 24 percent from 2008 to 2009, and has decreased by 75 percent since 1990 (USGS 2011, USGS 1995).

Similar to primary lead production, CO₂ emissions from secondary production result when a reducing agent, usually metallurgical coke, is added to the smelter to aid in the reduction process. CO₂ emissions from secondary production also occur through the treatment of secondary raw materials (Sjardin 2003). U.S. secondary lead production decreased from 2008 to 2009 by 3 percent, and has increased by 20 percent since 1990 (USGS 2011, 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 2009 (USGS 2011). In 2009, U.S. primary and secondary lead production totaled 1,213,000 metric tons (USGS 2011). The resulting emissions of CO₂ from 2009 production were estimated to be 0.5 Tg CO₂ Eq. (525 Gg) (see Table 4-78). The majority of 2009 lead production is from secondary processes, which accounted for 95 percent of total 2009 CO₂ emissions.

Table 4-78: CO₂ Emissions from Lead Production (Tg CO₂ Eq. and Gg)

Year	Tg CO₂ Eq.	Gg
1990	0.5	516
2000	0.6	594
2005	0.6	553
2006	0.6	560
2007	0.6	562
2008	0.6	551
2009	0.5	525

After a gradual decrease in total emissions from 1990 to 1995, total emissions have gradually increased since 1995

and emissions in 2009 were two percent greater than in 1990. Although primary production has decreased significantly (75 percent since 1990), secondary production has increased by about 20 percent over the same time period. Since secondary production is more emissions-intensive, the increase in secondary production since 1990 has resulted in a net increase in emissions despite the sharp decrease in primary production (USGS 2011, USGS 1994).

Methodology

Non-energy CO₂ 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 CO₂/metric ton lead. For secondary lead production, Sjardin (2003) and IPCC (2006) provide an emission factor of 0.25 metric tons CO₂/metric ton lead for direct smelting as well as an emission factor of 0.2 metric tons CO₂/metric ton lead produced for the treatment of secondary raw materials (i.e., pretreatment of lead acid batteries). The direct smelting factor (0.25) and the sum of the direct smelting and pretreatment emission factors (0.45) are multiplied by total U.S. primary and secondary lead production, respectively, to estimate CO₂ emissions.

The 1990 through 2009 activity data for primary and secondary lead production (see Table 4-79) were obtained through the USGS Mineral Yearbook: Lead (USGS 1994 through 2011).

Table 4-79: Lead Production (Metric Tons)

Year	Primary	Secondary
1990	404,000	922,000
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
2009	103,000	1,110,000

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) adds a CO₂ 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 4-80. Lead production CO₂ emissions were estimated to be between 0.5 and 0.6 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 14 percent below and 15 percent above the emission estimate of 0.5 Tg CO₂ Eq.

Table 4-80: Tier 2 Quantitative Uncertainty Estimates for CO₂ Emissions from Lead Production (Tg CO₂ Eq. and Percent)

Source	Gas	2009 Emission Estimate (Tg CO₂ Eq.)	Uncertainty Range Relative to Emission Estimate^a			
			(Tg CO₂ Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Lead Production	CO ₂	0.5	0.5	0.6	-14%	+15%

^a 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 2009. Details on the emission trends through time are described in more detail in the Methodology section, above.

Planned Improvements

Future improvements to the lead production source category involve evaluating facility level greenhouse gas emissions data as a basis for improving emission calculations from lead production. Beginning in 2010, all U.S. lead producing facilities (primary and secondary) that emit over 25,000 tons of greenhouse gases (CO₂ Eq.) are required to monitor, calculate and report their greenhouse gas emissions to EPA through its Greenhouse Gas Reporting Program. Under the Program, EPA will obtain data for 2010 from these facilities based on use of higher tier methods and assess how this data could be used to improve the methodology and emissions factors for calculating emissions from the U.S. lead production industry.

Recalculations Discussion

In previous Inventory reports, CO₂ emissions from secondary lead production were estimated by multiplying secondary lead production values from USGS by an emission factor of 0.2 metric tons CO₂/metric ton lead produced. This emission factor is provided by Sjardin (2003) and IPCC (2006) for the treatment of secondary raw materials (i.e., pretreatment of lead acid batteries). Due to a misinterpretation of language in Sjardin (2003) and IPCC (2006), this was the only emission factor applied to secondary lead production even though an emission factor of 0.25 metric tons CO₂/metric ton lead for direct smelting should have been applied as well. This issue has been corrected for the current Inventory, and increased 1990 through 2008 emissions from lead production by an average of 95 percent per year relative to the previous Inventory.

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

Trifluoromethane (HFC-23 or CHF₃) 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. Between 2000 and 2007, U.S. production fluctuated but generally remained above 1990 levels. In 2008 and 2009, U.S. production declined markedly. 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.¹¹⁷ Feedstock production, however, is permitted to continue indefinitely.

HCFC-22 is produced by the reaction of chloroform (CHCl₃) and hydrogen fluoride (HF) in the presence of a catalyst, SbCl₅. The reaction of the catalyst and HF produces SbCl_xF_y, (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 (CHCl₂F), HCFC-22 (CHClF₂), HFC-23 (CHF₃), 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 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 2009 were estimated to be 5.4 Tg CO₂ Eq. (0.5 Gg) (Table 4-81). This quantity represents a 60 percent decrease from 2008 emissions and a 85 percent decline from 1990 emissions. The decrease from 2008 emissions was caused by a 27 percent decrease in HCFC-22 production and a 46 percent decrease in the HFC-23 emission rate. The decline from 1990 emissions is due to a 34 percent decrease in HCFC-22 production and a 78 percent decrease in the HFC-23 emission rate since 1990. The decrease in the emission rate is primarily attributable to five factors: (a) five plants that did not capture and destroy the HFC-23 generated have ceased production of HCFC-22 since 1990, (b) one plant that captures and destroys the HFC-23 generated began to produce HCFC-22, (c) one plant implemented and documented a process change that reduced the amount of HFC-23 generated, and (d) the same plant began recovering HFC-23, primarily for destruction and secondarily for sale, and (e) another plant began destroying HFC-23. All three HCFC-22 production plants operating in the United States in 2009 used thermal oxidation to significantly lower their HFC-23 emissions.

¹¹⁷ 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]

Table 4-81: HFC-23 Emissions from HCFC-22 Production (Tg CO₂ Eq. and Gg)

Year	Tg CO₂ Eq.	Gg
1990	36.4	3
2000	28.6	2
2005	15.8	1
2006	13.8	1
2007	17.0	1
2008	13.6	1
2009	5.4	0.46

Methodology

To estimate HFC-23 emissions for five of the eight HCFC-22 plants that have operated in the United States since 1990, methods comparable to the Tier 3 methods in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories (IPCC 2006) were used. For the other three plants, the last of which closed in 1993, methods comparable to the Tier 1 method in the 2006 IPCC Guidelines were used. Emissions from these three plants have been calculated using the recommended emission factor for unoptimized plants operating before 1995 (0.04 kg HCFC-23/kg HCFC-22 produced).

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 2010, 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, 2010). 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 4-82.

Table 4-82: HCFC-22 Production (Gg)

Year	Gg
1990	139
2000	186
2005	156
2006	154
2007	162
2008	126
2009	91

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 plant-level emissions data for 2009 were not available, the relative errors yielded by the Monte Carlo simulation for 2006 were applied to the U.S. emission estimate for 2009. 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, and (2) although the distribution of emissions among the plants may have changed between 2008 and 2009 (because both HCFC-22 production and the HFC-23 emission rate declined significantly), the two plants that contribute significantly to emissions were estimated to have similar relative uncertainties in their 2006 (as well as 2005) emission estimates. Thus, changes in the relative contributions of these two plants to total emissions are not likely to have a large impact on the uncertainty of the national emission estimate.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-83. HFC-23 emissions from HCFC-22 production were estimated to be between 5.0 and 5.9 Tg CO₂ Eq. at the 95percent confidence level. This indicates a range of approximately 7 percent below and 10 percent above the emission estimate of 5.4 Tg CO₂ Eq.

Table 4-83: Quantitative Uncertainty Estimates for HFC-23 Emissions from HCFC-22 Production (Tg CO₂ Eq. and Percent)

Source	Gas	2009 Emission Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to Emission Estimate ^a			
			(Tg CO ₂ Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
HCFC-22 Production	HFC-23	5.4	5.0	5.9	-7%	+10%

^a Range of emissions reflects a 95 percent confidence interval.

Methodological recalculations were applied to the entire time-series to ensure time-series consistency from 1990 through 2009. Details on the emission trends through time are described in more detail in the Methodology section, above.

Planned Improvements

Beginning in 2010, all U.S. HCFC-22 production facilities are required to calculate and report their greenhouse gas emissions to EPA through its Greenhouse Gas Reporting Program. Data collected under this program will be used in future inventories to improve the calculation of national emissions from HCFC-22 production

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

Hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) are used as alternatives to several classes of ozone-depleting substances (ODSs) that are being phased out under the terms of the Montreal Protocol and the Clean Air Act Amendments of 1990.¹¹⁸ 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 4-84 and Table 4-85.

Table 4-84: Emissions of HFCs and PFCs from ODS Substitutes (Tg CO₂ Eq.)

Gas	1990	2000	2005	2006	2007	2008	2009
HFC-23	+	+	+	+	+	+	+
HFC-32	+	+	0.3	0.6	1.0	1.3	1.7
HFC-125	+	5.2	10.1	12.5	15.1	18.2	21.6
HFC-134a	+	60.4	75.1	75.0	72.3	69.3	66.7
HFC-143a	+	4.1	12.2	14.4	16.7	19.2	22.0
HFC-236fa	+	0.5	0.8	0.8	0.9	0.9	0.9

¹¹⁸ [42 U.S.C § 7671, CAA § 601]

CF ₄	+		+		+	+	+	+	+
Others*	0.3		4.0		5.6	6.0	6.3	6.7	7.0
Total	0.3		74.3		104.2	109.4	112.3	115.5	120.0

+ Does not exceed 0.05 Tg CO₂ Eq.

* Others include HFC-152a, HFC-227ea, HFC-245fa, HFC-4310mee, C₄F₁₀, 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 C₆F₁₄.

Note: Totals may not sum due to independent rounding.

Table 4-85: Emissions of HFCs and PFCs from ODS Substitution (Mg)

Gas	1990	2000	2005	2006	2007	2008	2009
HFC-23	+	1	1	1	1	2	2
HFC-32	+	26	505	971	1,465	1,977	2,540
HFC-125	+	1,855	3,619	4,453	5,393	6,486	7,730
HFC-134a	+	46,465	57,777	57,728	55,603	53,294	51,281
HFC-143a	+	1,089	3,200	3,782	4,402	5,044	5,798
HFC-236fa	+	85	125	131	136	141	144
CF ₄	+	1	2	2	2	2	2
Others*	M	M	M	M	M	M	M

M (Mixture of Gases)

+ Does not exceed 0.5 Mg

* Others include HFC-152a, HFC-227ea, HFC-245fa, HFC-4310mee, C₄F₁₀, and PFC/PFPEs, the latter being a proxy for a diverse collection of PFCs and perfluoropolyethers (PFPEs) employed for solvent applications.

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.¹¹⁹ 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 120.0 Tg CO₂ Eq. in 2009. 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 4-86 presents emissions of HFCs and PFCs as ODS substitutes by end-use sector for 1990 through 2009. The end-use sectors that contributed the most toward emissions of HFCs and PFCs as ODS substitutes in 2009 include refrigeration and air-conditioning (104.9 Tg CO₂ Eq., or approximately 87 percent), aerosols (9.1 Tg CO₂ Eq., or approximately 8 percent), and foams (3.9 Tg CO₂ Eq., or approximately 3 percent). Within the refrigeration and air-conditioning end-use sector, motor vehicle air-conditioning was the highest emitting end-use (45.9 Tg CO₂ Eq.), followed by refrigerated retail food and transport. Each of the end-use sectors is described in more detail below.

Table 4-86: Emissions of HFCs and PFCs from ODS Substitutes (Tg CO₂ Eq.) by Sector

Gas	1990	2000	2005	2006	2007	2008	2009
Refrigeration/Air Conditioning	+	61.6	93.1	97.6	99.8	102.3	104.9
Aerosols	0.3	10.1	7.3	7.7	8.2	8.6	9.1
Foams	+	0.3	1.9	2.1	2.3	2.5	3.9
Solvents	+	2.1	1.3	1.3	1.3	1.3	1.3
Fire Protection	+	0.2	0.5	0.6	0.7	0.7	0.8
Total	0.3	74.3	104.2	109.4	112.3	115.5	120.0

¹¹⁹ R-404A contains HFC-125, HFC-143a, and HFC-134a.

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/and 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 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-410A¹²⁰, R-404A, and R-507A¹²¹. These HFCs are emitted to the atmosphere during equipment 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 the industry has started 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 CO₂, 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, 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 (CCl₄) 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

¹²⁰ R-410A contains HFC-32 and HFC-125.

¹²¹ R-507A, also called R-507, contains HFC-125 and HFC-143a.

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 it tracks the use and emissions of various compounds for the annual “vintages” of new equipment that enter service in each end-use. The 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 nearly 60 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

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 nearly 60 end-uses. The uncertainty analysis, however, quantifies the level of uncertainty associated with the aggregate emissions resulting from the top 21 end-uses, comprising over 95 percent of the total emissions, and 5 other end-uses. These 26 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. 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 4-87. Substitution of ozone depleting substances HFC and PFC emissions were estimated to be between 111.8 and 129.3 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 7 percent below to 8 percent above the emission

estimate of 120.0 Tg CO₂ Eq.

Table 4-87: Tier 2 Quantitative Uncertainty Estimates for HFC and PFC Emissions from ODS Substitutes (Tg CO₂ Eq. and Percent)

Source	Gases	2009 Emission Estimate (Tg CO ₂ Eq.) ^a	Uncertainty Range Relative to Emission Estimate ^b			
			(Tg CO ₂ Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Substitution of Ozone Depleting Substances	HFCs and PFCs	117.1	109.0	126.5	-7%	+8%

^a 2009 emission estimates and the uncertainty range presented in this table correspond to selected end-uses within the aerosols, foams, solvents, fire extinguishing agents, and refrigerants sectors, 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.

^b Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Recalculations Discussion

An extensive review of the MDI aerosol, unitary air-conditioning, and domestic refrigerator foams markets resulted in revisions to the Vintaging Model since the previous Inventory. For MDI aerosols, the charge size for both the CFC and HFC propellants was revised. Based on research on substitutes and growth in the market, the percent of the CFC market that transitions to HFCs over the time series and the overall size of the MDI market decreased. For unitary air-conditioning, a review of air conditioner sales data reduced the quantity of air-conditioning equipment introduced into the market for 1990 through 1993 and 2008, while increasing the quantity of equipment sold into the market for 1994 through 2009. A review of the domestic refrigerator foams market increased the quantity of blowing agent consumed in the foam and decreased the quantity of blowing agent emitted during the foam manufacturing process. Overall, these changes to the Vintaging Model increased greenhouse gas emissions on average by 0.5 percent across the time series.

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 CHF₃), perfluoromethane (CF₄), perfluoroethane (C₂F₆), nitrogen trifluoride (NF₃), and sulfur hexafluoride (SF₆), although other compounds such as perfluoropropane (C₃F₈) and perfluorocyclobutane (c-C₄F₈) 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 C₂F₆ is used in cleaning or etching, CF₄ 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 2009, total weighted emissions of all fluorinated greenhouse gases by the U.S. semiconductor industry were estimated to be 5.3 Tg CO₂ Eq. Combined emissions of all fluorinated greenhouse gases are presented in Table 4-88 and Table 4-89 below for years 1990, 2000 and the period 2005 to 2009. The rapid growth of this industry and the increasing complexity (growing number of layers)¹²² of semiconductor products led to an increase in emissions of 148 percent between 1990 and 1999, when emissions peaked at 7.2 Tg CO₂ Eq. The emissions growth rate began to slow after 1998, and emissions declined by 26 percent between 1999 and 2009. Together, industrial growth and adoption of emissions reduction technologies, including but not limited to abatement technologies, resulted in a net increase in emissions of 83 percent between 1990 and 2009.

Table 4-88: PFC, HFC, and SF₆ Emissions from Semiconductor Manufacture (Tg CO₂ Eq.)

Year	1990	2000	2005	2006	2007	2008	2009
CF ₄	0.7	1.8	1.1	1.2	1.3	1.4	1.5
C ₂ F ₆	1.5	3.0	2.0	2.2	2.3	2.4	2.5
C ₃ F ₈	0.0	0.1	0.0	0.0	0.0	0.1	0.0
C ₄ F ₈	0.0	0.0	0.1	0.1	0.1	0.1	0.0
HFC-23	0.2	0.3	0.2	0.3	0.3	0.3	0.3
SF ₆	0.5	1.1	1.0	1.0	0.8	0.9	1.0
NF ₃ *	0.0	0.2	0.4	0.7	0.5	0.6	0.5
Total	2.9	6.2	4.4	4.7	4.8	5.1	5.3

Note: Totals may not sum due to independent rounding.

* NF₃ emissions are presented for informational purposes, using the AR4 GWP of 17,200, and are not included in totals.

Table 4-89: PFC, HFC, and SF₆ Emissions from Semiconductor Manufacture (Mg)

Year	1990	2000	2005	2006	2007	2008	2009
CF ₄	115	281	168	181	198	216	227
C ₂ F ₆	160	321	216	240	249	261	271
C ₃ F ₈	0	18	5	5	6	13	5
C ₄ F ₈	0	0	13	13	7	7	4
HFC-23	15	23	18	22	23	25	28
SF ₆	22	45	40	40	34	36	40
NF ₃	3	11	26	40	30	33	30

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 the absence of emission control strategies (Burton and Beizaie 2001).¹²³ The availability and applicability of Partner data differs across the 1990 through 2009 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 2009.

1990 through 1994

From 1990 through 1994, Partnership data was unavailable and emissions were modeled using the PEVM (Burton

¹²² 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.

¹²³ 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.

and Beizaie 2001).¹²⁴ 1990 to 1994 emissions are assumed to be uncontrolled, since reduction strategies such as chemical substitution and abatement were yet to be 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 size),¹²⁵ and (2) product type (discrete, memory or logic).¹²⁶ 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. 2010).

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. 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 2010).

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

¹²⁴ 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.

¹²⁵ By decreasing features of Integrated Circuit 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).

¹²⁶ 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.

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.^{127,128} 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 industry (see ITRS 2007 and Semiconductor Equipment and Materials Industry 2010).^{129,130,131}

2007 through 2009

For the years 2007 through 2009, 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 through 2009 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.¹³² Second, the scope of the 2007 through 2009 estimates is expanded relative to the estimates for the years 2000 through 2006 to include emissions from Research and Development (R&D) fabs. This was feasible through 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 in 2009 for non-partners. PEVM estimates were adjusted using technology weighted capacity shares that reflect relative influence of different utilization.

¹²⁷ 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.

¹²⁸ 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.

¹²⁹ 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 percent. 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.

¹³⁰ 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 are not Partners. Special attention was given to this occurrence when estimating the Partner and non-Partner shares of U.S. manufacturing capacity.

¹³¹ 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.

¹³² 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.

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 made 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 2009 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 2009 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 2009, it is assumed that most Partners used a method at least as accurate as the IPCC's Tier 2a Methodology, recommended in the 2006 IPCC Guidelines for National Greenhouse Inventories (IPCC 2006). 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) (e.g., Semiconductor Materials and Equipment Industry, 2010). Actual world capacity utilizations for 2009 were obtained from Semiconductor International Capacity Statistics (SICAS) (SIA, 2009). Estimates of silicon consumed by linewidth from 1990 through 2009 were derived from information from VLSI Research, Inc. (2010), 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 2009 is about ± 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 ± 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 ± 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.¹³³ A relative uncertainty of approximately ± 10 percent was estimated for the PEVM emission factor, based on the standard deviation of the 1996 to 1999 emission factors.¹³⁴ 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

¹³³ Error propagation resulted in Partnership gas-specific uncertainties ranging from 17 to 27 percent

¹³⁴ The average of 1996 to 1999 emission factor is used to derive the PEVM emission factor.

Monte Carlo analysis.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-90. The emissions estimate for total U.S. PFC emissions from semiconductor manufacturing were estimated to be between 4.8 and 5.9 Tg CO₂ Eq. at a 95 percent confidence level. This range represents 10 percent below to 11 percent above the 2009 emission estimate of 5.3 Tg CO₂ 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.

Table 4-90: Tier 2 Quantitative Uncertainty Estimates for HFC, PFC, and SF₆ Emissions from Semiconductor Manufacture (Tg CO₂ Eq. and Percent)

Source	Gas	2009 Emission	Uncertainty Range Relative to Emission Estimate ^b			
		Estimate ^a	(Tg CO ₂ Eq.)		(%)	
		(Tg CO ₂ Eq.)	Lower Bound ^c	Upper Bound ^c	Lower Bound	Upper Bound
Semiconductor Manufacture	HFC, PFC, and SF ₆	5.3	4.8	5.9	-10%	+11%

^a Because the uncertainty analysis covered all emissions (including NF₃), the emission estimate presented here does not match that shown in Table 4-88.

^b Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

^c Absolute lower and upper bounds were calculated using the corresponding lower and upper bounds in percentages.

Methodological recalculations were applied to the entire time-series to ensure time-series consistency from 1990 through 2009. 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 SF₆, 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 SF₆ 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 SF₆ from equipment manufacturing and from electrical transmission and distribution systems were estimated to be 12.8 Tg CO₂ Eq. (0.5 Gg) in 2009. This quantity represents a 55 percent decrease from the estimate for 1990 (see Table 4-91 and Table 4-92). This decrease is believed to have two causes: a sharp increase in the price of SF₆ during the 1990s and a growing awareness of the environmental impact of SF₆ emissions through

programs such as EPA's SF₆ Emission Reduction Partnership for Electric Power Systems.

Table 4-91: SF₆ Emissions from Electric Power Systems and Electrical Equipment Manufacturers (Tg CO₂ Eq.)

Year	Electric Power Systems	Electrical Equipment Manufacturers	Total
1990	28.1	0.3	28.4
2000	15.4	0.7	16.0
2005	14.1	1.1	15.1
2006	13.1	1.0	14.1
2007	12.4	0.8	13.2
2008	12.1	1.3	13.3
2009	12.1	0.7	12.8

Note: Totals may not sum due to independent rounding.

Table 4-92: SF₆ Emissions from Electric Power Systems and Electrical Equipment Manufacturers (Gg)

Year	Emissions
1990	1.2
2000	0.7
2005	0.6
2006	0.6
2007	0.6
2008	0.6
2009	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 2009 Emissions from Electric Power Systems

Emissions from electric power systems from 1999 to 2009 were estimated based on: (1) reporting from utilities participating in EPA's SF₆ 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, 2007, and 2010 Utility Data Institute (UDI) Directories of Electric Power Producers and Distributors (UDI 2001, 2004, 2007, 2010). (Transmission miles are defined as the miles of lines carrying voltages above 34.5 kV.) Over the period from 1999 to 2009, 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).¹³⁵

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 2009, non-reporting Partners accounted for approximately 8 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, SF₆ is contained primarily in transmission

¹³⁵ Partners in EPA's SF₆ Emission Reduction Partnership reduced their emissions by approximately 61% from 1999 to 2008.

equipment rated above 34.5 kV. The equations were developed based on the 1999 SF₆ emissions reported by a subset of 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 (fewer than 10,000 transmission miles, in kilograms):

$$\text{Emissions (kg)} = 1.001 \times \text{Transmission Miles}$$

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, 2006, and 2009 were obtained from the 2001, 2004, 2007, and 2010 UDI Directories of Electric Power Producers and Distributors, respectively (UDI 2001, 2004, 2007, 2010). The U.S. transmission system grew by over 25,000 miles between 2000 and 2003 and by over 52,000 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 1.3 percent between 2000 and 2003 and 2.6 percent between 2003 and 2006. This growth rate slowed to 0.2% from 2006 to 2009 as transmission miles increased by just 4,400 miles (approximately).

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 SF₆ 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 2009, modeling was used to estimate SF₆ 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 SF₆ 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 2006 IPCC Guidelines for National Greenhouse Gas Inventories (IPCC 2006).¹³⁶ (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.)

$$\text{Emissions (kilograms SF}_6\text{)} = \text{SF}_6 \text{ purchased to refill existing equipment (kilograms) + nameplate capacity of retiring equipment (kilograms)}^{137}$$

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 SF₆ 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 SF₆ 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

¹³⁶ 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 SF₆ during this time period, so it would not have been possible to conceal sensitive sales information by aggregation.

¹³⁷ Nameplate capacity is defined as the amount of SF₆ within fully charged electrical equipment.

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 SF₆ 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 SF₆ 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 SF₆ from electric power systems in 1999 (estimated to be 15.0 Tg CO₂ Eq.).

Two factors may affect the relationship between the RAND sales trends and actual global emission trends. One is utilities' inventories of SF₆ in storage containers. When SF₆ prices rise, utilities are likely to deplete internal inventories before purchasing new SF₆ at the higher price, in which case SF₆ sales will fall more quickly than emissions. On the other hand, when SF₆ prices fall, utilities are likely to purchase more SF₆ 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 SF₆ 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. SF₆ 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).

1990 through 2009 Emissions from Manufacture of Electrical Equipment

The 1990 to 2009 emission estimates for original equipment manufacturers (OEMs) were derived by assuming that manufacturing emissions equal 10 percent of the quantity of SF₆ provided with new equipment. The quantity of SF₆ 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 SF₆ provided with new equipment for 2001 to 2009 were estimated using Partner reported data and the total industry SF₆ nameplate capacity estimate (137.4 Tg CO₂ Eq. in 2009). 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 2009 was calculated. This ratio was then multiplied by the total industry nameplate capacity estimate to derive the amount of SF₆ 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

To estimate the uncertainty associated with emissions of SF₆ 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 SF₆ Emission Reduction Partnership include emissions from both reporting and non-reporting Partners. For reporting Partners, individual Partner-reported SF₆ 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 5.3 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 2009 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 57 percent of U.S. transmission miles in 2009) 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 SF₆ supplied with equipment by equipment manufacturers, which is projected from Partner provided nameplate capacity data and industry SF₆ nameplate capacity estimates, and (2) the manufacturers' SF₆ emissions rate.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-93. Electrical Transmission and Distribution SF₆ emissions were estimated to be between 10.2 and 15.7 Tg CO₂ Eq. at the 95 percent confidence level. This indicates a range of approximately 21 percent below and 22 percent above the emission estimate of 12.8 Tg CO₂ Eq.

Table 4-93: Tier 2 Quantitative Uncertainty Estimates for SF₆ Emissions from Electrical Transmission and Distribution (Tg CO₂ Eq. and percent)

Source	Gas	2009 Emission Estimate (Tg CO ₂ Eq.)	Uncertainty Range Relative to 2009 Emission Estimate ^a			
			(Tg CO ₂ Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Electrical Transmission and Distribution	SF ₆	12.8	10.2	15.7	-21%	+22%

^a Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

In addition to the uncertainty quantified above, there is uncertainty associated with using global SF₆ sales data to estimate U.S. emission trends from 1990 through 1999. However, the trend in global emissions implied by sales of SF₆ appears to reflect the trend in global emissions implied by changing SF₆ 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.

Several pieces of evidence indicate that U.S. SF₆ emissions were reduced as global emissions were reduced. First, the decreases in sales and emissions coincided with a sharp increase in the price of SF₆ 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 SF₆ recycling equipment, stated that most U.S. utilities began recycling rather than venting SF₆ 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.

Recalculations Discussion

SF₆ emission estimates for the period 1990 through 2008 were updated based on (1) new data from EPA's SF₆ Emission Reduction Partnership; (2) revisions to interpolated and extrapolated non-reported Partner data; and (3) a correction made to 2004 transmission mile data for a large Partnership utility that had been interpreted incorrectly from the UDI database in previous years. Updating the 2004 transmission mile data for the Partner changed the annual transmission mile growth rates used to extrapolate total U.S. transmission mile values for years in which a UDI database was not purchased (including 1999). This recalculation impacted emission estimates in two ways. First, the regression coefficients used to estimate emissions for non-Partners are based on 1999 transmission miles and emissions for Partners that reported emissions in 1999, so the change in 1999 transmission miles affected the regression coefficients. The result was that the regression coefficient for utilities with fewer than 10,000 transmission miles increased from 0.89 to 1.001 kg of emissions per transmission mile, while the regression coefficient for utilities with more than 10,000 transmission miles increased very slightly from 0.577 to 0.578 kg of emissions per transmission mile. The second impact of the updated annual transmission mile growth rates was that the total non-Partner transmission miles that the regression coefficients are applied to were also affected. Based on the revisions listed above, SF₆ emissions from electric transmission and distribution increased between 4 to 9 percent for each year from 1990 through 2008.

In addition, the method for estimating potential emissions from the sector was updated for the 1990-2009 Inventory. In previous years, potential emissions were assumed to equal total industry SF₆ purchases, which were developed from two components: (1) purchases by Partner utilities from bulk gas distributors, and (2) purchases by electrical equipment manufacturers from bulk gas distributors. This previous method led to concerns of double-counting since Partners sometimes were recording all SF₆ received in cylinders from any source (including equipment

manufacturers) as gas received from bulk distributors. Therefore, SF₆ that was purchased by a utility from an equipment manufacturer was sometimes counted as a purchase by both the equipment manufacturer and the utility. The new method still assumes that potential emissions are equal to industry purchases, but estimates total purchases for the industry by adding the total amount of gas purchased by all U.S. utilities from any source (bulk distributor or equipment manufacturer) to estimated emissions from equipment manufacturers. It is assumed that all SF₆ purchased by equipment manufacturers is either emitted or sent to utilities.

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_x), carbon monoxide (CO), and non-CH₄ volatile organic compounds (NMVOCs) from non-energy industrial processes from 1990 to 2009 are reported in Table 4-94.

Table 4-94: NO_x, CO, and NMVOC Emissions from Industrial Processes (Gg)

Gas/Source	1990	1995	2000	2005	2006	2007	2008	2009
NO_x	591	607	626	569	553	537	520	568
Other Industrial Processes	343	362	435	437	418	398	379	436
Chemical & Allied Product								
Manufacturing	152	143	95	55	57	59	61	55
Metals Processing	88	89	81	60	61	62	62	60
Storage and Transport	3	5	14	15	15	16	16	15
Miscellaneous*	5	8	2	2	2	2	2	2
CO	4,125	3,959	2,216	1,555	1,597	1,640	1,682	1,549
Metals Processing	2,395	2,159	1,175	752	788	824	859	752
Other Industrial Processes	487	566	537	484	474	464	454	484
Chemical & Allied Product								
Manufacturing	1,073	1,110	327	189	206	223	240	187
Storage and Transport	69	23	153	97	100	103	104	97
Miscellaneous*	101	102	23	32	30	27	25	29
NMVOCs	2,422	2,642	1,773	1,997	1,933	1,869	1,804	1,322
Storage and Transport	1,352	1,499	1,067	1,308	1,266	1,224	1,182	662
Other Industrial Processes	364	408	412	415	398	383	367	395
Chemical & Allied Product								
Manufacturing	575	599	230	213	211	210	207	206
Metals Processing	111	113	61	44	44	43	42	44
Miscellaneous*	20	23	3	17	14	10	7	15

* 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.

Methodology

These emission estimates were obtained from preliminary data (EPA 2010, 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. 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.

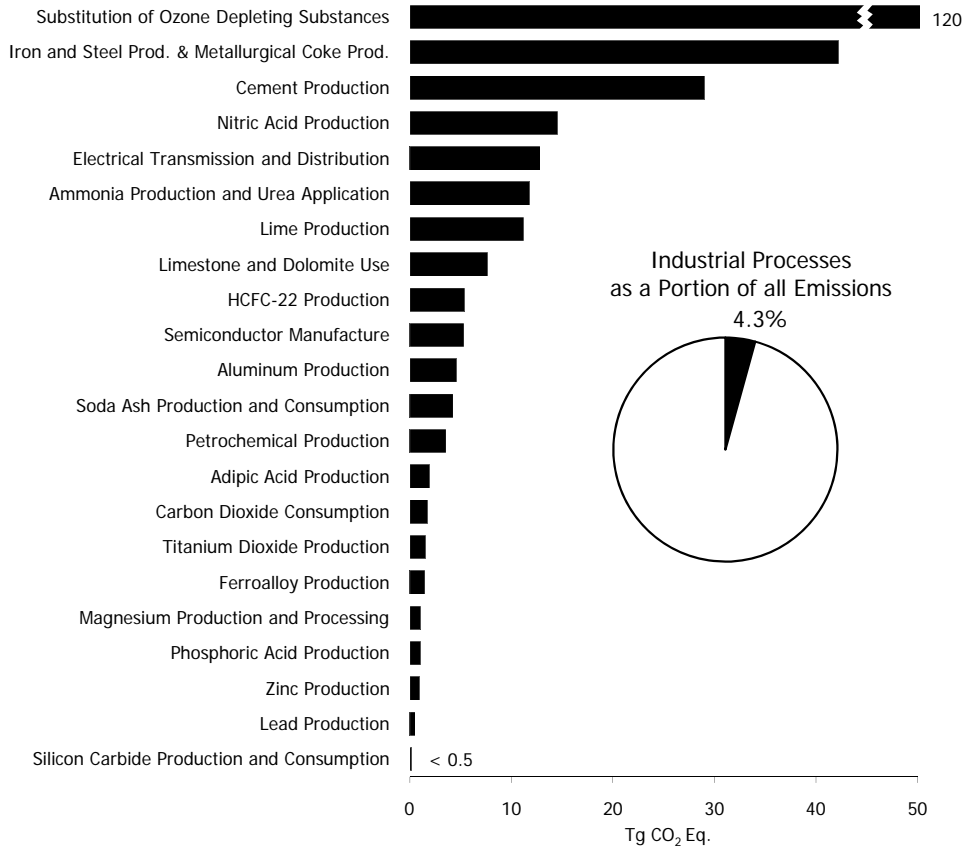


Figure 4-1: 2009 Industrial Processes Chapter Greenhouse Gas Sources

