

**Technical Support Document for the Phosphoric
Acid Production Sector: Proposed Rule for
Mandatory Reporting of Greenhouse Gases**

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

February 20, 2009

CONTENTS

1.	Industry Description	1
2.	Total Emissions	1
	2.1 Process Emissions	2
	2.2 Stationary Combustion	2
3.	Review of Existing Programs and Methodologies	2
4.	Options for Reporting Threshold	3
	4.1 Emissions Thresholds	3
	4.2 Capacity Thresholds	3
	4.3 No Emissions Threshold	3
4.4	Analysis of Emissions and Facilities Covered Per Threshold Option	3
	4.4.1 Emissions Thresholds	3
	4.4.2 Capacity Threshold	5
	4.4.3 No Emissions Threshold	5
5.	Options for Monitoring Methods	5
	5.1 Option 1: Simplified Emission Calculations	5
	5.2 Option 2: Hybrid Method	6
	5.3 Option 3: Direct Measurement using Continuous Emission Monitoring Data (CEMS)	7
6.	Procedures for Estimating Missing Data	7
	6.1 Procedures for Option 1: Simplified Emissions Calculations	7
	6.2 Procedures for Option 2: Hybrid Method	7
	6.3 Procedures for Option 3: Direct Measurement using CEMS	8
7.	QA/QC Requirements	8
	7.1 Stationary Emissions	8
	7.2 Process Emissions	8
	7.3 Data Management	9
8.	Types of Emissions to be Reported	9
	8.1 Other Information to be Reported	10
	8.2 Additional Data to be Retained Onsite	10
9.	References	11

1. Industry Description

Phosphoric acid is a chemical product derived from phosphate rock and is integral to the production of phosphate fertilizers. Four states mine phosphate rock (Florida, North Carolina, Idaho, and Utah) and facilities that produce phosphoric acid are generally located near phosphate rock mines. Of the 14 phosphoric acid facilities operating in 2006, only 3, located along the Gulf Coast, consumed phosphate rock imported from Morocco (USGS 2007). Phosphoric acid production in 2006 at each of the 14 facilities is presented in Table 1.

Table 1. U.S. Producers of Phosphoric Acid

Company	Plant Location	2006 Production (metric tons)
Agrifos, LLC	Pasadena, TX	NA
Agrium	Conda, ID	362,000
CF Industries	Plant City, FL	915,000
Mississippi Phosphates	Pascagoula, MS	NA
Mosaic Fertilizer	Bartow, FL	893,000
Mosaic Fertilizer	Riverview, FL	733,000
Mosaic Fertilizer	New Wales, FL	1,674,000
Mosaic Fertilizer	South Pierce, FL	432,000
Mosaic Fertilizer	Uncle Sam, LA	547,000
PCS Nitrogen	Geismar, LA	147,000
PCS Phosphate Co., Inc.	Aurora, NC	1,080,000
PCS Phosphate Co., Inc.	White Springs, FL	881,000
J.R. Simplot Co.	Rock Springs, WY	NA
J.R. Simplot Co.	Pocatello, ID	NA

Companies marked "NA" are privately-held and do not release financial information.

Source: Personal Communication with Stephen Jasinski, USGS.

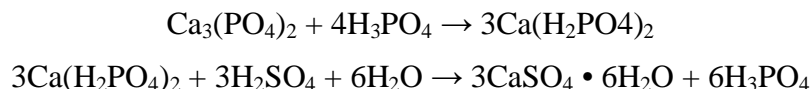
Phosphoric acid is a product of the reaction between phosphate rock and, typically, sulfuric acid (H_2SO_4). A byproduct called calcium sulfate ($CaSO_4$), or gypsum, is formed when calcium from the phosphate rock reacts with sulfate. Most companies in the United States use a dihydrate process in which two molecules of water (H_2O) are produced per molecule of gypsum ($CaSO_4 \cdot 2 H_2O$ or calcium sulfate dihydrate). Additionally, a second reaction occurs in which the limestone ($CaCO_3$) present in the phosphate rock reacts with sulfuric acid (H_2SO_4) releasing carbon dioxide (CO_2). The amount of carbon in the phosphate rock feedstock varies depending on the region in which it was mined. Phosphate rock is also used to produce triple super phosphate and elemental phosphorus.

2. Total Emissions

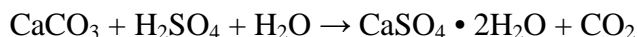
Combined, the 14 phosphoric acid plants in operation in 2006 emitted 3.8 MMT CO_2e . Process emissions from phosphoric acid production in 2006 totaled 1.17 tons CO_2 (U.S. EPA 2008). Combustion emissions (CO_2 , CH_4 , and N_2O) in 2006 totaled ~2.67 MMT CO_2e .

2.1 Process Emissions

Greenhouse gas emissions are generated from both the actual phosphoric production process. Phosphoric acid is produced by combining sulfuric acid and phosphate rock using a method known as “wet process production.” The chemical reactions that take place to produce phosphoric acid are shown below (U.S. EPA 2008).



A portion of the phosphoric acid produced is recycled to the reactor to sustain the reaction and ensure that an insoluble layer of calcium sulfate does not enclose the phosphate rock and inhibit interaction with sulfuric acid (EFMA 2000). Carbon dioxide (CO₂) is emitted when the limestone component (CaCO₃) of phosphate rock reacts with the sulfuric acid (H₂SO₄) (U.S. EPA 2008). The following reaction summarizes the emission process:



2.2 Stationary Combustion

Combustion-related greenhouse gas emissions from the production of phosphoric acid are limited to those from burning of fuel inputs used for equipment necessary to the manufacturing process. Auxiliary and packaged boilers are common combustion emission sources found at phosphoric acid manufacturing facilities (Wyoming DEQ 2006). Coal, natural gas, diesel fuel, distillate fuel oil, and residual fuel oil are all possible fuel inputs. The Manufacturing Energy Consumption Survey (MECS) data compiled by the Department of Energy (DOE) for NAICS code 325312, “Phosphatic Fertilizers” which includes phosphoric acid production, indicates 57 percent of the total fuel energy consumption (i.e., excluding purchased electricity) is natural gas and 39 percent is from a classification called “other fuels” (which includes steam and other energy used to produce heat and power). No other specifics of this classification are given by MECS.

3. Review of Existing Programs and Methodologies

Phosphoric acid production is not addressed by the 2006 IPCC guidelines, but the *Inventory of U.S. Greenhouse Gas Emissions and Sinks* provides a method for estimating process related CO₂ emissions from phosphoric acid production. CO₂ emissions from production of phosphoric acid from phosphate rock are estimated 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. 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 form 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.

The carbonate content of phosphate rock varies depending upon where the material is mined. The US inventory applies composition data for domestically mined and imported phosphate rock provided by the Florida Institute of Phosphate Research to regional phosphate rock production numbers to estimate emissions. Companies conduct analysis on the rock frequently to determine the P₂O₅ content and the level of impurities (Jasinski 2008). According to CF industries (Falls 2008), they analyze a composite of incoming phosphate rock for carbon contents on a daily basis. The phosphate rock consumed or entering the digestion process is also measured on a daily basis.

4. Options for Reporting Threshold

4.1 Emissions Thresholds

Four reporting threshold levels were considered for the phosphoric acid manufacturing sector. The emission thresholds, 100,000, 25,000, 10,000, and 1,000 mtCO₂e per year, were analyzed based on production data.

4.2 Capacity Thresholds

Four capacity threshold levels were considered for the phosphoric acid manufacturing sector. The thresholds, 1.5, 1.0, 0.5, and 0.15 million metric tons of phosphoric acid per year, were analyzed based on the capacity of the manufacturing sites. Because only production data was available, all facilities were assumed to operate at 90% of their capacity. The capacities were calculated based on production values.

4.3 No Emissions Threshold

The no emissions threshold includes all phosphoric acid manufacturing facilities regardless of their emissions or capacity.

4.4 Analysis of Emissions and Facilities Covered Per Threshold Option

4.4.1 Emissions Thresholds

All threshold levels were found to incorporate the entire phosphoric acid manufacturing sector. Table 2 provides the threshold analysis for the phosphoric acid manufacturing sector. The threshold analysis estimated a total emissions profile for the phosphoric acid production sector of 3,838,036 mtCO₂e. This total was the additive sum of process emissions (1,167,201 mtCO₂e) from the US GHG inventory and combustion emissions (2,670,836 mtCO₂e) which are described further below. The average emissions per facility equaled approximately 274,000 mtCO₂e, which placed all facilities above the maximum reporting threshold of 100,000 mtCO₂e.

Table 2. Threshold Analysis for Phosphoric Acid Production

Threshold Level (mtCO ₂ e)	Process Emissions (mtCO ₂ e /yr)	CO ₂ Emissions (mtCO ₂ e /yr)	Total National Emissions (mtCO ₂ e)	Number of Entities	Emissions Covered		Entities Covered	
					mtCO ₂ e /yr	%	Number	%
100,000	1,167,201	2,670,836	3,838,036	14	3,838,036	100	14	100
25,000	1,167,201	2,670,836	3,838,036	14	3,838,036	100	14	100
10,000	1,167,201	2,670,836	3,838,036	14	3,838,036	100	14	100
1,000	1,167,201	2,670,836	3,838,036	14	3,838,036	100	14	100

Source: Calculations based on U.S. production data

Process emissions were calculated by multiplying a default factor for inorganic carbon content within phosphate rock by the amount of phosphate rock used to produce phosphoric acid. The default factor varies by the region which mined the phosphate rock; a separate factor is applied to imported phosphate rock (See Table 3). It was not possible to prepare a detailed facility level analysis of process-related emissions. The US GHG inventory method requires having facility level information on the quantity of phosphate rock consumed which was not readily available.

Table 3. Chemical Composition of Phosphate Rock (percent by weight)

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

Source: Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2006

Calculations of process emissions followed the equation:

$$CO_2 = AD * EF$$

Where:

CO₂ = process emissions of CO₂

AD = Phosphate rock consumption

EF = Regional chemical composition factor of phosphate rock

The emissions analysis is an overestimate because it includes emissions from triple super phosphate and elemental phosphorus production. To calculate CO₂ emissions based on the equation above, it was assumed that all phosphate rock mined is used to produce phosphoric acid. However, approximately 7% of domestically-produced phosphate rock is used to manufacture elemental phosphorus and other phosphorus-based chemicals. Therefore, some greenhouse gas emissions resulting from the production of elemental phosphorus or triple super phosphate are included in the emission estimates used in the EPA Inventory (U.S. EPA 2008).

Emissions from triple super phosphate production may not be wholly accounted for in the process-related emissions estimate for phosphoric acid because the reaction to produce triple super phosphate includes reacting phosphoric acid with phosphate rock. While the process-related emissions from producing the phosphoric acid are accounted for by using phosphoric acid as the activity data, the emissions from reacting phosphoric acid with additional phosphate rock may be additive.

Emissions from elemental phosphorus production are not wholly accounted for in the emissions estimate for phosphoric acid because the reaction to produce elemental phosphorus includes reacting phosphate with petroleum coke. Consumption data was not available for the carbon-containing input (petroleum coke); therefore, it has been omitted from this analysis. It is known, however, that only a single facility in the United States currently produces elemental phosphorus and that about 5% of the phosphate rock mined is utilized for elemental phosphorus production (USGS 2007).

Combustion emissions from phosphoric acid production were estimated by using the Title V permit issued to the J.R. Simplot facility in Rock Springs, WY that listed the number, type, and fuel consumption rate of stationary emission sources. Two emission units were listed in the permit; a packaged boiler assumed to use natural gas at a rate of 350 MMBtu/hr, and an auxiliary boiler assumed to use natural gas at a rate of 106.5 MMBtu/hr. Assuming that each emission unit within the facility operated at 90% capacity continuously (24 hours a day, 365 days a year) emissions were estimated to be approximately 190,800 mt CO₂e (Wyoming DEQ 2006).

4.4.2 Capacity Threshold

Capacity-based thresholds are not presented here because preliminary estimates indicate that all facilities exceed the highest emissions-based thresholds.

4.4.3 No Emissions Threshold

The option of regulating all phosphoric acid manufacturing facilities regardless of their emissions profile is similar to the emissions threshold option because at each threshold level all phosphoric acid facilities would be regulated.

5. Options for Monitoring Methods

Three separate monitoring methods were considered for this technical support document: direct measurement (Option 1), an input-based method (Option 2), and a simplified emission calculation (Option 3). All of these options require annual reporting.

5.1 Option 1: Simplified Emission Calculations

Option 3 relies upon calculations based on each facility's raw material input and default carbon content of the phosphate rock. Specifically, the quantity of phosphate rock and the regional inorganic carbon percentage of the phosphate rock need to be known. The equation for calculating emissions is:

$$CO_2 = AD * EF$$

Where:

CO₂ = process emissions of CO₂

AD = Phosphate rock consumption

EF = Regional chemical composition factor of phosphate rock

The regional chemical composition factor of phosphate rock can be found in Table 3.

5.2 Option 2: Hybrid Method

Option 2 relies upon calculations based on each facility's raw material input. Specifically, the quantity of phosphate rock and the percentage of inorganic carbon present in the phosphate rock will need to be measured. An equation of the monitoring method is below:

$$E_m = \sum_{n=1}^z \frac{44}{12} * [IC_n * P_n] * \frac{2000}{2205}$$

Where:

E_m = Annual CO₂ mass emissions from a wet-process phosphoric acid process line m (metric tons)

44/12 = Ratio of molecular weights, CO₂ to carbon

IC_n = Inorganic carbon content of the batch of phosphate rock used during month n, from the carbon analysis results (percent by weight, expressed as a decimal fraction)

P_n = Mass of phosphate rock consumed in month n by wet-process phosphoric acid process line m (tons)

m = Each wet-process phosphoric acid process line

z = Number of months during which the process line m operates

2000/2205 = Conversion factor to convert tons to metric tons.

As noted earlier, many of the data inputs for this method are readily available. The Phosphoric Acid NSPS (40 CFR part 60, subpart T) requires continuous monitoring of phosphorus-bearing material (rock) to process. In addition, only 3 facilities within the United States are not vertically integrated with mines and may lack the necessary equipment to measure the inorganic carbon weight percent of the rock. In general, inorganic carbon test results and monthly production data should be readily available.

5.3 Option 3: Direct Measurement using Continuous Emission Monitoring Data (CEMS)

Another applicable monitoring method to estimate CO₂ emissions from phosphoric acid production facilities for which the process emissions and/or combustion GHG emissions are contained within a stack or vent is direct measurement using a Continuous Emissions Monitoring System (CEMS). In the case of phosphoric acid facilities, each stack emits both process and combustion emissions. Because a CEMS would continuously measure actual CO₂ emissions at a given phosphoric acid production facility when it is in operation, this method is the most accurate monitoring method for determining GHG emissions from a specific source. The costs for installing and operating a CEMS for direct measurements of GHG emissions from a given phosphoric acid production facility would be higher than for using one of the other monitoring method options. See stationary combustion TSD for information on estimating CH₄ and N₂O.

Direct measurements of the GHG concentration in the stack gas and the flow rate of the stack gas can be made using a CEMS. Elements of a CEMS include a platform and sample probe within the stack to withdraw a sample of the stack gas, an analyzer to measure the concentration of the GHG (e.g., CO₂) in the stack gas, and a flow meter within the stack to measure the flow rate of the stack gas. The emissions are calculated from the concentration of GHGs in the stack gas and the flow rate of the stack gas. A CEMS continuously withdraws and analyzes a sample of the stack gas and continuously measures the GHG concentration and flow rate of the stack gas.

6. Procedures for Estimating Missing Data

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

As noted, the Phosphoric Acid NSPS (40 CFR part 60, subpart T) requires continuous monitoring of phosphorus-bearing material (rock) to process. This requirement, along with the fact that the facility will closely monitor production inputs, results in low likelihood of missing data. Additionally, only 3 facilities within the United States are not vertically integrated with mines and may lack the necessary equipment to measure the inorganic carbon weight percent of the rock. In general, inorganic carbon test results and monthly production data should be readily available.

6.1 Procedures for Option 1: Simplified Emissions Calculations

For process sources that use a simplified emission calculation no missing data procedures would apply because the emission calculation is performed using default emission factors and activity data. Activity data such as production or consumption are readily available. Therefore, 100 percent data availability would be required.

6.2 Procedures for Option 2: Hybrid Method

For process sources that use a site-specific emission factor no missing data procedures would apply because the site-specific emission factor is derived from the analysis of the most recent phosphate rock batch and used in each calculation. The factor would be multiplied by the process input rate, which is readily available. Therefore, 100 percent data availability would be required.

6.3 Procedures for Option 3: Direct Measurement using CEMS

For options involving direct measurement of CO₂ emissions using CEMS, Part 75 establishes procedures for the management of missing data. Specifically, the procedures for managing missing CO₂ concentration data are specified in §75.35. In general, missing data from the operation of the CEMS may be replaced with substitute data to determine the CO₂ emissions during the period for which CEMS data are missing. Section 75.35(a) requires the owner or operator of a unit with a CO₂ CEMS to substitute for missing CO₂ pollutant concentration data using the procedures specified in paragraphs (b) and (d) of §75.35; paragraph (b) covers operation of the system during the first 720 quality-assured operation hours for the CEMS, and paragraph (d) covers operation of the system after the first 720 quality-assured operating hours are completed.

During the first 720 quality-assured monitor operating hours following initial certification at a particular unit or stack location, the owner or operator would be required to substitute CO₂ pollutant concentration data according to the procedures in §75.31(b). That is, if prior quality-assured data exist, the owner or operator would be required to substitute for each hour of missing data, the average of the data recorded by a certified monitor for the operating hour immediately preceding and immediately following the hour for which data are missing. If there are no prior quality-assured data, the owner or operator would have to substitute the maximum potential CO₂ concentration for the missing data.

Following the first 720 quality-assured monitor operating hours, the owner or operator would have to follow the same missing data procedures for SO₂ specified in §75.33(b). The specific methods used to estimate missing data would depend on the monitor data availability and the duration of the missing data period.

7. QA/QC Requirements

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

7.1 Stationary Emissions

For QA/QC options for stationary combustion refer to EPA-HQ-OAR-2008-0508-004.

7.2 Process Emissions

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

7.3 Data Management

Data management procedures should be included in the QA/QC Plan. Elements of the data management procedures plan are as follows:

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

8. Types of Emissions to be Reported

Based on the existing programs and the emission sources at phosphoric acid production facilities, GHG reporting for these facilities is limited to CO₂, CH₄, and N₂O. Phosphoric acid facilities should report both process (CO₂) and combustion related (CO₂, CH₄, and N₂O) greenhouse gas emissions. The data to be reported may vary depending on monitoring options selected. However, a phosphoric acid production facility should report its annual average phosphate rock consumption, number of wet-process phosphoric acid lines, percent inorganic carbon in phosphate rock consumed, annual phosphoric acid production and concentration, annual phosphoric acid production capacity, electricity usage (kilowatt-hours), and annual operating hours. For reporting options for stationary combustion refer to EPA-HQ-OAR-2008-0508-004.

8.1 Other Information to be Reported

Additional data for verification could include process raw material and product feed rates and carbon contents. Such data would illustrate the process operating conditions at which the emissions monitoring data were obtained. EPA could use such data, for example to check the reported emissions against activity-data-based emission factors for the process.

8.2 Additional Data to be Retained Onsite

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

9. References

EFMA (2000) "Production of Phosphoric Acid." Best Available Techniques for Pollution Prevention and Control in the European Fertilizer Industry. Booklet 4 of 8. European Fertilizer Manufacturers Association. Available online at <http://www.efma.org/Publications/BAT%202000/Bat04/section04.asp>.

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

Falls (2008). Personal Communication between Harold Falls of CF Industries and Erin Redmond of Research Triangle Institute (RTI), June 26, 2008.

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

Jaskinski (2008). Personal Communication between Stephen Jaskinski of the US Geological Survey and Mausami Desai of US EPA. June 25th, 2008.

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

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

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

U.S. EPA (2003) Part 75, Appendix B1, Available at <http://www.epa.gov/airmarkt/spm/rule/001000000B.htm>.

USGS (2007) Minerals Yearbook: Phosphate Rock Annual Report. U.S. Geological Survey, Reston, VA. Available online at: http://minerals.usgs.gov/minerals/pubs/commodity/phosphate_rock/myb1-2007-phosp.pdf.

Wyoming DEQ (2006) Air Quality Division Chapter 6, Section 3 Operating Permit. State of Wyoming Department of Environmental Quality Cheyenne, Wyoming. Available online at: <http://deq.state.wy.us/AQD/Title%20V%20Operating%20Permits/3-1-125.fin.pdf>.