Atmospheric Emissions and Air Quality Impacts from Natural Gas Production and Use

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Abstract

The US Energy Information Administration projects that hydraulic fracturing of shale formations will become a dominant source of domestic natural gas supply over the next several decades, transforming the energy landscape in the United States. However, the environmental impacts associated with fracking for shale gas have made it controversial. This review examines emissions and impacts of air pollutants associated with shale gas production and use. Emissions and impacts of greenhouse gases, photochemically active air pollutants, and toxic air pollutants are described. In addition to the direct atmospheric impacts of expanded natural gas production, indirect effects are also described. Widespread availability of shale gas can drive down natural gas prices, which, in turn, can impact the use patterns for natural gas. Natural gas production and use in electricity generation are used as a case study for examining these indirect consequences of expanded natural gas availability.

INTRODUCTION

Natural gas production in the United States is increasing, enabled by technologies such as horizontal drilling and hydraulic fracturing. In 2011, natural gas produced using hydraulic fracturing in shale formations (shale gas) accounted for 30% of US natural gas production. This percentage is projected to grow to 49% by 2035; total natural gas production is projected to increase by 30% (1). The implications of this transformation in the production of natural gas and associated hydrocarbon liquids in the United States will be profound. In 2012, the International Energy Agency predicted that the United States would become energy independent (on an energy basis) by 2035. The Agency also predicted that the additions to oil production associated with natural gas production could make the United States the largest global oil producer, surpassing Saudi Arabia, by 2020 (2).

Although the development of shale gas resources during the first decade of the twenty-first century has been more extensive in the United States than elsewhere, the resource base is global. **Table 1** provides global estimates of onshore, technically recoverable shale gas and oil (3). At current global rates of natural gas consumption [113 trillion cubic feet (tcf) per year (4)], these onshore resources (7,299 tcf) would represent more than 60 years of supply.

The widespread availability of natural gas, as well as its natural gas liquid and oil coproducts, will transform industrial sectors beyond oil and gas production. The projected long-term availability of natural gas at favorable prices is already beginning to change electricity generation in many parts of the United States (5), with natural gas generation replacing coal-fired electricity generation. Changes in the availability and pricing of methane, ethane, propane, and butane will change the chemical manufacturing sector, with natural gas liquids potentially replacing petroleum-derived feedstocks. Less-expensive natural gas will also lead to less-expensive hydrogen (produced by using steam reforming of methane), as well as the ammonia- and nitrogen-based fertilizers derived from methane. This, in turn, may affect agricultural practices. These are just a few examples of the potential impacts of increased availability of low-cost natural gas and natural gas coproducts.

Like all energy production and industrial processing, production and use of shale gas have environmental impacts. Among these impacts are land use, water use (6), water contamination (7–10), criteria air pollutant and air toxics releases (11–13), and greenhouse gas emissions (14–20).

Table 1 Estimates of global, technically recoverable shale oil and shale gas resources (3)

Rank	Country	Shale oil (10^9 barrels)	Country	Shale gas (10^{12} ft^3)
1	Russia	75	China	1,115
2	United States	58	Argentina	802
3	China	32	Algeria	707
4	Argentina	27	United States	665
5	Libya	26	Canada	573
6	Australia	18	Mexico	545
7	Venezuela	13	Australia	437
8	Mexico	13	South Africa	390
9	Pakistan	9	Russia	285
10	Canada	9	Brazil	245
World totals		345		7,299

Given the potential scope and magnitude of the economic and industrial transformations that shale gas production can lead to, it will be important to understand, as thoroughly as possible, the environmental implications of the transformations. This review focuses on the air quality implications of the production and use of natural gas from shale formations. Three types of air pollutants are considered: greenhouse gases, photochemical air pollutants and their precursors, and air toxics.

Estimating air pollutant emissions from shale gas operations can be challenging. The number of individual source locations is large; as an example, the Barnett Shale production region in North Central Texas has more than 10,000 individual gas wells (21). The number and types of emission sources at the well sites vary, and some of the operational practices are relatively new. Consequently, source-specific emissions data are just emerging.

In addition to the challenges associated with estimating emissions, there are challenges in characterizing impacts. The impacts of the air pollutant emissions occur over very different spatial and temporal scales, ranging from global and decadal (for greenhouse gases) to local and hourly (for air toxics). Consequently, the tools needed to characterize air pollutant impacts vary. For pollutants such as air toxics, local emission estimates and dispersion modeling are the primary tools of analysis. For regional photochemical air pollutants and their precursors, both local analyses and regional photochemical modeling (together with inventories of emissions over spatial scales of hundreds of kilometers) are used to assess impacts. For greenhouse gases, national or global emissions, coupled with an assessment of the relative potency of various emissions, is required.

GREENHOUSE GAS EMISSIONS FROM SHALE GAS PRODUCTION AND USE

Comparing Greenhouse Gas Emissions of Natural Gas to the Emissions of Other Fuels

When combusted to produce energy, the greenhouse gas emissions of natural gas, per unit of energy released, are lower than those of the other two principal fossil fuels, petroleum and coal. A simple calculation demonstrates the potential magnitude of the reductions in greenhouse gas emissions from combustion. A MJ of heat can be generated by combusting roughly 19.9 g of methane (the primary component of natural gas), assuming a lower heating value of 50.3 MJ/kg (22). Assuming complete combustion, 54.7 g of carbon dioxide would be released in combusting this amount of methane. In contrast, 44 g of coal would be needed to generate the same MJ of heat, assuming a lower heating value of 22.7 MJ/kg (**http://greet.es.anl.gov**). If the coal is 85% carbon, 137 g of carbon dioxide would be released in combusting this coal. Thus, focusing exclusively on combustion emissions, the carbon dioxide emissions of natural gas are substantially lower than those of coal (and petroleum) as a fuel.

Although the carbon footprint of methane combustion is lower than the carbon footprint associated with coal or petroleum combustion, methane emissions along the supply chain of natural gas can change this footprint. A conceptual diagram of the natural gas supply chain is shown in **Figure 1**. Methane, a potent greenhouse gas, can be emitted at multiple points along the supply chain, and if the methane emissions along the natural gas supply chain are large enough, they can change the greenhouse gas emission footprint of natural gas relative to other fuels. The amount of methane emissions that would lead to this change in the greenhouse gas footprint of methane, relative to other fuels, depends on the potency that is assumed for methane.

Potencies of greenhouse gases are typically expressed as global warming potentials (GWPs) and carbon dioxide equivalents (CO_{2e}). The CO_{2e} expresses the amount of carbon dioxide that would

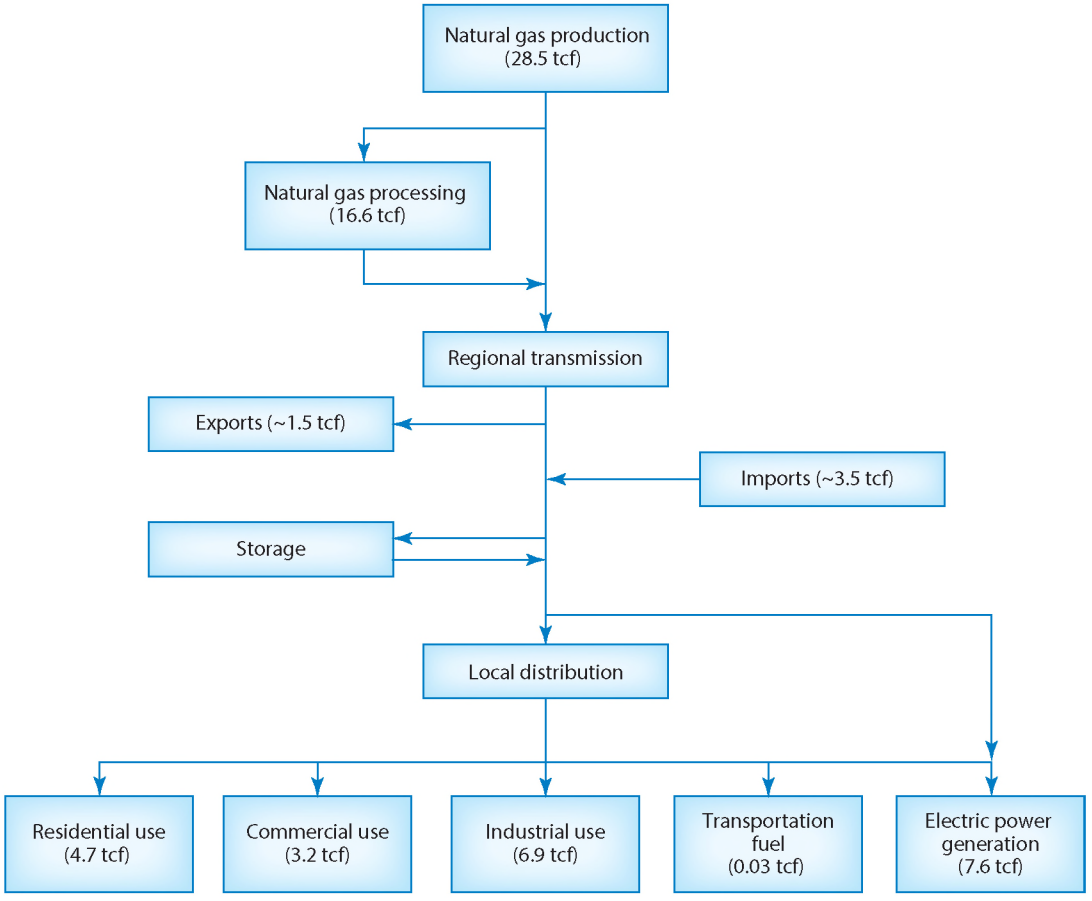

Figure 1

Natural gas supply chain in the United States (23). Flow data for 2011 are expressed in trillion standard cubic feet (tcf) of natural gas; the flow decreases along the supply chain owing to changes in the amount of gas stored, emissions, and the use of the gas as a fuel (for example, in compression during transmission) in the supply chain. Note that natural gas processing is shown as a side stream because some produced gas is of pipeline quality and does not need processing.

need to be emitted to produce the same radiative forcing of the atmosphere as the emission being reported. Methane has generally been assumed to have a GWP of 25 (24), indicating that for each kg of methane emitted, an emission of 25 kg of carbon dioxide would produce a similar radiative forcing of the atmosphere (a kg of methane has a CO_{2e} of 25 kg). However, methane GWPs of more than 100, relative to carbon dioxide, can also be assumed (25). Differences in assumed radiative forcings are due to the fact that methane is oxidized in the atmosphere to carbon dioxide, over roughly decadal timescales. A methane GWP of 25, relative to carbon dioxide, assumes that impacts are integrated over 100 years. For the first decade or so of this century-long period, the emitted carbon is in methane, but for most of this period, the emitted carbon has been oxidized to carbon dioxide. In contrast, a methane GWP of 102 (25) is based on the immediate difference in radiative forcing between methane and carbon dioxide.

Thus, the greenhouse gas impact of natural gas, relative to other fuels, will depend on the time horizon of the impact. Alvarez et al. (25) performed a series of analyses comparing natural

gas to other fossil fuels for a variety of uses, assuming a variety of methane GWPs. For example, they calculated that switching to natural gas combined-cycle electricity generation (with its high thermal efficiency and lower greenhouse gas emissions in combustion) will cause an immediate net climate benefit if the rate of methane leakage in the natural gas supply system is less than 2.9%. The leak percentage that can be accommodated while still producing a net climate benefit increases as the time horizon for the impact increases (and the GWP for methane decreases). Alvarez et al. (25) examined a variety of fuel-switching scenarios and came to the conclusion that net climate benefits sometimes require methane leakage rates of less than 1%, whereas other fuel-switching scenarios may lead to long-term climate benefits at leakage rates of 4% or more, depending on the GWP assumed for methane and the nature of the fuel switching.

These analyses provide a useful context for estimates of methane emissions along the natural gas supply chain; however, quantifying emissions as a percentage of natural gas produced or used can introduce confusion. The benchmarks and comparisons to other fuels reported by Alvarez et al. (25) rely on estimates of methane emissions integrated along the natural gas supply chain. Estimates of methane emissions as a percentage of natural gas production may or may not be adjusted for coproducts produced along with natural gas. Many natural gas wells also produce substantial amounts of natural gas liquids and oil. In these cases of wells producing multiple products, emissions are often allocated among the natural gas, natural gas liquids, and oil. The most commonly used allocation methods are based on energy, mass, and value (26–28). In an energy-based allocation, a well that produces 6,000 standard cubic feet (scf) of gas for every barrel (bbl) of hydrocarbon liquid would have equal energy content in the natural gas and oil products, assuming a heating value of 1,000 BTU/scf and 6 million BTU/bbl of hydrocarbon liquid. Because, in this simple example, the energy content of oil and gas products is the same, half of the emissions would be allocated to the gas and half to the liquid. In contrast, a mass-based allocation for the same simple example, based on a gas density of 25 g/scf and an oil density of 100 kg/bbl, would allocate 60% of the emissions to the natural gas and 40% to the oil. A value-based allocation, based on prices of $3.50 per thousand scf for gas and $90 per bbl for hydrocarbon liquid, would assign 19% of the emissions to gas and 81% to the liquid. Thus, whether and how coproducts are considered can have a significant impact on the reported leakage rate for methane in natural gas systems.

In summary, the greenhouse gas footprint of natural gas depends on the magnitude of the methane leaks along the supply chain. Leakages of methane along the natural gas supply chain, ranging from 1% to more than 4%, can change the greenhouse gas footprint relative to other fuels, depending on the type of use and the time horizon over which the radiative forcing impacts are integrated. However, practices vary in reporting methane emissions as a percentage of natural gas production and use; therefore, analyses must be interpreted carefully.

Current Estimates of Methane Emissions Along the Natural Gas Supply Chain

In the United States, estimates of greenhouse gas emissions, including those from the natural gas supply chain, are estimated annually by the Environmental Protection Agency (EPA) (29–32). This review focuses on methane emission estimates in this inventory. As noted in the previous section, emissions of methane along the natural gas supply chain can change the greenhouse gas footprint of natural gas, relative to other fuels, because of the potency of methane as a greenhouse gas. Emissions of carbon dioxide from combustion of natural gas are a substantial component of the total greenhouse gas emissions from the natural gas supply and use chain; however, these emissions can be estimated with a reasonable degree of accuracy from fuel consumption data. In contrast, emissions of methane have a much greater degree of uncertainty.

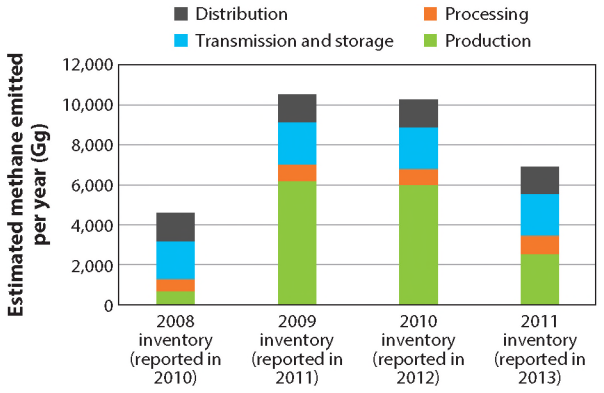

Figure 2

Estimated methane emissions along the natural gas supply chain, 2008–2011. Emission estimation methods, particularly for production processes, have varied over this period, producing large changes in estimates (32).

The magnitude of the uncertainties in methane emission estimates along the natural gas supply chain can be characterized by examining the annual inventories of methane emissions released by the US EPA over the past four years (29–32). The data are summarized in **Figure 2**. The emissions are categorized into production, processing, transmission/storage, and distribution segments. For the most recent reporting year, 2011 (data reported in 2013), emissions from production operations are estimated to be the largest contributor to methane emissions in this estimate, at 2,545 Gg. However, there has been substantial variation from year to year in production emission estimates. In 2008 and 2009, estimates of methane emissions in production operations were 6,205 and 6,002 Gg, respectively. In 2008, the emissions were estimated to be 674 Gg. This order-of-magnitude variation in methane emission estimates is due largely to changes in assumptions employed in emission estimation methods. If a consistent set of assumptions is used, production emissions are estimated to have decreased by 30% between 2008 and 2011 (from 3,640 Gg in 2008 to 2,545 Gg in 2011) (29–32).

For the other segments of the natural gas supply chain, emission estimates over the past four years have been far more stable. For the most recent reporting year, emissions from processing, transmission/distribution/storage, and local distribution segments are 932, 2,087, and 1,329 Gg, respectively.

Overall, methane leak rates in the natural gas supply chain (methane as a volume percentage of natural gas production with all methane emissions allocated to natural gas) reported in EPA inventories over the past several years have ranged from less than 1% in 2008 to 2.1% in 2009, with a current estimate of 1.3%. Other researchers have suggested that the leak rates may be much higher than 2%, with some values as high as 8% or more (17). A recent review of these estimates, based on US data, has been assembled by the Department of Energy and Climate Change in the United Kingdom (33), and their central estimate is similar to the most recent US EPA inventory.

More details on the major sources of methane emissions in the natural gas production sector, reported in the EPA national emission inventory, are given in **Table 2**. In assembling the national emission inventory, the EPA first estimates potential emissions for source categories then reduces the potential emissions by estimated voluntary reductions and reductions required by regulations. Potential emissions, emission reductions, and net emissions are reported in **Table 2** (32, 34). All regulatory reductions and some voluntary reductions are assigned to specific sources; however, some voluntary reductions are aggregated by source category. For example, the EPA estimates a total of 691 Gg of emission reductions for well-completion flowbacks and workovers with hydraulic

Table 2 National emission inventory estimates by source category (potential emissions, reductions, and net emissions in Gg methane per year) (adapted from 34)

Environmental Protection Agency source activity	Potential emissions (Gg)[a]	Emission reductions (Gg)[a]	Net emissions (Gg)
Completions with hydraulic fracturing	1,221	567	654
Refractures (workovers with hydraulic fracturing)	266	124	143
Pneumatic device vents	1,134	779	355
Chemical injection pumps	64	30	34
Equipment leaks: gas wells	52	24	172
Equipment leaks: separators	107	50	
Equipment leaks: meters/piping	102	48	
Equipment leaks: heaters	33	15	
Equipment leaks: dehydrators	31	15	
Workovers without hydraulic fracturing	0.6	0.3	0.3
Liquids unloading	257	0	257
Kimray pumps	365	180	930
Condensate tanks	313	167	
Gas engines	276	49	
Dehydrators vents	114	73	
Reciprocating compressors	84	35	
Pipeline leaks	170	80	
Well drilling	0.8	0.4	
Blowdowns	6.7	2.3	
Compressor starts	6	3	
Pressure relief valves	0.7	0.3	
Mishaps	2	1	
Emissions from coal bed methane and offshore production			
Coal bed methane–produced water	59	27	
Offshore and deepwater platforms	289	136	
TOTAL	4,949	2,405	2,545

[a]Potential emissions data are from US Greenhouse Gas Inventory 13 Annex 3, Table A-134 (32, 34). Emission reductions data are from Tables A-132 and A-133.

fracturing combined. In cases such as this, the allocation of combined reductions in **Table 2** was assumed to be proportional to the potential emissions [see Allen et al. (34) for more details].

The largest single source category is emissions from completion flowbacks. Completion is the process of readying a well for continuous production. Specifically, after drilling and fracturing, and before natural gas production can begin, the well must be cleaned of sand and liquids of various types that have been injected into the well. The recovery of these liquids is referred to as flowback, and gas, including methane, can be dissolved or entrained in the flowback liquids. Some of the methane in the liquids can be sent to sales or emission control devices, but some can be emitted (34). Other significant source categories include emissions from pneumatic devices, venting from tanks, liquids unloadings, workovers, and equipment leaks. If the sources along the entire supply

chain are added to the emissions from the production sector, emissions from compressors also emerge as a significant source category (32, 35).

Insights from New Measurements

Emission estimates for many of the source categories in the US national methane emission inventory are based on measurements that were performed in the 1990s as part of a joint effort between the Gas Research Institute and the US EPA (36). However, over the past two decades, practices and processes in some parts of the natural gas supply chain, particularly natural gas production, have changed significantly. Therefore, new data may be expected to lead to additional insights into methane emissions along the natural gas supply chain.

Horizontal drilling and hydraulic fracturing are among the practices that have become more widely used over the past two decades. In the current US national inventory for methane from the natural gas supply chain, completion flowbacks are estimated to be the largest source of methane emissions; however, these estimates have been based on very limited data and are subject to change owing to evolving use of reduced emission completions. Allen et al. (34) have recently reported detailed data for methane emissions from 27 hydraulically fractured well completions in the United States. The durations of the completions ranged from 5 to 339 h (2 weeks). Measured methane emissions over an entire completion flowback event ranged from less than 0.01 Mg to more than 17 Mg, with an average value of 1.7 Mg and a 95% confidence interval of 0.67–3.3 Mg. In the most recent EPA national greenhouse gas emission inventory (2011 inventory, released April 2013) (32), a total of 8,077 well completions with hydraulic fracturing are estimated to result in 654 Gg per year of emissions (see **Table 2**), for an average of 81 Mg of methane per completion flowback [compared to 1.7 Mg per flowback reported by Allen et al. (34)]. To understand the reasons for the much lower emissions per event reported by Allen and coworkers, it is useful to carefully distinguish potential emissions from net emissions. The potential of a flowback to emit can be defined as the methane that would be emitted if all of the methane leaving the well during the flowback were vented to the atmosphere. Potential emissions reported by Allen et al. (34) ranged from 0.2 Mg to more than 1 Gg of methane, with an average of 124 Mg. The average from the EPA national inventory is only slightly higher, at 151 Mg. In the EPA national inventory, net emissions are calculated by reducing potential emissions by estimates of methane captured or controlled owing to regulatory or voluntary emission reductions. In the current national inventory, emission reductions are roughly half of potential emissions (see **Table 2**). Net emissions to the atmosphere reported by Allen et al. (34) are 98% less than potential emissions. This large difference between the net emissions measured by Allen and coworkers and the net emissions estimated in the national inventory is due to several factors. First, consistent with emerging regulatory requirements for reduced emission completions [40 C.F.R. 60, Subpart OOOO (2012); 40 C.F.R. 63, Subpart HH (2012); 77 Fed. Reg. 49490 (2012)] and improved operating practices, two-thirds of the wells Allen and coworkers examined in 2012 sent methane to sales or control devices. In late 2012, these practices became required for well completions in the United States. For those wells with methane capture or control, 99% of the potential emissions were captured or controlled. In addition, the wells with uncontrolled releases observed by Allen and coworkers had much-lower-than-average potential to emit, less than 1% of the average potential to emit in the national inventory (34).

To summarize this evolving situation for emissions from well completions, if all methane leaving the well during a completion were vented to the atmosphere, methane emissions from well-completion emissions would be the largest single source category along the natural gas supply chain. Reduced emission completion practices can reduce these emissions by 99%, and if these

practices are widely employed, methane emissions from completions become a relatively small source category. Consistent with emerging regulatory requirements in the United States, and consistent with the evidence reported by Allen et al. (34), reduced emission completions are being performed in the United States and are effective at reducing methane emissions. The evidence also suggests that if only a portion of wells have reduced emission completions, well operators will deploy that equipment to wells that have the largest potential for methane emissions. For some studies that estimate a very large percentage of methane leaks along the supply chain (17), large estimated emissions from completion flowbacks have been a significant fraction of the emission estimates. Therefore, data on current emissions from this source category are particularly important in assessing methane emissions along the natural gas supply chain.

Well completions provide a case study of how emissions can evolve as operating practices change and as practices for controlling emissions evolve. Additional insights are provided by the case study of emissions from pneumatic controllers. Pneumatic controllers use the pressure from on-site natural gas to drive devices that actuate valves controlling flow from units such as separators to units such as tanks. As the controllers sequentially increase and decrease pressure to control valve actuators, methane may be vented. Pneumatic controllers have been used for decades in the natural gas supply chain; therefore, emission factors from the 1990s might be expected to lead to reliable emission estimates. However, because emissions from pneumatic devices can depend on the frequency of accuation, the average emissions from a liquid level controller on a separator may depend on the gas-to-oil ratio in the well. In addition, controller equipment has evolved, as have regulations regarding the type of equipment that can be deployed in various regions. Therefore, it is not surprising that Allen et al. (34) report emissions different than emission factors based on data from the 1990s; the emissions are higher than in the current national inventory. This case of pneumatic devices suggests that as features of gas wells (such as gas-to-oil ratio) change, as equipment changes, and as regulations change, emissions may change in complex ways, even those from device types that have been used for decades.

Finally, improved understanding of methane emissions in the natural gas supply chain can also be provided by ambient measurements made at ground level and aloft using aircraft. Ground-level measurements, made downwind of natural gas sites, have made use of a variety of techniques designed to infer emission rates from ambient concentrations. A procedure that enables some of the most precise measurements is generally referred to as a tracer technique (34, 37–41). In this method, tracer compounds (e.g., SF_6, N_2O, and C_2H_2) are released at a known rate at or near a methane emission source; downwind measurements of methane (minus background) and the tracers (minus background) are equal to the ratio of emission rates if the dispersions of the methane and the tracer are identical. Methane emissions are estimated by multiplying the known emission rate of the tracer by the background corrected downwind concentration ratio of methane to the tracer. If two tracers are used, the assumption of equivalent dispersion can be quantitatively tested. Several of these studies have pointed to a skewed distribution of emissions among sites, with a small number of sites accounting for a large fraction of emissions. This may be due to high emitting sources (e.g., a pneumatic controller valve that emits much more than the average pneumatic controller), and there is evidence in direct source measurements that such high emitters exist (34, 42). However, these distributions must be interpreted carefully. The amount of equipment, and therefore the potential emission sources, at natural gas sites varies. For example, in a study by the City of Fort Worth (43), which reports on emissions from 375 well sites in the Barnett Shale production region (sites were randomly selected from the well sites that were within the City of Fort Worth), 30% of the sites had one well, 63% had between 2 and 6 wells, and one site had 13 wells. Similarly, whereas 78% of the sites had between 1 and 4 tanks, 16% had more than 4 tanks, and one site had 20 tanks. The potential sources of fugitive emissions, such as valves

and flanges, varied by an order of magnitude or more between sites. Ten percent of the sites had less than 62 valves, but 10% had more than 446 valves. Ten percent of the sites had 390 or less connectors (such as flanges), but 10% had more than 3,571 (34, 43). Because of this heterogeneity in the equipment among sites, simple comparisons of methane emissions among sites, without adjustments for equipment counts, should be viewed with caution.

Ambient measurements made by aircraft have also been used to assess emissions from the natural gas supply chain. In these studies, average aloft concentrations, upwind and downwind of a natural gas production region, are determined. The difference between downwind and upwind concentration multiplied by the advection rate of the air over the basin (mixing height multiplied by the average wind velocity and the horizontal dimension of the basin) leads to a basin total for emissions. If the emissions from livestock, landfills, and all other nonnatural gas sources in the region can be estimated, and are subtracted from the total methane emissions in the area, emissions from natural gas operations can be estimated. In some regions, these types of analyses have led to very high emissions estimates as a percentage of the region's natural gas flow. For example, for a natural gas and oil field in Utah, aircraft measurements suggest an emission rate that is 6.2–11.7% of the natural gas production rate. In aircraft-based analyses of methane emissions in Los Angeles, fugitive losses from natural gas pipelines and the urban distribution system, along with geological seeps, were identified as the dominant emission sources (44–46). These analyses suggest emissions sources that are not accurately accounted for in current emission inventories for both natural gas production and natural gas delivery systems. Again, however, these data must be interpreted with care. The attribution of methane emissions to the natural gas supply chain from regions that have both oil and gas production should be done carefully. Some emissions of methane may come from oil rather than gas production and therefore should be allocated to oil, rather than gas, supply chains. In addition, natural gas production operations, and their emissions, vary over the life of a gas field. For example, early in a field's life, drilling and well-completion activities will be more common than later in a field's life. Late in a field's life, wells may accumulate liquids, and methane venting may occur as part of a process called liquids unloading, which removes liquids from the well bore. Therefore, the age of a field and other factors can influence emissions. Consider a detailed example of how liquids unloadings may skew instantaneous measurements. Allen et al. (34) have observed emission rates for single liquids unloading events that ranged from roughly 100 g per min to more than 30,000 g per min. These rates are much higher than emission rates for production sites (typically tens of g of methane per min per well) or from completions (typically a few hundred g per event per min). At these emission rates, a single unloading event could, during the period that it is occurring, result in emissions that are the equivalent of just a few wells in routine production to the equivalent of up to several thousand wells in routine production. Because not all gas fields have wells that unload, and because gas wells may unload for only part of their production life cycle, emissions from different gas fields would be expected to vary, and an individual gas field would be expected to vary in its emissions over time. Overall, reconciliations between instantaneous ambient measurements should carefully account for the status of the wells in a gas field.

Collectively, recent measurements suggest that both ambient and direct source measurements will be important in examining emissions along the natural gas supply chain. Much work is currently under way. In direct source measurements (sometimes referred to as bottom-up measurements), Allen et al. (34) have reported initial results for the production portion of the supply chain, and additional measurements on selected source categories (including pneumatic controllers and liquids unloadings) are being performed. Similar efforts are under way in gathering and gas-processing operations, transmission, and local distribution (47–49). For ambient measurements designed to assess regional emissions (sometimes referred to as top-down measurements), several groups are continuing to collect data in and over large natural gas production regions (44–46). Over

the next several years, these studies can be expected to produce an evolution in the understanding of the sources that contribute to the greenhouse gas footprint of the natural gas supply chain.

REGIONAL AIR POLLUTANT EMISSIONS AND IMPACTS FROM SHALE GAS PRODUCTION AND USE

Although greenhouse gas emissions from natural gas production and use have attracted a great deal of attention in the scientific literature, they are not the only atmospheric emissions from natural gas production and use. Regional air quality can also be impacted. Regional impacts are driven by the emissions of criteria air pollutants and the precursors of criteria air pollutants, specifically volatile organic compounds (VOCs), nitrogen oxides (NOx), and particulate matter. The sources of these emissions include the source categories responsible for greenhouse gas emissions, discussed in the last section, but also include the vehicles used to transport materials to and from natural gas production sites.

Rather than attempting to briefly survey regional air quality impacts of natural gas production and use in many regions, this review focuses on analyses and data for the Barnett Shale production region in North Central Texas. Because the Barnett is one of the most mature shale gas production regions in the United States, it has a record of data that has been used to assess questions of regional air quality impacts. The Barnett is also located adjacent to the Dallas–Fort Worth metroplex, which currently violates US National Ambient Air Quality Standards for ozone (50).

The Barnett Shale region in Texas has shown significant growth in gas-production activity during the past ten years, producing 0.11 billion cubic feet per day in 2000 and increasing to 5 billion cubic feet per day by 2011 (51, 52). For comparison, total natural gas withdrawals in the United States in mid-2011 were approximately 70 billion scf/day (bcf/day), with approximately 22 bcf/day in Texas (53). At 5 bcf/day of production, the Barnett Shale is one of the largest natural gas production regions in the United States. The region includes 24 counties to the north and west of Fort Worth, with a total of more than 20,000 oil- and gas-producing wells (54). In a recent assessment of the future production activity in the Barnett, the Bureau of Economic Geology at the University of Texas (55) projected that, although new wells will continue to be drilled in the region, the field as a whole has likely reached its peak rate of natural gas production. It is anticipated, however, that the field will continue to produce significant quantities of natural gas for decades, with an ultimate production in the range of 50 trillion scf.

Current Emission Inventories of Criteria Air Pollutants from the Natural Gas Supply Chain and Insights from Ambient Measurements

Just as top-down and bottom-up measurements provide complementary information for greenhouse gas emissions, top-down and bottom-up methods have been used to assess emissions that affect regional air quality. Bottom-up data are available from the Texas Commission on Environmental Quality (TCEQ), which reports emissions from individual production sites in the Barnett Shale special inventory (21). The VOC emissions data in this inventory contain information on a total of 19,914 point sources, which report a total of 19,833 tons per year of VOC emissions. **Table 3** shows the total VOC emissions by source type from the TCEQ inventory. Condensate tanks are the largest source of VOC emissions, followed by fugitives, engines, and water tanks.

The performance of these bottom-up emission estimates in predicting changes to regional air quality owing to natural gas operations can be evaluated by using ambient data. Since 2010, the TCEQ has deployed automated gas chromatographs that have recorded hourly averaged atmospheric concentrations of hydrocarbons in the Barnett Shale production region and neighboring

Table 3 Total volatile organic compound (VOC) emissions by source type in the Barnett Shale Special Inventory (21)

Type of source	Total VOCs (tons per year)	% of total
Amine unit	6.1	0.03
Boiler	0.7	0.004
Condensate tank	11,549	58.2
Engine	1,236	6.23
Flare	20.0	0.10
Frac tank	3.5	0.02
Fugitives	4,260	21.5
Glycol dehydrator	207	1.04
Heater	3.9	0.02
Loading	553	2.79
Oil tank	291	1.47
Other	11.7	0.06
Separator	161	0.81
Thermal oxidizer	2.1	0.01
Vent	187	0.94
Water tank	1,343	6.77
Total	19,835	100.0

areas (56). **Figure 3** illustrates the locations of three of the monitoring sites, as well as their spatial relationship to the estimated sources of natural gas supply-chain emissions. The three sites are Eagle Mountain Lake (EML), Flower Mound Shiloh, and Hinton. EML is located northwest of the Fort Worth urban area, in approximately the geographical center of the Barnett Shale natural gas production region. Under typical wind conditions, with flow from the south, the Flower Mound Shiloh site, located northeast of the EML site, is not as strongly influenced by natural gas production activities as the EML site. The Hinton site is located in the Dallas downtown area.

Figures 4*a* and **5*a*** show measured diurnal and monthly average concentrations of hydrocarbons at the EML site. Light alkanes dominate, with ethane, propane, and butane accounting for approximately 70% of the identified hydrocarbon concentrations, expressed as ppbC. This composition is consistent with the expected composition of emissions from natural gas production activities. The concentrations show diurnal and monthly patterns; however, as shown in **Figures 4*b*** and **5*b***, the relative concentrations of the hydrocarbons are constant at all times of day and during all months, suggesting a constant source of emissions (57).

For the Flower Mound Shiloh and Hinton sites, the dominant species are also ethane, propane, and butane; however, in addition to being associated with emissions from natural gas production, these species are commonly found in regional background hydrocarbon samples. The concentrations of light alkanes at EML, within the Barnett Shale, are higher than at the sites at the periphery of and outside the natural gas production region. At EML, the average morning maximum concentrations of ethane, propane, and butane total close to 100 ppbC, whereas at Flower Mound Shiloh and Hinton the morning totals are 60 ppbC and 40 ppbC, respectively. Summed over all days and hours in a 20-month sampling period, the average concentrations at EML for ethane, propane, and butane are 31.3, 19.4, and 9.2 ppbC, respectively. For Flower Mound Shiloh, those

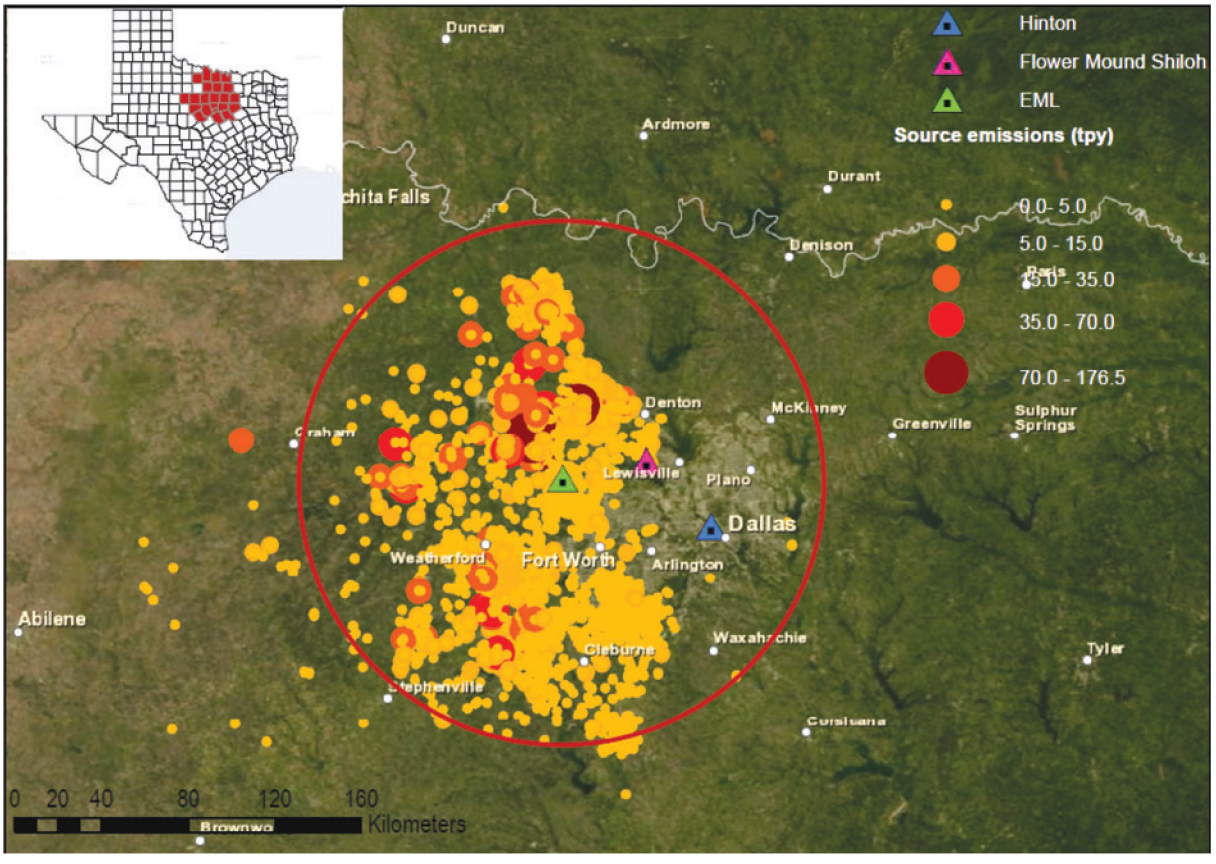

Figure 3

Location of ambient monitoring sites in the Barnett Shale region (*triangles*), relative to sources of volatile organic compound (VOC) emissions from natural gas production (*yellow*, *orange*, *and red circles*; size and color of circle scale with magnitude of emissions); large red open circle denotes a 100-km distance from a central monitoring site (57). Abbreviation: EML, Eagle Mountain Lake.

averages are 18.4, 13.0, and 7.8, respectively. In the case of Hinton, the averages are 15.5 for ethane, 11.0 for propane, and 6.5 for butane (57).

These top-down measurements can be quantitatively compared to the bottom-up emission inventory data assembled by the TCEQ by using dispersion models. When this is done for the Barnett Shale region, the predicted concentrations of VOCs owing to natural gas production were generally within ~20% of background corrected measurements, with a slight underprediction bias. Hourly and daily variations in observed, background-corrected concentrations were explained primarily by variability in meteorology. This analysis for the Barnett Shale suggests that VOC emissions associated with shale gas production are reasonably well accounted for by current emission inventory methods (57).

Reconciliation between top-down and bottom-up methods of estimating emissions of NOx from natural gas production sites in the Barnett Shale are more ambiguous than for VOCs. NOx is emitted as a by-product of combustion, and the engines associated with vehicles and compressors in the natural gas supply chain will emit NOx. Unlike ethane, propane, and butane, which are relatively stable in the atmosphere, NOx can react relatively quickly in the atmosphere, and top-down estimates of emission rates must account for these transformations. Satellite data,

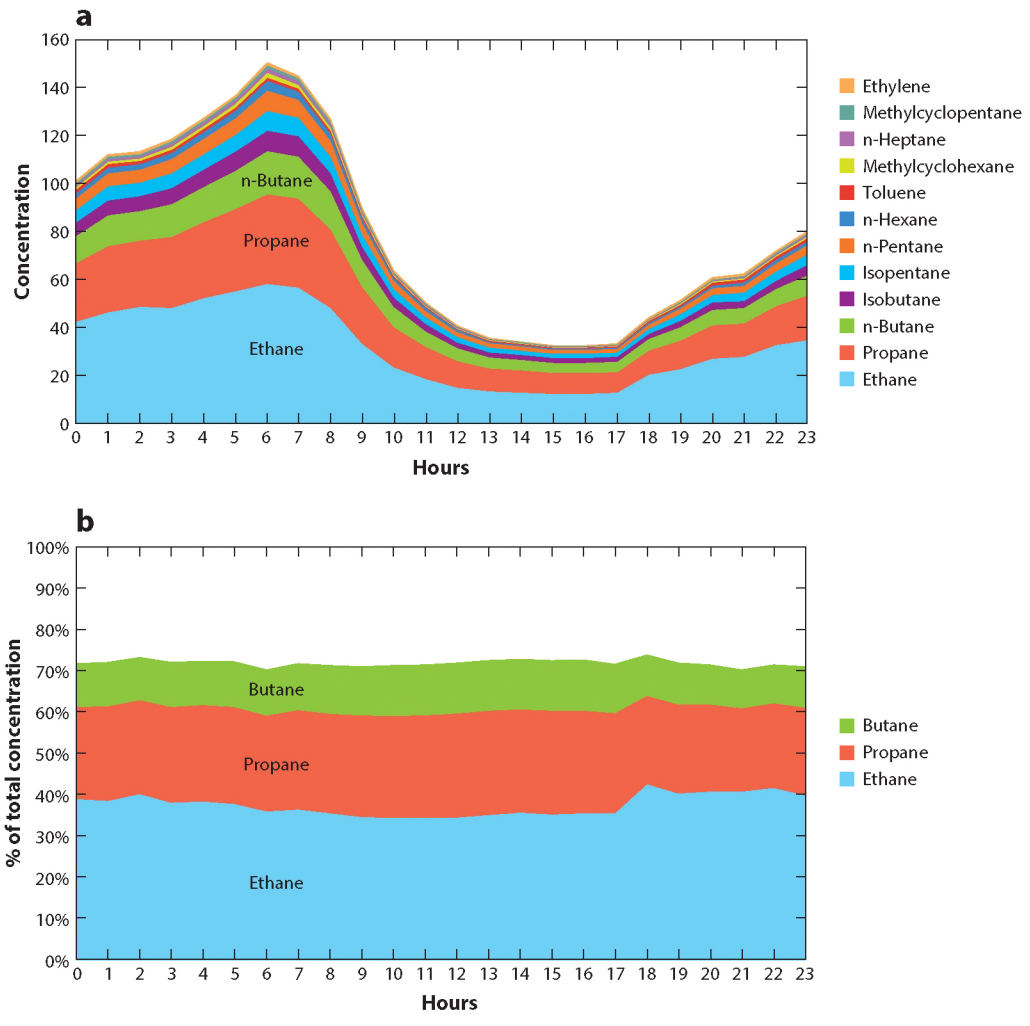

Figure 4

(*a*) Average diurnal pattern of hydrocarbon concentrations (ppbC) at Eagle Mountain Lake (EML); data for each hour are averaged over 20 months of sampling. (*b*) Percentage of ppbC accounted for by ethane, propane, and butane at EML (57).

coupled with regional photochemical models, provide one such tool for top-down estimates of NOx emissions. For example, the Ozone Monitoring Instrument (OMI) aboard the *Aura* satellite (58, 59) uses differential optical absorption spectroscopy applied to the range 405–465 nm, which can be used to determine a vertical column density for NO_2. The OMI instrument has been used to evaluate several regional emissions inventories for NOx (60–64). **Figure 6** shows an example of an overall NO_2 column density over Texas based on OMI observations (65). These top-down measurements of column NO_2 density can be compared to predictions of total column NO_2 generated by a gridded regional photochemical model, such as the Comprehensive Air Quality Model with Extensions (65; **www.camx.com**). These predictions rely on an inventory of all NOx emissions and accurate representation of the fraction of the NOx that is NO_2. **Figure 6** also shows column NO_2 predictions for eastern Texas, consistent with the time periods of the

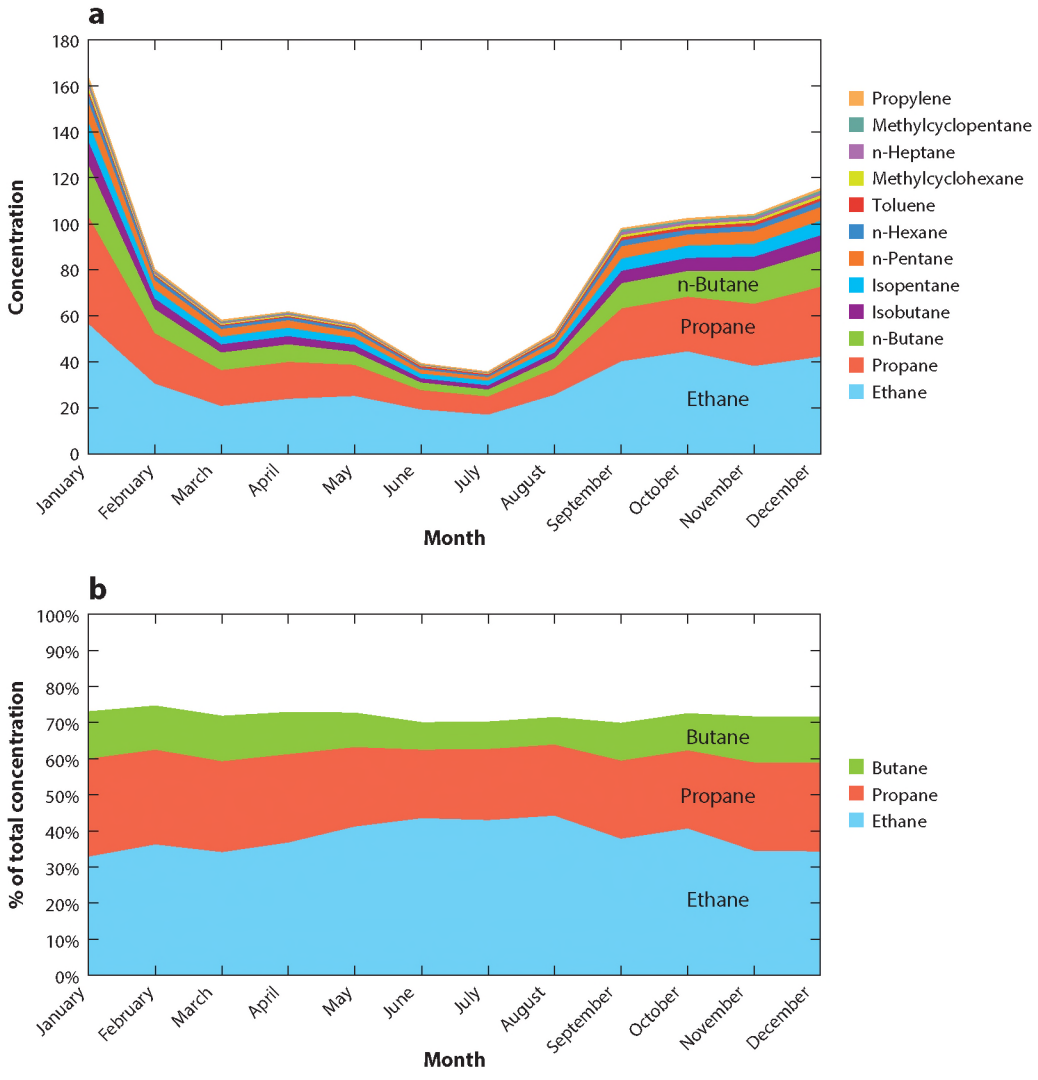

Figure 5

(*a*) Monthly average hydrocarbon concentrations at Eagle Mountain Lake (EML) (ppbC); data are averaged over all hours and over 20 months of sampling. (*b*) Percentage of ppbC accounted for by ethane, propane, and butane at EML (57).

OMI observations. Comparison suggests some underprediction of column NO_2 by the emission inventory and regional photochemical model over broad regions of the state where oil and gas production activity occurs, but the spatial resolution of the measurements and modeling makes it difficult to use this type of analysis to perform a quantitative assessment of NOx inventories in natural gas production (65).

Supply-Chain Estimates of Criteria Air Pollutant Emissions and Their Impacts

To this point, this review has emphasized the air pollutant emissions associated with the natural gas supply chain; however, as noted in the introduction, the widespread availability of natural

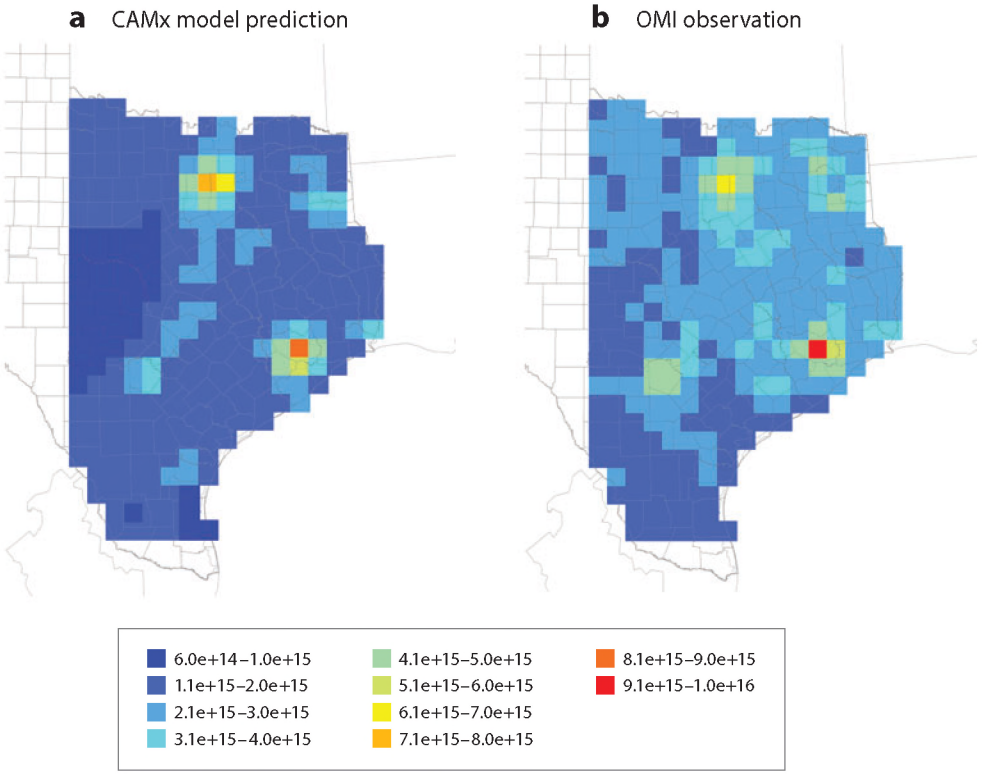

Figure 6

NO_2 column densities (molecules cm^{-2}) estimated from satellite measurements (*b*) and emission inventories coupled with photochemical modeling (*a*) (65). Abbreviations: CAMx, Comprehensive Air Quality Models with Extensions; OMI, Ozone Monitoring Instrument.

gas will likely have impacts on sectors other than oil and gas production. The potential impacts of natural gas production on electricity production can serve as a case study of the air quality implications of changes in natural gas use patterns.

Electricity generation is one of the dominant uses of natural gas. In the Texas electrical grid, operated by the Electricity Reliability Council of Texas (ERCOT), a fuel mix consisting of 39% coal, 40% natural gas, 12% nuclear, and 8.5% wind has been used in the past several years. This represents an increase in natural gas use. Historically, coal has been used for base-load electricity generation, with natural gas used to meet peak loads, but recently natural gas has begun to displace coal for some base load. Overall, generation capacity in ERCOT is 23% coal, 57% natural gas, 7% nuclear, and 13% wind (66), so even more natural gas capacity exists in the current operation of the grid.

Over the past decade, natural gas prices have decreased from peak levels above $10 per million BTU of heating value to prices approaching $2 per million BTU. These decreasing prices for natural gas have driven changes in the use of natural gas generation in ERCOT. Pacsi et al. (13) have modeled the electricity generation shifts that would be expected in ERCOT as natural gas prices change from $7.74 per million BTU (a representative price from 2006–2008) to $3.87 per million BTU, $2.88 per million BTU (an average price in late 2012), and $1.89 per million BTU (a price

equivalent to coal on an energy basis). Decreasing natural gas prices relative to coal drives a shift in electricity generation from coal-fired units to natural gas–fired units. Because the natural gas–fired units have lower air pollutant emissions per kW h of generation, relative to the coal plants that they displace, total air pollutant emissions are driven downward. Associated with these downward shifts in emissions in electricity generation are increases in emissions associated with natural gas production. Pacsi et al. (13) found that overall, for the entire supply and use chain, emissions are lowered by the shift from coal to natural gas in ERCOT, but emissions increase in some areas and decrease in others. Similar results have been reported for other regions in the United States (67, 68). If changes in emissions, and their spatial distributions, are used in conjunction with regional air quality models, these changes in emissions can be used to predict overall changes in air quality. Pacsi and coworkers (13) report that, even though emissions increase locally in natural gas production areas as natural gas production increases, overall ambient concentrations of ozone and particulate matter decrease in the entire region (including the natural gas production regions) because of the large decreases in emissions from electric power generation that are upwind of the natural gas production regions. This type of result is likely to vary regionally, but it points to the importance of considering air quality impacts of natural gas along the entire life-cycle chain, from production to use.

TOXIC AIR POLLUTANTS FROM SHALE GAS PRODUCTION

In principle, the same types of tools employed in greenhouse gas and regional air pollutant assessments of natural gas production and use can also be applied to toxic air pollutants. These tools include bottom-up and top-down emission inventory assessments, dispersion and photochemical modeling, and life-cycle (supply and use chain) analyses. In practice, however, data are sparse on toxic air pollutant impacts of natural gas production and use. Benzene, which would be expected to be emitted with other VOCs, has been measured in some regions (for example, see Reference 69). Other measurements have focused on detailed speciation of organics in air samples collected near production sites. Some of these samples have included species such as formaldehyde, chloroform, carbon tetrachloride, and other halogenated organics (70–71). Species such as formaldehyde may be associated with engine emissions (70); however, chlorinated organics (71) are not typical components of oil and natural gas or their combustion products, and their origin is unclear. Hypotheses include fracturing fluid constituents or the reaction products that may occur as fracturing fluids interact with reservoir fluids and surfaces at the elevated temperatures and pressures experienced downhole. These reaction products may be vented during processes such as flowbacks. Overall, our understanding of the issue of toxic air pollutants associated with natural gas production is limited.

SUMMARY

Hydraulic fracturing of shale formations and the production of shale gas are transforming the industrial and energy landscapes in the United States. Like all energy production and industrial processing, the production and use of shale gas have environmental impacts. This review has summarized the current state of knowledge of air quality impacts, focusing on greenhouse gas emissions, regional air pollutants, and toxic air pollutants. In each of these areas, a combination of direct source emission measurements (bottom-up methods) together with ambient measurements (top-down analyses) is improving our level of understanding. Nevertheless, uncertainties remain in all of these areas, and the multifaceted air quality impacts of shale gas are likely to remain a very active area of research.

DISCLOSURE STATEMENT

David Allen has worked on research projects funded by a variety of governmental, nonprofit, and private sector sources, including the National Science Foundation, the Environmental Protection Agency (EPA), the Texas Commission on Environmental Quality, the American Petroleum Institute, and the Environmental Defense Fund (EDF). Recently, he was the lead investigator for a study of methane emissions in natural gas production funded by the EDF; Anadarko Petroleum Corporation; BG Group plc; Chevron; Encana Oil & Gas (USA), Inc.; Pioneer Natural Resources Company; SWEPI LP (Shell); Southwestern Energy; Talisman Energy USA; and XTO Energy, an ExxonMobil subsidiary. A second phase of the methane emission study is under way, with nine of the original sponsors (EDF and eight of the original companies) and two additional sponsors (ConocoPhillips and Statoil).

The author has also served as an external reviewer on Environmental Sciences for ExxonMobil's Corporate Strategic Research and as an external reviewer for Eastern Research Group. The author serves as a member of two Scientific Advisory Panels for other university studies EDF is sponsoring of methane emissions along the natural gas supply chain.

The author chairs the US EPA Science Advisory Board; however, this review does not necessarily represent the views of the Board or the Agency, and no official endorsement should be inferred.

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Annual Review of Chemical and Biomolecular Engineering

Volume 5, 2014

Contents

Indexes

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