The Influence of Marcellus Shale Extraction Emissions on Regionally Monitored Dry Reactive Nitrogen Deposition

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ABSTRACT: Emissions of nitrogen oxides (NOx) in the United States (U.S.) from large stationary sources, such as electric generating units, have decreased since 1995, driving decreases in nitrogen deposition. However, increasing NOx emissions from emerging industries, such as unconventional natural gas (UNG) extraction, could offset stationary source emission reductions in shale gas producing regions of the U.S. The Marcellus Shale in the northeastern U.S. has seen dramatic increases in the number of wells and associated natural gas production during the past 10 years. In this study, we examine the potential impacts of shale gas development on regional NOx emission inventories and dry deposition fluxes to Clean Air Status and Trends (CASTNET) sites in Pennsylvania and New York. Our results demonstrate that the current distribution of CASTNET sites is ineffective for monitoring the influence of Marcellus well NOx emissions on regional nitrogen deposition. Despite the fact that existing CASTNET sites are not influenced by UNG extraction activity, NOx emissions densities from shale gas extraction are substantial and are estimated to reach up to 21 kg NOx ha−1 year−1 in some regions. If these emissions deposit locally, UNG extraction activity could contribute to critical nitrogen load exceedances in areas of high well density.

INTRODUCTION

Since the Industrial Revolution, global emissions of nitrogen oxides (where NOx = NO + NO2) have surpassed natural inputs primarily due to inputs from fossil fuel combustion.1 Under the Clean Air Act (CAA) of 1970, the U.S. Environmental Protection Agency (EPA) created the National Ambient Air Quality Standards (NAAQS) which designate maximum allowable concentrations of six criteria air pollutants, including nitrogen dioxide (NO2) and ozone (O3). NOx can have acute effects on populations’ respiratory systems, most notably asthmatic individuals.2 NOx is also a precursor to O3 formation, which has negative impacts on respiratory systems of sensitive populations, such as children and the elderly.3−5 Further, deposition of NOx oxidation products, including nitrate (NO3−) and nitric acid (HNO3), can have detrimental impacts to sensitive ecosystems.6 Recently, critical load evaluations have been utilized in the U.S. to determine whether ecosystems are adversely affected by fluxes of atmospheric nitrogen deposition.7,8 Following implementation of the CAA Amendments of 1990, monitoring efforts in the U.S. focused on reducing regional-scale transport of atmospheric pollutants, particularly across the northeastern U.S.9 As a result, electric generating unit (EGU) NOx emissions in the northeastern U.S. have declined by roughly 70% over the last 20 years.10 Previous studies have documented declines in stationary EGU NOx emissions resulting in (1) decreased dry and wet reactive nitrogen [Nr, where Nr = NOx, gaseous nitric acid (HNO3(p)), particulate nitrate (NO3−(p)), gaseous ammonia (NH3(g)), and particulate ammonium (NH4+(g))] deposition fluxes at regional monitoring network sites [e.g., the Clean Air Status and Trend Network (CASTNET) and National Atmospheric Deposition Program (NADP)], (2) lower O3 concentrations in the eastern U.S., and (3) lower annual NO3 concentration columns in the Ohio River Valley.11−14 Although EGU emissions continue to decline with increasingly efficient emission reduction technologies, other emerging industrial processes may potentially counteract these air quality improvements realized under the CAA Amendments. For example, unconventional natural gas (UNG) extraction activities across the U.S. represent one such process that could counteract these air quality advances. UNG extraction involves the combined processes of horizontal drilling and hydraulic fracturing within a natural gas reservoir, requiring the utilization of heavy machinery associated with NOx emissions. As the number of UNG wells in development and production phases continues to rise,15 UNG well NOx emissions may begin to offset the progress in reactive nitrogen deposition reduction.

The Marcellus Shale is a ~240 000 km2 Devonian rock formation found in Maryland (MD), New York (NY), Ohio (OH), Pennsylvania (PA), and West Virginia (WV). Advances
in horizontal drilling and enhanced recovery techniques in shale reservoirs have enabled the extraction of large volumes of natural gas from the Marcellus play.\textsuperscript{16} In 2011, the U.S. Geological Survey estimated that the Marcellus Shale reservoir contained a technically recoverable, undiscovered reservoir of 2.4 billion m\(^3\) of natural gas and 3.4 million barrels of natural gas liquids.\textsuperscript{17} Currently, the Marcellus Shale is producing roughly 430 000 m\(^3\) of natural gas per day.\textsuperscript{18} The various phases of UNG extraction require large diesel engines, used to power drill rigs and pumps, and are significant NO\(_x\) sources.\textsuperscript{19} While selective catalytic reduction (SCR) technology in diesel engines reduces NO\(_x\) emissions, SCRs can also be a source of NH\(_3\) release during engine slippage due to the use of urea (CO(NH\(_2\))\(_2\)) reducing agents.\textsuperscript{20} In addition, recent modeling demonstrates that UNG extraction activities can significantly impact near-source ambient O\(_3\) concentrations.\textsuperscript{21,22}

Although several studies have used tracers to estimate emissions of methane, volatile organic compounds, and NO\(_x\), no studies have directly measured NO\(_x\) emissions from large diesel sources on Marcellus UNG well pads.\textsuperscript{23,24} For example, one tracer study estimated NO\(_x\) emissions of 21–72 kg NO\(_x\) day\(^{-1}\) during the development phase of a well (i.e., site clearance, drilling, hydraulic fracturing, and completion).\textsuperscript{24} In addition to those emissions emitted directly from well pad equipment, ancillary activities such as water transport during the hydraulic fracturing phase can necessitate increased diesel truck traffic to and from well pads. This heavy automobile traffic can serve as an additional source of Nr emissions and deposition near well pads and along roadways.\textsuperscript{25,26} Given the recent proliferation of UNG well pads and their associated activities throughout the Marcellus Shale Basin, these sites of concentrated industrial activity have the potential to influence patterns of Nr deposition both locally and regionally. Therefore, characterization of NO\(_x\) emission and deposition dynamics surrounding these sites is necessary to contextualize the potential environmental and public health impacts of these UNG extraction activities.

Because of the lack of direct measurements of NO\(_x\) emissions from sources used on-site in the Marcellus Basin, regional assessments of potential NO\(_x\) impacts have been largely based on emission factor estimates.\textsuperscript{27,28} Studies based on emission factors for diesel sources report large ranges for NO\(_x\) emissions and span from 1.3 to 16 tons per well during the development phase of UNG extraction.\textsuperscript{27} Upper ranges of this estimate are derived from 2011 emissions factor estimates, which have lower emission factors than 2011 due to the expectation that new emission reduction technologies will be available by 2020.\textsuperscript{25,27} Currently, there are discrepancies between literature-estimated NO\(_x\) emissions and state-reported NO\(_x\) emissions. Litovitz et al. (2013) estimated that in 2011, statewide UNG NO\(_x\) emissions in PA ranged from roughly 17 000 to 28 000 tons NO\(_x\) for the development, production, and compressor station phases of natural gas extraction,\textsuperscript{27} while the PA Department of Environmental Protection (DEP) reported NO\(_x\) emissions of 16 500 tons in the Marcellus emission inventory for the same year.\textsuperscript{28} One factor potentially contributing to this discrepancy is the source of data used to generate estimates. Literature-based estimates utilize a bottom-up approach of process-level emissions factor estimates to determine regional-scale emissions from UNG activity while state-reported emissions inventories are determined using a similar bottom-up approach, but are calculated using individual well-scale emissions factor estimates that companies report to the state agency. Inconsistencies between industry-reported data and literature-based estimates inhibit the accurate quantification of human health and ecosystem impacts caused by UNG extraction activity.

The relationships between UNG well NO\(_x\) emissions and on-site NO\(_x\) concentration or Nr deposition fluxes remain uncharacterized in the existing literature. Determining the additional nitrogen deposition resulting from UNG wells has implications for addressing potential ecosystem impacts from UNG well activity in active and future shale plays. In this study, we evaluate whether UNG activity in the Marcellus Shale basin influences regional dry Nr deposition in PA and NY and whether the current CASTNET site distribution is effectively capturing effects of NO\(_x\) emissions from Marcellus Shale UNG wells. Specifically, we compare dry Nr deposition fluxes measured at CASTNET sites from 2011 to 2013 with modeled NO\(_x\) emission densities from EGU and UNG wells.

\section{MATERIALS AND METHODS}

\subsection*{Emissions data.} EGU NO\(_x\) emissions data were retrieved from the EPA’s Air Markets Program—Acid Rain Program.\textsuperscript{10} Annual emissions and location data were obtained for the years 1995–2013 in five states including PA and surrounding states (MD, NY, OH, and WV) and were aggregated to the facility level (Figure 1).

![Figure 1. Maps of the (a) distribution of UNG wells and CASTNET sites in Pennsylvania and New York (USA) in 2013 and (b) distribution of EGUUs and CASTNET sites in operation in the five state area in 2013. The inset shows the relative location of the five state area in the USA.](image)

Annual Marcellus UNG well NO\(_x\) emissions were retrieved for all wells in Pennsylvania from the industry-reported emissions data collected by the PA DEP for the years 2011–2013.\textsuperscript{28} Well locations were determined from the PA DEP’s SPUD (drilling commencement date) report (Figure 1).\textsuperscript{15} Locations were generated for only PA unconventional wells with SPUD dates on or after January first and on or before December 31st for each respective year. Well emissions data were joined to SPUD location data using the unique name of the well as the primary identifier (site locations and American Petroleum Industry well numbers were not included in the statewide emissions inventories). Compressor stations were removed prior to these joins and the joins resulted in 91–93\% join percentages between industry-reported emissions and...
SPUD location data for the years 2011–2013. The remaining ~8% of well emission data that was not joined to location data was attributed to misspellings, discrepancies of when drilling actually began, or data not listed in the SPUD or emissions inventory reports. These unmatched data comprised ~10% of all UNG well emissions and were excluded from the analysis because of the inability to determine location data.

To compare the relative magnitude between EGU and UNG well NO\textsubscript{x} emissions prior to 2011, statewide UNG well NO\textsubscript{x} emissions were estimated for Pennsylvania using literature-based well development emission estimates (low and high estimates for 2011 and 2020) and the PA DEP SPUD report data. The SPUD-reported number of wells that began drilling in a single year were multiplied by the low (2020) and high (2011) NO\textsubscript{x} emissions estimates for single well development for the years 2006–2013.\textsuperscript{25,27} We assumed that wells were developed during the same year as their SPUD date.

CASTNET Dry Deposition Data. A total of seven CASTNET sites from PA and NY were included in our analysis for the years 1995–2013 (Figure 1). CASTNET location and deposition data were retrieved from EPA’s CASTNET data set.\textsuperscript{33} CASTNET deposition measurements were collected according to EPA CASTNET protocols (see Supporting Information).

Modeling NO\textsubscript{x} Emission Densities. Wells, EGUs, and CASTNET sites were mapped and analyzed with ArcMap 10.2.2.\textsuperscript{30} Several buffers (referenced buffer sizes are equal to buffer radius) were delineated around EGU, UNG well, and CASTNET sites to compare NO\textsubscript{x} emissions densities to CASTNET deposition fluxes of NO\textsubscript{3}\textsuperscript{(p)}, NH\textsubscript{4}\textsuperscript{(p)}, and HNO\textsubscript{3}\textsuperscript{(g)} during different years (Table SI-1). Buffer areas around CASTNET sites represent assumptions about the area of regional deposition around the site monitors. NO\textsubscript{x} emissions densities originating from UNG well and EGU sources were estimated by using circular buffers around each NO\textsubscript{x} emission source and assuming a uniform distribution of annual NO\textsubscript{x} emissions across the buffer area (Figure 2, step 1).

This approach (Figure 2) utilizes a modified version of previous methods relating NO\textsubscript{x} emissions from EGUs to deposition measured at monitoring sites.\textsuperscript{31,32} Modeled NO\textsubscript{x} emission density buffers were then spatially intersected with monitoring network site buffers (Figure 2, step 2). The intersecting area (ha) was calculated and the proportion of NO\textsubscript{x} emissions density attributable to these overlapping areas was transformed to a mass by multiplying the emissions density by the intersected area. The comparison of buffers around emission sources and monitoring sites assumes that emissions from a point source travel to areas of intersection and affect regional Nr deposition. Additionally, no background NO\textsubscript{x} from soil, vehicles, or long-range transport that could affect Nr deposition is assumed in the model. NO\textsubscript{x} emissions masses from all intersected source buffers within a single CASTNET buffer were then summed, and a new emission density within the entire CASTNET buffer was determined, and then compared with regional Nr deposition (Figure 2, step 3). This final emission density was determined using eq 1:

$$D = \sum_{i=1}^{n} \frac{E_i}{A}$$

where $D$ is the total annual modeled NO\textsubscript{x} emission density (kg NO\textsubscript{x} ha\textsuperscript{−1} year\textsuperscript{−1}) from all sources contributing to deposition in an individual CASTNET buffer, $E_i$ are the NO\textsubscript{x} emissions attributable to the ith area intersection (kg NO\textsubscript{x} year\textsuperscript{−1}), and $A$ is the CASTNET monitoring site buffer area (ha). NO\textsubscript{x} deposition was kept in units of kg NO\textsubscript{x} ha\textsuperscript{−1} year\textsuperscript{−1} in order to avoid assumptions about regional NO\textsubscript{2}/NO\textsubscript{x} ratios. Statistical analyses comparing emissions density and Nr deposition were then conducted using SAS version 9.4 (see Supporting Information).\textsuperscript{33}

RESULTS

NO\textsubscript{x} Emissions from UNG Wells and EGUs. The total number of wells that had SPUD dates between the years 2011 to 2013 was 4285. Total annual average, statewide reported UNG well NO\textsubscript{x} emissions (PA) were 11,084 ± 733 tons NO\textsubscript{x} year\textsuperscript{−1} for 2011–2013. On an individual well basis for 2011–2013, industry-reported NO\textsubscript{x} emissions for UNG wells ranged from zero to 148 tons NO\textsubscript{x} year\textsuperscript{−1}. When UNG wells with zero annual NO\textsubscript{x} emission reported are included, median UNG well emissions...
NOx emissions were 0.5 tons NOx year\(^{-1}\) over the same time period (Figure S1). When UNG well NOx emission values of zero are removed, the median value for UNG well NOx emissions from 2011 to 2013 increases to 1.9 tons NOx year\(^{-1}\). Total statewide reported UNG well NOx emissions in PA have not widely fluctuated from 2011 to 2013 (10,071 to 11,782 tons NOx year\(^{-1}\)).

Since 1995, EGU NOx emissions have decreased as facilities have implemented more stringent emission controls. For example, in 1995, the total of the NOx emissions from all emission-reporting EGUs (MD, NY, OH, PA, WV) was 127,900 tons NOx year\(^{-1}\). However, in 2015, the total of the NOx emissions from all emission-reporting EGUs in those same states was 296,000 tons NOx year\(^{-1}\). Statewide EGU NOx emissions have been reduced by 92%, 92%, 90%, 70%, and 82% from 1995 to 2015 for MD, NY, OH, PA, and WV, respectively. Even though the number of emission-reporting EGUs (from all states in this analysis) has increased from 106 to 173 when comparing 1995 to 2015 data, implementation of SCR technology in individual facilities has greatly reduced EGU NOx emissions. For example, in 1995, the median individual EGU NOx emissions (from all states in this analysis) was 5,500 tons NOx year\(^{-1}\) compared to only 120 tons NOx year\(^{-1}\) in 2015; 84.5% of the individual EGU NOx emissions in this analysis (1995–2015) were below 10,000 tons NOx year\(^{-1}\). This average individual EGU emission rate is roughly equivalent to mean annual statewide PA UNG well NOx emissions for a single year (Figure S1).

Dry Nitrogen Deposition in PA. From 1995 to 2013, the average HNO3\(_{(g)}\) deposition flux at the seven CASTNET sites included in this study decreased from 2.74 to 0.76 kg N ha\(^{-1}\) year\(^{-1}\). Among these sites, ARE128 had the highest HNO3\(_{(g)}\) flux, whereas either KEF112 or LRL117 had the lowest flux from 1995 to 2013 (Figure S2). NH4\(^{+}\)\(\text{(p)}\) deposition fluxes follow a similar general trend as the HNO3\(_{(g)}\) deposition fluxes from 1995 to 2013 (Figure S2). In 1995, average NH4\(^{+}\)\(\text{(p)}\) deposition flux at the CASTNET sites was 0.51 kg N ha\(^{-1}\) year\(^{-1}\), while average NH4\(^{+}\)\(\text{(p)}\) deposition flux in 2013 was 0.22 kg N ha\(^{-1}\) year\(^{-1}\). Similarly, the average particulate NO3\(^{-}\)\(\text{(p)}\) deposition flux in 2013 (0.06 kg N ha\(^{-1}\) year\(^{-1}\)) is lower than the 1995 NO3\(^{-}\)\(\text{(p)}\) deposition flux (0.09 kg N ha\(^{-1}\) year\(^{-1}\)) (Figure S2). From 2012 to 2013, one site measured a decrease in NO3\(^{-}\)\(\text{(p)}\) deposition flux (ARE128), while the other six sites measured increases.

NOx Emissions Densities vs Measured Nr Deposition. EGU NOx emissions densities and HNO3\(_{(g)}\), NH4\(^{+}\)\(\text{(p)}\), and NO3\(^{-}\)\(\text{(p)}\) deposition fluxes measured at CASTNET sites were compared using regression analyses for the years 1995, 2000, 2005, and 2011–2013. Years prior to UNG well activity were used in the EGU-CASTNET regression analyses to examine whether the inclusion of UNG well NOx emissions influenced the relationship between EGU NOx and Nr species deposition during multiple regression analyses, assuming EGU NOx emissions were the dominant predictor of Nr deposition. CASTNET deposition of HNO3\(_{(g)}\), NH4\(^{+}\)\(\text{(p)}\), and NO3\(^{-}\)\(\text{(p)}\) was positively associated with EGU NOx emissions densities regardless of source or receptor buffer size variants. There were strong relationships between EGU NOx emission densities and Nr deposition, where \(r^2\) values ranged between 0.21 and 0.61 (\(p < 0.05\)). Furthermore, HNO3\(_{(g)}\) showed consistent strongly correlated relationships, likely due to the oxidation of NOx during long-range transport (see Supporting Information for oxidation processes). The strongest relation-

 ships across all Nr species were observed using a CASTNET buffer of 50 km and EGU buffer of 50 km (Figure 3). It is likely that NH4\(^{+}\)\(\text{(p)}\) is well correlated with NOx emissions due to the formation of ammonium nitrate as a consequence of the reactions that tropospheric NOx undergoes, leading to particulates subsequently dissociating and depositing in the form of NO3\(^{-}\)\(\text{(p)}\) and NH4\(^{+}\)\(\text{(p)}\).

LRL117 did not follow the same trend as the other six sites (Figure S3). LRL117 is near some of the highest EGU NOx-emitting facilities in the northeastern U.S., which creates overpredictions of anomalously large depositions. LRL117 received the largest proportion of NOx emissions from the top 10% of NOx-emitting EGUs of all CASTNET sites in the states analyzed; roughly 33% of EGU “super-emitters” were located within 150 km of LRL117. Therefore, LRL117 was treated as an outlier and removed from our regression analyses.

In contrast, UNG well NOx emissions were negatively associated with CASTNET HNO3\(_{(g)}\), NH4\(^{+}\)\(\text{(p)}\), and NO3\(^{-}\)\(\text{(p)}\) deposition regardless of source and receptor buffer size variants. The strongest (negative) relationships were observed when UNG well buffers were 20 km and CASTNET buffers were 25 km, but the CASTNET buffer was held constant at 50 km to be comparable to the EGU analysis (Figure 4). Additionally, wet Nr deposition was also examined, and showed weakly correlated, negative relationships between wet Nr deposition and UNG well NOx emission densities (Figure S4), but was not the primary focus of this study. Differences in optimal buffer sizes between well and EGU emissions are likely due to EGUs that emit NOx from stack heights usually greater than 100 m, and allow for further regional transport than well pad sources that release NOx near the ground level and thus likely deposit more locally.
**DISCUSSION**

**UNG Well NOx Emissions.** Industry-reported NOx emissions from individual UNG wells from 2011 to 2013 spanned a large range (0–148 tons NOx year⁻¹), and the majority of reported single UNG well NOx emissions were below ranges estimated by previous studies. The single development UNG well NOx emissions estimated by Roy et al. (2014), derived from 2020 fleet emissions factors (1.3–16 tons NOx year⁻¹), were higher than 57% of reported individual UNG well NOx emissions. This discrepancy could be due to the inclusion of UNG well NOx emissions from the production phase in the industry-reported emission inventories, differences in estimation procedure, or different emissions factors chosen by operators for the same type of equipment. Across the three years, 20% (~1900 wells) had a NOx emission value of 0.0 (Figure S1). This large number of wells with NOx emissions could be due to (1) UNG wells listed in the emission inventory that were not in development or production phases during the corresponding year, (2) unreported data, or (3) data entry errors. Within state reported natural gas activity emissions inventories, the rationale for reported emissions of 0.0 tons NOx year⁻¹ should be clarified (e.g., qualifiers) to reduce uncertainty in average individual and statewide emissions calculations.

Annual statewide development-phase NOx emissions from all UNG wells in PA ranged from 2.6 to 32 and 1453–17 888 tons NOx year⁻¹ in 2006 and 2013, respectively, based on low and high literature-based NOx emissions per well (2020 fleet estimate) and the SPUD-reported number of wells (Figure S5). In 2011, industry-reported statewide UNG well NOx emissions in PA were equivalent to 5% of statewide NOx emissions from the transportation sector but were larger than the individual statewide biogenic, fire, and solvent source sectors. PA statewide reported UNG well NOx emissions were equivalent to 13% of total PA EGU NOx emissions in 2013. The high 2020 fleet statewide PA UNG well development NOx emissions estimate increases to 15% of total PA EGU NOx emissions in 2013 because the literature-based UNG well NOx emission estimate is higher than the average industry-reported value (Figure 5). Production-phase NOx emissions were not included in the annual statewide literature-based NOx emission calculation because SPUD reports do not detail when wells begin production. However, inclusion of these emissions would increase our annual estimates by roughly 450 tons NOx per year, according to literature emissions factors.

EGU NOx emissions densities were strongly correlated with HNO3(g), NH4⁺(g), and NO3⁻(g) deposition recorded at the six CASTNET sites included in this study. In comparison, UNG well NOx emissions densities were negatively correlated to HNO3(g), NH4⁺(g), or NO3⁻(g) when used as a sole predictor. In general, the spatial distribution of UNG wells across the state creates cases where some CASTNET sites are closer to UNG NOx emissions and further from EGU emissions (Figure 1). Although these cases occur, the modeled NOx emissions densities at CASTNET sites derived from UNG well NOx emissions is roughly an order of magnitude lower than that of EGU NOx emissions densities (Figure S5). CASTNET sites relatively distant from UNG activity measure large Nr fluxes, likely due to EGU activity. Likewise, CASTNET sites relatively close to UNG activity also tended to be distant from EGU sites (Figure S5). CASTNET sites having large NOx emission densities from EGUs have the lowest influence from UNG activity and vice versa (Figure S5). Additionally, EGUs emit NOx emissions close to the planetary boundary layer, allowing for efficient regional transport of NOx and its oxidation products. In contrast, diesel sources found on well pads emit NOx from exhaust pipes near the ground surface, likely not allowing for migration of NOx to the free troposphere. As EGU NOx emissions continue to decline with the implementation of SCR technologies, UNG wells are expected to contribute larger relative proportions of NOx air pollution in regions impacted by both sources.

**Limited UNG Well NOx Emission Detection by Federal and State Monitoring Networks.** The regression analyses indicate that the CASTNET network, as currently configured in...
PA and NY, does not capture the effects of UNG well activity in the Marcellus Shale Basin. Because UNG well NO$_x$ emission densities were negatively correlated withNr deposition at CASTNET sites, multiple regressions did not reveal additive interactions between UNG well and EGU NO$_x$ sources. Additionally, the strong positive relationships between EGU NO$_x$ emission densities andNr deposition demonstrate the dominance of EGU emissions on regional Nr deposition. EGU NO$_x$ emissions have previously been found to oxidize to HNO$_3$ preferentially, and this is consistent with our findings as HNO$_3$ deposition has a strong relationship with modeled NO$_x$ emissions densities from EGUss (Figure 3). Previous studies have found particulates form preferentially relative to HNO$_3$ formation near petrochemical facilities due to the presence of hydrocarbons. However, in this study a positive correlation was observed between EGU and particulate Nr deposition, but not UNG well NO$_x$ emission densities. Additionally, vehicles emit a large amount of NO$_x$ along major traffic corridors, and could be having an additive effect on regional deposition that is not included in the modeled NO$_x$ emissions densities.

The current spatial distribution of CASTNET sites in PA and NY does not effectively detect nitrogen deposition from UNG activity in the Marcellus Shale formation, nor do NADP wet deposition sites in PA (Figure S4 and Figure S6). Recently, the PA DEP has established additional source-oriented, state and local air monitoring stations (SLAMS) to monitor volatile organic compound, PM$_{2.5}$, and NO$_x$ emissions from natural gas facilities and well pads in counties with large amounts of UNG activity. Because these additional SLAMS sites were generally established following the increase in Marcellus Shale natural gas production, long-term trend analyses are not possible at this time. Further, since NO$_x$ emissions from UNG well pads are intermittent due to activities characterized by varying emission magnitudes (e.g., horizontal drilling, well pad development), these annual emissions estimates may not be conducive to high temporal resolution analyses of well emissions’ effects on regional deposition or regional air monitoring, unlike previously conducted studies. While this study concludes that UNG well activity is not effectively monitored on regional scales by the current federal deposition and state air monitoring network configurations, it does not preclude that local air quality degradation and ecosystem impacts from nitrogen deposition do indeed occur.

Implications for Deposition and Critical Loads. Atmospheric nitrogen loads to eastern temperate forests are in exceedance of nitrogen critical loads, ranging from roughly 3 to 17.5 kg N ha$^{-1}$ year$^{-1}$, depending on ecosystem component. Individual UNG well NO$_x$ emission densities, applied across a 20 km buffer around a single well, ranged from 0 to 1.1 kg NO$_x$ ha$^{-1}$ year$^{-1}$. While nitrogen deposition from the development of a single well may not individually cause exceedance of a critical load, the fact that well pads typically contain multiple wells and high densities of well pads are common, the...
combined influence of multiple UNG wells could cause high deposition fluxes that exceed critical nitrogen loads in active UNG plays in the northeastern US.

To examine the potential cumulative impact of individual UNG well emissions to Marcellus Shale-rich regions, overlapping well emissions densities (20 km buffer) were summed across the state of PA for 2011–2013. The highest aggregate emissions densities occurred in Greene, Washington, Susquehanna, and Lycoming counties (Figure 6). Some areas in these counties contained emission densities of 18–21 kg NO\textsubscript{x} ha\textsuperscript{-1} year\textsuperscript{-1}. The nearest CASTNET site was 90–130 km away from these high emission density areas, which would not allow for accurate deposition tracking of influences from NO\textsubscript{x} emitted primarily near ground level. Previous studies have found that nitrogen deposition ranging from >3–8 kg N ha\textsuperscript{-1} year\textsuperscript{-1} in eastern temperate forests can result in decreased growth of native tree species, changes in lichen community composition, and increased surface water loading of NO\textsubscript{3}.\textsuperscript{38–40} In high well density areas, aggregate NO\textsubscript{x} emission densities could result in N deposition ranges of 5–6 kg N ha\textsuperscript{-1} year\textsuperscript{-1}, assuming NO\textsubscript{x} was fully converted to NO\textsubscript{2} and there was 100% deposition within a localized area. This deposition range results in an exceedance range of the critical load for eastern temperate forests by 2–3 kg N ha\textsuperscript{-1} year\textsuperscript{-1}. Additional research to quantify Nr emissions and deposition fluxes attributable to well pad activity are needed to clarify the magnitude of UNG well impacts to critical loads. This will allow accurate assessments of critical load exceedances in areas experiencing UNG development and production. As other shale plays are developed in the U.S. and globally, consideration of aggregate Nr contributions to local and regional Nr deposition should improve management of environmental systems surrounded by UNG extraction activities.

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