Regional air quality impacts of hydraulic fracturing and shale natural gas activity: Evidence from ambient VOC observations

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HIGHLIGHTS

- Ambient VOC measurements from EPA PAMS sites were analyzed.
- Ethane concentrations have increased recently in the Baltimore/Washington area.
- Shale natural gas operation emissions appear to be transported downwind.

ARTICLE INFO

ABSTRACT

Over the past decade, concentrations of many anthropogenic pollutants have been successfully reduced, improving air quality. However, a new influx of emissions associated with hydraulic fracturing and shale natural gas operations could be counteracting some of these benefits. Using hourly measurements from Photochemical Assessment Monitoring Stations (PAMS) in the Baltimore, MD and Washington, DC areas, we observed that following a period of decline, daytime ethane concentrations have increased significantly since 2010, growing from ~7% of total measured nonmethane organic carbon to ~15% in 2013. This trend appears to be linked with the rapidly increasing natural gas production in upwind, neighboring states, especially Pennsylvania and West Virginia. Ethane concentrations failed to display this trend at a PAMS site outside of Atlanta, GA, a region without new widespread natural gas operations.

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1. Introduction

As global energy demands continue to grow, new and alternative energy sources have been sought out. One emerging energy source, natural gas, is gaining favor over coal because of lower emissions of CO_2 and significantly lower nitrogen oxides (NO_x) and sulfur oxides (SO_x) (deGouw et al., 2014; EPA, 2014a). In the United States, natural gas production has quickly increased and its cost has dropped, making it an economically viable energy source (EIA, 2014a). Because of these advantages, natural gas usage is expected to grow rapidly and displace coal as the second largest source of energy by 2025 (ExxonMobil, 2014).

An increasingly popular method of obtaining natural gas resources is through the combination of horizontal drilling to allow access a large amount of the shale, followed by hydraulic fracturing, where a mixture of water, sand, and chemical additives is pumped at high pressure to free and extract natural gas trapped within shale layers (USGS, 2014). According to the U.S. Energy Information Agency (EIA) the amount of natural gas obtained from shale gas wells in the United States has tripled between 2009 and 2012 (EIA, 2014b), providing more than a third of total U.S. natural gas production by 2012 (EIA, 2014c). The major shale plays which account for more than 60% of total U.S. shale gas production since 2010 are the Barnett in Texas, the Haynesville in Texas and Louisiana, and the Marcellus, centered in Pennsylvania and West Virginia where about a third of natural gas production since 2013 has occurred (EIA, 2014d).

Although its composition can vary due to geographical location, shale gas is predominately, and sometimes almost entirely, methane, a greenhouse gas with climate implications (Bullin and

Krouskop, 2009). Compared to coal, combustion of natural gas for generating electricity produces only about half the CO_2 and reduces climate forcing, but only if less than about 3% of the methane escapes into the atmosphere (Howarth et al., 2011; Alvarez et al., 2012). Several studies have been conducted to determine the total leakage-based emissions from natural gas operations; estimates range from as low as 0.42% up to 17.3% (Allen et al., 2013; Caulton et al., 2014; Howarth et al., 2011; Karion et al., 2013; Kirchgessner et al., 1997; Petron et al., 2012; Pieschl et al., 2013; Schneising et al., 2014). In 2013 the Intergovernmental Panel on Climate Change increased the 100 year global warming potential of methane to be 28 to 34 times greater than that of CO_2 (IPCC, 2013). Thus, it is vital to quantify the leakage rate, and apply necessary control technologies to curtail emissions.

In addition to climate impacts from methane emissions, air quality can also be affected by natural gas operations and the numerous emission sources associated with the drilling, hydraulic fracturing, and production processes and associated equipment. In the Mid-Atlantic States, the Marcellus shale in the Appalachian basin is estimated to contain 4×10^{12} m^3 of unproved technically recoverable shale gas (EIA, 2012). A modeling effort for this shale play by Roy et al. (2014) considered numerous emission sources such as completion venting, a process in which fluid and debris are cleared from the well, and the natural gas and diesel engines powering various trucks, compressors, drilling rigs, and pumps. This study predicted that for the year 2020, Marcellus shale activities would, on average, account for 12% of the total NO_x and volatile organic compound (VOC) emissions and 14% of the total particulate matter (PM) in the region, and these emissions could complicate attainment of PM and ozone standards.

Along with these standard emissions associated with drilling and fracturing a well, there are other sources related to hydraulic fracturing to consider. When liquid unloadings are performed to clear a well bore of accumulated liquids for increased production, methane can be released to the atmosphere, and most of the methane emitted in these instances comes from a small fraction of wells which are frequently unloaded (Allen et al., 2014). Large emissions of VOCs have been observed on oil and gas well pads because of leaks from dehydrators, storage tanks, compressor stations, and pneumatic devices and pumps, as well as evaporation and flow back pond water (Warneke et al., 2014). Another non-negligible source of methane emissions are abandoned wells — those no longer active in the natural gas production process. There are an estimated 300,000–500,000 abandoned wells in Pennsylvania, and it has been suggested that they could account for up to 7% of Pennsylvania's 2010 anthropogenic methane emissions (Kang et al., 2014).

While the consequences for localized pollution from emissions associated with hydraulic fracturing processes are certainly of significance, the transport of these emissions to downwind regions is also a major issue, especially for major metropolitan areas already struggling to attain current standards (Kemball-Cook et al., 2010). Although the State of Maryland does not currently have extensive shale natural gas operations within its borders (MDE, 2015), the neighboring states including Pennsylvania and West Virginia house thousands of wells responsible for a tenfold increase in natural gas production volumes from 2009 to 2013 (PADEP, 2014). Fig. 1 shows counties in neighboring states where new unconventional natural gas wells were drilled from 2005 through 2012, the most recent year for which well production information is available for all four states, and is also indicative of regions where hydraulic fracturing occurs.

Ethane emissions in the Northern Hemisphere are mainly anthropogenic with about 70% originating from fossil fuels (mostly evaporative), and biomass burning and biofuel use making up the remainder of emission sources (Simpson et al., 2012). In northwestern Pennsylvania with nearby areas of oil and gas production, Pekney et al. (2014) observed average ethane concentrations of 9.2, 10.3, and 15.9 ppb. These concentrations are well above the ~1 ppb Northern Hemisphere background concentration of ethane (Rinsland et al., 1987; Rudolph et al., 1996) and indicate the local impact of emissions from oil and gas wells. The transport of emissions by prevailing winds is a well-documented occurrence affecting Maryland and other East coast states (Hains et al., 2008; He et al., 2013a, 2013b, 2014; Ryan et al., 1998; Taubman et al., 2004, 2006). A back-trajectory investigation by Taubman et al. (2006) found that the majority of wind trajectories arriving in the Mid-Atlantic U.S. passed through the regions where hydraulic fracturing now occurs. Wind data collected at the wind profiler in Beltsville, MD also show a high frequency of winds arriving from the northwest and west (Fig. 2). Additional wind roses are available in the supporting information (Figs. S1–S3). In this paper, we quantify how observed concentrations of ethane monitored in Baltimore, MD and Washington, DC, have risen as a likely result of the development of the Marcellus Shale Play.

2. Methods

The U.S. Environmental Protection Agency (EPA) has established numerous sites for monitoring pollutants. Following the 1990 Clean Air Act Amendments, Photochemical Assessment Monitoring Stations (PAMS) were created to monitor ozone, its precursors of NO_x and VOCs, and surface meteorology in regions of ozone non-attainment (EPA, 2014b). The monitor at Essex, MD was set up to track emissions for the Baltimore ozone nonattainment area. This is the monitor closest to the Marcellus shale which provides a historical record of VOC measurements with hourly resolution. During the summer months of June, July, and August when ozone levels can often be hazardous to human health, concentrations are recorded every hour, providing a rich dataset for analysis. A suite of 56 VOCs are measured by GC-FID and calibrated weekly to maintain analytical precision to within ± 5% (Acefaw Belay, MDE, personal communication). Although methane is not included, ethane is measured and can be used as a tracer for fugitive natural gas production emissions, as the ethane recovered from natural gas production is separated from the methane ultimately distributed commercially. The composition varies geographically, but ethane makes up a significant portion (3–16%) of the Marcellus shale gas (Bullin and Krouskop, 2009). Methane, with an atmospheric photochemical lifetime of about a decade, is relatively well mixed in the troposphere. Ethane, with a photochemical lifetime of several weeks (Blake and Blake, 2003), is essentially inert with respect to photochemical loss on time scales of transport from the sources to the monitors (1–2 days), but still shows strong spatial and temporal gradients, making it a useful tracer.

In addition to the Essex, MD location, another Mid-Atlantic PAMS location with similar surroundings and conditions was considered: McMillan Reservoir in Washington, DC. Like Maryland, Washington, DC does not currently have hydraulic fracturing operations within its borders, but could easily be affected by transported emissions from neighboring states. Measurements from 1996 to 2013 are shown for these locations. A site outside the city of Atlanta, Georgia in Rockdale County was selected to serve as a control environment, as its air quality is influenced by urban emissions from heavy motor vehicle traffic and natural gas delivery, as well as biogenic emissions, similar to the Baltimore/Washington region, but Georgia and nearby states do not have extensive natural gas production. At this location, measurements from 1996 to 2013 are also shown.

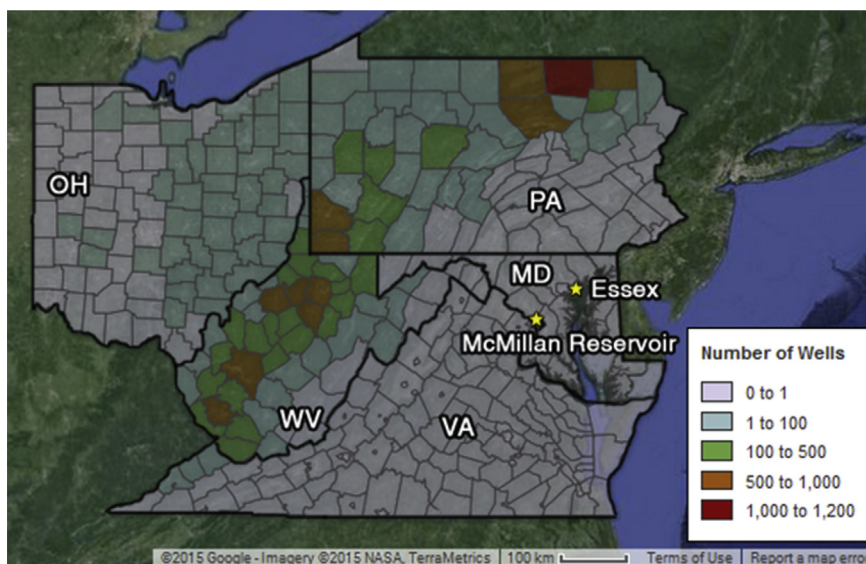As the boundary layer collapses following sunset, the

Fig. 1. Number of total unconventional natural gas wells drilled by county in the Marcellus shale region from 2005 through 2012. The northern and southeast counties of Pennsylvania contain the most newly-drilled wells. Essex, MD and McMillan Reservoir (DC) monitor locations are also shown.
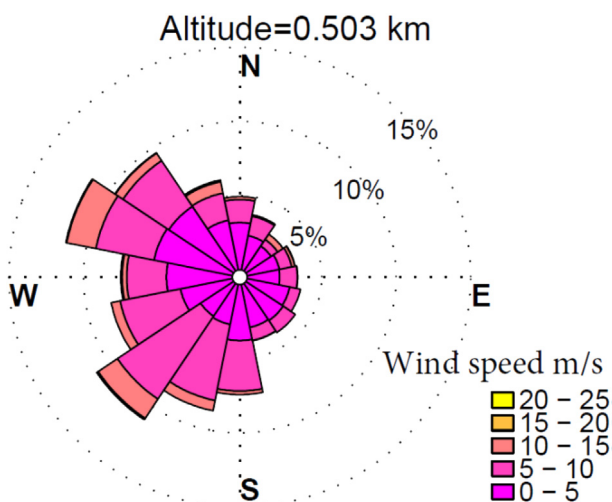

Fig. 2. Wind rose showing wind velocity frequencies and direction at 503 m AGL provided by the wind profiler at Beltsville, MD. Wind velocities are taken from daytime hours (10am – 7pm) during the month of July in years 2012–2014. Winds are predominantly from the west where natural gas operations have increased in recent years.

Fig. 3. Daytime TNMOC concentrations at Essex, MD from 1996 to 2013 are shown by box and whisker plots. The box provides the 25th and 75th percentiles, with the median represented by the red bar, and the whiskers extend to the 10th and 90th percentiles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

concentrations of ethane increase due to the change in mixing volume. Because of this strong dependency on boundary layer height, only the concentrations during local daytime hours from 10am to 7pm were considered since the boundary layer depth should show little long-term trend. For each site, each year analyzed in this study contains at least 200 concentration observations from at least two different months, with the exception of June only for 2010 and August only for 2013 at Rockdale County.

3. Results and discussion

3.1. Trend analysis

The historical decline of total non-methane organic compounds (TNMOC) at Essex, MD (Fig. 3) shows that strategies to curtail VOC emissions from sourc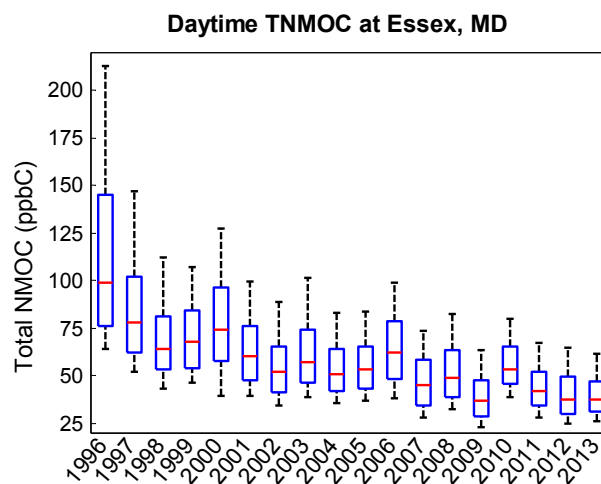es such as solvent usage, gasoline storage and distribution, and other industrial processes have been successful (MDE, 2011; EPA, 2015). In Fig. 4a, Essex, MD ethane concentrations followed this same general downward trend continuing for about a decade beginning in 1996. However, around the same time that hydraulic fracturing operations began in surrounding states (circa 2009), ethane concentrations stopped decreasing, and were unmistakably increasing by 2012 and 2013 (Fig. 4).

To test for the possibility that ethane is increasing at Essex, MD because of a local source, the site at McMillan Reservoir in Washington, DC was also considered. Fig. 4b shows an increase in ethane concentrations at McMillan Reservoir during the most recent years, despite several years exhibiting a decreasing trend. This new trend of increased ethane concentrations at more than one location suggests that several downwind areas could be affected by the transport of fugitive emissions and other pollutants associated with natural gas operations.
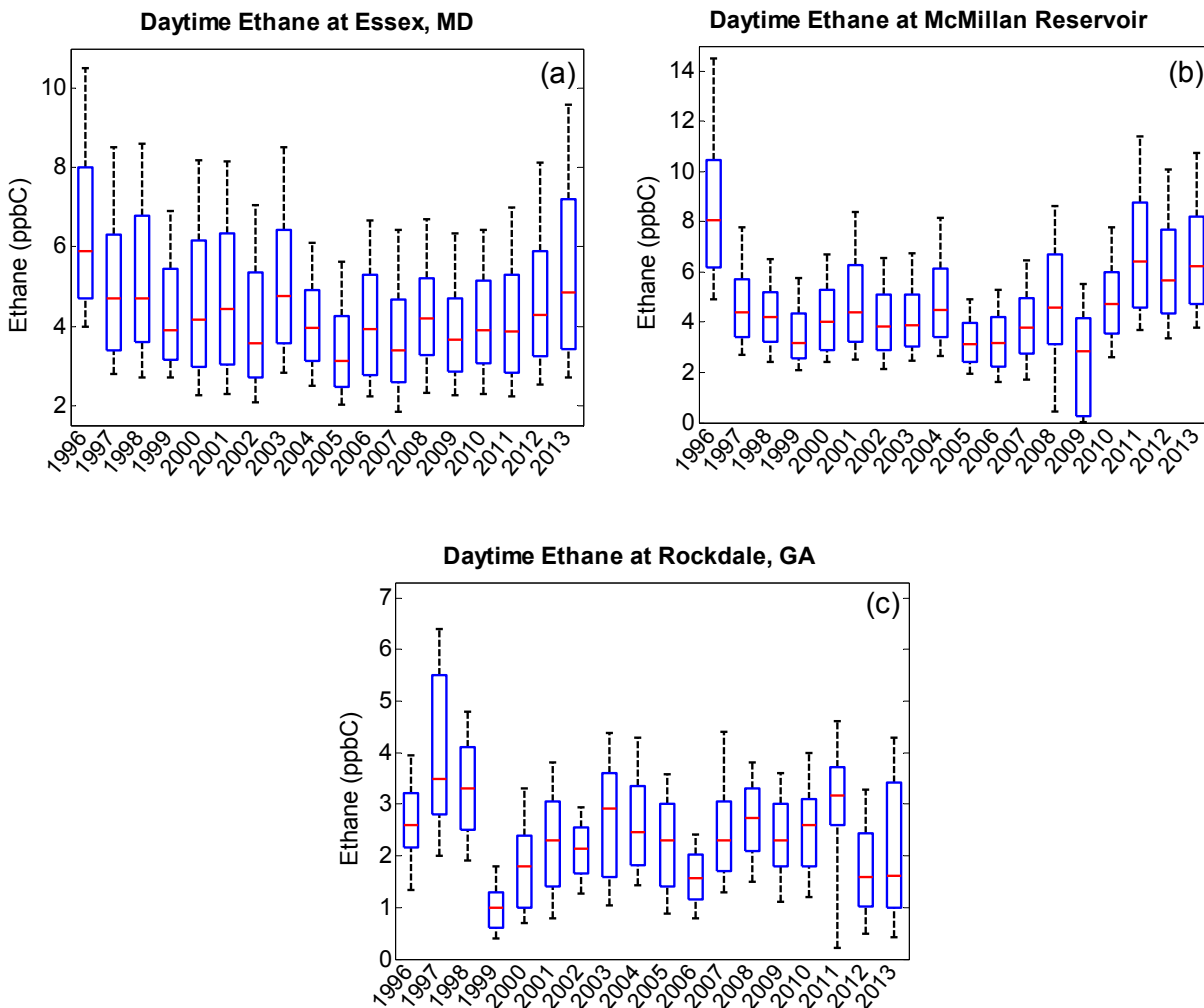
Fig. 4. From 1996 to 2013, hourly daytime ethane concentrations from a) Essex, MD, b) McMillan Reservoir (DC), and c) Rockdale County, GA are presented by box and whisker plots with the same statistical parameters as Fig. 3.

In contrast (Fig. 4c), ethane concentrations have continued to trend slightly downward since 1996, and no discernible increasing trend is evident in the Atlanta region in the more recent years. If increased ethane concentrations were attributable to sources other than natural gas production and associated operations, then this site should show similar increases, but the State of Georgia has no major hydraulic fracturing activity within its borders or in neighboring states. TNMOC plots for the McMillan and Rockdale sites are available in the supporting information (Figs. S4 and S6).

Another approach taken was considering how the diurnal cycle of ethane has shifted at the Essex, MD site. Fig. 5 demonstrates the departure of concentrations of ethane from a previously established baseline over the most recent years. While there are year-to-year differences in ethane concentrations from 2004 to 2010 shown in Fig. 4a, the overall trend is nearly flat for the time period. As a result the concentrations from these years were averaged together to establish the lowest placed diurnal cycle seen as the (in web version) blue squares in Fig. 5. The overall concentrations of ethane have increased annually— in the past three years the baseline has increased by 1.1 ppbC. This sudden rise, especially given that TNMOC is decreasing, is indicative of a rapidly growing emission source such as natural gas operations.

Finally, the ratio of ethane to TNMOC at Essex, MD was examined and compared to natural gas production in the Marcellus shale
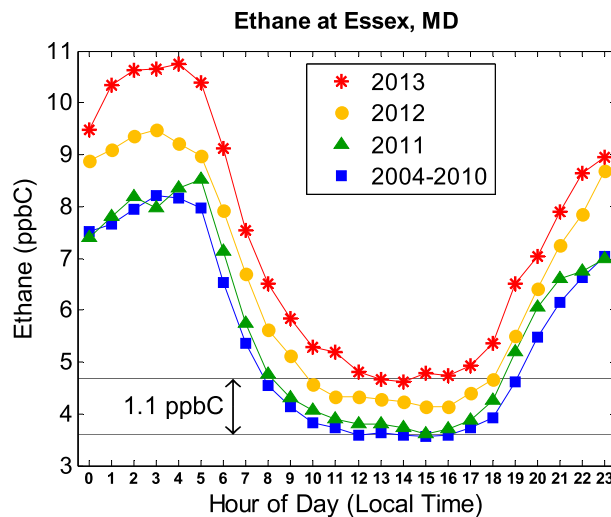

Fig. 5. The diurnal cycle of ethane at Essex, MD showing the geometric mean concentration at each hour. Concentrations of ethane from 2004 to 2010 were averaged to establish a period unaffected by natural gas operations, and subsequent years show a continuing departure from this baseline.
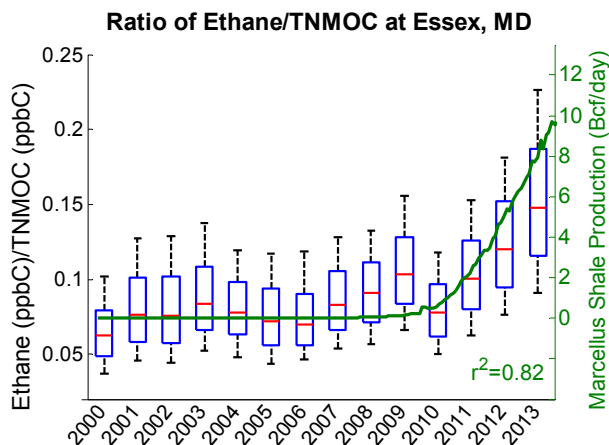
Ratio of Ethane/TNMOC at Essex, MD

Fig. 6. The ratio of ethane to TNMOC observed at Essex, MD is shown by box and whisker plots with the same statistical parameters as Fig. 3. In addition, the production rates from the Marcellus shale in Pennsylvania and West Virginia are shown in green. A strong correlation was observed with an r^2 value of 0.82. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(Fig. 6). From 2000 to 2007, the median amount of ethane remained around 7–8% of the total NMOC, but rose quickly after 2010 to nearly 15% by 2013. The upwind production rates exhibit a similar rapid increase. For each year, the median production rate from June through August was compared to the median observation at Essex, MD during the same months. With $r^2 = 0.82$, a strong correlation was found between the Essex, MD ethane to total ratio and natural gas production in the Marcellus shale. Likewise, a positive correlation of $r^2 = 0.59$ was found when daytime ethane concentrations at Essex, MD from June, July, and August of 2010–2013 were compared to production rates from the Marcellus shale (Fig. 7). Additional ratio (Figs. S5 and S7) and correlation (Figs. S8–S10) plots are available in the supporting information.

3.2. Other measured VOCs at Essex, MD

In both Essex, MD and Washington, DC, the sum of observed VOC (TNMOC) has generally decreased over the past decades,
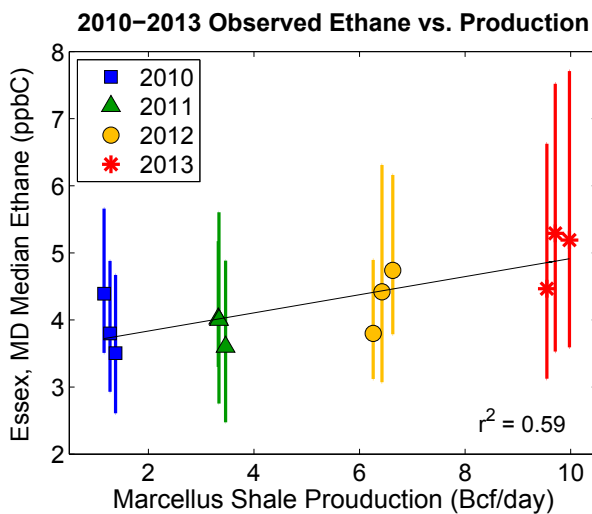
2010−2013 Observed Ethane vs. Production

Fig. 7. Monthly summer values from 2010 through 2013 of observed daytime ethane concentrations at Essex, MD vs. Marcellus Shale production. The uncertainty bars provide the 25th and 75th percentiles of measured ethane during each month.

leveling off since about 2009 (Figs. 3 and S4). Rockdale County, GA, has shown no discernable trend (Fig. S6). Propane has shown no increase in Essex, but has increased in Washington, DC (Figs. S11 and S12). The diversified uses of propane such as cooking, heating, and equipment and vehicular use (EIA, 2015a) might hide slight increases from upwind natural gas operations. From the limited measurements of well gas composition available in the public domain, propane is estimated to make up about 5% of wet Marcellus shale gas (Conder and Lawlor, 2014; Foster, 2013; Pace Global, 2010); the driest reported regional composition was 1% propane (Bullin and Krouskop, 2009). Only 30% of the shale gas produced in Pennsylvania since 2010 is wet gas (down from 35% in 2009) (PADEP, 2014), indicating shale gas propane is much less abundant as ethane. At the Atlanta site, the ethane to propane ratio is near unity, much lower than that found in natural gas, reflecting the use of propane fuel in urban areas (Figs. S13 and S14). The ratio of ethane to propane in Essex is rising to approach the natural gas emissions ratio (Fig. S21). Total production of propane and propylene in the East Coast region slightly increased in 2013 (EIA, 2015b), but a production increase at natural gas plants (EIA, 2015c) has been offset by an overall decline from refineries (EIA, 2015d), and thus, industrial emissions are expected to have remained relatively constant. The Sasol refinery in Baltimore was taken out of service in July 2007, and this removed source of VOCs might also hide slight recent increases from upwind sources (Christopher Wheeling, MDE, personal communication).

Concentrations of n-butane have decreased significantly from initial values in 1996, but slight increases in 2012 and 2013 were observed (Fig. S15). Concentrations of n-pentane, isopentane, ethylene, and benzene have continued to decrease from 1996 (Figs. S16–S19). Isoprene, a dominant VOC from biogenic sources, shows no trend (Fig. S20).

The ratios of ethane to n-butane, n-pentane, and ethylene were also investigated (Figs. S22–S24) and demonstrated an increasing trend from around 2011, similar to what is seen in Fig. 4. Finally, the ratio of isopentane to n-pentane was evaluated (Fig. S25). Gilman et al. (2013) showed this ratio to be lower in regions with natural gas production and greater in urban environments. Essex, MD had a median ratio of 2.7 from 2000 to 2003, but the median ratio has since decreased to about 2, indicating an influence of natural gas production.

3.3. Statistical analysis

It is necessary to apply statistical tests for significance. Because of the lognormal distribution of ethane concentrations, nonparametric tests were performed using the JMP Pro 10.0.2 statistical software. The Essex, MD PAMS hourly daytime ethane concentrations from 2004 to 2013 were collected and grouped by year for comparisons. To test for differences between years, the Kruskal−Wallis test (McBean and Rovers, 1998) was used to determine if daytime ethane concentrations during at least one year were different from the concentrations during other years. The result returned a p-value less than 0.0001, indicating at least one of the years contained significantly different concentrations.

To determine which year(s) had significantly different daytime ethane concentrations when compared to other years, the Steel-Dwass post-hoc test (SAS Institute Inc., 2013) was used, assuming a 95% confidence interval. The results (Table S2) suggest that, in general, the years of 2005, 2007, 2012, and 2013 had ethane concentrations significantly different from each of the other years. Looking at Fig. 4a, it can be inferred that the years of 2005 and 2007 had significantly lower ethane concentrations, while 2012 and 2013 have significantly higher concentrations. It is also significant that a p-value less than 0.0001 was returned when comparing 2013 to

2012, indicating that ethane concentrations in 2013 were already significantly greater than they were a year prior.

This procedure was repeated for daytime ethane concentrations from 2004 to 2013 at the other two sites. At McMillan Reservoir, ethane concentrations in 2005, 2006, 2007 and 2009 were significantly lower than in the other years, and in 2011, 2012, and 2013 ethane concentrations were significantly greater (Table S4). McMillan Reservoir observed significant ethane concentration increases in recent years, but unlike Essex, these ethane concentrations have not significantly increased over each passing year. At the Rockdale County site, ethane concentrations were significantly lower in 2005, 2006, and 2012 and significantly greater in 2008 and 2011 (Table S6). The shift from significantly greater in 2011 to lower in 2012 suggests long-term effects are not causing increases in ethane concentrations at this location. Descriptive statistics for daytime ethane concentrations from all three sites are also available in the supporting information (Tables S1, S3, and S5).

3.4. Local natural gas sources

The recent increase in ethane concentrations at Essex, MD has been demonstrated and coincides with the spread of wells promoting increased natural gas production, but it is also important to rule out other possible local natural gas sources. Landfills and waste water treatment plants are known sources of methane, but do not emit ethane (Aydin et al., 2011). Natural gas storage fields exist in Garrett County, MD (~250 km west of Essex, MD) but there is no evident recent change in usage (EIA, 2014e), and it is unlikely that these storage fields have started to degrade so quickly since 2009 (Cleveland, 2004).

The use of compressed natural gas in the transportation sector was also considered. Only ~0.5% of total Maryland natural gas consumption is used for vehicles, whose usage peaked in 2006 and 2008, only to decline rapidly thereafter (EIA, 2014f). Additionally, while other metropolitan areas chose to convert public transportation vehicles to use natural gas, the Maryland Transit Authority instead switched diesel buses to diesel-electric hybrid buses (MDOT, 2013). The state of Maryland has ten compressed natural gas fueling stations: seven have been operational prior to 2006, two recently added stations are located more than 60 km away, and one was opened in 2012 over 10 km away from the Essex, MD receptor (DOE, 2014). Although nearby leaks from these stations could be significant, none of them are in the immediate vicinity of the monitor.

Finally, fugitive emissions from pipeline leaks were evaluated as a source responsible for the observed increase in atmospheric ethane concentration. Information on methane loss for local utility companies was ambiguous, but Maryland's total natural gas consumption has remained nearly constant from 1997 to 2013 (EIA, 2014e). If fugitive loss rates were constant, fugitive emissions would also be expected to remain constant during this time period.

4. Conclusion

Recently, ethane concentrations have significantly increased at Essex, Maryland, and the emissions associated with hydraulic fracturing operations appear to be the only plausible source for this trend. This indicates that a substantial fraction of natural gas is escaping uncombusted, and the signal is detectable hundreds of kilometers downwind. This effect was also noticed in nearby Washington, DC, but not outside Atlanta, GA, a city without upwind hydraulic fracturing. As shale natural gas production continues to expand, this increasing trend will continue in downwind regions until more efficient control technologies are applied. Although ethane is not a criteria pollutant, additional pollutants are likely transported at increasing rates; these could cause ozone and PM to rise and complicate attainment of air quality standards for major urban centers downwind. The observed increase in ethane (1.1 ppbC) corresponds to an expected regional increase in methane of ~5 ppb. In future analyses, we will evaluate concentrations of shorter-lived (e.g., NO_x) monitored closer to natural gas operations, and incorporate back-trajectory analysis and source apportionment to further evaluate the influence of natural gas operations on climate and regional air quality.

Acknowledgments

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2015.03.056.

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