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Characterization of methane plumes downwind of natural gas compressor stations in Pennsylvania and New York (click to view paper on ScienceDirect)

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ABSTRACT

The extraction of unconventional oil and natural gas from shale energy reservoirs has raised concerns regarding upstream and midstream activities and their potential impacts on air quality. Here we present *in situ* measurements of ambient methane concentrations near multiple natural gas compressor stations in New York and Pennsylvania using cavity ring-down laser spectrometry coupled with global positioning system technology. These data reveal discernible methane plumes located proximally to compressor stations, which exhibit high variability in their methane emissions depending on the weather conditions and on-site activities. During atmospheric temperature inversions, when near-ground mixing of the atmosphere is limited or does not occur, residents and properties located within 1 mile of a compressor station can be exposed to rogue methane from these point sources. These data provide important insight into the characterization and potential for optimization of natural gas compressor station operations.

1. Introduction

The rise in unconventional oil and gas development (UD) has stimulated increased measurement and confirmation of methane emissions in both upstream and midstream processes in the commercial natural gas system. Such emissions are problematic given methane is a significant greenhouse gas (GHG) with an estimated global warming potential 28 to over 100 times greater than that of carbon dioxide (Stocker et al., 2013). Methane is emitted by natural and anthropogenic sources. Natural sources include wetlands and oceans, while predominant manmade sources are agriculture and the production, transportation and use of fossil fuels (Bosquest et al., 2006). Methane emissions are also associated with landfills and biomass burning.

Several studies have focused on the detection and quantification of methane emissions associated with UD across multiple shale formations have revealed that methane has the potential to leak during each stage of the natural gas production pathway including compressor stations (Allen, 2014; Allen et al., 2013; Caulton et al., 2014a; Omara et al., 2016; Schneising et al., 2014; Yacovitch et al., 2015). Large methane emissions averaging 34 g CH_4/s per well were observed at drilling sites in the Marcellus Shale formation (Caulton et al., 2014b), while a study in the Denver-Julesburg Basin reported 64.4% of carbon emitted from a dehydration unit was in the form of methane (Brantley et al., 2015). Subramanian et al. (2015) measured methane emissions from 45 compressor stations (midstream process) across 16 states, and found 10% of the sites tested were responsible for 50% of the total methane emissions measured. These high emitters are referred to as "superemitters". Superemitters can appear anywhere along the natural gas supply chain making it difficult to determine a national average for methane emissions. Collectively, the United States Environmental Protection Agency (USEPA) estimated a total 7045 Gg methane emissions from the U.S. natural gas supply chain for 2014, with 4359 Gg from field production, 960 Gg from processing, 1282 Gg from transmission, and 444 Gg from distribution (USEPA, 2016). Furthermore, Brandt et al. (2014) postulate that inventories based on emission factors, like those reported by the EPA, are consistently lower than estimates based on direct methane measurements.

In most situations where methane is of concern as a pollutant or explosion hazard, it is due to a concentrated source, such as a septic tank, a landfill, or a natural gas pipeline, compressor station, or other infrastructure. When methane is emitted from such sources the concentrations are high and are usually associated with other malodorous gases that are either byproducts of microbial methane production or natural gas additives, such as mercaptan, to assure leaks are noticed before explosion hazards can develop. Consequently, if one can collect measurements close to the point source, identifying and characterizing such leaks is relatively easy. However, in many cases quantifying ambient methane is inherently difficult due to accessibility issues. Some sources are located underground, like most gas pipelines, natural gas deposits that seep to the surface, and underground areas of

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biological methane production. Furthermore, most larger natural gas infrastructure is not readily accessible for safety and security reasons. Therefore, the practical reality is that methane leaks have to be detected by measuring methane concentrations in the air above ground and often at considerable distances from methane sources. Additionally, there are instrumental limitations when quantifying methane *in situ* that have recently fielded significant scrutiny (Allen et al., 2015; Howard, 2015). According to Touché Howard, the chemical engineer who invented and developed the popular Bacharach Hi Flow Sampler, this device is known to give low, inaccurate readings for high methane leakers under certain conditions (Johnson, 2016). This means that the Hi Flow Sampler is known to grossly underestimate the percentage of methane present in a natural gas leak when it is emitting at a high rate. Howard also claims there is a sensor transition failure between low and high range sensors, which can lead to an underestimation of emission rates by up to 2 orders of magnitude (Howard, 2015; Howard et al., 2015). The data reported in this work were collected using entirely different instrumentation, along survey paths remote from likely methane sources, measuring much lower methane concentrations in ambient air (no-net-flow conditions with respect to methane), and, hence, not subject to the aforementioned types of errors.

Methane is the most mobile and abundant (> 90%) component of natural gas, and has the potential to escape at every stage of the natural gas supply chain including compressor stations. Methane is also less dense than air and will diffuse more quickly from the point source than any other contaminant that might be released from natural gas facilities. Consequently, leaked methane disperses rapidly. Concentrations near methane sources drop relatively quickly to the local background methane concentration, which typically ranges from 1.7–2.1 ppm (0.00017–0.00021%). Given this rapid dispersion of methane, detection of methane leaks, and especially associated plumes, requires analytical instrumentation capable of accurately and consistently measuring trace levels of the gas. Previously, the potential usefulness of methane as an indicator of environmental contamination from commercial natural gas systems or other sources was limited by the difficulties involved in effective air sampling and analysis for trace levels of the gas (Baldocchi et al., 2011). However, recent developments in analytical technology, such as cavity ring-down laser spectroscopy, have made it possible to measure trace levels of methane in the field while continuously logging the results to perform point source attribution (Crosson, 2008).

The measurement of trace gases in the environment offers a useful approach for stand-off, semi-remote detection of emissions of methane and potential co-contaminant gases from compressor stations. Here we report cavity ringdown laser spectrometer measurements of ambient air methane concentrations in the vicinity of natural gas compressor stations in the Marcellus Shale region.

2. Methods & materials

Methane was quantified using a mobile Picarro G2301 Cavity Ring-Down Spectrometer (CRDS) equipped with an onboard GPS unit to record time, location, and methane concentration in ambient air (parts-per-million, ppm), every 0.25–5.00 s. In CRDS, light from a frequency tunable laser is introduced into the ring-down cavity (RDC), which contains two or more high reflectivity mirrors, at least one of which passes a small, but consistent fraction (typically < 0.1%) of incident light (Fig. 1). The mirrors are oriented so that the input laser light is reflected within the RDC until it is dissipated due to non-reflection losses. A photo detector located behind the partially transmissive mirror determines in real time the amount of light passing the mirror. When the laser is turned off, the light trapped inside the cavity decays exponentially with time, or "rings down". A given RDC will have a characteristic ring down time. When an analyte enters the RDC, it absorbs light, shortening the ring down time in proportion to the amount of analyte. An absorption spectrum of the analyte is determined by measuring the decay rate, the inverse of the decay time constant, τ, as a function of wavelength, and then subtracting the background decay rate for the empty RDC (Crosson et al.,

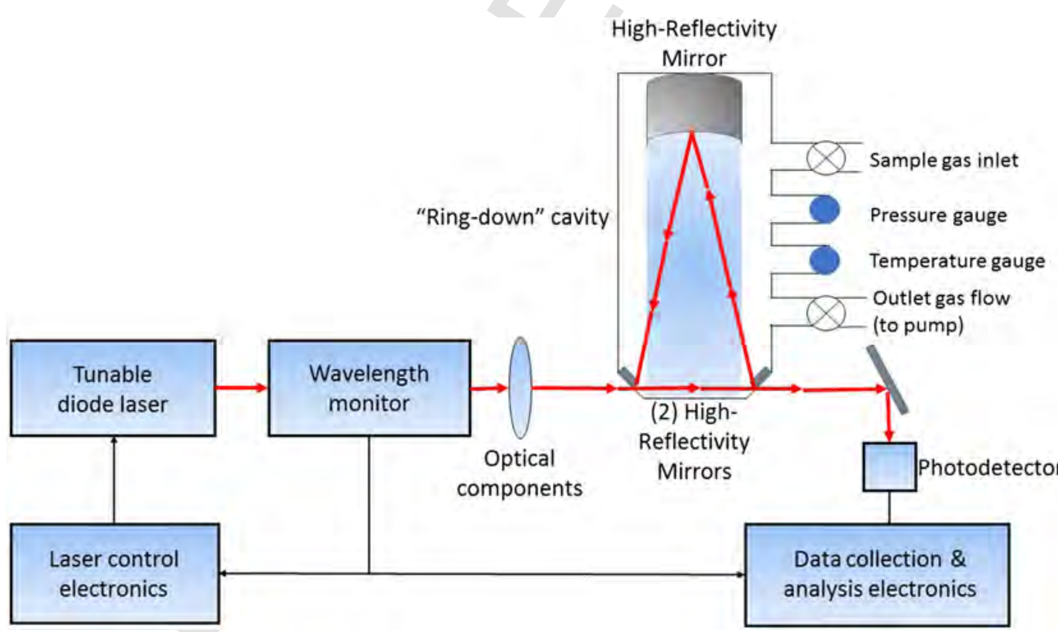

Fig. 1. Diagram of cavity ring-down spectrometer. Single-frequency laser light tuned to the absorbance of methane is introduced to the ring-down cavity (RDC). The mirrors are oriented so that the input laser light is reflected within the RDC at an effective path length of approximately 20 km until it is dissipated due to non-reflection losses through/in the mirrors. A photodetector is located behind the low-pass mirror to determine in real time the amount of light passing through that mirror. When the laser is turned off, the light trapped inside the cavity decays exponentially with time, or "rings down".

1999). The Picarro instruments we used contained a laser tuned to the absorption spectrum of methane, an RDC with three mirrors providing an effective path length of > 20 km, and sensitivities to < 1 ppb methane. The unit was mobile and contained an onboard GPS instrument to continuously record time, location, and methane concentration data. The instrument was factory calibrated, and stability was verified at least twice per day under field conditions using commercial reference gases with known levels of methane at 0, 5, and 50 ppm.

Data was processed using a custom program in R statistical language. Prior to analysis, non-essential data (reference gas check data, data from vehicle stops, instrument system function verification data, out of range data, *etc.*) were removed. Data files were converted to .kml files using the Picarro KML Converter program and plotted using Google Earth™.

Measurements of ambient methane were collected within the vicinity of compressor stations in Dimock and Milford Townships in Pennsylvania, and the Towns of Minisink and Hancock in New York. The methane data reported for compressor stations were collected during general methane surveys of areas where methane emissions from shale gas well operations, and related natural gas infrastructure, were suspected in the Marcellus Shale play. Seven compressor stations in Pennsylvania were surveyed: CDPI (New Milford, PA), Central and Franklin Forks stations (Montrose, PA), Hurkey and Lathrop (Springville, PA), Church and Herb Button Road (Dimock, PA). In New York, the towns of Minisink and Hancock were surveyed prior to construction of the compressor stations and again after the stations were operational. Methane surveys were typically performed during daytime hours, though scheduling, weather, and other factors occasionally imposed need to perform surveys at night. The Dimock area was surveyed in November 2014, the seven Pennsylvania compressor stations in November 2015 (Table 1), and the New York compressor stations pre-construction surveys in January and June 2013 and post-construction surveys in September 2014 (Table 2). Methane surveys were conducted along publicly accessible roads throughout rural areas of interest with the CRDS logging data constantly. Interference from other vehicles was accounted for during data collection using filtering provisions within the R program suite that also removed all collected while the CRDS was idle.

Methane plume delineation was determined through visual examination of the methane survey data plot to identify values that exceed the locally typical atmospheric concentrations (in range of 1.7–2.1 ppm). We define one edge of a plume as the location where an initial and sustained rise above the expected atmospheric condition begins, the other edge at the location where that elevated level returns to the expected atmospheric condition. In practice, this analysis can be accomplished with reasonable accuracy by visual examination of the plotted data.

Table 1
Methane measurements collected at seven Pennsylvania compressor stations on November 14, 2015.

Location	$[CH_4]$, ppm	Local average $[CH_4]$, ppm
CDPI compressor station near New Milford, PA	5.53	1.90
Central compressor station near Montrose, PA	2.05	1.90
Franklin Forks compressor station, 13.2 km north of Montrose, PA	2.07	1.90
Hurkey compressor station, 11.3 km south of Springville, PA	6.35	1.79
Lathrop compressor station, 1.6 km north of Springville, PA	3.62	1.90
Church compressor station, 2.8 km west of Dimock, PA	2.10	1.90
Herb Button Road compressor station, 4.7 km southeast of Dimock, PA	7.40	1.79

Table 2
Methane measurements collected before and after construction of compressor stations in Dimock, PA, Minisink and Hancock, NY.

Location	Collection date	Comments	$[CH_4]$, ppm	Local average $[CH_4]$, ppm
Dimock area	11/22/2014	Plume 3.2 km downwind of compressor station	4.145	1.966
Dimock area	11/22/2014	502 m downwind of compressor station	22.3	1.966
Dimock area	11/23/2014	Extensive plume	2.386	1.966
Minisink, NY	01/02/2013	Pipeline prior to construction of compressor station	1.930	1.870
Minisink, NY	09/18/2014	Compressor station operational	2.738	1.938
Hancock, NY	06/03/2013	Prior to construction of compressor station	1.812	1.800
Hancock, NY	09/16/2014	Compressor station operational, plume present	2.044	1.959
Hancock, NY	09/18/2014	Compressor station operational, plume present	2.890	1.961

3. Results and discussion

Methane concentration data collected during methane baseline surveys are not necessarily proportional to the strength of methane sources in the survey area. This lack of correlation between methane survey data and strength of causative methane sources is due to variable, uncontrollable and usually unknown distances between methane sources in the area and the survey path. Restricted access to natural gas infrastructure, as well as local wind conditions, effects of local terrain on methane mixing rates, and potentially other factors, can limit the ability to attribute individual methane concentrations to individual point sources. Any data that could not be confidently assigned to a compressor station as the most likely source, *i.e.*, due to proximity of another potential source, such as animal farm or sewage treatment operations, or landfills, were eliminated. Further, the data presented in the images do not necessarily present the highest methane levels encountered in the respective study areas, even if that highest level was associated with the compressor station. When more extreme elevated methane survey data occurred in the vicinity of a compressor station and its inclusion interfered with the clarity of the image depicting the data indicating an apparent methane plume associated with a compressor station or stations in the area, the higher data were excluded. Figs. 2–6 (and Supplementary Figs. 1–8) are presented to clarify the extent of the apparent methane plumes associated with the areas of interest.

3.1. *Pennsylvania compressor stations*

A retrospective analysis of methane survey data collected from the vicinities of 7 compressor stations in 4 different geographical locations (summarized in Table 1) indicates a consistent presence of elevated methane levels downwind from the compressor stations. Methane levels downwind of the CDPI compressor station in New Milford, PA were measured at 5.53 ppm, while levels of 6.35 ppm were measured at the Hurkey compressor station near Springville, PA (Figs. 2 and 3, respectively). Methane levels at the Central compressor station near Montrose, PA appeared negligible (Supplementary Fig. 1). There was a notable methane peak down-

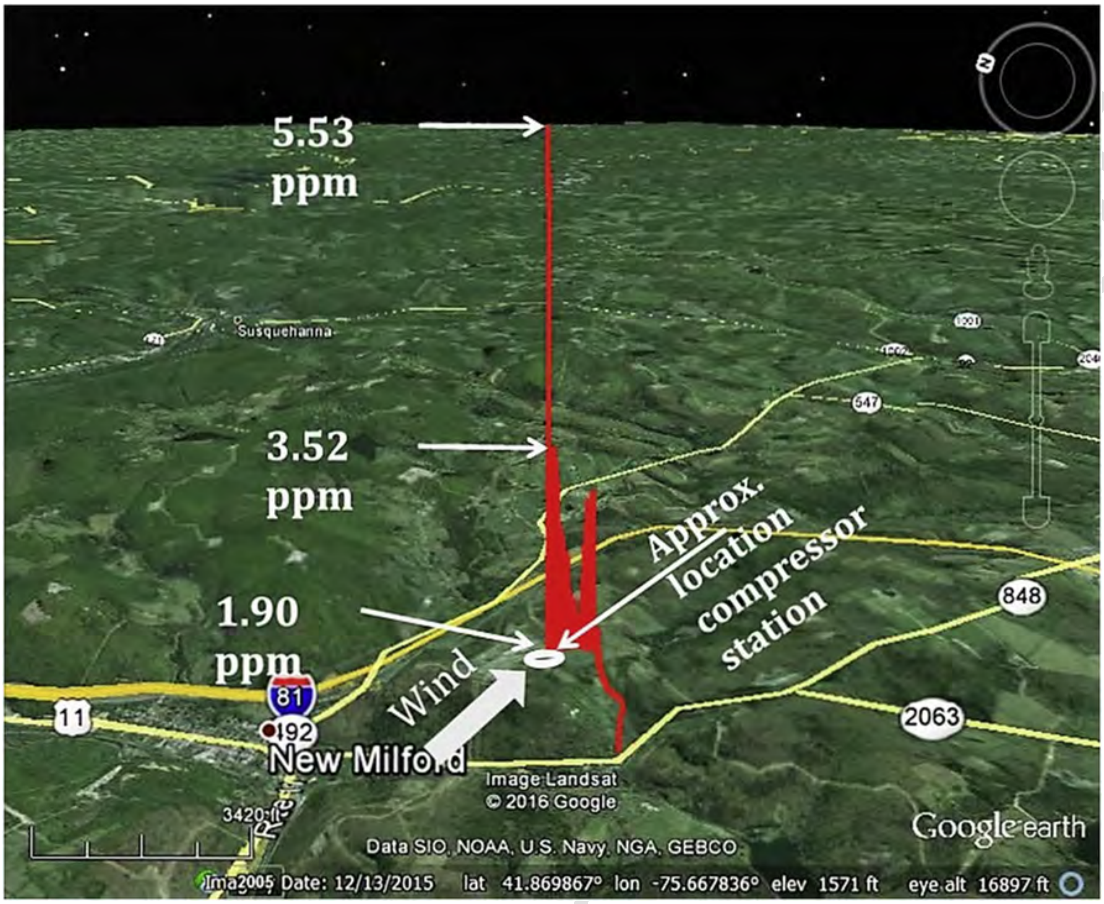

Fig. 2. Methane survey data collected adjacent the CDPI compressor station near New Milford, PA (eastward view). Each vertical red line indicates the approximate location of a methane measurement. The height of each vertical red line is proportional to the elevation of methane over 1.90 ppm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

wind of the compressor station, but that peak occurred slightly off of downwind from a gas well pad. We, therefore, concluded the more likely source was infrastructure on the gas well pad. There was little effect on methane levels from the Franklin Forks station near Montrose as well, with the highest level of 2.07 ppm near the compressor station decreasing to near the local average further downwind (Supplementary Fig. 2). The Lathrop compressor station near Springville showed evidence of a plume downwind of the station with methane levels up to 3.62 ppm (Supplementary Fig. 3). In Dimock, PA, the Church compressor station generated a methane plume from 0.74–1.3 km downwind of the station with a maximum methane concentration of 2.10 ppm (Supplementary Fig. 4). The Herb Button Road compressor station emitted methane levels as high as 7.40 ppm directly adjacent the station (Supplementary Fig. 5).

This data indicates that the areas downwind of compressor stations during periods with winds exceeding 3 m/s will be exposed to methane plumes, and any other co-emitted pollutants released by compressor stations. Residents and properties downwind under prevailing wind conditions will likely be subjected to a disproportionate burden of contaminants from compressor stations, especially those closer to the station under light prevailing wind conditions. Conditions at night and during other low wind periods may result in particularly high methane burdens for residents and properties located downslope from compressor stations especially during atmospheric temperature inversions. Temperature inversion is a condition in which the temperature of the atmosphere increases with altitude in contrast to the normal decrease in temperature with increasing altitude. When temperature inversion occurs, cold air underlies warmer air at higher altitudes. When cold air is close to the ground there is little to no near-ground mixing of the atmosphere and the concentration of methane is maintained. Ultimately, this results in a greater exposure of contaminants for the residents in the area. This phenomenon has been found to have a significant impact in other atmospheric (Bintanja et al., 2011) and epidemiological (Tunno et al., 2016) studies.

In the Dimock, PA area, there is a great deal of natural gas infrastructure, all of which could be short, occasional, or longer-term sources of methane emissions. The coincidence of elevated methane concentrations, the timing of construction or expansion of three compressor stations in southern Dimock Township, and the lack of other nearby methane sources where elevated methane levels were observed clearly suggest compressor stations are likely sources of substantial portions of the methane in the air in southern and eastern Dimock Township. We believe that atmospheric methane levels measured downwind of Dimock were due to release from the nearby compressor stations. Of particular note in this regard was the compressor station on Herb Button Road, where methane levels were measured at their highest concentration 503 m from the compressor station and dissipated downwind (Fig. 4). Elevated methane conditions were measured up to 3.2 km from the compressor station. Based on local terrain and weather and wind conditions we estimated an implied emission rate of 0.42 m^3/s at station at that time.

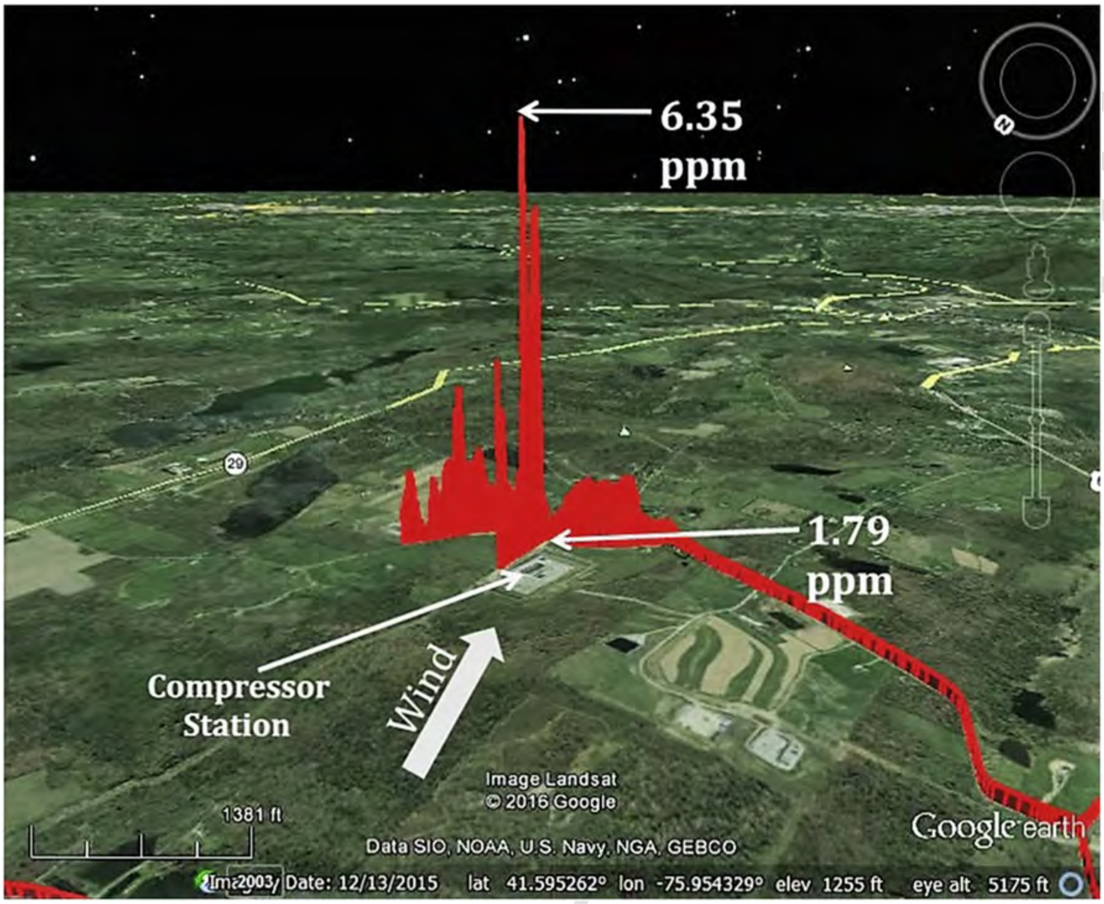

Fig. 3. Methane survey data collected near the Hurkey compressor station located 7 miles south of Springville, PA (southeastward view). Each vertical red line indicates the approximate location of a methane measurement. The height of each vertical red line is proportional to the elevation of methane over 1.79 ppm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.2. *New York compressor stations*

In Minisink and Hancock, NY, methane measurements were collected before and after the construction of compressor stations (Table 2). In January 2013, methane measurements were collected near the then-planned natural gas compressor station in the town of Minisink, NY. Relatively low and uniform methane levels were detected. At that time maximum methane levels in the vicinity were 0.060 ppm above the local average of 1.870 ppm (Supplementary Fig. 6). Measurements collected after the construction of the compressor station (September 2014), revealed methane levels of 0.800 ppm above the local average (Fig. 5). In the second set of measurements, the basal levels of methane in the entire vicinity of the compressor station appear to be uniformly elevated compared to the previous measurements. Substantially higher methane levels were observed immediately downwind of the compressor station, diminishing to the north and east (Fig. 4-blue line). It should be considered, that on that day the wind was blowing approximately parallel to the run of the pipeline, and only one survey pass roughly perpendicular to both the pipeline and the wind was performed. Even with such constrained survey access, methane concentrations within the plume reached 800 ppb above the local average.

In June 2013, methane measurements were taken near the then-planned natural gas compressor station in the town of Hancock, NY. Prior to construction of the compressor station, methane levels were detected at approximately 12 ppb above the local average of 1800 ppb (Supplementary Fig. 7). After the compressor station was constructed, methane data collected on September 16th, 2014 indicated the presence of a methane plume directly downwind of the station at levels 85 ppb above the average (Supplementary Fig. 8). This compressor station is on terrain that is elevated with respect to the path of the survey. Consequently, due to wind and terrain effects, it is reasonable to expect that the measured methane levels were lower than actual levels. The same area was surveyed again on September 18th, 2014 under conditions of low wind and insolation. Methane emissions were measured at 929 ppb above background (Fig. 6). The elevated concentration was likely due to methane drifting downslope. Notable increases in atmospheric methane at both New York sites post-construction suggest that these natural gas supply infrastructure could be responsible for significant releases of methane and likely co-emitted contaminants.

4. Conclusion

Our data indicate that compressor stations are likely sources of methane emissions and presumably co-emitted air contaminants, and can sporadically/episodically emit methane at relatively high levels. While these analyses provide significant insight into contamination events during specific periods in time, they are not sufficient to project how often high emissions occur, or to characterize basal emission rates. Nonetheless, these data provide an impetus for more thor-

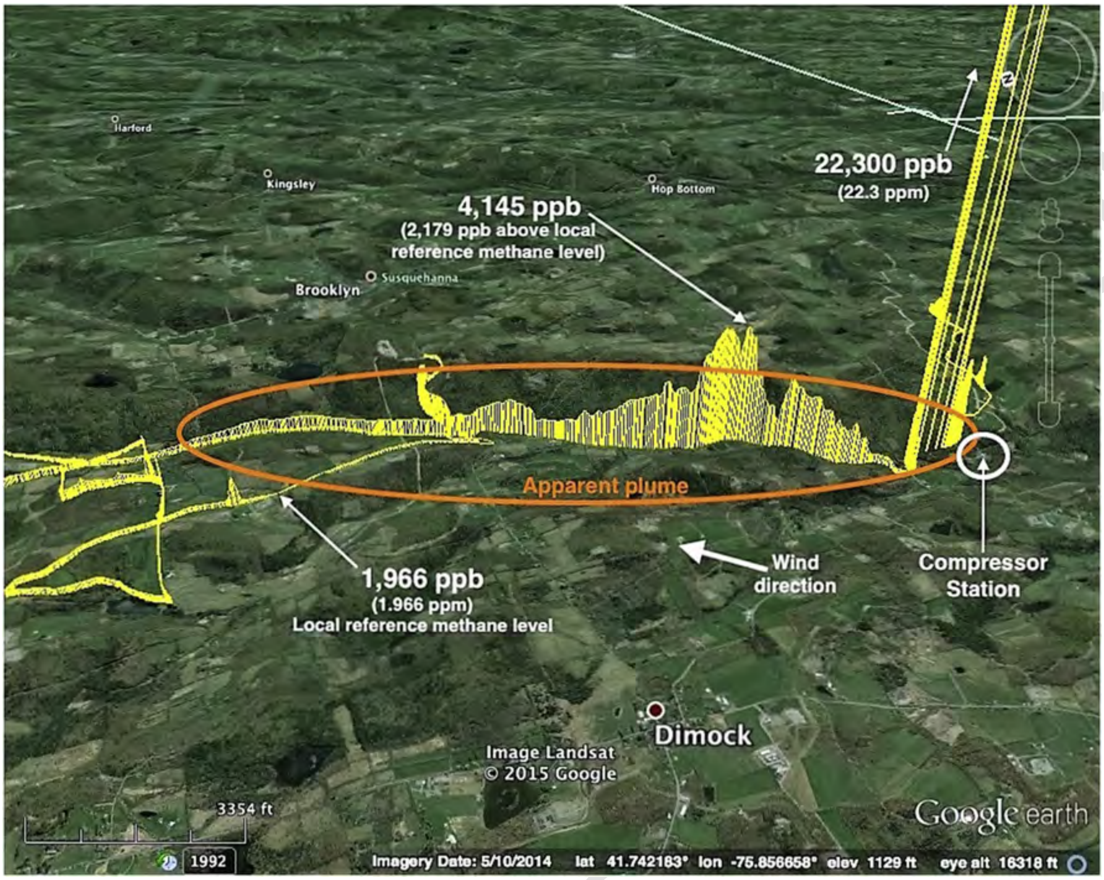

Fig. 4. Ambient methane measurements collected from a survey of area in Dimock, PA. Yellow lines indicate locations of methane measurements. The vertical height of each line is proportional to the elevation of the methane concentration at that location above the local reference methane level that day (1966 ppb). The highest methane level encountered in the Dimock area up to the time of this survey (22, 300 ppb) was encountered about 503 m downwind of the compressor station. Methane levels began to rise at the closest approach to the compressor station, about 750 ft (230 m), just prior to encountering the maximum methane level. An apparent plume extended for over 2 miles downwind in the Meshoppen Creek valley. Data indicated this plume may have been dissipating at the time of the survey as return survey passes along the margins of the plume encountered lower methane levels. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

ough environmental investigations of natural gas infrastructure in general. It would seem appropriate, therefore, that if such facilities are to be permitted to release specified amounts of contaminants, those amounts should be actively measured and verified. Without measurement there can be no assurance that permit conditions are being met. Baseline measurements of methane emissions from compressor stations should be collected to better understand how midstream activities in the natural gas supply system contribute to overall anthropogenic emissions, while simultaneously aiding in the early detection of environmental contamination events, and guiding the subsequent improvement of natural gas infrastructure.

Author contributions

BFP and RA designed research; BFP and RA performed research; BFP, RA, APW and ZLH analyzed data; and BFP, APW, ZLH, DDC, and KAS wrote the paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2016.12.082.

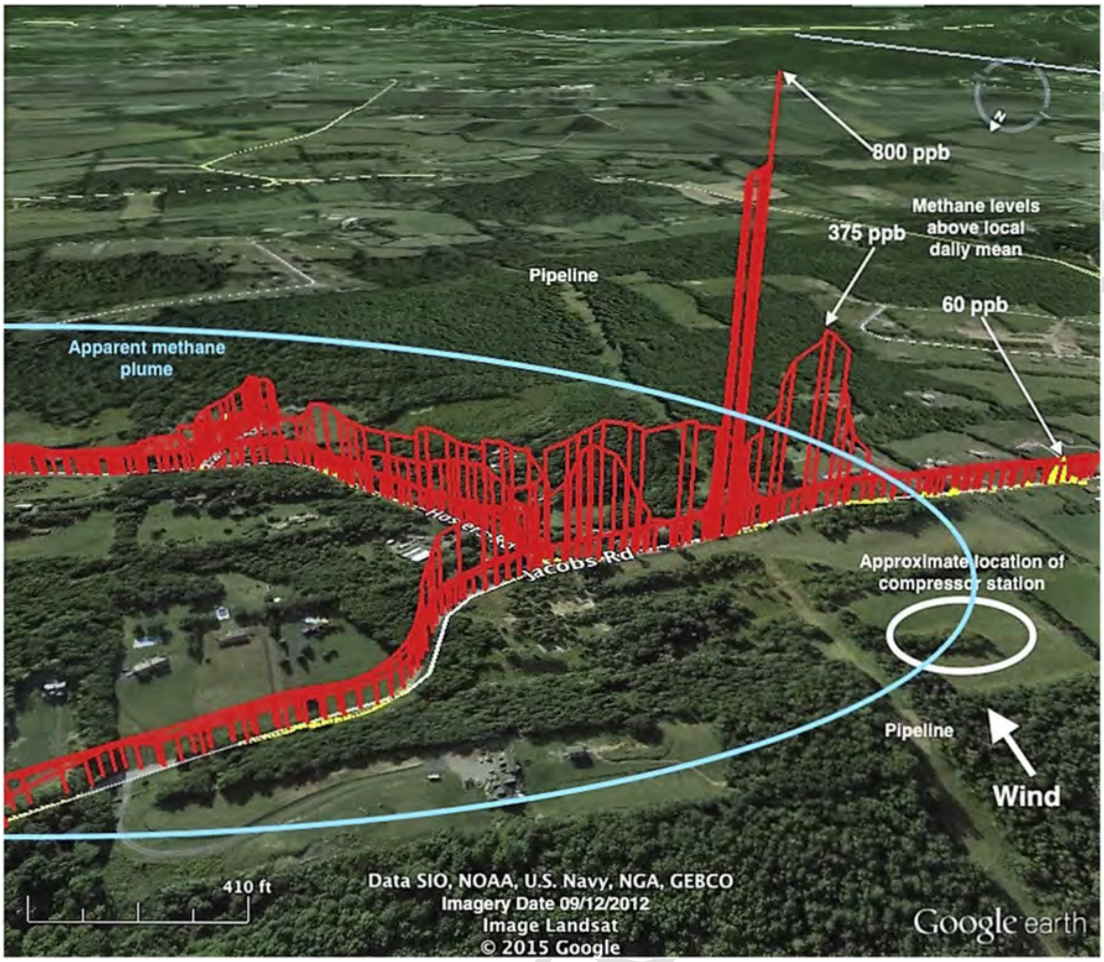

Fig. 5. Southeastward view of methane measurements collected after the construction of a natural gas compressor station in the Town of Minisink, NY. The methane survey data of the area after the construction of the compressor station is superimposed (red) over the survey data collected prior to construction (yellow). Each vertical red line indicates the approximate location of a methane measurement. The height of each vertical red line is proportional to the elevation of methane above the local average methane level (1938 ppb). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

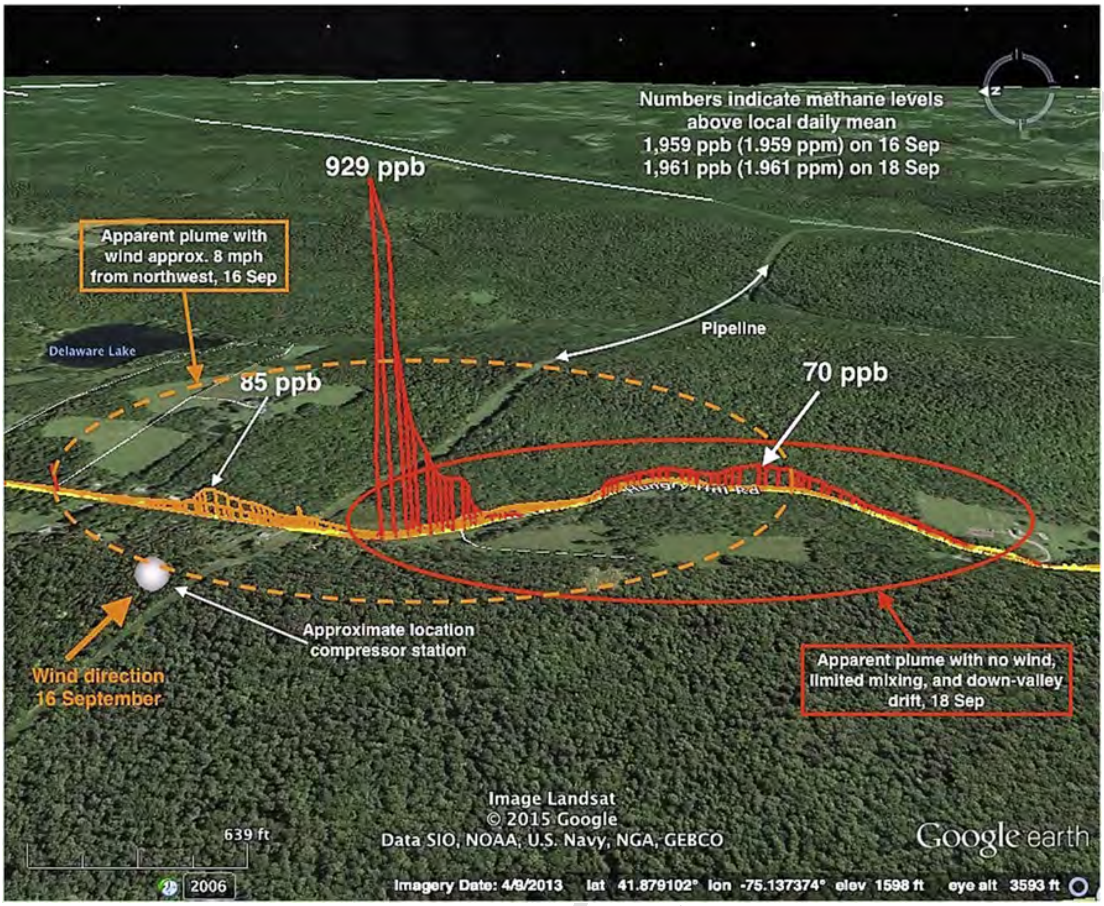

Fig. 6. Methane data from the September 18th survey (displayed in red) superimposed on top of measurements from September 16th (orange). Both sets of measurements were collected after the completion of a natural gas compressor station in Hancock, NY. Initial baseline measurements are illustrated in yellow. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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