Distributions of air pollutants associated with oil and natural gas development measured in the Upper Green River Basin of Wyoming

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Abstract

Diffusive sampler monitoring techniques were employed during wintertime studies from 2009 to 2012 to assess the spatial distribution of air pollutants associated with the Pinedale Anticline and Jonah Field oil and natural gas (O&NG) developments in the Upper Green River Basin, Wyoming. Diffusive sampling identified both the extent of wintertime ozone (O3) episodes and the distributions of oxides of nitrogen (NOx), and a suite of 13 C5+ volatile organic compounds (VOC), including BTEX (benzene, toluene, ethylbenzene and xylene isomers), allowing the influence of different O&NG emission sources to be determined. Concentration isopleth mapping of both diffusive sampler and continuous O3 measurements show the importance of localized production and advective transport. As for O3, BTEX and NOx mixing ratios within O&NG development areas were elevated compared to background levels, with localized hotspots also evident. One BTEX hotspot was related to an area with intensive production activities, while a second was located in an area influenced by emissions from a water treatment and recycling facility. Contrastingly, NOx hotspots were at major road intersections with relatively high traffic flows, indicating influence from vehicular emissions. Comparisons of observed selected VOC species ratios at a roadside site in the town of Pinedale with those measured in O&NG development areas show that traffic emissions contribute minimally to VOCs in these latter areas. The spatial distributions of pollutant concentrations identified by diffusive sampling techniques have potential utility for validation of emission inventories that are combined with air quality modeling.

1. Introduction

Increased onshore oil and natural gas (O&NG) production, driven in part by the development of hydraulic fracturing and directional drilling techniques, continues to reshape the United States (US) energy economy. Natural gas, in particular, has become increasingly important, a trend expected to be sustained in the future, such that by 2040, its share of total primary energy production is predicted to rise to a high of 30%. Furthermore, it is expected to become the most important fuel source for electricity generation by 2040 (US EIA, 2014).

Wyoming has a long history of O&NG development with oil production dating back to the late 19th Century. Currently, the Jonah field and Pinedale Anticline, both in the sparsely populated Upper Green River Basin (UGRB) of Sublette County, Wyoming, are ranked 8th and 6th respectively among US producing gas fields for 2013 (US EIA, 2015). In 2012, ~4,000 wells from these two fields produced 807.5 million Mcf of natural gas, 6.3 million barrels of oil and 23.9 million barrels of water (Wyoming Oil and Gas Conservation Commission, 2015). The relatively wet nature of the gas allows for production of oil (condensate) that leads to both fields also being ranked within the top hundred of US producing oil fields, with the Jonah field 94th and the Pinedale Anticline 85th, respectively (US EIA, 2015).
Accompanying O&NG development has been the inevitable addition of new atmospheric pollutant emission sources. The large number and diversity of emission sources have accentuated the difficulty of developing quantitatively accurate emission inventories for O&NG field operations. One approach to combating these difficulties is the development of a new inventory for small point (also termed ‘area’), upstream O&NG sources. Discrepancies have emerged between measurement-based emissions estimates over, for example, an entire local gas field and calculated inventory source strengths. The latter appear to be under-predicted (Brandt et al., 2014). Efforts to reconcile these differences are already underway (Pétron et al., 2014).

Pollutants from O&NG development and production operations contribute to the photochemical formation of surface ozone (O₃). High levels of wintertime O₃ were first observed in 2005, close to the developing Jonah and Pinedale Anticline O&NG fields. Since that time a large number of winter O₃ episodes have been reported in the UGRB (during 2005, 2008, 2011) and the Uintah Basin of Utah (during 2011, 2013 and 2014). Schnell et al. (2009) summarized the early observations and described the requisite conditions necessary for episode occurrence. These include relatively stagnant conditions and snow cover to both increase the actinic flux and foster the formation of a low-level capping inversion above a ‘cold pool’ that facilitates the accumulation of primary O₃ precursor pollutants, specifically volatile organic compounds (VOC) and oxides of nitrogen (NOₓ) (Carter and Seinfeld, 2011; Oltmans et al., 2014). Under favorable conditions, O₃ production rates in the UGRB can exceed 10 ppbv/hr, leading to maximum hourly mixing ratios in excess of 160 ppbv (Rappenglück et al., 2014). The National Ambient Air Quality Standard for O₃ is based upon the average of the fourth highest 8-hour average for 3 years of monitoring. An area is defined as being in non-attainment when this 3-year average exceeds 75 ppbv. Fourth highest 8-hour averages have exceeded 75 ppbv in 2005, 2008 and 2011 in the UGRB (Field et al., 2015).

Ozone episodes have typically been associated with urban areas in summer with precursor species from traffic and industrial emissions. The Los Angeles (LA) basin provides an archetypical scenario for these events. In recent years, air quality in the LA basin and many other metropolitan areas has improved, largely because of the implementation of stringent emission controls for traffic produced VOCs and NOₓ (Pollack et al., 2013; Warneke et al., 2012). The dominance of traffic related pollutant sources has eased the characterization and design of effective pollution control strategies. Emission profiles from O&NG activities are varied and also depend on the basin considered due to differences between characteristics of the extracted hydrocarbon product and the operational approaches. Alkanes are typically the most important VOC class arising from fugitive emission sources, whereas aromatics are emitted in particular during wet gas dehydration operations and water treatment processing (Field et al., 2015). Major VOC sources also include those associated with well completions, venting, processing, and distribution activities, in addition to a wide range of combustion engines (Field et al., 2014). Combustion sources are also the primary source of NOₓ.

Characterization of the relationship between precursor mixing ratios and the potential for wintertime O₃ production under optimal formation conditions has progressed significantly. The importance of the spatial distribution of emitted VOCs and their concentrations has been recognized. Both modeling studies (Carter and Seinfeld, 2011; Edwards et al., 2014) and observations (Field et al., 2015) suggest that O₃ production is radical limited and therefore sensitive to VOCs. Thus VOC reductions should lower peak O₃ whereas NOₓ reductions could lead to increases in O₃, until a critical lower threshold of NOₓ is reached. Under VOC sensitive/NOₓ saturated conditions, modest reductions in NOₓ can lead to an increase in the rate of O₃ production by decreasing the rate of diversion of HO₂ radicals to inactive HNO₃, thereby causing the concentration of NO-oxidizing peroxy radical production from VOCs to rise. Larger decreases in NOₓ can result in the system becoming NOₓ rather than VOC sensitive, leading to a reduction in the rate of NOₓ photodecomposition, and a consequent lowering of the O₃ formation rate (Sillman, 1999). Available measurement data (Field et al., 2015) suggest that O₃ precursor concentrations vary across the UGRB, implying that uniformity of O₃ formation is highly unlikely. For example, daily average ambient toluene mixing ratios during winter at monitoring locations in the UGRB, described elsewhere (Field et al., 2015), typically vary over two orders of magnitude within a range of 0.0 to ~50 ppbv. At additional sites considered as proximate to sources, including a fence line location next to a water treatment and recycling facility, toluene values reached 1 ppbv. O₃ mixing ratios measured in the UGRB have recently been shown to be strongly influenced by both toluene and m+p-xylene (Field et al., 2015). Modeling studies attempting to compute spatially resolved time dependent wintertime O₃ concentrations are clearly limited by the resolution of precursor concentration data (Ahmadov et al., 2015), and are potentially compromised by the difficulties of successfully simulating the topographically influenced weak wind fields in the very shallow surface cold pool. The need for spatially distributed measurements of VOC and NOₓ with reference to current regulatory modeling approaches, was also noted by Carter and Seinfeld (2011).

Early State of Wyoming Department of Environmental Quality (WDEQ) modeling studies aimed at understanding UGRB wintertime O₃ episodes were based on measurements from two locations, namely Jonah and Boulder. They were subsequently supplemented by four additional air quality network stations outside the O&NG development areas, together with a suite of more extensive measurements at the Boulder site (WDEQ, 2015a). Unfortunately, these network upgrades did not provide enough data to characterize the spatial distribution of pollutants across the basin (Carter and Seinfeld, 2011). The distribution of VOC...
and NO₃ in wintertime varies due to the non-uniform spatial distributions of their emission sources, and is further influenced by meteorological conditions that affect local advection and pollutant redistribution in the surface cold pool below the capping temperature inversion.

This study aims to characterize the spatial extent of elevated O₃ during days anticipated to experience episodic ozone production. A similar characterization during wintertime conditions in the UGRB was performed for O₃ precursors, VOC and NOₓ, at locations in O&NG development areas with primary pollutant emission sources. Local population centers were included as both contrast, to emissions, and due to concerns related to pollution impacts. Achieving these aims greatly facilitates the identification and strength of major pollutant emission sources, understanding cold pool meteorology in the basin, and identifying communities potentially at risk for experiencing degraded air quality. The study builds on surveys that used canister sampling for VOC measurements (Field et al., 2015), by employing a passive diffusive sampler network to measure the spatial distributions of O₃, NOₓ, and VOC (including benzene, toluene, ethylbenzene and xylene isomers (BTEX)), over a wider area of the UGRB, and with a greater number of sampling sites. The resultant observational dataset could be used to assess the quality and accuracy of the WDEQ spatially resolved emissions inventory, which has yet to be made publicly available.

2. Materials and methods

Measurement surveys of the spatial distributions of species of interest were conducted using passive diffusive samplers. This technique was first developed in 1973 (Palmes and Gunnison, 1973), and has been subsequently refined and is now well established (e.g., Varns et al., 2001; Carmichael et al., 2003; Muckerjee et al., 2004; Bruno et al., 2005; Gerboles et al., 2006; Pérez Ballesta et al., 2008; Cocheo et al., 2008; Buczynska et al., 2009; Martin et al, 2014). The method, which relies on the diffusion of a pollutant species to a collection medium, typically an adsorbent material, allows a wide range of trace gas concentrations to be measured in both indoor and outdoor environments (Zabiegala et al., 2010). Brown (2000) has described the underlying theory of diffusive sampling in detail, while Carmichael et al. (2003), among others, have discussed the prerequisites for its successful operation, which include an appropriate consideration of sampler design, sampling rate, sampler orientation during sample collection, exposure conditions, and analytical procedures.

Diffusive sampling yields averaged species concentrations for the chosen sampling time period, which may range from a few hours, appropriate for O₃ episode monitoring, to a week or more, an often useful time period for VOC measurements in this context. A particular advantage of the method, especially in remote areas, is the flexible ease of sampler placement, because no electricity is required for sampler operation. In Europe diffusive sampling has qualified as an indicative method for European Air Quality Directives, by achieving defined accuracy requirements (Buzio et al., 2005). For example, the Radiello® diffusive sampler meets the quality requirements according to the European standard for measuring benzene in ambient air (Pennequin-Cardinal, 2005). Diffusive sampling is regularly employed in Europe and frequent inter-comparison studies are performed to ensure the quality of diffusive samplers and their application as a technique for assessing ambient air quality (Martin et al, 2014).

2.1 Sampling approach

In this study, sampling surveys were conducted in the UGRB of Sublette County, Wyoming, using species specific diffusive passive samplers deployed at over 60 sites. Table 1 summarizes the sampler types deployed, the analysis laboratories and analytical methods employed, sampling duration periods, and survey dates. Table 2 shows a summary of key quality assurance parameters for the different diffusive sampling and analysis methodologies. Ozone surveys were performed to determine both the spatial extent of episodes, and whether observed high O₃ concentrations resulted from long-distance regional transport or local production driven by precursor emissions related to UGRB O&NG development. BTEX and NOₓ surveys were performed to show the distribution of these O₃ precursors. A single survey of VOC was carried out at 13 sites to determine the variability of these pollutants at selected established monitoring sites within the basin.

Potential monitoring locations were initially determined by dividing the study area into a 10 × 10 grid and evaluating each of the 100 grid boxes in the field for potentially suitable sites. The primary criteria used for site subsequent selection were accessibility, representativeness, and safety. Site locations, Pinedale Anticline and Jonah field wells, and select geographical markers are shown in Figure 1. The UGRB, at an elevation of approximately 2150 m msl, is enclosed by the Wyoming mountain range to the west, the Gros Ventre range to the north, and the Wind River mountains to the northeast. To the south it broadens and opens onto lower elevation plains and the Interstate-80 corridor. Monitoring sites were located towards the center of the basin in and around O&NG developments. As funding was from the Pinedale Anticline Project Office the designated oversight agency (WDEQ) did not support the placement of many samplers in and around the Jonah field. The greater density of passive samplers in the Pinedale Anticline compared to the Jonah field is evident in Figure 2, as is the wider distribution of continuous O₃ monitors, which extend further to the south into the Jonah field and beyond.
Air pollutant distributions measured in a Wyoming basin

Table 1. Diffusive sampler methods

<table>
<thead>
<tr>
<th>Species</th>
<th>Sampler</th>
<th>Analysis</th>
<th>Analysis group</th>
<th>Duration</th>
<th>Survey dates (m/yy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O3</td>
<td>Ogawa</td>
<td>IC</td>
<td>RTI Int.</td>
<td>8-hours</td>
<td>2/09; 6/09</td>
</tr>
<tr>
<td>NOx</td>
<td>Ogawa</td>
<td>IC</td>
<td>RTI Int.</td>
<td>3-7 days</td>
<td>2/11; 11/11; 2/12</td>
</tr>
<tr>
<td>BTEX</td>
<td>Radiello®</td>
<td>TD/GC/MS</td>
<td>Air Toxics Inc.</td>
<td>3-7 days</td>
<td>2/11; 11/11; 2/12</td>
</tr>
<tr>
<td>VOC</td>
<td>PODs</td>
<td>TD/GC/FID</td>
<td>ERLAP</td>
<td>3-days</td>
<td>2/12</td>
</tr>
</tbody>
</table>

*IC = ion chromatography; TD = thermal desorption; GC = gas chromatography, MS = mass spectrometry; FID = flame ionization detection

Table 2. Overview of methodology quality assurance

<table>
<thead>
<tr>
<th>Species</th>
<th>Analysis group</th>
<th>Accuracy</th>
<th>Detection limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>O3</td>
<td>RTI Int.</td>
<td>15%</td>
<td>3 ppbv</td>
</tr>
<tr>
<td>NOx</td>
<td>RTI Int.</td>
<td>20%</td>
<td>0.3 ppbv</td>
</tr>
<tr>
<td>BTEX</td>
<td>Air Toxics Inc.</td>
<td>30%</td>
<td>0.1 ppbv</td>
</tr>
<tr>
<td>VOC</td>
<td>ERLAP</td>
<td>20%</td>
<td>0.1 ppbv</td>
</tr>
</tbody>
</table>

A key experimental requirement was that samplers should be deployed and retrieved at similar times, ideally simultaneously, especially for short duration samples. To achieve this objective, short deployment routes were designed, each with 3 to 5 sampling sites, thereby ensuring that the monitoring periods for each sampler were within ±15 minutes of the target start and duration times. Up to fourteen teams of trained volunteers, representing employees of the State of Wyoming, the Federal Government, Sublette County, the City of Pinedale, the University of Wyoming, and the natural gas industry, together with local citizens, carried out coordinated sampler deployment on days when meteorological forecasts predicted conditions expected to allow O3 production and/or pollutant accumulation. Consistency of handling was ensured through in-person training with respect to standardized operating procedures. Each team was supplied with a clear route map.
and easy to follow sampler-handling instructions. This approach ensured that only 1 sample out of a total of ∼400 was lost due to handling issues.

Samplers were mounted on isolated custom-installed or existing posts at ∼1.5 m above ground level. After exposure, they were prepared for analysis immediately upon receipt from the placement teams. Samplers were refrigerated overnight and were express shipped in an insulated container to the analysis laboratory (an unnecessary procedure for sorbent tubes). The week-long extended sampling period of the first O3 precursor survey yielded samplers with relatively high mass loadings of adsorbed material, such that while they were within the sampler saturation limit for BTEX, they required split flow during analysis. A reduced sampling duration was therefore adopted during the second and third surveys, to eliminate the need for split flow analysis. Prototype Pocket Diffusive (POD) samplers developed by the European Reference Laboratory of Air Pollution (ERLAP) of the European Commission (Pérez Ballesta et al., 2014) were used for VOC.

2.2 Analytical approach

Samples were analyzed following protocols recommended by the requisite sampler manufacturer. The analytical approach differed based upon the compound considered and the sample collection approach.

Ogawa samplers were used for determination of ambient mixing ratios for O3 and NOx. This sampler, developed by Koutrakis et al. (1993), has a tubular design with two chambers at each end that each hold a collection pad set within stainless steel shields behind an end cap. Each end cap has a series of holes engineered to ensure an appropriate airflow rate, and thereby diffusion, to a cellulose fiber analyte collection pad. The collection pads for O3 measurements are coated with a nitrite based solution that is oxidized to nitrate during sampling. After sampling the pad is extracted and analyzed with ion chromatography Dionex 2000i series. The nitrate ion concentration is used to determine O3. This determination relies upon calculations

Figure 2

Ozone mixing ratio (ppbv) isopleth contour plots for February 22, 2009.

Upper panel, Figure 2a: Contour plot constructed from 8 hour average O3 passive diffusion sampler data. Locations of sampling sites are indicated by pink triangles. Lower panel, Figure 2b: Contour plot is constructed from 8 hour averaged data from continuous monitors located at the sites marked by pink triangles. The dashed outline rectangle shows the area depicted in the upper panel. Wells are superimposed to aid as geographic markers.

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that consider the diffusion path (length and area of diffusion) and diffusion coefficient (determined by the collection temperature and pressure). The measurement of NOx with the Ogawa sampler follows the same principles as those for O3 measurement, albeit with different collection pads, analytical procedures and diffusion co-efficient. For determination of NOx in ambient air, Ogawa sampling pads are coated with triethanolamine. After exposure the collection pads were stored in vials prior to shipping for analysis. They were subsequently extracted and the NOx content determined by the spectrophotometric Saltzman reaction using a TCI-NOx 1000 automatic flow injection analyzer (Tokyo Kasei Kogyo). RTI International performed the analyses of Ogawa samplers and supplied us with spreadsheets of the mass loading results for each sampled adsorbent. Corresponding raw O3 and NOx mixing ratios were then calculated using the appropriate concentration conversion coefficients incorporating ambient temperature, relative humidity, and the water vapor pressure coefficient, as described by Ogawa (2006). Ambient O3 and NOx mixing ratios were derived with an uptake rate suitable for the sampling conditions with blank correction applied from five travel blanks for each survey.

Radiello® samplers (Fondazione Salvatore Maugeri (FSM)) were used to determine the ambient mixing ratios of BTEX. This sampler, developed by Cocheo et al. (1996), consists of a cylinder set within a microporous polyethylene membrane, held by a polycarbonate support plate. The sample is collected by adsorption upon 350 ± 10 mg of graphitized carbon (Carbograph 4) sorbent material. The design of the stainless steel net cylinder containing the sorbent promotes radial diffusion to the sorbent surface. After sampling the exposed sorbent cylinders were individually stored in glass vials prior to shipping. Collected analyte is recovered by thermal desorption, with analyses performed by capillary gas chromatography with MS detection. Sampling times for typical ambient environments may be up to two weeks. Given the possibility of high ambient levels in the UGRB, sampling times were reduced to 3-days to minimize the possibility of back diffusion, while allowing sufficient time for collection of a suitable quantity of the target compounds. Air Toxics Inc. performed the analyses of Radiello® samplers and supplied spreadsheets with a mass loading for each sampler. Corresponding mixing ratios were subsequently calculated using appropriate concentration conversion coefficients incorporating ambient temperature, relative humidity, and the water vapor pressure coefficient as described by FSM (2006). Ambient mixing ratios were derived with uptake rates suitable for the sampling conditions with blank correction applied from five travel blanks for each survey.

POD samplers were used for the determination of ambient mixing ratios of VOC. This was the first field deployment of POD samplers, so the results presented here are regarded as a pilot project. This sampler, developed by Pérez Ballesta (2014), is a zero equilibrium interface concentration device (Mayer et al., 2003). The POD sampler consists of a metallic diffusion body with a porosity of 20 µm and an adsorbent cartridge located inside the diffusion body. The adsorbent cartridge contains 34±1 mg of Carbopack-X 60–80 mesh (Supelco). The diffusion body is held on a support body for sampling and is hermetically closed with a PTFE cover for transport and storage. After sampling sealed samplers are shipped in sets of three within glass tubes. Collected analyte is recovered by thermal desorption, with analysis performed by capillary gas chromatography with MS detection. Sampling rates were experimentally evaluated in laboratory tests. For VOCs the effect of concentration (0.1 to 50 µg/m³ depending on the compound), temperature (-30 to 40°C), humidity (10 to 70%) and air speed (0.1 to 4 m/s) was evaluated. The sampling rate was not significantly influenced by concentration (variation <10%) humidity (≤15%) and air speed (<6%). Sampling rate was lower for compounds with the higher diffusion coefficients. Laboratory tests allowed the estimation of sampling rates for VOCs that were not evaluated, as a function of their diffusion coefficient. Ambient VOC mixing ratios were derived for thirteen compounds, with uptake rates suitable for the sampling conditions with blank correction applied from five travel blanks and five laboratory blanks.

Reported values for each sampler were calculated by applying standard uptake rates and blank corrections (based on travel blanks) to the mass loadings. Average UGRB meteorological conditions reported at WDEQ monitoring sites were used to calculate species mixing ratios. Data quality comparisons were conducted by

<table>
<thead>
<tr>
<th>Species</th>
<th>Sampler</th>
<th>Linear regression parameters</th>
<th>Survey dates (m/yy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O3</td>
<td>Ogawa</td>
<td>Cx = 0.93 Cx, b = -1.1; R² = 0.98; n = 8</td>
<td>2/09; 6/09</td>
</tr>
<tr>
<td>NOx</td>
<td>Ogawa</td>
<td>Cn = 1.02 Cn, b = 0.6; R² = 0.85; n = 18</td>
<td>2/11; 11/11; 2/12</td>
</tr>
<tr>
<td>BTEX</td>
<td>Radiello®</td>
<td>Cn = 0.93 Cn, b = 0.0; R² = 0.99; n = 120</td>
<td>2/11; 11/11; 2/12</td>
</tr>
<tr>
<td>VOC</td>
<td>PODs</td>
<td>Cn = 1.06 Cn, b = 0.0; R² = 0.99; n = 169</td>
<td>2/12</td>
</tr>
</tbody>
</table>

*O3 with Thermo Scientific 4% using UV photometric analysis; NOx with Thermo Scientific 42i using UV photometric analysis BTEX using Markes thermal desorption and Hewlett Packard MS analysis; VOC with Entech canister sampling followed by thermal desorption and FID analysis with a Perkin Elmer OPA system

1Linear regression best-fit model (y = mx + b) with y (independent variable diffusive sampler, Cx) and x (dependent variable established method, Cn). The slope (m), y-intercept (b) and coefficient of determination (R²) value for the number of paired samples (n) is also stated.

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co-located measurements, with identical sampling times, using independent methodologies. Table 3 shows linear regression results for O$_3$ and NO$_x$ from Ogawa diffusive samplers compared to averaged hourly values from WDEQ stations, and also for BTEX species from Radiello® diffusive samplers with those from UW canister measurements (Field et al., 2015). The results confirm that Ogawa and Radiello® passive samplers perform well, indicating that they can accurately assay the targeted pollutants. For VOC, excellent agreement was also found for thirteen C$_5$ to C$_8$ species mixing ratios measured by POD diffusive samplers that were measured with co-located canister sampling at thirteen sites performed during the study of Field et al. (2015) (C$_{POD}$ sampler $= 1.06$ C$_{canister}$, $R^2 = 0.99$).

### 3. Results and discussion

Summary results for each survey for O$_3$, NO$_x$ and benzene are given in Table 4. The winter survey yielded higher O$_3$ mixing ratios than that in summer. NO$_x$ mixing ratios are similar in the three winter surveys with measured values ranging from 0.1 ppbv to 16 ppbv. For BTEX surveys, benzene mixing ratios range from 0.1 to 10 ppbv. By contrast benzene peaks at over 50 ppbv during the VOC survey that was performed concurrently with VOC canister sampling (Field et al., 2015). Diffusive VOC sampling sites were selected from those used for BTEX surveys with the exception of one site which was positioned at the fence line of the water treatment facility discussed in sections 3.2 and 3.3. While Table 4 show elevated pollutant levels, spatial distributions of pollutant species can be visualized by constructing concentration contour plots of their ambient concentrations (or mixing ratios). Mixing ratio zones on such plots are defined with greater confidence in areas where the density of monitoring sites is high. Contour plots shown here were created with the Surfer® software plotting routine available from Golden Software LLC, Golden, CO. The plotting routine uses point kriging and a default linear variogram (Isaaks and Srivastava, 1989). Such plots are critically dependent upon the relationship between pollutant emissions and meteorological conditions, in particular wind speed and direction. Wind roses for all surveys are given in the supplemental materials Figure S1.

#### 3.1 Ozone

Eight-hour average O$_3$ mixing ratio data obtained for UGRB diffusive sampling surveys are plotted for February 22$^{nd}$ 2009 (9:00 to 17:00) in the contour map shown in Figure 2a. This plot indicates that on this day O$_3$ levels present throughout the Pinedale Anticline and Jonah field were elevated above the background levels observed to the west. Higher O$_3$ values likely extended into nearby areas to the northwest. During the day winds were variable with speeds less than 10 m/s.

An analogous O$_3$ contour plot extending further south, can also be constructed for the same time period (February 22, 2009) using data from continuous monitors. A special study conducted by WDEQ during this period increased the total number of O$_3$ monitors in the Pinedale Anticline and Jonah field to 21 (Environ, 2010). The data they provide allow the O$_3$ contour plot shown in Figure 2b to be constructed from hourly averaged data for the same time period as Figure 2a. The distribution patterns of O$_3$ mixing ratio in Figures 2a and 2b are similar. Furthermore, in areas where passive samplers and continuous monitors are located in close proximity, or where the spatial proximity of measurements from both techniques is high, observed O$_3$ mixing ratios are in excellent mutual agreement. The largest differences occur in areas where passive samplers and continuous monitors are not co-located and coverage is sparse. Contour plot patterns for these areas,
especially in Fig. 2b, should therefore be interpreted with caution. The greater geographic coverage provided by the continuously operating monitors allows the approximate southern boundary of elevated \( O_3 \) levels to be roughly delineated, as shown in Figure 2b. The plot confirms that on this day, high \( O_3 \) mixing ratios are essentially confined to the gas development fields and their immediate surroundings, rather than being distributed throughout the entire region.

The four panels of Figure 3 show the development of \( O_3 \) distributions constructed from the continuous monitor data at 06:00, 12:00, 17:00, and 22:00 MST on March 2, 2009. This day experienced some of the highest \( O_3 \) values during the winter of 2009. Animations of hourly \( O_3 \) mixing ratio distributions illustrate the development pattern more clearly. Higher \( O_3 \) mixing ratios, centered in particular on the Pinedale Anticline, are observed in the afternoon. Other days (not shown) exhibit similar temporal behavior, but also show slightly different \( O_3 \) spatial variability, that presumably results from small differences in the prevailing wind fields. The weak episode on February 22, 2009 (Figure 2) was centered upon the Jonah field, when winds throughout the day were generally light and variable. On March 2, 2009, winds were also variable with speeds less than 10 m/s during the morning, but became southeasterly in the late afternoon. It is possible that these southeasterlies are an incipient barrier wind that occasionally forms along the western flank of the Wind River mountains and subsequently extends over the UGRB (Emery et al., 2015). This wind results in the advection of \( O_3 \) and its precursors from source regions in the Pinedale Anticline and Jonah field towards the northwestern boundary of the basin.

The \( O_3 \) distributions on February 22, 2009 and March 2, 2009, when elevated \( O_3 \) is found largely in the Pinedale Anticline and Jonah field, are typical of those found on days with similar wind patterns, suggesting that localized production processes (Schnell et al., 2009) are dominant. Measurements of high wintertime \( O_3 \) in surrounding areas only occurs under particular wind regimes when advection transports \( O_3 \) and/or its precursors to those areas, such as during barrier wind events as noted above (Emery et al. 2015). In 2011 the observation of elevated \( O_3 \) levels at WDEQ monitoring stations in the town of Pinedale, and in undeveloped
rural areas on the northwestern perimeter of the basin, was evident when southerly wind flow occurred from areas that had earlier experienced episodic O₃ production. While meteorology remains an important factor, a lack of wintertime O₃ episodes from 2012 to 2015 is most likely due to reduced emissions from O&NG sources, from a combination of voluntary efforts by operators (e.g. leak detection and repair programs), regulatory actions (WDEQ, 2015b) and reduced explorations activities, as indicated by rig counts in the Green River Basin (Sublette, Lincoln, Sweetwater and Lincoln counties) declining from a peak of 32 in 2011 to ~14 from 2012 to 2014 (Baker Hughes, 2015).

3.2 BTEX

Passive diffusive sampling surveys of BTEX were carried out on three occasions. The first survey was performed over a one week period (2/2011), whereas surveys two (11/2011) and three (2/2012) were each of 3 days duration. Figures 4a–4e illustrate BTEX distributions in a series of iso-concentration contour maps for the third survey. The depicted third survey was dominated by northwesterly winds up to 10 m/s. Within the O&NG development areas, mixing ratios are clearly above background levels with two significant ‘hotspots’ evident. Contour plots for the other two sampling surveys (not shown) exhibit very similar mixing ratio patterns with the same two hotspots. Benzene mixing ratios are greatest (> 4 ppbv) at the more northerly hotspot (designated ‘Hotspot 1’), whereas ethylbenzene and xylenes are largest at the southerly hotspot (designated ‘Hotspot 2’), indicating different predominant emission sources at the two locations. Peak toluene mixing ratios are similar at the two hotspots, while the extent of the northern hotspot is greater.

Hotspot 1 (~42.75°N, 109.85°W) is located in the Mesa area of the Pinedale Anticline natural gas field, an area with widespread production and numerous exploration activities. Intensive drilling was occurring in this area during the survey, with some 11–16 actively operating drill rigs, powered by engines known to emit VOC. In addition, ancillary activities associated with well drilling and completion, such as flow back, are known to have high BTEX emissions (Field et al., 2015). The area has also been observed to contain...
grandfathered uncontrolled dehydration units. In sum, measurements suggest that elevated BTEX levels at this hotspot may be attributed to intensive local O&NG operations. The southerly Hotspot 2, shown in Figure 4 at 42.65°N, 109.75°W, indicates the influence of BTEX emissions from a wastewater treatment and recycling facility. While not defined as a Title V facility, it is known to be an important point source of VOC (Field et al., 2015), with a far higher emission density than elsewhere in the UGRB.

These non-uniform distributions of elevated BTEX mixing ratios illustrate the utility of detailed, high-resolution spatial measurements when evaluating emissions in O&NG development areas. For the UGRB, the origin of the southerly hotspot, the wastewater treatment facility, is now well established. Additional fence line measurements, to be reported elsewhere, performed in 2014 and 2015, utilizing passive sampling with GC-MS analysis and mobile monitoring using PTR-TOF-MS analysis, have confirmed the hotspots noted here. However, the relative contributions of the specific sources associated with gas well drilling, completion, and production operations such as those close to Hotspot 1 on the Mesa have yet to be unambiguously determined. It is clearly important that the influence, strength, and temporal behavior of emission sources are quantitatively characterized, not only to develop better emissions inventories, but to enable observed ambient levels of hazardous pollutants and their concentration gradients to be both explained and predicted. To this end we are conducting on-going investigations to better understand the importance of the role of wet gas processing at Hotspot 1, and at other locations, to ambient BTEX levels. By contrast to typical well pads, as evident in the Jonah Field, that have on site storage of produced water and condensate, those at the Pinedale Anticline are directly connected to liquids gathering facilities that transport water and condensate off site in pipelines, eliminating the need for storage tanks at well pads.

3.3. Oxides of nitrogen

Diffusive sampling surveys of NO, were performed in conjunction with BTEX measurements, for the same time periods. Nitrogen oxides are generated from internal combustion engines, and the presence of NO, in ambient air often signifies a traffic source, especially when highway vehicle densities are high (Beevers et al., 2012). Measurements in the UGRB are in line with this conclusion (Soltis and Field, 2012a), and, as samplers were placed at roadside locations, traffic influences are to be expected. Traffic surveys have shown the dominance of traffic related to O&NG activities (Field and Soltis, 2009a) with ∼70% pickup trucks and ∼30% multi-axle vehicles. Figure 4f illustrates NO, distributions as an iso-concentration contour map for the third survey, carried out in February 2012. All three surveys exhibited similar pollutant distributions and NO, mixing ratios. While two hotspots are shown, they are close to but not coincident with those for BTEX. The more northerly hotspot (NO, Hotspot 1 at 42.70N, 109.80W) is associated with the Pinedale Complex in an area known as Gobblers Knob near the junction of Paradise and North Anticline Roads. Gas compression facilities are also present in this area. The second area (NO, Hotspot 2 at 42.60N, 109.70W) includes the junctions of US Highways 191 and 351, and Middle Crest Road. The passive sampler data show that NO, mixing ratios are generally less than 10 ppbv above the background level (<1 ppbv), while those at the two hotspots are up to 20 ppbv above background.

One purpose of the construction of BTEX and NO, contour plots was to assist on-going photographic grid modeling studies designed to predict O₃ formation in the UGRB. Unfortunately, the WDEQ emissions inventory database used in these studies (Rodriguez et al. 2014) could not be evaluated or refined using the BTEX and NO, observations as it has yet to be released for external review. Rodriguez et al. (2014) report that their O₃ modeling efforts are unable to replicate episodic O₃ production, in part because the emissions database includes VOC data that appear to be an order of magnitude too low. Comparisons of ambient data measured at the University of Wyoming Boulder South Road monitoring site and the WDEQ winter emission inventory show excellent agreement in terms of relative masses of VOC (as total NMHC), n-hexane, benzene, toluene and xylenes (R² = 0.99). However if NO, values are correct then the VOC emissions rates in the 2011 WDEQ winter (February and March) inventory could be a factor of approximately 5 too low. Edwards et al. (2014) and Ahmadov et al. (2015) demonstrate that measurement based model inputs of appropriate values of VOC and NO, together with appropriate derivation of radicals for photochemical mechanisms, are critical to ensure effective modeling of wintertime O₃ in the Uintah Basin, Utah. Model development for the UGRB remains critical, despite a lack of O₃ episodes in the past few years, so that further development activities in the basin do not result in 8-hour O₃ averages that exceed the current 75 ppbv standard value, or the new standard value of 70 ppbv set in October 2015 (US EPA, 2014).

3.4. Volatile organic compounds

Diffusive sampling of VOC was also performed, in conjunction with a longer-term VOC monitoring project that included canister sampling (Field et al., 2015) at 13 UGRB monitoring sites. Diffusive sampling results from six of the sites are shown in Figure 5, from a pilot survey for prototype samplers conducted in and around the Pinedale Anticline commencing on February 14, 2012 and extending for 72 hours. This survey was dominated by northwesterly winds up to 10 m/s. Four of the sites in Figure 5 are the identified NO,
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and BTEX hotspots. Also shown are data from the WDEQ Boulder monitoring station, which typically receives air containing well-mixed O&NG emissions. A site on the heavily trafficked main street in the town of Pinedale is also included. Concentrations for four of thirteen measured VOC species are shown, selected as marker compounds because their relative abundances reflect the strengths of different emission sources. For example, the ratio by mass of \( n \)-pentane to toluene is typically about 4:1 in fugitive natural gas emissions, but only about 1:4 in condensate (Wyoming Oil and Gas Conservation Commission, 2014). While fugitive unprocessed wet natural gas emissions should match those of wet natural gas, emissions from condensate may vary depending on the adopted product handling approach and other environmental conditions. The \( i \)-pentane to \( n \)-pentane ratio (\( iC_5/nC_5 \)) can also be used to contrast areas with significant O&NG emissions from those with greater influence from traffic (Gilman et al., 2013). The \( iC_5/nC_5 \) ratio of \( \sim 1:2:1 \) (median) from the VOC survey, excluding town of Pinedale sites, indicates the dominance of O&NG emissions and is similar to that reported in natural gas (1.4:1). However while the \( iC_5/nC_5 \) ratio is almost constant (\( r^2 = 0.98 \)), that of toluene to \( n \)-pentane shows greater variation. Emissions from traffic sources within the Pinedale Anticline are reported to contribute minimally to VOC levels compared to O&NG sources (Field et al., 2015). Higher ratios of toluene to \( n \)-pentane suggest a greater contribution of emissions other than those from fugitive natural gas. Aromatic compounds appear to be relatively elevated in the Pinedale Anticline compared to measurements in the Uintah basin (Helming et al., 2014; Warneke et al., 2014), when considering ratios expressed relative to mixing ratios of alkanes. This difference is likely due to a combination of the selection of hotspot sites (closer to emission sources in the UGRB), the consistently high non-methane hydrocarbon content of natural gas in the Pinedale Anticline, the hydrocarbon product handling approach, and the density of development in the UGRB. With the exception of BTEX Hotspot 2 and the town of Pinedale site, species distributions suggest that a mix of O&NG emission sources determine the observed compound concentrations at the remaining four sites shown in Figure 5. At BTEX Hotspot 2, relatively high toluene to benzene (\( \sim 3:1 \)), and \( n \)-octane to \( n \)-pentane (\( \sim 1:1 \)) ratios represent nearby emissions rich in heavier VOC, as expected due to the close proximity of this site to a water treatment and recycling facility. By contrast, at the town of Pinedale site, low ratios for both toluene to benzene (\( \sim 1:1 \)) and \( n \)-octane to \( n \)-pentane (\( \sim 0.01:1 \)) indicate the predominance of traffic emissions, albeit at low mixing ratios due to the low traffic flows compared to more populous urban areas (Schauer et al., 2002).

4. Conclusions

Passive diffusive sampling measurements were carried out to determine spatial distributions of O\(_3\), NO\(_x\), VOC, and BTEX in the UGRB of Wyoming, where emissions are dominated by O&NG sources. Visualization of pollutant distributions, facilitated by constructing iso-concentration contour plots, enable an appreciation of geographical differences driven by contributing emission sources. Contour maps for O\(_3\) reveal locations where episodic levels of photochemically produced O\(_3\) are found in winter. Measurements from continuously operating O\(_3\) monitors, including long-term WDEQ sites, confirm the diffusive sampler O\(_3\) distribution patterns, while providing a clear resolution of the localized nature of wintertime episodes. BTEX contour maps show two hotspots with mixing ratios elevated above background. The first of these, in the Mesa area of the Pinedale Anticline, is associated with production activities, whereas the second results from emissions from a wastewater treatment and recycling facility. While NO\(_x\) mixing ratios were also elevated above background levels, two hotspots different from those for BTEX were identified, both associated with traffic emissions. Diffusive sampling of VOC supports the findings of the more extensive BTEX sampling. BTEX hotspots have minimal traffic influence, a finding supported by the observed patterns and ratios of VOC species, confirming the dominance of O&NG sources.
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Passive diffusive sampling is an inexpensive and simple-to-use measurement technique that provides valuable quantitative assessments of pollutant spatial distributions that are readily visualized by contour mapping. In addition to providing spatial distribution information such mapping techniques have the potential to support the development and evaluation of emission inventories and air quality modeling. Model output invariably forms a key factor influencing regulatory air quality management. Photochemical grid modeling approaches are reliant upon the accuracy of spatially aggregated emissions. Spatially distributed and temporally integrated ambient air quality measurements can provide supplemental information for input parameters (e.g. O₃ precursors) to assess emission inventories and air quality model simulations (e.g. O₃). The value of future diffusive air sampling studies can be enhanced by increasing both the number of reported chemical species, which for VOCs increases the utility of the data for source apportionment analysis, and the sampler distribution density, which improves the confidence of derived species spatial distributions. Besides serving as an effective tool for local and regional studies, longer term temporal monitoring is also likely to become serving more common as the technique becomes better accepted as a methodology with known, and relatively low, detection limits and measurement uncertainty.

References


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Contributions
• Contributed to conception and design: RAF, JJS
• Contributed to acquisition of data: RAF, JJS
• Contributed to analysis and interpretation of data: RAF, JJS, DCM, EG, PPB
• Drafted and/or revised the article: RAF, JJS, DCM
• Approved the submitted version for publication: RAF, JJS, DCM, EG, PPB

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Competing interests
The authors declare that they do not have competing interests.

Supplemental material

Wind roses for days with diffusive sampling of air pollutants in the UGRB at the WDEQ Boulder monitoring site are shown. These figures are shown as support for iso-contour concentration plots. doi: 10.12952/journal.elementa.000074.s001

Data accessibility statement
The data used for this article are available from the corresponding author upon request. The data for the O3i and PASQUA projects are also available from the Wyoming Department of Environmental Quality.

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