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Extensive regional atmospheric hydrocarbon pollution in the southwestern United States

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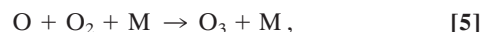
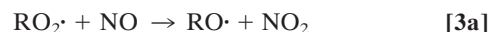
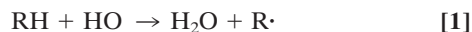
Contributed by F. Sherwood Rowland, August 15, 2003

Light alkane hydrocarbons are present in major quantities in the near-surface atmosphere of Texas, Oklahoma, and Kansas during both autumn and spring seasons. In spring 2002, maximum mixing ratios of ethane [34 parts per 10⁹ by volume (ppbv)], propane (20 ppbv), and *n*-butane (13 ppbv) were observed in north-central Texas. The elevated alkane mixing ratios are attributed to emissions from the oil and natural gas industry. Measured alkyl nitrate mixing ratios were comparable to urban smog values, indicating active photochemistry in the presence of nitrogen oxides, and therefore with abundant formation of tropospheric ozone. We estimate that 4–6 teragrams of methane are released annually within the region and represents a significant fraction of the estimated total U.S. emissions. This result suggests that total U.S. natural gas emissions may have been underestimated. Annual ethane emissions from the study region are estimated to be 0.3–0.5 teragrams.

We have performed two regional studies in different seasons of hydrocarbon and halocarbon mixing ratios in surface-level air sampled within the southwestern United States. Elevated atmospheric mixing ratios of C₁–C₄ alkanes and C₂–C₄ alkyl nitrates (RONO₂) were measured over much of the region during both studies. The alkyl nitrate enhancements show that significant photochemistry analogous to urban smog formation is occurring within the source region. The release of hydrocarbons into the atmosphere contributes to photochemical ozone (O₃) production, with related adverse health effects, reduction in plant growth, and climate change (1–3). The production, storage, and transport of oil and natural gas are a major global source of hydrocarbons into the atmosphere (4), and the southwestern states have some of the largest oil and natural gas reserves in the United States. Although the U.S. natural gas industry has been estimated to account for ≈20% of the total U.S. anthropogenic methane (CH₄) emissions (5), the global budgets of light (C₂–C₄) alkanes, including their emissions from the oil and natural gas industry, are more poorly assessed.

The C₂–C₄ alkanes have globally averaged lifetimes ranging from ≈2 months for ethane to several days for the butanes (6). Because of their short lifetimes, the atmospheric concentrations of light alkanes are variable and depend on the number and strength of nearby emission sources. By contrast, CH₄ is by far the most abundant hydrocarbon in the atmosphere, in part because of its 8-year atmospheric lifetime (7), which allows it to be widely distributed throughout both the northern and southern hemispheres. The greater reactivity of C₂–C₄ alkanes relative to CH₄ ensures that a much larger fraction of the former will react in the area where the emissions occur, making the combined C₂–C₄ alkane contributions more important for local and regional O₃ formation than the influence of the incremental local increases in CH₄.

In the troposphere, photochemical O₃ production begins with the attack of parent hydrocarbons (RH) by tropospheric hydroxyl radicals (HO), and proceeds through the following key reactions (2):



where R· is an alkyl radical, and RO₂· and RO· are its alkylperoxy and alkoxy counterparts, respectively. Hydroxyl radicals have a strong seasonal concentration dependence, peaking in the summer in temperate and polar regions (8). Therefore, if emissions are independent of season, the shorter-lived alkanes should show maximum local mixing ratios during late winter in each hemisphere and a minimum during summer when there are higher HO concentrations and longer days.

Methods

Initial surveys of the urban atmospheric composition in six U.S. cities (Chicago, Houston, New York, Oklahoma City, Salt Lake City, and San Diego) during August 1999 showed much higher mixing ratios of C₂–C₄ alkanes in Oklahoma City than in the other five cities (Fig. 1). Samples collected upwind of Oklahoma City also showed substantial alkane enhancements, suggesting a regional rather than a local urban source. We then conducted two follow-up studies between September 23–25, 2001 and April 28–May 3, 2002 to determine the geographical extent and locations of the elevated light alkane mixing ratios. During the September study, a total of 85 samples were collected in a 1,600-km-wide clover-leaf configuration centered around Oklahoma City (Fig. 2). Four research group members separately drove 800 km to the north, east, south, and west of Oklahoma City on the first day of sampling. On the second day, each drove ≈600 km along an arc to the right of the original direction, and then on the third day returned 800 km to Oklahoma City. Air samples were collected in ≈30 s by ambient pressure introduction into evacuated canisters at a height of 6 feet above ground. Sampling was carried out within open fields approximately every 80 km along the route during daylight hours (10 a.m. to 6 p.m.) to allow for expansion of the planetary boundary layer. Each sampling position was determined by using a Global Positioning Sensor (GPS). Time, date, wind direction, and distance to the nearest town were also noted for each sample. The wind during this period was predominantly from the north, and the wind speed was generally between light and moderate. During the spring 2002 study, six group members were deployed to the southwestern U.S., and a total of 261 surface air samples were collected in a grid sampling configuration at ≈80-km intervals in both north-south and east-west directions (Fig. 3). As in 2001, collections were made during daylight hours within open fields, and GPS position was noted. The 2002 sampling pattern was

Abbreviations: 2-BuONO₂, 2-butyl nitrate; 2-PrONO₂, 2-propyl nitrate; pptv, parts per 10¹² by volume; ppbv, parts per 10⁹ by volume; Tg, teragrams.

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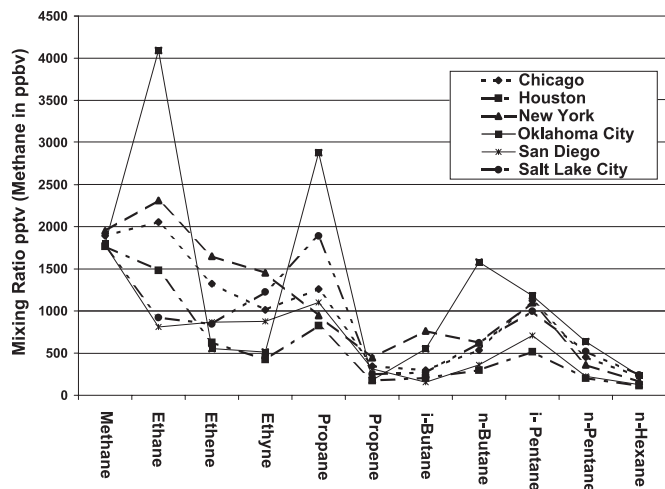


Fig. 1. Average hydrocarbon mixing ratios in six U.S. cities in August 1999.

spatially denser than in September 2001. The predominant wind direction during this spring 2002 study period was southerly.

The whole air samples were returned to our laboratory at the University of California, Irvine, and analyzed for methane, nonmethane hydrocarbons, halocarbons, and alkyl nitrates. Methane was analyzed by flame ionization detection after gas chromatographic separation. The gas chromatographic analytical system used for quantitative assay of all gases except methane pre-concentrated the sample on a stainless steel loop filled with glass beads and immersed in liquid nitrogen, with subsequent vaporization of the entire sample. The material was then flushed to a splitter that partitioned the flow stream into five different aliquots, with each separate stream directed to one of five column/detector combinations: DB-1/FID, DB5/ECD, RESTEK1701/ECD, PLOT/FID, and DB5/MS. The measurement for each individual compound was taken from the most favorable column/detector combination, but the data for those compounds cleanly identifiable on more than one combination were fully consistent with one another. The complete analytical details are available elsewhere (9).

Results

For the September 2001 study, the highest C₂-C₄ alkane mixing ratios were found in western Texas (Table 1; the ethane values

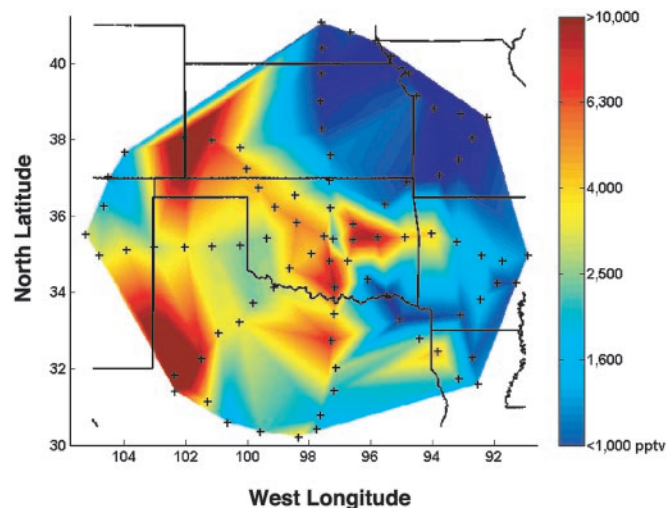


Fig. 2. Surface-level mixing ratios of ethane in the southwestern United States, September 23–25, 2001. Crosses show individual sampling locations.

are in Fig. 2). The maximum C₂-C₄ alkane mixing ratios for the 85 samples were 30–150 times higher than observed minimum regional values (Table 1). Other local maxima were found in central Oklahoma and southwestern Kansas. The propane mixing ratios correlated very well with those of ethane throughout the entire region ($r^2 = 0.97$). By comparison, *n*-butane mixing ratios did not correlate quite as well with ethane ($r^2 = 0.86$) because of the variability of alkane emission sources and the differences in atmospheric lifetimes. The mixing ratios of the light alkanes are close to seasonal background levels (Table 1) on the northern and eastern perimeters of the region (Fig. 2).

The goals of the second study of the southwestern U.S. (April–May 2002) were to determine the concentrations of light alkanes in a different season, the full extent of the area over which they are enhanced, and the source of the enhancements. A color contour plot fitted to the 261 samples reveals a larger area enhanced in the C₂-C₄ alkanes than during the previous study (Fig. 3A and B). The spring 2002 data again showed alkane hotspots in Texas, Oklahoma, and Kansas. By comparison, much lower concentrations of the light alkanes were observed to the west in New Mexico. The correlations between ethane and propane ($r^2 = 0.91$) and between ethane and *n*-butane ($r^2 = 0.84$) were comparable to the 2001 study. The methane concentrations show a pattern of enhancement similar to the C₂-C₄ alkanes (Fig. 3C). In contrast, trace gases such as ethyne did not show the same geographic distribution as the alkanes (Fig. 3D), indicating that the enhanced alkane concentrations were not associated with local or regional combustion sources.

Discussion

The alkane enhancements show a similar pattern to the locations of liquefied natural gas sites in the southwestern United States (10), which have clusters in western Texas, northern Texas, and western Oklahoma. Although there are fewer liquefied natural gas plants in Kansas compared with Texas and Oklahoma, the southerly wind direction during the sampling period is expected to have transported alkane-rich air masses north to Kansas from Texas and Oklahoma. U.S. liquefied natural gases are associated with C₁-C₈ alkane components (10). A source sample collected downwind of a working oil well with an oil storage tank showed elevated levels of CH₄ and C₂-C₇ alkanes (Table 2). The composition of hydrocarbons in this sample was similar to the composition of “associated gas” (i.e., found in conjunction with crude oil) (10, 11). “Nonassociated gas” typically contains a higher percentage of methane and lower percentages of heavier alkanes (10).

Color contour plots of the alkyl nitrate concentrations measured in these air samples show a similar geographic distribution to their parent alkanes, although in 2002 the maximum alkyl nitrate values were shifted northward. The concentrations of 2-butyl nitrate (2-BuONO₂), the major daughter nitrate of *n*-butane oxidation, are shown in Fig. 3E. Alkyl nitrates are photochemically produced from the reaction of light alkanes as shown in Eqs. 1–3. The branching ratios leading to alkyl nitrate formation (reaction 3b) are 0.073 for 2-BuONO₂ and 0.029 for 2-propyl nitrate (2-PrONO₂) (12). The branching ratio favoring alkyl nitrate formation increases with increasing carbon number (12), whereas the ambient mixing ratios of parent *n*-alkanes decrease with increasing carbon number because of lower emission ratios and/or higher chemical reactivity. The net effect of these two factors is maximum photochemical production of C₃-C₄ alkyl nitrates, in particular 2-PrONO₂ and 2-BuONO₂. In spring 2002, maximum mixing ratios of 2-PrONO₂ [51 parts per 10¹² by volume (pptv)] and 2-BuONO₂ (68 pptv) were sampled in south-central Kansas. The mean (± 1 SE) 2-PrONO₂ and 2-BuONO₂ mixing ratios were 9.2 ± 0.5 and 9.7 ± 0.7 pptv, respectively. The northerly offset of the alkyl nitrate maxima (compared with their parent *n*-alkanes) is consistent with alkyl

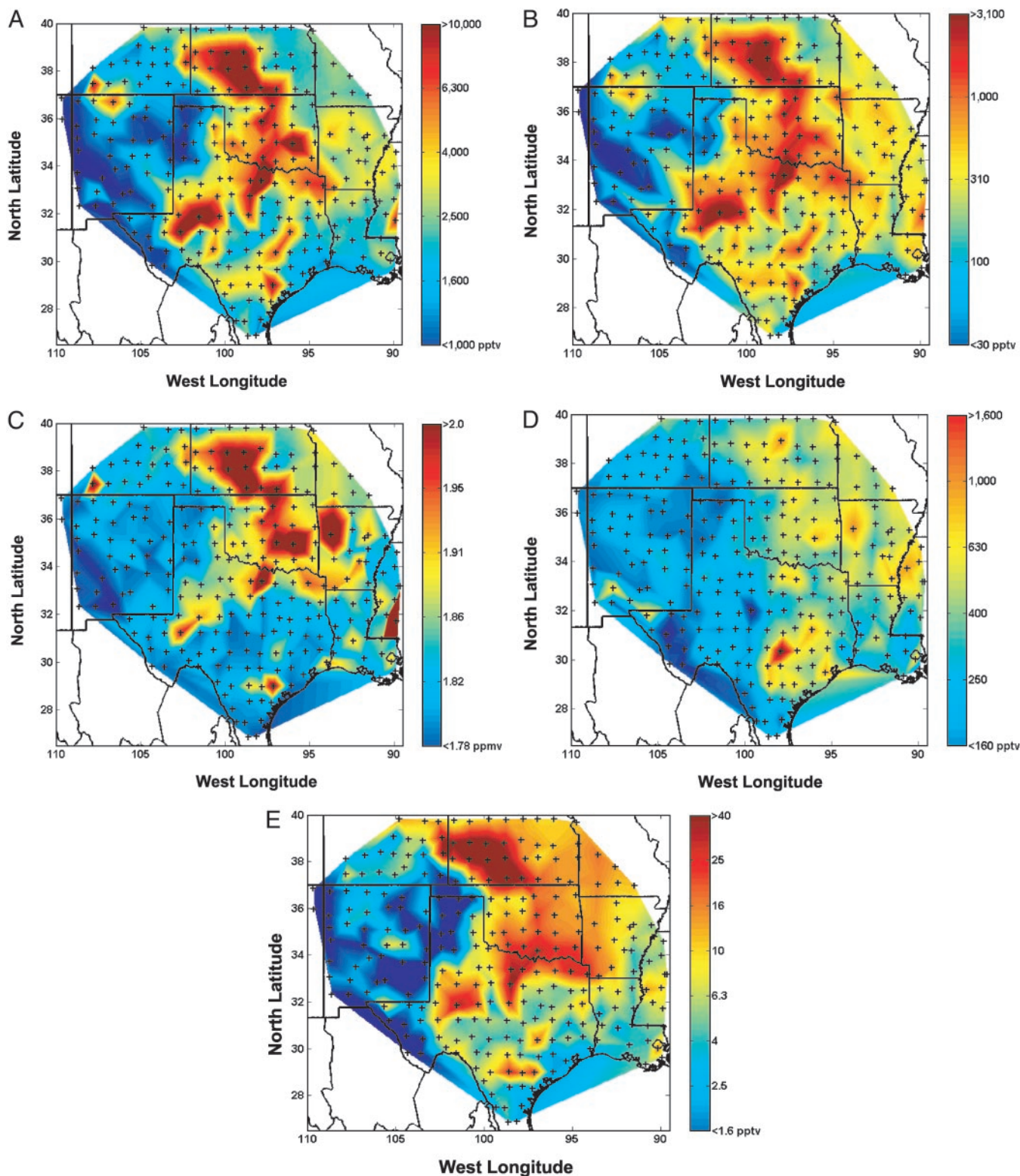


Fig. 3. Surface-level mixing ratios of ethane (A), *n*-butane (B), methane (C), ethyne (D), and 2-BuONO₂ (E) in the southwestern United States, April 28–May 3, 2002. Crosses show individual sampling locations.

nitrate production during the northerly transport of the air masses from Texas and Oklahoma to Kansas.

The maximum alkyl nitrate mixing ratios that we measured in rural Kansas are much larger than maxima we have measured even within major cities such as Karachi, Pakistan (2-PrONO₂,

34 pptv; 2-BuONO₂, 45 pptv) (13). The maximum alkyl nitrate concentrations observed in the 1999 city study (compare Fig. 1) were New York (2-PrONO₂, 25 pptv; 2-BuONO₂, 22 pptv) and Houston (2-PrONO₂, 10 pptv; 2-BuONO₂, 8 pptv). The amount of a daughter alkyl nitrate that is produced from its parent

Table 1. Light alkane mixing ratios in the southwestern United States in September 2001 (85 samples) and April–May 2002 (261 samples)

Mixing ratio	Methane, ppmv	Ethane, ppbv	Propane, ppbv	<i>n</i> -Butane, ppbv	<i>i</i> -Butane, ppbv
September 2001					
Maximum	2.10	24.5	18.9	7.0	4.7
Minimum	1.79	0.8	0.2	0.08	0.03
Mean	1.87	3.4	2.1	0.91	0.42
SE	0.01	0.4	0.3	0.13	0.07
April–May 2002					
Maximum	3.29	33.9	19.5	13.1	5.3
Minimum	1.74	0.6	0.06	0.01	0.07
Mean	1.85	3.4	1.6	0.59	0.29
SE	0.01	0.2	0.1	0.07	0.03

ppmv, Parts per 10⁶ by volume.

hydrocarbon by means of Eqs. 1–3 can be modeled for alkyl nitrates, by assuming that (i) HO reaction with the parent hydrocarbon is the rate-limiting step in photochemical alkyl nitrate formation, and (ii) the initial concentration of the alkyl nitrate is zero (14, 15). Using the average *n*-butane mixing ratio (± 1 SE) measured during the spring 2002 campaign (590 ± 70 pptv) and an estimated diurnally averaged HO concentration of $0.9 \times 10^6 \text{ mol}\cdot\text{cm}^{-3}$ gives a predicted 2-BuONO₂ mixing ratio of 7 pptv after 1 day of photochemical processing and 12 pptv after 2 days. The mean 2-BuONO₂ mixing ratio measured during the spring 2002 campaign (9.7 pptv) thus corresponds to ≈ 1.5 days of photochemical processing. These results indicate that sufficient nitrogen oxide (NO_x) levels are present for active photochemistry within the region of alkane enhancements. The enhanced alkyl nitrate concentrations also imply significant ozone formation by reactions 3a, 4, and 5, which would contribute to overall background O₃ levels in this region and further downwind. Of course, because the branching ratios leading to alkyl nitrate formation are usually < 0.1 , most of reaction 3 goes directly toward ozone formation.

The alkane mixing ratios from the 2002 study can be used to calculate rough emission estimates from the southwestern United States. Based on CH₄ mixing ratio enhancements integrated within the 2002 study area, a boundary layer height of 1 km, and a ventilation time of 2–3 days from the study area, a CH₄ emission estimate of 4–6 teragrams (Tg) per year is obtained. These calculations assume a constant emission of alkanes from the study area (720 × 820 km). The estimated boundary layer height of 1 km was selected as follows. During the airborne Pacific Exploratory Mission-Tropics B, a daytime descent near Amarillo, Texas on March 10, 1999 showed alkane enhancements peaking at the lowest sampling altitude of 200 m [ethane, 12 parts per 10⁹ by volume (ppbv); propane, 7 ppbv; *i*-butane, 1 ppbv; *n*-butane, 2 ppbv] and decreasing to background values at an altitude of ≈ 2.4 km. A boundary layer height of 1 km was selected as a midway point for the integration of measured alkane enhancements throughout the boundary layer. The ventilation time of 2–3 days was selected based on predominant surface wind speeds of 3–5 m s⁻¹, a relatively constant wind

Table 2. Hydrocarbon composition of a source sample collected in the southwestern United States downwind of an oil storage tank with a working oil well (September 2001)

Compound*	Mixing ratio, ppbv	Percent by volume
Methane	3,370	69.5 [†]
Ethane	246	10.8
Propane	224	9.9
<i>i</i> -Butane	26	1.1
<i>n</i> -Butane	115	5.1
<i>i</i> -Pentane	24	1.0
<i>n</i> -Pentane	40	1.8
<i>n</i> -Hexane	11	0.5
<i>n</i> -Heptane	4	0.2

*There were no differences in upwind or downwind alkyl nitrate concentrations (e.g., both were ≈ 0.02 ppbv for 2-BuONO₂), indicating that they were not emitted directly from the storage tank. The level of C₂H₂ in this sample was 370 pptv, comparable to ≈ 400 pptv in samples collected a few miles away. The level of other unsaturated compounds were also comparable to local background values (the sum of the mixing ratios for ethyne, ethene, propene, benzene, and toluene was < 2 ppbv).

[†]A local background CH₄ mixing ratio of 1,790 ppbv has been subtracted; background values for other gases were found to be negligible.

direction during the sampling period, and a conservative estimate of entrainment to the free troposphere.

Conclusion

By comparison to the calculated 4–6 Tg of CH₄ released annually from the study area, global natural gas drilling has been estimated to release 45 Tg of CH₄ per year (16), of which the U.S. natural gas industry alone has been credited with 6 ± 2 Tg of CH₄ per year (4). These results show that the southwestern states account for a significant portion of U.S. CH₄ release from natural gas sources. Because only 37% of the U.S. natural gas industry is located in Texas, Oklahoma, and Kansas, with another 25% offshore in the Gulf of Mexico, our results suggest that the actual CH₄ emissions from the fossil fuel industries may be larger than currently estimated. Using similar conditions to the CH₄ calculations, an emission rate of 0.3–0.5 Tg per year is calculated for ethane. By comparison, global natural gas emissions are believed to release 6 Tg of ethane yr⁻¹ out of a global ethane budget of 13–15.5 Tg per year (17, 18).

In this study, the elevated light alkane levels were measured within a region that encompasses the Anadarko Basin, which contains one of the largest natural gas and oil reserves in the continental U.S. Whereas individual sources of alkane emissions from this region (e.g., natural gas and/or oil production, natural gas storage, and perhaps natural gas seepage from the ground) are poorly quantified, sampling this region in a grid configuration was very effective in identifying locations with elevated alkane mixing ratios. Similar studies of natural gas and oil regions in other countries would help to constrain global emission estimates for methane and other light alkanes.

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