Methane emissions from the 2015 Aliso Canyon blowout in Los Angeles, CA

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Abstract: Single-point failures of the natural gas infrastructure can hamper deliberate methane emission control strategies designed to mitigate climate change. The 23 October 2015 blowout of a well connected to the Aliso Canyon underground storage facility in California resulted in a massive release of natural gas. Analysis of methane (CH_4) and ethane (C_2H_6) data from dozens of plume transects from 13 research aircraft flights between 7 Nov 2015 and 13 Feb 2016 shows atmospheric leak rates of up to 60 metric tonnes of CH_4 and 4.5 tonnes of C_2H_6 per hour. At its peak this blowout effectively doubled the CH_4 emission rate of the entire Los Angeles Basin, and in total released 97,100 tonnes of methane to the atmosphere.

Main Text:

Underground storage of large volumes of processed natural gas is used to accommodate variability in energy demand on diurnal to seasonal time scales. Underground storage facilities constitute strategic gas reserves in many countries worldwide, with a volume equal to 10% of global annual consumption (*1*). Roughly 86% of stockpiled natural gas in the U.S. is stored at high pressure in depleted subsurface oil reservoirs (*2*). The Aliso Canyon storage facility, a depleted subsurface oil reservoir in the San Fernando Valley 40 km northwest of Los Angeles, CA, has a total capacity of 4.79×10^9 m^3 at standard temperature and pressure [168 billion standard cubic feet (SCF)], of which only 86 billion SCF (the "working capacity") is routinely accessed for commercial use (*2*). It is the fourth largest facility of its kind in the U.S., accounting for 2.1% of the total U.S. natural gas storage in 2014 (*2*). Processed natural gas is composed primarily of methane (CH_4), a powerful greenhouse gas, and ethane (C_2H_6), both of which can lead to background tropospheric ozone production; at sufficiently high concentrations, natural gas leaks pose an explosion hazard and if inhaled can induce nausea, headaches, and

impaired coordination. Exposure to odorants added to natural gas, typically sulfur-containing compounds such as tetrahydrothiophene ($(CH_2)_4S$) and 2-methylpropane-2-thiol (*t*-butyl mercaptan; $(CH_3)_3CSH$) can cause short-term loss of the sense of smell, headaches, and respiratory tract irritation. Major natural gas leaks therefore can have adverse impacts on climate, air quality, and human health.

On 23 October 2015 a major natural gas leak of indeterminate size was reported in the Aliso Canyon area and was later identified as originating from SS-25, one of 115 wells connected to the subsurface storage reservoir. The SS-25 well began oil production in 1954 and was converted to a gas storage well in 1973 (*3*). Seven unsuccessful attempts to shut in the leak have been reported. A relief well intercepted the leaking pipe at a depth of ~8500 feet, below the subsurface breach; heavy fluid injection (a "bottom kill") temporarily halted the leak on 11 February, and cement injection sealed the well on 18 February 2016 (*4*).

We deployed a chemically-instrumented Mooney aircraft in 13 flights from 7 November 2015 to 13 February 2016. We measured CH_4 and C_2H_6 to quantify the atmospheric leak rate and to assess air quality downwind of the leaking well (*5*). Ground-based whole-air sampling (WAS) into stainless-steel canisters on 23 Dec 2015 followed by laboratory analysis provided chemical speciation of the leaking hydrocarbon mixture. We used the continuous airborne data and the ground-based WAS canister data to fingerprint the plume chemical composition, quantify the atmospheric leak rate, and document trends in the leak rate over time.

The airborne chemical data show the continuing transport on northerly winds of exceptionally high concentrations of CH_4 and C_2H_6 into the densely populated San Fernando Valley a few kilometers south of the leaking well (Fig. 1). The plume C_2H_6-to-CH_4 enhancement ratio (ER) derived from linear-least-squares regression fits to the continuous airborne data on 23 Dec 2015 is identical, within total uncertainties propagated by quadrature addition of errors (*6*), to the plume ER derived from WAS canister data taken at the surface on the same day (Fig. 2A).

The hydrocarbon composition of WAS canister samples taken at surface locations in the San Fernando Valley (Fig. 1) on 23 Dec 2015 (*5*) is consistent with a leak of pipeline-quality processed natural gas with a hydrocarbon composition of ~95% CH_4, ~4% C_2H_6, and ~0.3% C_3H_8 (propane) (Table S1). Plume enhancements of natural gas liquids (ethane through butanes) and condensates (pentanes and higher hydrocarbons that are liquid at ambient temperature and pressure) were detected (Table S1) and are likely responsible for reports of oily deposits on surfaces in affected residential areas downwind. Trace enhancements of benzene, toluene, ethylbenzene, and xylene isomers (the so-called BTEX compounds) were also detected at ratios of 0.001% or lower relative to CH_4 (Table S1).

Benzene is a known human carcinogen (*7*); thus population exposure to benzene from the Aliso Canyon leak has received particular attention. Composition data from the WAS canisters indicates a benzene-to-CH_4 enhancement ratio of $(5.2 \pm 0.1)\times10^{-6}$ (uncertainties throughout are ±1 standard error of the mean), broadly consistent with an ER of $\sim7\times10^{-6}$ derived from highly concentrated samples collected ~10 feet downwind of the SS-25 well site and posted online (*8*). Together these samples suggest minimal variation over time in the benzene composition of the leaking gas. Publicly available benzene data reported in near-daily 12-hour air samples (*9*) were often below the 1 nanomole/mole (part-per-billion; ppb) detection limit of the contract laboratories used for the analyses, but also show a relatively constant ER over time. We note that plume benzene enhancements can be estimated from the abundant CH_4 data by multiplying

plume CH_4 enhancements by the benzene-to-CH_4 ER determined using the research-grade WAS canister samples.

Sulfur-containing odorants were not measured, but concentrations above the odor threshold are estimated similarly (Fig. 1) from observed CH_4 enhancements by assuming an industry-standard value of ~5 parts per million of total odorant in processed natural gas (*10*).

Continuous airborne CH_4 and C_2H_6 data were taken on each flight between 11 AM and 3:30 PM local time with a resolution of 30 m along track during repeated crosswind transects at multiple altitudes from 60 to 1400 m above ground. These data define the horizontal and vertical extent of the leaking natural gas plume on each flight (Figs. 1, S1). These flights provided highly spatially resolved data from which an atmospheric mass flux can be accurately calculated (*11*) within well-defined uncertainties (*12*). Plumes from nearby landfills have low concentrations of CH_4, are clearly identified by lack of co-emitted C_2H_6, and were eliminated from further analysis. Background levels of CH_4 and C_2H_6 were measured during aircraft transects on multiple flights immediately upwind, confirming the SS-25 well as the dominant source of enhanced natural gas to the region. Operational restrictions on aircraft flight patterns were imposed by the elevated terrain at the leak site, the highly controlled airspace of the San Fernando Valley, and proximity to approach corridors of the nearby Van Nuys airport (Fig. 1). These restrictions were overcome by performing crosswind transects at multiple altitudes immediately downwind of the leak site which afforded accurate reconstruction of a vertical concentration profile, even before the plume completely mixed through the full vertical extent of the atmospheric boundary layer (*5*).

The chemical data show that the airborne sampling captured the full vertical extent of the lofted plumes on each flight day (Fig. S1). Atmospheric mass fluxes calculated from the chemical data during each downwind transect (*5*) suggest an average leak rate of 53 ± 6 tonnes of CH_4 and 3.9 ± 0.5 tonnes of C_2H_6 per hour for the first six weeks of the leak, and decreasing thereafter (Fig. 2B, Table S2). The decreasing trend beginning around the first week of December 2015 (Fig. 2B, Table S2) is consistent with decreasing reservoir pressure following withdrawal of gas, in a deliberate effort to slow the leak rate, via the other storage wells connected to the subsurface reservoir (*13*). The absence of a decrease in the leak rate after the first week of January 2016 is consistent with cessation of withdrawals to maintain a minimum working pressure in the reservoir, which throughout the leak duration supplied natural gas to customers in the greater Los Angeles Basin.

These data demonstrate the blowout of a single well in Aliso Canyon temporarily created the largest known anthropogenic point source of CH_4 in the U.S. (*14*), effectively doubling the leak rate of all other sources in the Los Angeles Basin combined (*15, 16*). Further, at its peak this leak rate exceeded that of the next largest point source in the U.S. – an underground coal mine in Alabama – by over a factor of 2 (*14*) and was a factor of 10 larger than the CH_4 leak rate reported from the Total *Elgin* rig blowout in the North Sea in 2012 (*17*). The Aliso Canyon CH_4 leak rates were comparable to total CH_4 emission rates of entire oil and gas production regions in the U.S. (*e.g.*, Barnett shale, 76 tonnes per hour (*18*); Haynesville shale, 80 tonnes per hour (*19*); Fayetteville shale, 39 tonnes per hour (*19*); northeastern Marcellus shale, 15 tonnes per hour (*19*)).

Our aircraft flights following the "bottom kill" confirmed cessation of flow from the SS-25 well on 11 February 2016 and revealed a residual leak rate of < 1 ton per hour of CH_4 (Fig. 2B, Table

S2), consistent with nonzero leak rates observed from other natural gas, oil, and petrochemical facilities nationwide (*16, 18-24*). These data show the Aliso Canyon natural gas leak duration of 112 days released a total of 97,100 tonnes (5.0 billion SCF) of CH_4 (Fig. 2C) and 7,300 tonnes of C_2H_6 to the atmosphere, equal to 24% of the CH_4 and 56% of the C_2H_6 emitted each year from all other sources in the Los Angeles Basin combined (*16*).

This CH_4 release is the second-largest of its kind recorded in the U.S., exceeded only by the 6 billion SCF of natural gas released in the collapse of an underground storage facility in Moss Bluff, TX in 2004, and greatly surpassing the 0.1 billion SCF of natural gas leaked from an underground storage facility near Hutchinson, KS in 2001 (*25*). Aliso Canyon will have by far the largest climate impact, however, as an explosion and subsequent fire during the Moss Bluff release combusted most of the leaked CH_4, immediately forming CO_2. The total release from Aliso Canyon will substantially impact the State of California greenhouse gas (GHG) emission targets for the year (*26*) and is equivalent to the annual energy sector CH_4 emissions from medium-sized EU nations (*27*). The radiative forcing from this amount of CH_4, integrated over the next 100 years, is equal to that from the annual GHG emissions from 572,000 passenger cars in the U.S. (*28*). The volume of CH_4 released represents only 3% of the total capacity of the Aliso Canyon storage facility, raising the possibility of substantial additional emissions if the leaking SS-25 well had not been sealed, or the remaining natural gas not completely withdrawn through other wells, before the reservoir had been completely exhausted to the atmosphere.

We note that the agreement reached at the 21st Conference of the Parties (COP21) to the Framework Convention on Climate Change (*29*) includes specific requirements for the Parties to account for anthropogenic GHG emissions with accuracy and completeness. In the post-COP21 world, rapid evaluation of episodic releases of GHGs like the Aliso Canyon blowout will be an essential contribution to meeting these requirements.

Our analysis quantifies a massive CH_4 release using a rapid, direct, and repeatable method with known accuracy. As such, results from this method serve as reference values for less direct and timely estimates using retrievals of surface (*30, 31*), airborne (*32*), and/or satellite remote sensing observations (*33*). For example, our airborne method offers an *a priori* estimate of the Aliso Canyon leak rates for inverse modeling methods that analyze continuous *in situ* CH_4 monitoring data from fixed ground sites (*15, 34*). This incident highlights the utility of rapid-response airborne chemical sampling method in providing an independent, time-critical, accurate, spatially and temporally resolved leak rate, as well as plume location and plume composition. Such information helps document human exposure, formulate optimal well control intervention strategies, quantify the efficacy of deliberate control measures, and assess the climate and air quality impacts of major unanticipated chemical releases to the atmosphere (*35, 36*).

Figures.

Figure 1. Aliso Canyon gas plume transport into populated areas. Airborne chemical data from multiple flights demonstrate transport into the San Fernando Valley; data from 10 November 2015 are shown. Plume enhancements above the local background (colored markers) are plotted along the flight track (white line) and can be scaled using the legends at top to yield measured CH_4, measured C_2H_6, estimated benzene based on the WAS benzene-to-CH_4 ER, and estimated total odorant assuming 5 ppm in the leaking gas.

Figure 2. Time series of the Aliso Canyon natural gas leak. A. Plume C_2H_6-to-CH_4 enhancement ratios from airborne measurements (black circles) and ground-based WAS measurements (red square). **B.** CH_4 (black) and C_2H_6 (blue) leak rates from airborne measurements. Red line is a fit to the airborne CH_4 data assuming an average leak rate from blowout to day 43, an exponential decrease between days 43 and 80, and an average leak rate thereafter to day 112 when control was restored. **C.** Total amount of CH_4 released calculated from the fit in 2B. Error bars indicate ±1 standard error of the mean.

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Supplementary Materials.

Materials and Methods

Figs S1 to S2

Tables S1 to S2

References (37-52)