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Air Pollution News: Aliso Canyon Methane Leak

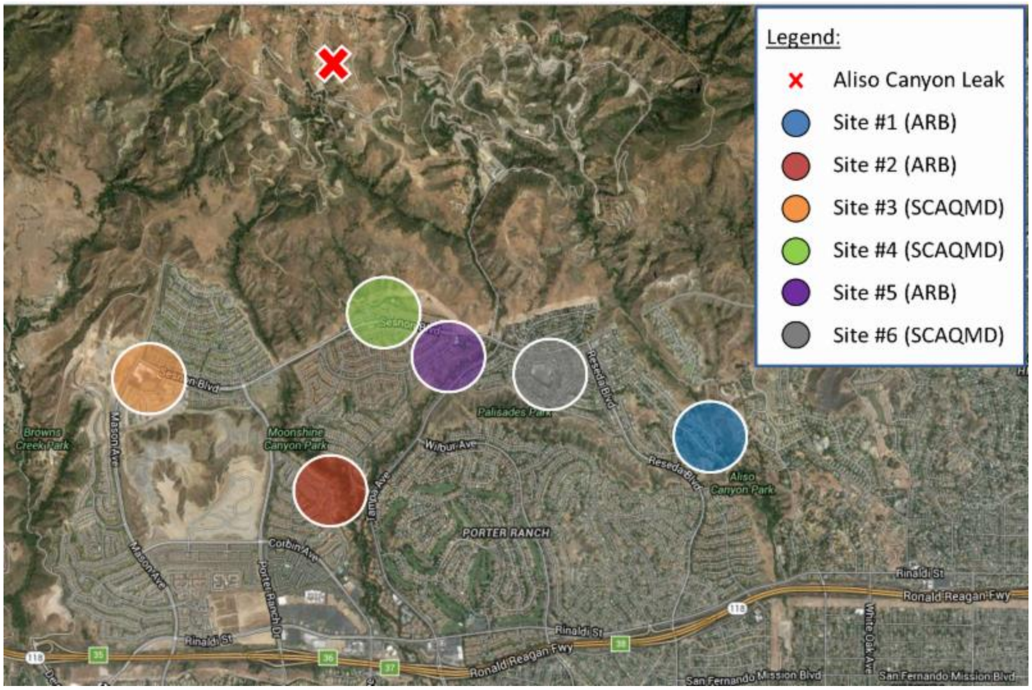
On October 23, 2015 a leak in the Aliso Canyon Natural Gas Storage facility near Los Angeles, CA was reported by its owner, Southern California Gas. The amount of methane that has been released since October has become a significant environmental disaster. In one month, the leak has released the equivalent of a quarter of the entire State of California's total methane emissions for 2015.

Infrared image of the methane plume from the Aliso Canyon natural gas leak. Image from Environmental Defense Fund. See video of flight around the plume here.

The leak resulted from a damaged well casing 500 feet underground. The difficulty in accessing the damage and making the repair means the leak is not expected to be stopped until February or March of this year.

Aside from the massive scale of the leak, nearby residents have been relocated due to headaches and nausea resulting from the strong rotten egg-like odor. The odor is due to the mercaptans and tetrahydrothiophene that are added to odorless methane to aid in leak detection. Leaked benzene, a constituent of natural gas, is the main risk to human health; however, measurements to date have not indicated dangerous levels.

Instruments placed by the California Air Resources Board (CARB) and the South Coast Air Management District (SCAQMD) in neighborhoods near the leak have reported methane concentrations up to 230 ppm. Normal background concentrations of methane are typically around 2 ppm.



Location of monitoring stations relative to the Aliso Canyon Leak. Image from the California Air Resources Board.

The leak is also being monitored from airplanes, towers, and satellites. Rough estimates show that 4.4 billion cubic feet of natural gas have been lost to date, enough to supply all of Delaware's natural gas needs for over a month.

The energy lost in the leak is significant, but more significant is its impact on climate. Methane is an extremely potent greenhouse gas. This and other natural gas leaks bring up the question, is natural gas better for the environment than coal after all?

The answer is not clear. Although burning natural gas produces about half as much carbon dioxide as coal per unit of electrical energy produced, fugitive methane emissions related to drilling, transporting and storing natural gas release significant amounts of methane. Since methane as a greenhouse gas is 86 times as potent as carbon dioxide over a 20-year time scale, the fugitive emissions call the benefits of natural gas into question.

It is estimated that global natural gas leakage rates are between 2 and 4 percent. Leakage above 3 percent would negate the climate benefits of natural gas over coal for the next two decades, making the Aliso Canyon leak part of a larger debate over our energy future.

For more information see: UC Davis and Scientific American

Featured Product: Model 408 Nitric Oxide Calibration Source

The Model 408 Nitric Oxide Calibration Source is a portable source of nitric oxide that allows one to calibrate any nitric oxide monitor. The instrument scrubs NO from ambient air and produces either zero air or air having a mixing ratio of NO in the range 10-1,000 parts-per-billion by volume (ppbv). The desired NO concentration is chosen from the easy-to-use menu using a rotary select switch. The instrument can be programmed to output up to 10 individual NO step concentrations over a chosen time interval. The total output volumetric flow rate is 3.0 L/min, and the NO mixing ratio is controlled so as to be independent of ambient temperature, pressure and humidity.

You can attach the NO Calibration Source output directly to the inlet of any nitric oxide monitor (providing that its sampling rate is less than 3.0 L/min), with the excess flow vented through an external overflow tee. Besides portability, an important advantage of the Model NO Calibration Source is that it provides a known concentration of NO in ambient air containing the same level of humidity as the air sample to be measured. The NO Calibration Source is factory calibrated against a NIST-traceable standard.

Features:

- Method for producing NO: Photolysis of N_2O at 185 nm
- N_2O conveniently provided by "Whippit" cartridges
- Output concentration: 0 and 10-1,000 ppb
- Precision and accuracy of NO output: Greater of 3 ppbv or 3% of reading
- Operating temperature range: 0 to 40 deg C
- Total output flow rate: 3 liter/min
- Rise time: < 30 s to reach 95% of selected concentration

- Diagnostic data output: R5232

For more detailed information on the Model 408 Nitric Oxide Calibration Source, see Model 408 NO Calibration Source.

Monitoring Tip: Vertical Profiling to High Altitudes Using 2B Tech Ozone Monitors

2B Tech Models 202 and 205 Ozone Monitors have been used to measure ozone to altitudes as high as 30 km in the past. Such profiles have agreed well with electrochemical ozonesondes. However, the following modifications are required to accommodate the very low temperatures and pressures encountered in the stratosphere:

- For altitudes above ~13.5 km (pressures below 15 kPa) the standard pressure sensor (Honeywell MPX5100) needs to be replaced with our high altitude upgrade sensor (Honeywell ASDX015).
- The instrument case should be enclosed in approximately 2 in (5 cm) of styrofoam or other insulation, similar to what is done for ozonesondes in order to maintain adequate internal temperature.
- The inverter that supplies high voltage to the lamp must be potted in order to prevent corona discharge breakdown at low pressures.
- As an option you might want to include a cold weather upgrade as well, which includes a heater for the lamp and air pump that operates down to 5 ^{o}C.

Please contact us if you would like our help in making modifications of your ozone monitor for high altitude measurements.

Opinion: Water Vapor Interferences in Ozone and NO_x Measurements and Inconsistencies in National Ambient Air Quality Standards (NAAQS)

There continues to be confusion in the air monitoring community about the origin of water vapor interferences in measurements of ozone and NO_x species and the consequences of various approaches taken to minimize those interferences. The aim of this brief article is to provide a better understanding of how water vapor affects analytical measurements of these pollutants and to raise the question of whether ozone and NO_x measurements for compliance monitoring should be made as mixing ratios in dry or ambient (humid) air. Another issue discussed here is whether air quality standards should be based on mixing ratios or concentrations.

Ozone by UV Absorbance. A water vapor interference in ozone measurements by UV absorbance has long been recognized. Based on the Ph.D. thesis work of Kevin Wilson (Wilson and Birks, 2006), this interference is now understood to be due principally to a refractive index effect. The interference manifests itself as an offset that occurs when there is a sudden change in humidity of sampled air. Since the 254-nm light source is not collimated, with light reflecting from the interior surfaces, the transmission of UV light through the detection cell is affected by adsorbed water layers on the interior of the cell. In order to make low ppb measurements of ozone, the flow of sample air entering the detection cell alternately goes through a solid-phase scrubber or bypasses the scrubber, providing light intensity measurements of I_o (ozone-scrubbed air) and I (unscrubbed), respectively. Unfortunately, ozone scrubbers act as a "sponge," either adsorbing water molecules from the air stream or releasing water molecules to it, depending on the past history of the scrubber. If the humidity level does not change over a long period of time, the ozone scrubber will come into equilibrium with the humidity of ambient air and no longer modulate the water vapor concentration. But if ambient humidity suddenly changes, the humidity levels within the detection cell during I and I_o measurements will differ and a false component to the ozone reading (an offset) will occur. This offset will be positive or negative, depending on the direction of humidity change. 2B Technologies solves this problem by placing a Nafion tube (our DewLine™) on the inlet of the detection cell.* Nafion (a sulfonated fluorocarbon polymer) has the property of selectively transporting water molecules across the walls of the tube at a very rapid rate. Air passing through the interior of a Nafion tube reaches the same humidity level as the surrounding air (air within the instrument case). Thus, our DewLine™ assures that air entering the detection cell is at the same humidity (approximately ambient humidity) during both I_o and I measurements of light intensity even if there is a sudden change in humidity (e.g., transitioning from a dry calibration to an ambient measurement, or an episodic change in humidity due to a weather event). No other UV-based ozone monitors make use of a Nafion tube.

Ozone by Chemiluminescence. It has long been known that one can reverse the chemistry of a conventional NO chemiluminescence monitor to measure ozone instead of NO by supplying the instrument with NO reagent gas in place of ozone. In both cases, chemiluminescence is produced in the reaction of NO with O_3 at reduced pressure. However, since water molecules quench the chemiluminescence, it is necessary to dry the sample at the entrance to the instrument. Air dryers make use of Nafion tubes, but instead of equilibrating with ambient air, they remove most of the water in the air sample. The result is that the mixing ratio (the ratio of ozone molecules to air molecules in ppb), is measured in dry rather than ambient air. Drying enhances ozone values relative to those measured by UV absorbance instruments, since by removing water vapor the ozone is concentrated by up to several percent, depending on ambient temperature and relative humidity. This water vapor interference in NO-chemiluminescence measurements of ozone was recently investigated in detail by Boylan *et al.* (2014). They found two partially offsetting factors - a signal quenching by remaining water molecules since the dryer was not 100% efficient and an enhancement in ozone mixing ratio due water vapor removal.

The Teledyne API Model T265 Chemiluminescence O_3 Analyzer was recently proposed by the U.S. Environmental Protection Agency (EPA) as a new Federal Reference Method (FRM). This instrument also dries the air sample. It is unclear from the product literature whether this new FRM measures ozone as a dry or ambient mixing ratio. If it measures the ozone mixing ratio in dry air, then there will be a few percent bias between this new FRM and the more than 1,300 Federal Equivalent Method (FEM) UV absorbance instruments in the U.S. State or Local Air Monitoring Stations (SLAMS) compliance monitoring network.

Ozone by Scrubberless UV Measurements. The new 2B Technologies Model 211 Scrubberless Ozone Monitor avoids both interferences from UV-absorbing compounds and water vapor by replacing the solid-phase scrubber in a UV absorbance instrument with a gas-phase titration of ozone with ppm levels of NO. This FEM instrument also is being considered for designation as a FRM, but no time line for consideration has been established, and it is unclear whether the

EPA will continue the evaluation now that a new FRM has been recommended.

NOx Monitors. Nitric oxide (NO) and the Criteria Pollutant NO_2 have long been measured primarily by chemiluminescence. A major disadvantage of this method for NO_2 is that it is determined by difference between NO_x and NO, where NO_x represents the sum of NO and the NO_2 converted to NO via a molybdenum or photolytic converter. Conversion efficiencies for NO_2 are significantly less than 100% and variable. Also, the method is well known to have many interferences (e.g., Beaver and Long, 2012). The Cavity Attenuated Phase Shift (CAPS) method, a variant of the cavity ring down technique, recently was developed to measure NO_2 directly, a major advantage, and instruments based on CAPS are now being marketed by several companies. However, CAPS also relies on drying of the sample air. FRM chemiluminescence measurements of NO_x species do not dry the sample air. The same question arises, as to what is the appropriate mixing ratio to report, a mixing ratio in dry or ambient air?

The new 2B Technologies Model 405 nm measures NO_2 directly in ambient air (without drying). It also has the advantage of measuring NO in addition to NO_2 by alternately adding ppm levels of ozone to convert NO to NO_2 with nearly 100% efficiency.

In our opinion, the EPA needs to clarify whether the NAAQS for gaseous pollutants, which are expressed as mixing ratios (ppb or ppm), apply to dry or ambient air. It is not uncommon for water vapor to comprise up to 4% or more of air molecules. At the level of the new 70 ppb ozone standard, this amounts to an enhanced ozone reading of 2.8 ppb if the standard is now based on dry air, an amount that can easily place a region out of compliance by making the new standard effectively 67 ppb of ambient air. It seems reasonable that the standard should continue to be a mixing ratio in ambient air since the NAAQS is established based on health effects studies in which the reported ozone values were measured in ambient air, not dry air.

NAAQS and Altitude. A related issue is whether compliance monitoring of criteria air pollutant gases should report mixing ratios (molec/molec), as done now, or concentrations (molec/vol). For example, ambient pressure in the mile-high city of Denver, CO is about ~83% of sea level. In Denver, 70 ppb of ozone has a concentration equivalent to 58 ppb in Miami, FL. In terms of an inhaled concentration of ozone, Denver is being held to a much stricter standard than lower elevation cities. EPA also notes this unresolved issue in its recent ozone risk assessment document (EPA, 2014).

The question as to whether NAAQS standards for gaseous pollutants should be based on mixing ratios or on concentrations needs to be addressed. It is noteworthy that the particulate matter standards, $PM_{2.5}$ and PM_{10}, are based on mass concentrations (mg/m^3) where the volume is the true volume (volumetric flow rate x time) at ambient temperature and pressure.

For gas-phase air quality standards to be consistent with particulate standards, the measured gas phase mixing ratios could be corrected to "equivalent ppb" by multiplying by (P/P_o) where P is ambient pressure and P_o is the pressure at sea level. Of course, a thorough review of the effects of altitude on health effects of air pollutants would be required to make this judgement, but there may not be sufficient data. In any case, it seems unlikely that the health effects of gases would scale with mixing ratio while the health effects of particles scale with concentration.

-John Birks

*Note that our DewLine™ is often referred to in EPA documents as a "drier" (meaning "dryer") even though it does not dry air; instead, it equilibrates air to a nearly constant humidity very near ambient levels just prior to entering the detection cell.

EPA (2014) Health Risk and Exposure Assessment for Ozone, Final Report, pp. 6-8/9.
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Beaver, M. and R. Long, Characterization and Development of Measurement Methods for Ambient Nitrogen Dioxide (NO_2), EPA Presentation, 16 May 2012.
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Boylan, P., D. Helmig and J. -H. Park, Characterization and Mitigation of Water Vapor Effects in the Measurement of Ozone by Chemiluminescence with Nitric Oxide (2014) *Atmos. Meas. Tech.* **7**, 1231-1244.

Wilson, K.L. and J.W. Birks (2006) Mechanism and Elimination of a Water Vapor Interference in the Measurement of Ozone by UV Absorbance, *Environ. Sci. Technol.* **40**, 6361-6367.

Please contact us for copies of these papers: johnb@twobtech.com