Measuring gases: links between cows, volcanoes and fighting terrorism

by Angelina Souren

Contrary to popular belief among many university scientists, science does not only take place within academia. Instead, it is a matter of give and take on both sides, like most good things. Many impulses for developments within academia - including funding - actually come from the "rest of the world". Herb Dempsey, who works there (at the Durham, North Carolina, office of ARCADIS), provided the inspiration for this article. Herb is very enthusiastic about open-path optics. In these techniques, the path runs through part of the atmosphere when, for instance, a beam is sent through a contaminant plume. The atmosphere thus usually replaces the (multiple-pass) cell or cuvette. It may sound easy, but involves a great deal of calculating and modeling.

One area where Herb sees possibilities for these open-path technologies is the BioWatch program, in which Herb and his colleagues are involved. Research related to biological and other terrorist attacks has been going on for many years, but was accelerated by the tragic events of September 2001. The "BioWatch" program is one of the results. It will become a warning system that samples the air in major metropolitan areas for pathogens and other substances, such as traces of explosives. daily. It will protect 80% of the population of the United States. Pilots were set up in twenty metropolitan areas in the United States last year, based on prototype equipment that was tested during the 2002 Winter Olympics. This equipment, called BASIS, almost literally "sniffs the air" (see Fitch et al., 2003). Open-path optics would allow real-time monitoring for some substances.

Let us take a quick look at some of these open path techniques. They are currently mainly used to study pollutants, meteorology and atmospheric chemistry. The latter is also a form of geochemistry, of course, and a few papers have already been published in which these techniques were applied to (bio)geochemistry closer to the earth's surface. In the future, it may be possible to track down ores (mercury fumes) and other gas or particle sources this way.

OP-FTIR: Open-path Fourier-transform Infrared
Herb and his Durham colleagues are already applying open-path optical technologies to environmental problems. One of these colleagues is Ram Hashmonay. As a post-doc at the Department of Environmental Health of the University of Washington, he and Michael Yost developed a method based on Open-Path Fourier Transform Infra-Red (OP-FTIR) spectroscopy for mapping air pollution by, for instance by hog farms. It uses a radial plume mapping (RPM) approach: non-overlapping multiple beams from a single-beam instrument. In combination with the use of a tomography algorithm, it enables them to map concentrations across a much larger area than was traditionally possible. It works from a distance (a few hundred meters) as well and is relatively easy and cheap. The instrument sends out a beam of IR light to reflectors at a distance of up to a kilometer (light from the sun is also suitable). In FTIR, the incoming signal is split in two and the length of one of the beams' pathways is slowly changed. This produces a slowly changing interferogram; a Fourier transform is used to extract the spectral distribution. From this, compounds can be identified (either through their emission or through their absorption characteristics, depending on the background) and their concentrations calculated.


cows

DOAS: differential optical absorption spectroscopy
DOAS appears to be the most popular open-path method at the moment and is quite similar to traditional spectrophotometry. DOAS is based on differences in absorption at different wavelengths. Weibring et al. (2002) wrote one of the still relatively few geochemistry papers in which open-path optical methods were applied. These authors investigated the sulfur dioxide emissions of St. Etna and Stromboli by letting a ship pass under the volcanic plumes and using DOAS to determine the concentration. Both the sun and sky radiation can act as the light source; the latter tends to be more difficult to interpret. In such a study, it is necessary to model the atmosphere to account for scattering. DOAS is


Tampo Lake crater

relatively cheap and can use UV/Vis but also IR.

DIAL: differential absorption lidar

In addition to DOAS, Weibring et al. (2002) also employed DIAL, which is faster but also more expensive. The instrument emits a laser beam and uses the beam's reflection by a reflector or backscattering by the atmosphere (clouds). The difference in absorption between two different wavelengths is then used to calculate the concentration. Initially, mainly the thickness of clouds and other atmospheric layers was measured with lidar (light detection and ranging). DIAL is now often used for ozone measurements.

TDL(A)S: tunable laser diode (absorption) spectroscopy

In The Netherlands, TDLAS recently made the news on TV. The "sniffing van" of the Energy Centre of The Netherlands (ECN) drives past farms and measures, for instance, methane production by cows. It uses a TDLAS method developed by Arjan Hensen of ECN. The Netherlands is trying to assess the effects of measures taken to reduce greenhouse gas emissions (Kyoto protocol). Eighteen other European institutes and ECN are now mapping greenhouse gas emissions associated with dairy production (MID-AIR project). ECN also studies methane emissions at landfills and NO_2 at, for instance, fertilizer plants. In TDL, the wavelength can be adjusted. ECN's TDLAS method actually is not an open-path technique: air is sucked into the van's instrument (Aerodyne Research Inc., Billerica, MA).


Mt. Vesuvius, Italy

In TDLS, a laser beam is sent out and reflected and the absorption is measured. Like DIAL, TDLS tends to be limited to the determination of one or two compounds, but new developments are making it more suitable for measuring more compounds simultaneously. TDLS is costly, but fast. Open-path TDLS does not appear to be very common yet (relatively few papers). In regular TDLS, the pressure is reduced in the cell so that the absorption lines become narrower and there is less interference (it also means that the laser can be adjusted across a small range, which diminishes noise effects). In open-path measurements at ambient pressure, the absorption line becomes a broad band. Brassington (1995), however, already gave examples in which OP-TDLS was used to measure gases like carbon monoxide, methane, ethane and ethylene and produced useful results. Brassington also mentioned stratospheric measurements (at 30 km), of which the results are good because of the low pressure at that altitude.

Biogeochemical cycles

Open-path optical methods may help determine the magnitude of all sorts of fluxes in biogeochemical cycles (such as organic volatiles released by plants). Undoubtedly, many interesting applications will follow.

This article is mainly based on a brief look at a few papers and web pages, and is not an exhaustive review. The author is a geologist and marine biogeochemist. She is the owner of SmarterScience (a consultancy and service business specialized in marine, earth and environmental sciences), board member of the Environmental Chemistry Section of KNCV (the Dutch version of ACS) and associate editor for The Geochemical News. She has not personally worked with these open-path optical methods and any errors in this article are solely hers. She can be contacted at Angie-at-smarterscience.com.

For more information:

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