

# ACTIVE OPEN-PATH SPECTROSCOPIC MEASUREMENTS OF MARINE ATMOSPHERIC BOUNDARY LAYER COMPOSITION

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Air quality in developed nations has significantly improved through regulatory action in transportation and electricity sectors [1]. In 2012, the Canadian Council of Ministers of the Environment (CCME) adopted a new national air quality management system which uses updated and more stringent Canadian Ambient Air Quality Standards (CAAQS) for ground-level O<sub>3</sub> and Particulate Matter (PM) as drivers of regulatory action [2]. The CAAQS are being expanded to include SO<sub>2</sub> and NO<sub>2</sub> at the same time as, e.g., fuel sulphur content regulations in marine transport have been reduced from 1.5% to 1.0% (2010) and further to 0.1% (2015) within Emission Control Areas (ECAs). It is in this changing regulatory framework as well as rapid economic growth (and changes to power generation, heating and transportation sectors) that air quality measurement and modeling activities now take place, requiring greater capacity and integration across the measurement and modeling communities.

With this in mind, the mobile spectrometer described below was acquired and commissioned to study atmospheric trace gas concentrations in the boundary layer, initially in Halifax. Understanding boundary layer air composition *in situ* is complementary to satellite observations, which most often detect integrated column amounts with limited or no vertical sensitivity to trace gas concentrations. As to the measurement location, while Halifax is relatively clean, it nonetheless occasionally exceeds [2] desirable 1-hour average ground level O<sub>3</sub> levels (>50 ppb) due to a combination of a rapidly changing local industry, long-range pollution transport, and biogenic precursors of O<sub>3</sub> formation from surrounding forests. The relative

contribution of each of these factors to local air quality is an open research question.

## MEASUREMENT TECHNIQUE

Boundary layer trace gas concentrations are derived from infrared absorption spectra recorded by an Open-Path Fourier Transform Infrared (OP-FTIR) spectrometer. FTIR spectroscopy has a long history of application in ground- and satellite-based observations of atmospheric composition due to the numerous and strong mid-infrared (~2 to ~20 μm) rotational-vibrational absorption features of gases with a permanent dipole moment. In solar absorption FTIR spectroscopy, the Sun is the infrared source and absorption spectra reflect an underlying vertical distribution of trace gases in a slant column through the entire atmosphere (0-100 km). The open-path configuration described here uses an active broadband IR source (Fig. 1) which is modulated by a Fourier transform spectrometer and then passed through a second beamsplitter to a modified transmitting 12" telescope [3]. The collimated IR beam traverses a horizontal open path of ~500 m (one-way) before encountering a retroreflecting corner cube array, which doubles the optical path and target trace gas absorption and sends the beam back to the same telescope, now serving as a receiving unit. The second beamsplitter passes the returning radiation to a broadband IR detector, in our system a Mercury Cadmium Telluride (MCT) element with Stirling cycle cryocooling, which eliminates the need for liquid nitrogen in field applications and greatly increases system mobility. Each pass through the second beamsplitter reduces the signal by 50%, which is a trade-off in the much simplified monostatic configuration that employs a single transmitting and receiving telescope, a two-way open path and a collocated detector, as well as completely passive non-translating retroreflecting optics. Under normal conditions, the system can be unpacked and aligned in the field in less than 1 hour.

Electronic signal processing ensures that only the modulated returning radiation is detected, while unmodulated emitted atmospheric radiation in the same wavelength range as the IR source is ignored. In practice the separation between the telescope and retroreflector must



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## SUMMARY

We commissioned a mobile spectrometer to study atmospheric trace gas composition in the boundary layer. Technique details and first diurnal trace gas concentrations are presented.

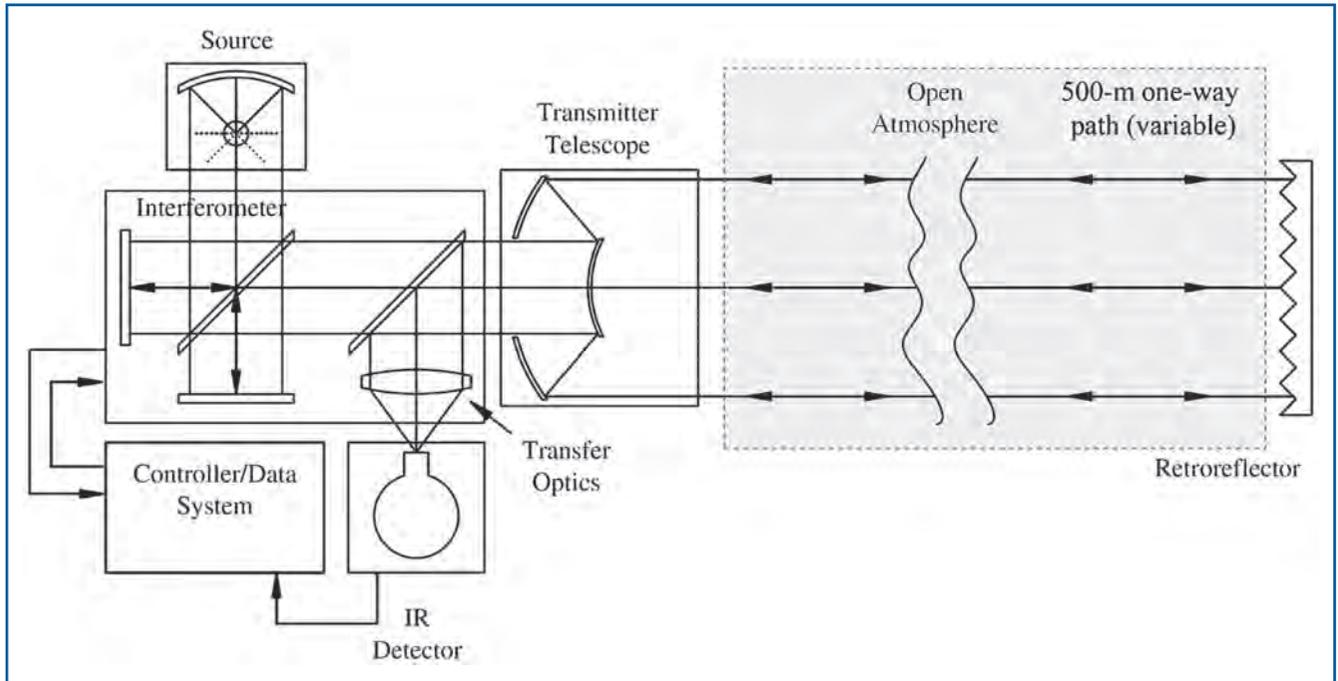


Fig. 1 Components of an Open Path Fourier Transform Infrared (OP-FTIR) system in a monostatic configuration with a single receiving and transmitting telescope and two beamsplitters (image adapted from [3]).

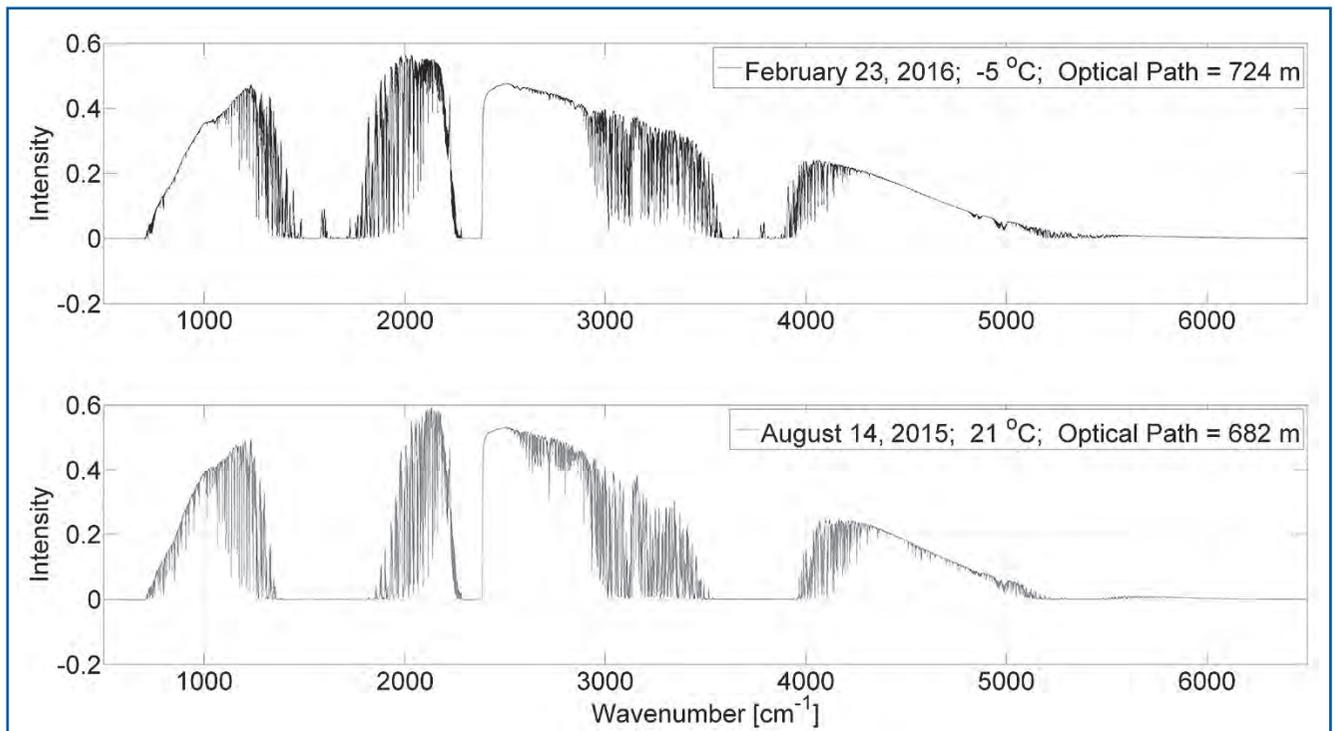


Fig. 2 Sample measured open-path spectra in winter and summer, showing saturated absorption due to water (1500-1800 cm<sup>-1</sup> and 3500-3800 cm<sup>-1</sup>) and carbon dioxide (2300 cm<sup>-1</sup>).

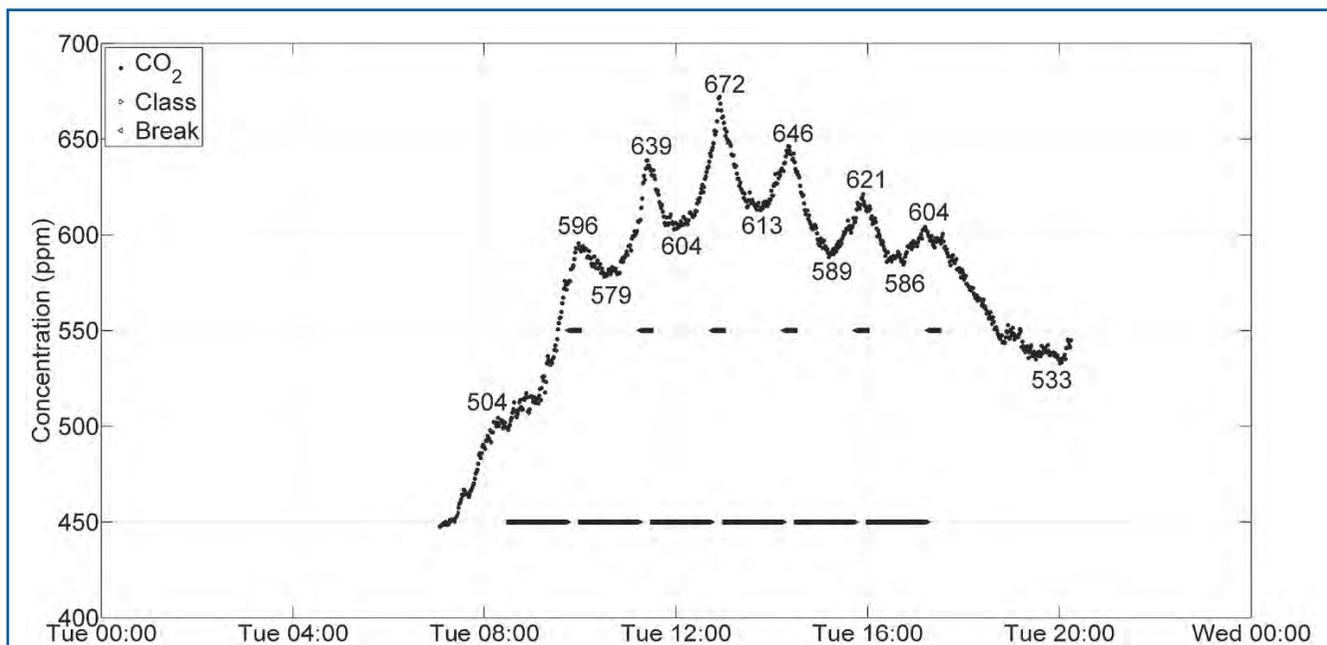


Fig. 3 Retrieved carbon dioxide concentration over a 30-m one-way open path in an indoor campus environment (November 10, 2015). 15-minute class breaks and 75-minute class times are shown with left and right triangles, respectively.

be large enough that sufficient absorption for detection can be achieved, which is different for each target trace gas. One-way open paths larger than 500 m lead to diminishing returns due to imperfect beam collimation, which in our system leads to overfilling the retroreflector array at and beyond separations of about 300 m. Moreover, with increasing atmospheric path, strong interfering absorption from water vapour and carbon dioxide increases (Fig. 2), reducing overall signal levels in the spectrum and strongly overlapping other target gas absorptions.

As with the solar absorption technique, open-path absorption spectra contain the fingerprints of dozens of air quality (AQ) and greenhouse gases (GHGs) present in detectable quantities. The spectra represent a permanent record of atmospheric composition in the open path sampled and “new” gases may be analyzed at any point in the future from the appropriate spectral region. One advantage of the open-path configuration is that the ~500 m horizontal path is well defined spatially in the planetary boundary layer, and bridges the spatial scales of *in situ* point measurements on one hand and space-based satellite measurements on the other. Another major advantage of an active source system is that measurements are possible during both sunny and cloudy atmospheric conditions, during both day and night. By definition, solar absorption FTIR spectroscopy is possible only during sunny conditions, which leads to a dry, sunny, daytime sampling bias in trace gas concentrations. Due to weak scattering of infrared radiation by condensed phase fog and rain droplets in the beam, we have

also made successful measurements during light fog and rain, which opens the possibility of studying heterogeneous atmospheric chemistry processes. Finally, the maximum spectral resolution of our system is  $0.5 \text{ cm}^{-1}$ , as is appropriate for sampling strongly Lorentz-broadened rotational-vibrational gas absorption features at 1 atm. This translates into fast acquisition speeds, up to a maximum of 5 Hz. To improve signal to noise ratios, we co-add 240 interferograms operating at 4 Hz to produce a single spectrum once per minute when sampling ambient atmospheric conditions.

Trace gas concentrations are derived from transmittance spectra through an iterative fitting process that minimizes a least squares cost function between measured and calculated spectra, taking into account target and interfering gas absorptions, spectrum baseline shape, as well as instrumental line shape parameters describing line broadening and asymmetry under both ideal and real spectrometer conditions [4]. The forward spectral model does not assume linearity in Beer’s Law for absorbance vs. concentration, meaning that both weakly and strongly absorbing spectral features can be used in the analysis. Forward spectra are either calculated based on temperature- and pressure-dependent line-by-line absorption coefficients from the HITRAN database [5] or are based on measured reference spectra, e.g., from the PNNL reference library [6]. The inverse result is not unique because of noise in the spectra and represents the most probable set of trace gas concentrations, baseline coefficients and instrumental parameters given the measured spectrum. Retrieval pressures and

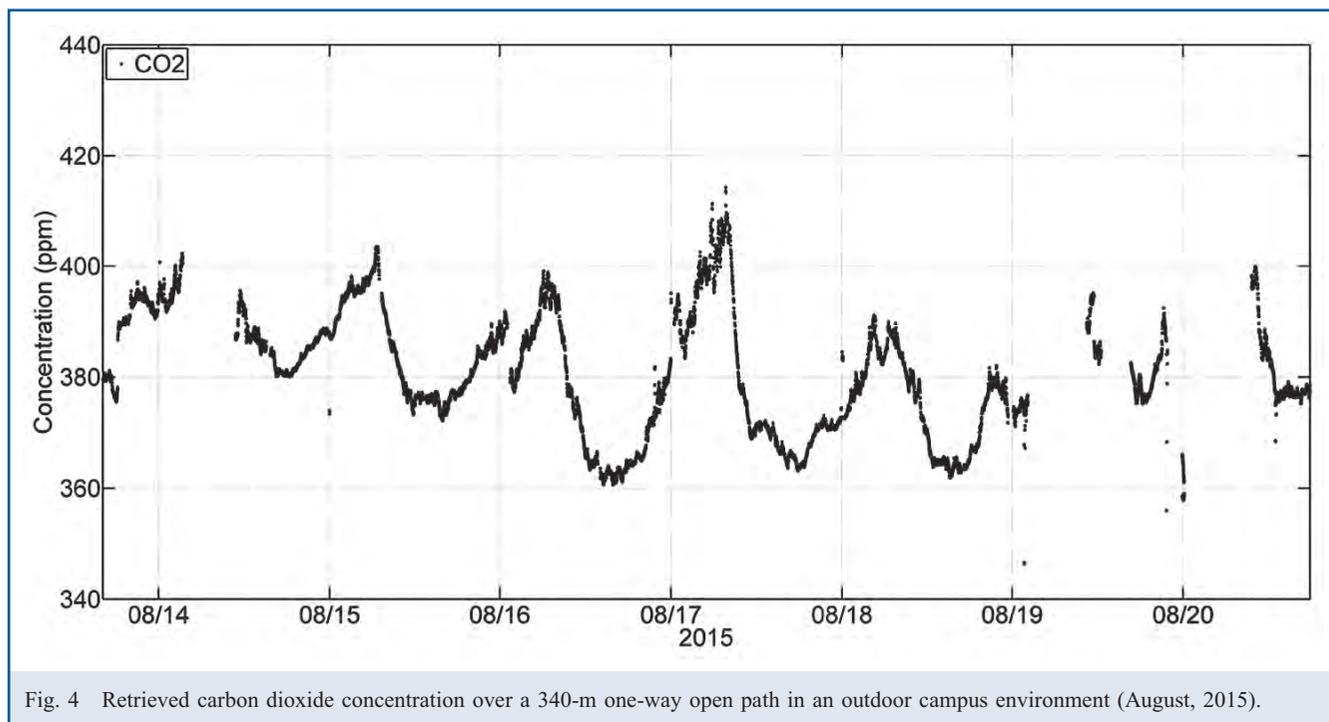


Fig. 4 Retrieved carbon dioxide concentration over a 340-m one-way open path in an outdoor campus environment (August, 2015).

temperatures are measured at one point as close as possible to the open path sampled.

### FIRST RESULTS

To date, we have conducted field campaigns in Halifax Harbour, on campus (outdoors and indoors), near traffic emission sources, as well as in coastal forest and Nova Scotia wildfire-influenced environments. One-way atmospheric open paths ranged from 30-500 m and measurements lasted from just 2 hours to 6 weeks. Figure 3 illustrates the sensitivity of our measurement technique and shows retrieved carbon dioxide concentrations over a 30-m open path in an indoor campus environment on November 10, 2015. The space sampled is a three-storey Atrium where students gather on the ground floor during class breaks, while our measurements are sampling the air above them from the second floor balconies. The concentration of CO<sub>2</sub> is lowest early in the morning, but – as expected – still 50 ppb higher than ambient outdoor CO<sub>2</sub> levels of 400 ppm in a global annual mean. Gradually, CO<sub>2</sub> levels rise and peak just after noon at ~700 ppm, then begin to taper off again around 8 PM. Health Canada sets a CO<sub>2</sub> exposure limit at 3500 ppm and CO<sub>2</sub> levels below 1000 ppm in occupied spaces indicate good air quality and ventilation. The comb-shaped pattern of pronounced CO<sub>2</sub> peaks correlates extremely well with 15-minute class breaks shown with short dashes on the 550 ppm line. During class times, shown with long dashes on the 450 ppm line, the Atrium occupancy is reduced, leading to a quick reduction in CO<sub>2</sub> levels due to efficient ventilation.

Figure 4 shows ambient outdoor carbon dioxide concentrations over the course of a week of nearly continuous observations on campus. In August, average concentrations are below 400 ppm, as expected for northern hemisphere mid-latitudes, which experience a minimum in CO<sub>2</sub> concentration at this time due to strong plant growth and the associated CO<sub>2</sub> drawdown. (The peak-to-peak amplitude in the CO<sub>2</sub> seasonal cycle at 45°N is ~10 ppm.) Superimposed on the average concentration are strong diurnal variations due to daytime photosynthesis (consumes CO<sub>2</sub>) and nighttime respiration (releases CO<sub>2</sub>). Indeed, our measurements indicate decreasing CO<sub>2</sub> levels from sunrise until sunset and increasing CO<sub>2</sub> levels from sunset until sunrise. Each day is characterized by slightly different levels of photosynthesis and respiration, with unclear results due to fog and rain on August 19<sup>th</sup> and 20<sup>th</sup>. Overall reasonable results of our indoor and outdoor CO<sub>2</sub> tests increase confidence in our spectral measurement and trace gas retrieval process.

### SUMMARY AND FUTURE WORK

As part of a new research program dedicated to understanding atmospheric composition, we have initiated measurements of marine boundary layer trace gases using the active source technique of Open-Path Fourier Transform Infrared Spectroscopy (OP-FTIR). First test results with indoor and outdoor CO<sub>2</sub> concentrations show reasonable and expected patterns of temporal variation. The recently acquired system (2015) significantly expands the measurement capability of atmospheric trace gases in Halifax and in Atlantic Canada. A long-term

marine boundary layer composition observatory is being designed to house the instrument and make automatic measurements when weather conditions permit. The retrieval process is being optimized to robustly target greenhouse gases (CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O), ozone and its precursors (CO, NO<sub>x</sub> and many VOCs), trace gases implicated in particle formation (SO<sub>2</sub>, HNO<sub>3</sub>, NH<sub>3</sub>), and other IR-active species permanently imprinted in stored absorption spectra above detection limits. A future focus of measurements and analysis will be the quantification of shipping emissions' contributions to Halifax ambient air quality.

#### ACKNOWLEDGEMENTS

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