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Solar absorption infrared spectroscopic measurements over Mexico City: Methane enhancements

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RESUMEN

En este trabajo se describe el experimento para realizar mediciones espectroscópicas de absorción solar en el infrarrojo desde el observatorio atmosférico de la Universidad Nacional Autónoma de México (UNAM), ubicado en el campus de Ciudad Universitaria en la ciudad de México. El espectrofotómetro por transformada de Fourier en el infrarrojo (FTIR, por sus siglas en inglés) opera con el rastreador solar desde junio de 2010, y a partir de los espectros medidos se calculan las densidades totales de columna de varios gases atmosféricos. Se presentan los resultados para el metano (CH_4), un contaminante que participa en la formación de ozono y que es importante como gas de efecto invernadero. Las columnas totales obtenidas con alta resolución temporal muestran gran dispersión y variabilidad diaria. Para los análisis que comprenden el periodo junio de 2010 a diciembre de 2011 se obtuvo un valor promedio de 2.88×10^{19} moléculas/cm^2 (1.829 ppm) con un intervalo de confianza del 95% entre las 2.62 y 3.14×10^{19} moléculas/cm^2. No se puede identificar un ciclo anual claro de los promedios mensuales, lo cual sugiere una afectación significativa de la concentración natural de fondo como resultado de las emisiones locales. Se presentan algunos días con aumentos extraordinarios, y un análisis sencillo de las trayectorias apunta a una dirección predominante desde el noreste del sitio de mediciones. Sin embargo, es probable que las masas contaminadas con metano que pasan sobre el observatorio atmosférico de la UNAM se originen no en una sino en varias fuentes distribuidas por la ciudad de México. Se requiere análisis más detallado de la dinámica de estas masas de aire mediante modelación.

ABSTRACT

In this work, the experiment for performing solar-absorption infrared measurements from the atmospheric observatory of the Universidad Nacional Autónoma de México (UNAM) located at the university campus in Mexico City is described. The Fourier transform infrared (FTIR) spectrometer and solar-tracking system have been operating since June 2010, and from the recorded spectra the total column amounts of several atmospheric gases can be derived. The current study presents the results obtained for methane (CH_4), an important pollutant involved in ozone production and a rapidly increasing greenhouse gas. The total column amounts, retrieved with high temporal resolution, present a large dispersion and day-to-day variability. A mean value of 2.88×10^{19} molecules/cm^2 (1.829 ppm), with a 95% confidence interval between 2.62 and 3.14×10^{19} molecules/cm^2, has been obtained for the period from June 2010 to December 2011. No clear annual cycle can be determined from the monthly means due to the large variability in the measurements, suggesting a significant effect of local emissions on the natural background concentrations. Some days with extraordinary enhancements are presented and a simple back trajectory analysis points to a predominant source direction from the northeast of the measurement site. The methane-contaminated air masses passing over the UNAM atmospheric observatory, however, originate presumably not from one but several dispersed sources. A more detailed analysis with modeling of the dynamics of these air masses is required.

Keywords: FTIR spectroscopy, solar absorption, inverse theory, methane.

1. Introduction

Solar absorption infrared spectroscopy is a remote sensing technique, which has been used with increasing interest to determine changes in the composition of the atmosphere. It is based on the measurement of direct solar radiation in the infrared part of the spectrum to derive the total integrated column amount of individual gases, which absorb part of the light along the optical path. A Fourier transform infrared spectrometer (FTIR) in conjunction with a solar-tracker, a device that follows the sun and directs the radiation into the spectrometer, serve to record the infrared spectra. Instruments with enough spectral resolution, such as those participating in the Network for the Detection of Atmospheric Composition Change (NDACC, http://www.acd.ucar.edu/irwg/) have the possibility to report vertical columns of gases such as O_3, HNO_3, HCl, HF, CO, N_2O, CH_4, HCN, C_2H_6 and $ClONO_2$. At first, these observations were aimed at understanding the chemistry and evolution of the ozone layer but the objectives of the network has widened to other areas of research. The Total Carbon Column Observing Network (TCCON, http://www.tccon.caltech.edu/), on the other hand, is focused on deriving accurate and precise column-averaged abundances of greenhouse gases mainly involved in carbon chemistry. Data from the various NDACC and TCCON sites operating instruments of this kind also have been widely used to validate column amounts measured with other techniques (Rinsland *et al.*, 2006; Wiacek *et al.*, 2007; Sepúlveda *et al.*, 2012; Viatte *et al.*, 2011a) and from satellite instruments (Vigouroux *et al.*, 2007; Bergamaschi *et al.*, 2009; Stremme *et al.*, 2012; Buchwitz *et al.*, 2013). FTIR spectrometers with lower spectral resolution also have been employed with other advantages such as lower-cost and higher temporal resolution (Stremme *et al.*, 2009; Viatte *et al.*, 2011b; Gisi *et al.*, 2012).

Methane is the second most important greenhouse gas influenced by human activities after carbon dioxide, which in a 20-year time horizon has a global warming potential 84 times greater than CO_2 (Prather *et al.*, 2012). With a lifetime of 12 years, defined mostly by its reaction with the OH radical, methane is considered together with tropospheric ozone and black carbon, one of the short-lived climate forcers (SLCF) thought to account for 40-45% of the anthropogenic radiative forcing. Thus, reducing emissions of SLCF could significantly slow the warming of the atmosphere according to recent studies (Bond *et al.*, 2013; IGSD, 2013). The radiative forcing of methane alone was estimated to be 0.48 [0.43 to 0.53] W/m^2 in 2011, which is about 26% of the radiative forcing due to CO_2 (IPCC, 2013). CH_4 emissions are, however, still increasing and could accelerate with current interests to exploit natural gas reserves.

In the past decade, the main anthropogenic sources were agriculture and waste, fossil fuels and biomass burning (including biofuels) with 209, 96 and 30 $Tg(CH_4)\ yr^{-1}$, respectively. These include rice-paddies agriculture, ruminant animals, sewage and waste, landfills, and fossil fuel extraction, storage, transformation, transportation and use (coal mining, gas and oil industries). Natural sources, which account for 35-50% of the total global emissions, are dominated by wetlands, which are highly sensitive to climate change and variability. The global methane concentration has increased by a factor of 2.5 since preindustrial times, from 720 ppb in 1750 to 1803 ppb in 2011, and has been steadily increasing at a rate of 4-5 ppb yr^{-1} in recent years (Sussmann *et al.*, 2012).

In this work, we have used the solar absorption infrared spectroscopic technique to retrieve methane column amounts over Mexico City. Due to the importance of this gas and because its sources in most cities are poorly quantified, the total column of methane is studied above the Mexico City metropolitan area (MCMA), one of the most densely populated areas of the world. There are important sources that could contribute to the methane abundance above the measurement site, such as water treatment plants, landfills, the sewage system, and the transportation of natural gas used in households and industry, delivered both by trucks and a complex pipe system. Another source that can contribute to methane enhancements in the air is biomass burnings in the surrounding areas and the transport of polluted air from the north of the city, where large industrial areas are located. The MCMA is surrounded by hills and mountains except to the north, forcing polluted air masses to stay over the city. A recent study suggests that methane emissions in large urban areas could be as high as twice from what is reported by the official inventory (Wunch *et al.*, 2009).

2. Instrumental set-up

The solar-absorption infrared spectrometer is located at the atmospheric observatory of the Universidad