

Open-path FTIR spectroscopic studies of the trace gases over Mexico City

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A long open-path Fourier transform infrared (OP-FTIR) spectrometer was used to detect and monitor the concentrations of the main gaseous pollutants near downtown Mexico City. The modulated infrared beam, with a spectral resolution of 0.5 cm^{-1} , was transmitted and collected by a pair of Cassegrainian telescopes after traveling 426 m horizontally across the atmosphere. The concentrations from the spectra were retrieved by a classical least-squares regression using measured, when available, and synthetically generated spectra as references. Results are presented on measurements carried out during February 2002. The concentration profiles of acetylene, ethylene, ethane, propane, and methane are reported for the first time in the region with a high temporal resolution. The data are coupled with meteorological information so that rose-wind generation is performed and the possible common sources for these compounds are analyzed and discussed.

Introduction

The Mexico City metropolitan area (MCMA), like many other megacities in the world, suffers from air quality problems caused mainly by the abundant emissions of volatile organic compounds (VOCs) and nitrogen oxides (NO_x) into the atmosphere.^{1–3} In 1998, the local emissions inventory⁴ reported a contribution only by mobile sources of 187773 and 165838 tons of these group of compounds per year, respectively. These quantities represent 80% from all the NO_x and 40% of all the hydrocarbons emitted within the metropolitan basin. The importance of considering specific information about the individual VOCs in order to design more effective control strategies has been addressed.⁵ The relative ozone-forming potentials of the hundreds of different VOCs emitted by anthropogenic activities, as well as the emission profiles of the individual sources, need to be appropriately known for establishing efficient regulations which will result in cost-effective reductions.⁶

Open-path Fourier transform spectroscopy (OP-FTIR) is a reliable, fast, and accurate analytical method used in recent years for measuring atmospheric gases^{7–9} and has increasingly been accepted as a monitoring tool by different environmental agencies.^{10–12} The OP-FTIR is an optical remote sensing technique, which consists of transmitting an infrared beam several hundred meters across the atmosphere in order to spectroscopically detect absorption by individual gases. Among the various applications it has successfully been used to measure volatile organic compounds in traffic exhaust,^{13–15} to estimate emission fluxes in different environments,^{16–19} to perform biomass burning studies,²⁰ and to analyze smog episodes in urban areas.²¹

In this contribution, an OP-FTIR instrument was operated near downtown Mexico City and the time series of specific hydrocarbons are reported. The

diurnal patterns of important ozone precursors such as acetylene and ethylene are discussed as well as the behavior of the saturated compounds (methane, ethane and propane) regarding their possible sources in the area. The measurements were carried out near downtown Mexico City, next to one of the 32 stations from a local network of atmospheric monitoring (RAMA): Merced, at $19^\circ 24' 27''\text{N}$, $99^\circ 7' 15''\text{W}$, $\sim 2240\text{ masl}$. The results presented in this work are based on measurement data acquired during February of 2002, corresponding to the dry season and distinguished by low temperatures and frequent thermal inversions.

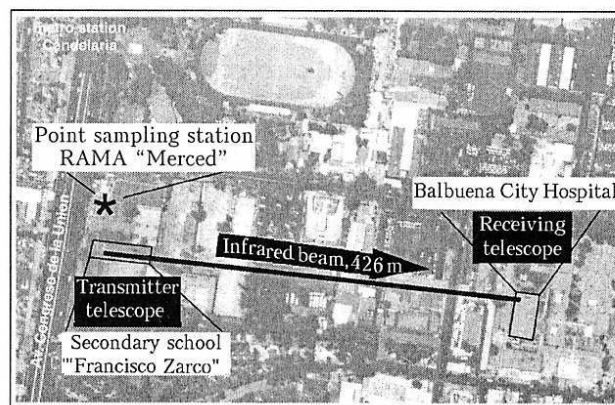


Fig. 1. Areal photograph of the measuring site showing the IR beam trajectory (line) and the point sampling station (asterisk).

In the aerial photograph shown in Fig. 1, one can see the optical remote sensor (line) going from the roof of a secondary school to a city hospital. The point sampling station is marked with an asterisk. The infrared beam traveled horizontally at about 20 m above the surface reaching an optical path of 426 m. This urban site is surrounded by several avenues, parking lots, and some green areas and can be

characterized by having intense vehicular and commercial activity. There are several markets, shops, and cooking establishments in the vicinity. An important bus station is located 1 km to the northeast and the only airport of the MCMA is approximately 3 km to the east.

Experimental

The instrument used for measuring the atmospheric gases along an open path is shown in Fig. 2. It consists of a Fourier transform infrared spectrometer (Nicolet®, maximum unapodized resolution of 0.125 cm^{-1}), equipped with a ZnSe beamsplitter covering a spectral range of $600\text{--}4000\text{ cm}^{-1}$. The modulated beam is sent across the atmosphere by means of an optical transfer bench and a Cassegrainian-type telescope. All mirrors are made of polished aluminum with silicon oxide coatings and the telescope's field mirror has a diameter of 30 cm. At the receiver end, an identical telescope collects the radiation and focuses it onto a liquid-nitrogen cooled MCT (mercury cadmium telluride) detector. The entire arrangement was constructed by Industrial Monitor and Control Corp. (IMACC, Austin TX) and its bistatic design is favored from the fact that no infrared interferences from the background affect the signal, however, a cable is needed to connect the detector with the spectrometer.

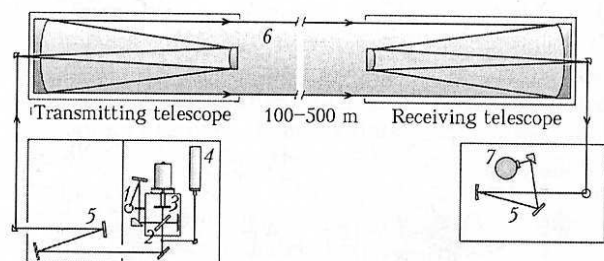


Fig. 2. Optical arrangement of the open-path FTIR spectrometer: infrared source 1, beamsplitter 2, Michelson interferometer 3, He-Ne laser 4, transfer optics 5, modulated IR beam 6, MCT detector 7.

The acquisition system was set to co-add 179 interferograms in order to have one transmission spectrum stored every five minutes in the computer. The corresponding spectrum in absorbance was obtained by using an artificially generated background and the trace-gas concentrations were then retrieved running a CLS (classical least squares) regression on nearly real-time scale. Both measured and calculated reference spectra were used for the analysis, depending on availability and reliability. The synthetic references were generated using the E-Trans code (Ontar Corp. North Andover, MA) and the molecular parameters from the HITRAN database.²² All measurements in this work were performed with the spectral resolution of 0.5 cm^{-1} and the optical path was set at 426 m. This distance was determined by the geo-referenced image (0.5 m resolution) shown in Fig. 1.

Results and discussion

Apart from the criteria, pollutants such as carbon monoxide, nitrogen oxides, and ozone, which are routinely monitored for evaluating pollution levels in Mexico City, the diurnal cycles of many other trace gases have been obtained with the OP-FTIR spectrometer. As an example, the time series of several hydrocarbons are presented in Fig. 3. The curves show 15-minute averages of the retrieved concentrations and correspond to the week of the 1–7 of February, 2002. For Julian day 35, which is a Monday, there is a clear growth in the observed carbon monoxide, acetylene, and ethylene emissions as a result of the increased vehicular activity. The peak concentration for these gases during weekdays appears at around 7:30 LST. Acetylene is known to be a main product of internal-combustion engines and since it possesses a much longer lifetime than ethylene, it can be considered a tracer for automotive activity. The reactivity of these hydrocarbons in terms of reaction rate constants, lifetimes, and ozone-forming potentials are given in Table 1.²³ Exhaust emission studies of motor vehicles have been done previously in the MCMA using gas chromatographic methods.^{24,25}

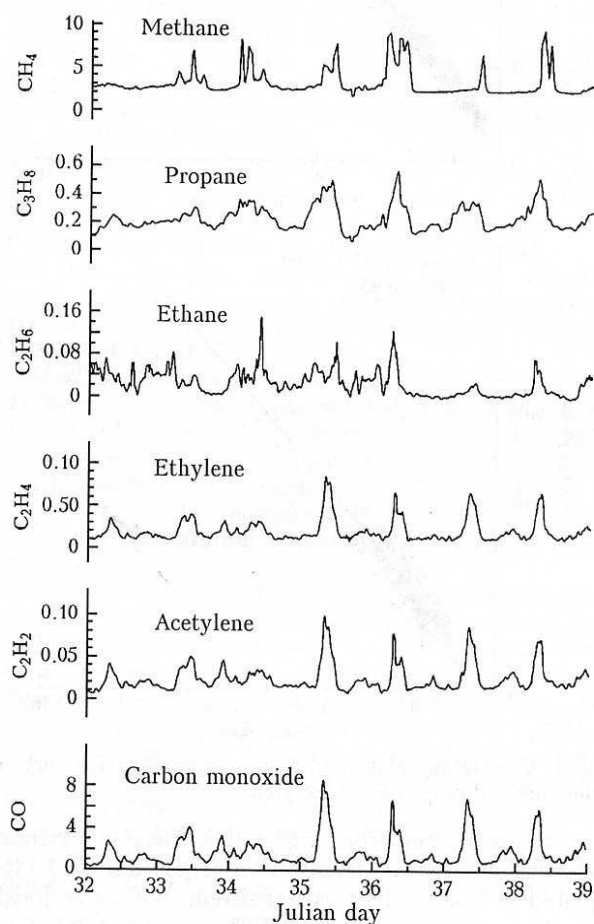


Fig. 3. Time series showing the concentrations (in ppm) of several hydrocarbons measured with the open-path FTIR spectrometer at 426 m. The data plotted represent 15 min. averages for the period 1–7 of February, 2002.

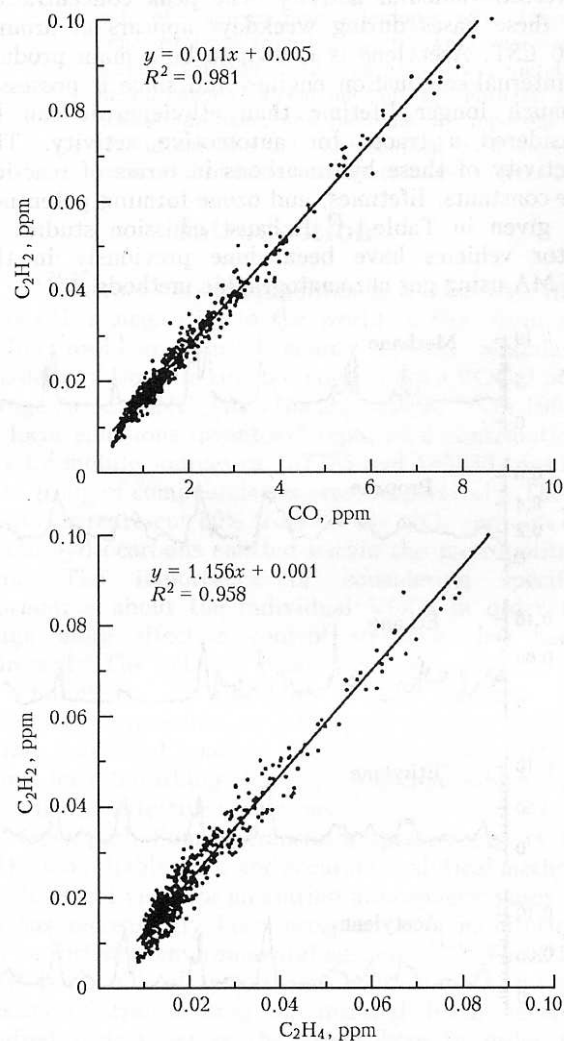
Table 1. Rate constants $k(\text{OH})$, lifetimes τ , and ozone-forming potentials for selected hydrocarbons (Ref. 23)

Compound	Formula	$k(\text{OH})^a \cdot 10^{-12}$, $\text{cm}^3 \cdot \text{molec}^{-1} \cdot \text{s}^{-1}$	Lifetime ^b $\tau = 1/k(\text{OH})$	O ₃ -forming potential ^{b,c} , ppb/hr
Ethylene	C ₂ H ₄	8.52	6.5 hrs	0.206
Propane	C ₃ H ₈	1.15	2.2 days	0.033
Acetylene	C ₂ H ₂	0.815	2.8 days	0.041
Ethane	C ₂ H ₆	0.257	9 days	0.018
Methane	CH ₄	0.006	1 year	—

^a Rate coefficient based on their reaction with OH at 298 K.

^b Assuming a 12 h daytime mean concentration of $5 \cdot 10^6$ molecules/cm³.

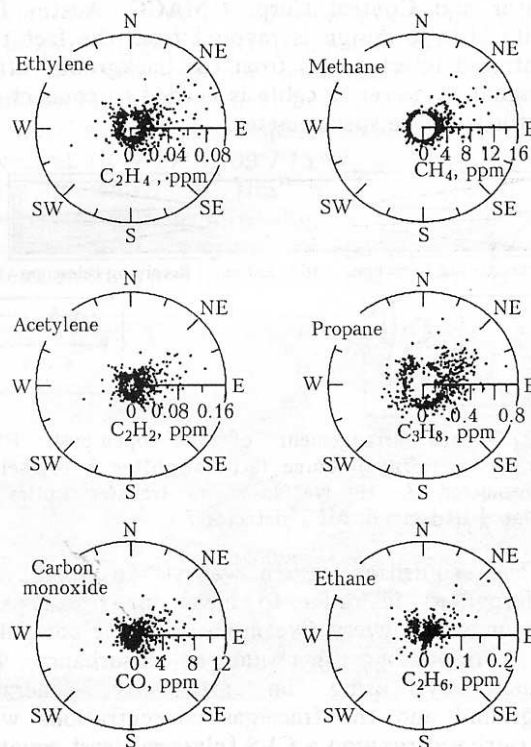
^c Ozone production rate assuming no NO_x present.

**Fig. 4.** Correlation plots and linear regressions for carbon monoxide and ethylene vs. acetylene.

It can be seen from Fig. 4 that there is a strong correlation between the levels of C₂H₂ and CO ($R^2 = 0.981$). This is consistent with the local inventory, which associates 98% of the total CO emissions with the mobile sector, which uses mostly gasoline and some diesel as its main fuels in the MCMA.⁴ Since ethylene has a much larger reactivity it persists not enough long and can be observed

relatively close to the sources. One can see in Fig. 4 that the variance of C₂H₄ with respect to C₂H₂ is somewhat larger, which could suggest alternative sources. Nevertheless, it appears from the correlation that C₂H₄ primarily originated from the same mobile sources as C₂H₂ and CO.

The time series of ethane, propane, and methane in Fig. 3 shows a more independent behavior from the automotive peak hours and are evidently governed by other sources. Liquefied petroleum gas (LPG) is the most widely used domestic fuel in Mexico City and is the main contributor for the large concentrations of propane detected. A background concentration of propane in this region of at least 100 ppb is seen in Fig. 3. Methane appears also to have a background level of about 2.3 ppm, which is considerably higher than the reported global average of 1.76 ppm.²⁶ Strong emission and frequent short-lived features peaking above 7 ppm characterizes the CH₄ curve. From its temporal profile, ethane is strongly influenced by sources other than the mobile ones. This is revealed by a strong variation in its behavior during Julian days 32–35, followed by more calmed days correlated somewhat better to vehicular rush hours.

**Fig. 5.** Wind roses containing concentration data of CO, C₂H₂, C₂H₄, C₂H₆, C₃H₈, and CH₄ for the week of 1–7 February, 2002.

The wind roses for the compounds considered in this study are presented in Fig. 5. The plots represent the concentration data for the week in hand as a function of wind direction. The meteorological sensors were located at the point sample station, marked with an asterisk in Fig. 1, approximately at the same height as the infrared beam. An excellent agreement is observed for the CO and C₂H₂ distributions,

confirming the common origin of these compounds. Ethylene and ethane seem somewhat more dispersed and have angular distributions, which are independent of CO and acetylene. The propane data is even more scattered in all directions and its background concentration is also visible from this plot. The background level of methane just above 2 ppm is clearly seen and the excess concentrations tend to be coming from the east and northeast. Although not seen in the plots, a general pattern for all the compounds is observed in terms of the wind speeds. The larger concentrations seem to be associated with lower wind speeds indicating that local emissions govern the higher levels observed.

Conclusions

In this paper the technique for measuring trace gases with an open-path FTIR is described. The concentration profiles of acetylene, ethylene, ethane, propane, and methane are reported for the first time in the MCMA with a high temporal resolution. Specific correlation between the profiles and their relation to wind direction was evaluated in order to identify the main sources contributing to the levels detected for these compounds.

Carbon monoxide shows a strong correlation with acetylene and ethylene. Also, the concentration vs. wind-direction plots of CO and acetylene show the same patterns indicating the common source for these two gases. CO is known to be emitted by the combustion of fossil fuels. Large amounts of this pollutant in an urban setting is expected from important point sources such as power plants, from area sources (stoves, home boilers, etc.) as well as by mobile sources. On the other hand, acetylene is considered to be a finger-print element for the incomplete combustion in gasoline-powered vehicles. The almost perfect match between carbon monoxide and acetylene indicates that mobile sources are by large the dominant source of carbon monoxide at this particular site. Ethylene also appears to be dominated by vehicular emissions, although a slightly more dispersed wind rose is indicative of alternative sources.

Ethane showed an independent concentration profile with respect to the gases discussed above. This reveals that for the most part, C_2H_6 originates from sources other than mobile ones. Some possibilities present the large amounts of services in the vicinity such as cooking establishments, mechanical workshops (motor-cleaning facilities, paint shops, etc.), as well as a road-construction site less than 1 km to the east. These are also possible contributors to the large propane levels detected, although the background concentration above 100 ppb observed for this pollutant is mainly due to the distribution and consumption of LP gas. The concentration profile of methane indicates some relation to vehicular sources, but also some strong independent features with no particular diurnal patterns recognizable. A relatively high background level of methane at 2.3 ppm is persistent at this location and can be partly due to

the large amounts of organic wastes generated by several food markets in the region.

Acknowledgments

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References

1. H. Mayer, *Air pollution in cities*, Atmospheric Environment **33**, 4029–4037 (1999).
2. G.B. Raga, D. Baumgardner, T. Castro, A. Martínez-Arroyo, and R. Navarro-González, *Mexico City air quality: a qualitative review of gas and aerosol measurements (1960–2000)*, Atmospheric Environment **35**, 4041–4058 (2001).
3. M.J. Molina and L.T. Molina, *Air Quality in the Mexico MegaCity: An Integrated Assessment* (Kluwer Academic Publishers, Dordrecht, (2002).
4. *Inventario de emisiones de la zona metropolitana del valle de México*, Comisión Ambiental Metropolitana, Secretaría de Medio Ambiente del GDF, Secretaría de Ecología del Edo. de México, SEMARNAT ed. México, (1998).
5. A. Russell, J. Milford, M.S. Bergin, S. McBride, L. McNair, Y. Yang, W.R. Stockwell, and B. Croes, *Urban ozone control and atmospheric reactivity of organic gases*, Science **169**, 491–495 (1995).
6. *Rethinking the ozone problem in Urban and Regional Air Pollution*, National Research Council. Committee on Tropospheric Ozone Formation and Measurement ed. (National Academy Press, Washington D.C., 1992).
7. R. Beer, *Remote sensing by Fourier transform spectrometry*, in: *Monographs on Analytical Chemistry and Its Applications* (Wiley-Interscience, Pasadena, California, 1992), Vol. 120, p. 153.
8. M.W. Sigrist, *Air Monitoring by Spectroscopic Techniques*, in: *Monographs on Analytical Chemistry and Its Applications* (Wiley-Interscience, Zurich, 1994), Vol. 127, p. 531.
9. T.L. Marshall, C.T. Chaffin, R.M. Hammaker, and W.G. Fateley, *An introduction to open-path FT-IR atmospheric monitoring*, Environ. Sci. Technol. **28**, 224A–231A (1994).
10. EPA, *Compendium Method TO-16: Long-path open-path Fourier transform infrared monitoring of atmospheric gases, and Test Method 320, Appendix A to Part 63: Measurement of vapor phase organic and inorganic emissions by extractive Fourier transform infrared (FTIR) spectroscopy*, U.S. Environmental Protection Agency, Cincinnati, OH, (1997).
11. ASTM, *Standard test method for determination of gaseous compounds by extractive direct interface Fourier Transform Infrared (FTIR) Spectroscopy*, D6348, American Society for Testing and Materials, PA, USA, (1998).
12. VDI, *Remote Sensing: Atmospheric measurements near ground with FTIR spectroscopy*, VDI 4211 (Verein Deutscher Ingenieure, Düsseldorf, 2000).
13. A. Sedlmaier, K. Schäfer, K.H. Becker, K. Brockmann, J. Heland, R. Kurtenbach, J. Lörzer, and P. Wiesen, *Determination of VOCs in traffic exhaust by FTIR absorption spectrometry*, in: SPIE **3821**, *Environmental Sensing and Applications* (München, 1999).

14. G.M. Russwurm, R.H. Kagann, O.A. Simpson, and W.F. Herget, *Long-path FTIR measurements of volatile organic compounds in an industrial setting*, J. Air & Waste Management Association **41**, 1062–1066 (1991).
15. K.S. Bradley, K.B. Brooks, L.K. Hubbard, P.J. Popp, and D.H. Stedman, *Motor vehicle fleet emissions by OP-FTIR*, Environ. Sci. Technol. **34**(5), 897–899 (2000).
16. R.A. Hashmonay, D.F. Natschke, K. Wagoner, D.B. Harris, E.L. Thompson, and M.G. Yost, *Field evaluation of a method for estimating gaseous fluxes from area sources using open-path Fourier infrared*, Environ. Sci. Technol. **35**(11), 2309–2313 (2001).
17. K. Schäfer, S. Emeis, M. Stockhause, A. Sedlmaier, H. Hoffmann, G. Depta, and A. Gronauer, *Emission rates of benzene and ammonia area sources determined by spectroscopic remote measurements and inverse dispersion modeling*, in: Proc. SPIE **3534**, 212–219 (1998).
18. B. Galle, J. Samuelsson, B.H. Svensson, and G. Borjesson, *Measurements of methane emissions from landfills using a time correlation tracer method based on FTIR absorption spectroscopy*, Environ. Sci. Technol. **35**(1), 21–25 (2001).
19. K.J. Hargreaves, F.G. Wienhold, L. Klemedtsson, J.R.M. Arah, I.J. Beverland, D. Fowler, B. Galle, D.W.T. Griffith, U. Skiba, K.A. Smith, M. Welling, and G.W. Harris, *Measurement of nitrous oxide emission from agricultural land using micrometeorological methods*, Atmos. Environ. **30**, 1563–1571 (1996).
20. R.J. Yokelson, *Open-path Fourier transform infrared studies of large-scale laboratory biomass fires*, J. Geophys. Res. **101**(D15), 21067–21080 (1996).
21. E.C. Tuazon, R.A. Graham, A.M. Winer, R.R. Easton, J.N. Pitts, and P.L. Hanst, *A kilometer pathlength Fourier-transform infrared system for the study of trace pollutants in ambient and synthetic atmospheres*, Atmos. Environ. **12**, 865–875 (1978).
22. L.S. Rothman, C.P. Rinsland, A. Goldman, S.T. Massie, D.P. Edwards, J.-M. Flaud, A. Perrin, C. Camy-Peyret, V. Dana, J.-Y. Mandin, J. Schroeder, A. McCann, R.R. Gamache, R.B. Wattson, K. Yoshino, K.V. Chance, K.W. Jucks, L.R. Brown, V. Nemtchinov, and P. Varanasi, *The HITRAN molecular spectroscopic database*, J. Quant. Spectrosc. Radiat. Transfer **60**, 665–710 (1998).
23. C.N. Hewitt, *Reactive Hydrocarbons in the Atmosphere* (Academic Press, London, 1999).
24. V. Mugica, E. Vega, J.L. Arriaga, and M.E. Ruiz, *Determination of motor vehicle profiles for non-methane organic compounds in the Mexico City metropolitan area*, J. Air & Waste Management Association **48**, 1060 (1998).
25. E.D. Gamas, L. Diaz, R. Rodriguez, E. Lopez-Salinas, and I. Schifter, *Exhaust emissions from gasoline- and LPG powered vehicles operating at the altitude of Mexico City*, J. Air & Waste Management Association **49**, 1179 (1999).
26. IPCC, *Atmospheric chemistry and greenhouse gases*, in: *Climate Change 2001: The Scientific Basis. Contribution of Workgroup I to the third Assessment Report of the Intergovernmental Panel on Climate Change*, M. Prather, D. Ehhalt, F. Dentener, R. Derwent, E. Dlugokencky, E. Holland, I. Isaksen, J. Katima, V. Kirchhoff, P. Matson, P. Midgley, and M. Wang, eds. (Cambridge University Press, Cambridge, UK and NY, USA, 2001).