Tropospheric trace gases at Bremen measured with FTIR spectrometry


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The total column densities of acetylene ($C_2H_2$), carbon monoxide (CO), hydrogen cyanide (HCN) and ethane ($C_2H_6$) measured in Bremen (Germany, 53.107°N, 8.854°E) were compared with data from Mace Head/Ireland (MHD) and GEOS-Chem model simulations. The data were obtained between August 2002 and October 2006 with the ground based high resolution Fourier Transform Infra-Red (FTIR) Spectrometry, using the sun as the light source. The analysis showed good agreements between all the three data sets for the seasonal cycle of CO. Enhancements in summer 2003 and summer 2004 due to influence of biomass burning were identified in all three data sets. The high correlations between $C_2H_2$ and $C_2H_6$, $C_2H_2$ and CO, and for $C_2H_6$ and CO support the similarities in their sources and sinks. The results suggest that the background air in Bremen is mainly influenced by long-ranged transport of biomass burning products. Local pollution plays a minor role for the measurements performed in Bremen.

1. Introduction

The atmospheric concentrations of $C_2H_2$, CO, HCN and $C_2H_6$ are important indicators of tropospheric pollution and transport because they are primarily emitted from biomass burning and anthropogenic sources. The reaction of CO with OH has an important role in the oxidising capacity of the troposphere and hence the lifetime of many atmospheric species. CO, $C_2H_2$ and $C_2H_6$ are precursors of tropospheric ozone ($O_3$) such that the budget of $O_3$ could be affected by changes in their tropospheric concentrations. Thus, the issue of the resulting environmental pollution due to increases in the atmospheric concentrations of these trace gases and others with anthropogenic origin had been of great concern. Hence, we are interested in their distributions because continuous increase in their concentrations may adversely alter air quality, affect composition and chemistry of the atmosphere which can lead to health problems and long-term climate change, etc. It has been observed that reactions with hydroxyl radicals (OH) are their primary sink, while ocean uptake and reactions with $O(1D)$ are part of the suggested sinks of HCN. Thus, the purpose of this paper is to report and analyse the time series of the vertically integrated total column densities of these trace gases in Bremen and compare the data with both in situ and model results. This will be helpful in validating satellites and as source of complementary information to the satellite measurements. The data could also be useful for the interpretation of atmospheric trace gas composition. It will improve our understanding of global features of trace gases and the overall tropospheric pollutant loading at Bremen.

2. Measurements and data analysis

2.1. Sampling site

The measurements were carried out using a high resolution FTIR instrument (Bruker 125 HR) placed at 23.6 m above the ground level, on the rooftop of the Institute of Environmental Physics, University of Bremen (53.107°N, 8.854°E, sea level), Germany. Better understanding of the sources and sinks of trace gases require establishing observatories at low altitude. Hence this site is an ideal one for FTIR measurements because of its location in the mid-latitude with flat topography and low altitude. It is one of the complementary sites of the Network for the Detection of Atmospheric Composition Change (NDACC) and a primary station of the Total Carbon Column Observing Network (TCCON). Bremen is an industrial town with a population of over 500 000 people; the studying site is about 4 km away from the city centre. Local sources of emissions include industrial and automobile emissions, natural gas, biogenic, vegetative activities, agriculture and fossil fuel combustions.

The instrument is equipped with MCT (Mercury–Cadmium–Tellurium) and InSb (Indium–Antimony) detectors, cooled with liquid nitrogen. It has an active solar tracker that follows the course of the sun, using a quadrant-diode and two movable mirrors. The solar beam is focussed on the entrance aperture of the interferometer. Using sun as the direct light source we could measure the concentrations (vertical columns) of about 20 trace gases along the instrument’s lines of sight from the earth’s surface to the sun. Since the trace gases we are considering in our analysis reside in the troposphere with very little concentrations above it, the concentrations measured are their tropospheric total columns with negligible contributions from the stratosphere and mesosphere above.

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2.2. Data analysis

The data analysis is based on the fact that trace gases absorb light at certain wavelengths, which are characteristics of their chemical bonds, leading to vibrational or rotational motions of the molecules. Information on the concentrations of the atmospheric species in the air volume is based on the amount of light they absorbed. In our instrument, a Michelson interferometer, records the intensity of an interferogram, the interferograms were apodized using the Boxcar apodisation, which allows to keep the maximum information content of the measurements. The final spectra is obtained by performing a Fourier Transform of the interferogram. The atmospheric molecules lead to absorption features in the spectra, which will be analysed in the next step by comparison with simulated spectra. The measured spectra we got between August 2002 and October 2006 were analysed using a nonlinear least squares spectral fitting algorithm (GFIT) developed at the Jet Propulsion Laboratory (NASA/JPL) that is freely available upon request. Atmospheric absorption coefficients were calculated line-by-line for each gas in a chosen spectral window. These were used together with the NCEP (National Centres for Environmental Prediction) pressure and temperature profiles, and with assumptions on the volume mixing ratio (VMR) from balloon profiles\textsuperscript{13,14} to calculate the atmospheric transmittance spectrum. The absorption line parameters were taken from High Resolution Transmission, HITRAN (2004) molecular absorption data base. The simulated spectra were compared with the measured ones and the VMR profiles were iteratively scaled until the RMS differences between the calculated and measured spectra were minimized. Further details of the algorithm are available in the literature.\textsuperscript{13,14} The final output is the total column along the line of sight through the atmosphere. This column has been transformed to yield finally the vertical column amount of each trace gas (in molecules cm\textsuperscript{-2}) above the site of measurement.

The measurements were done at a resolution of 0.005 cm\textsuperscript{-1} using single scans, where the resolution is defined as 0.9/OPD (OPD: maximum optical path difference of the interferogram). The time required for a single complete spectra scan is about 5 min. Depending on the spectral region and solar zenith angle, the signal-to-noise ratio in our data ranges from 300–700. The precision, given as the root mean square (RMS) of the individual fits for each trace gas vary from 0.3% to 0.7%. The individual results were averaged, yielding daily averages, which we presented below. The spectral microwindows (and corresponding widths) used for the four trace gases are 3250 cm\textsuperscript{-1} (0.34), 2160 cm\textsuperscript{-1} (6.0), 3287 cm\textsuperscript{-1} (0.17) and 2976 cm\textsuperscript{-1} (1.0) for C\textsubscript{2}H\textsubscript{2}, CO, HCN and C\textsubscript{3}H\textsubscript{6}, respectively. The spectroscopic analysis requires considering potential interfering gases. The interfering gas for C\textsubscript{2}H\textsubscript{2} in the spectral region used is H\textsubscript{2}O (water) while those for C\textsubscript{3}H\textsubscript{6} are H\textsubscript{2}O, CH\textsubscript{4} (methane) and HDO (heavy water). For the analysis of CO the interfering gases H\textsubscript{2}O, O\textsubscript{3} (ozone), N\textsubscript{2}O (nitrous oxide) need to be considered. For HCN the trace gases CO and C\textsubscript{2}H\textsubscript{4} (ethene) have been considered. The total column densities of each molecule in their respective window were plotted to reveal their seasonal cycles, Fig. 1.

3. Discussion of results

3.1. Seasonal cycles

Since measurements are only possible on sunny days with clear sky, there are periods without measurement due to bad weather, restricting the number of observation days. Therefore, the numbers of measurement days in each year are 15, 31, 33, 24 and 58 days for the year 2002, 2003, 2004, 2005 and 2006 respectively. Given below are the daily averages of the results. The daily averages of the measured total columns of CO, C\textsubscript{2}H\textsubscript{2} and C\textsubscript{3}H\textsubscript{6} reach maxima values between February and March and minima between July and September while that of HCN is at a maximum between August–September and minimum around December–January (Fig. 1). The error bars indicate the associated 1\textsigma errors in the retrievals, based on the RMS of the measurements. Generally, the tropospheric lifetimes of these trace gases depend on the seasons and latitudes with global averages of about 2 months for CO and C\textsubscript{2}H\textsubscript{6}, approximately 1 month for C\textsubscript{2}H\textsubscript{2} and between 2 months–4 months or several years for HCN.\textsuperscript{13,16,11} Their seasonal cycles are mainly controlled by changes in biomass burning emissions and OH concentrations due to the influence of solar flux.\textsuperscript{15} However, estimates of the roles of HCN in atmospheric chemistry, biogeochemistry, global sources, sinks and the lifetime are still uncertain due to insufficient data. The observed seasonal cycle of HCN is out of phase with those seen in the other molecules and the seasonal cycles of

![Fig. 1](image-url) Seasonal variations of tropospheric total column densities of C\textsubscript{2}H\textsubscript{2}, C\textsubscript{3}H\textsubscript{6}, CO and HCN over Bremen.
all the four molecules are marred by lots of variations, but they are still consistent with previously observed 2–4 months lifetime.\textsuperscript{1,5,6,10,11} The agreements between CO, C\textsubscript{2}H\textsubscript{2} and C\textsubscript{2}H\textsubscript{6} is expected due to similarities in their sources and atmospheric sinks while their deviations from HCN seasonal cycles might be associated with differences in the observed HCN sources and their removal rates.

3.2 Comparison of FTIR results with other data

3.2.1. Comparison with \textit{in situ} surface data from MHD. We compared our CO column data with the tropospheric average volume mixing ratios (VMR) using the relation:

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\text{Column average VMR} = \frac{\text{column}}{\text{total dry column}}
\]

The CO VMR obtained from the FTIR data was lower than data from \textit{in situ} surface measurement from Mace Head (MHD, County Galway, Ireland, 53.33\textdegree\N, 9.9\textdegree\W) with a factor of 1.438 (obtained from the slope of the Bremen’s CO FTIR-VMR data with respect to the data from MHD). The reason is most probably the assumption of a constant mixing ratio throughout the atmosphere, as assumed in the equation above, while the MHD data are \textit{in situ} data measured at the surface. Thus, we scaled our FTIR result by a factor of 1.438 to get better agreement with the \textit{in situ} data. The final outcome was plotted together with the CO VMR from both MHD and that from Baltic Sea, BAL (not shown), Poland (55.35\textdegree\N, 17.22\textdegree\E). Both were obtained from the archived data of the Earth System Research Laboratory, Global Monitoring Division (GMD) of National Oceanic and Atmospheric Administration (NOAA).\textsuperscript{6,17,18} The comparisons were made for periods covering August 2002 to October 2006. As shown in Fig. 2a (except for BAL), their seasonal variations agree well with the FTIR data but the BAL data was not shown because it contains higher scatter points that might be due to the influences of pollutions from local sources as opposed to the MHD station that measured clean Atlantic air. Though surface measurements are very accurate, they are liable to errors due to their limited vertical coverage and proximity to local sources, especially for sites located in the continental interiors. Deviations might also be the outcome of differences in the sensors used for the measurements, errors from interfering gases\textsuperscript{6} and inaccuracies in the assumptions or constraints used in the retrieval algorithms.\textsuperscript{6,17,18} Since the spectral data used have an accuracy of only a few percent, and since the interfering gases have been considered correctly in the analysis we estimate these errors to be within 5–10%.

Furthermore, the seasonal anomalies of the trace gases of each year compared to the long-term averages were analysed. The anomalies were calculated by dividing both results with the monthly mean of the smoothed, interpolated and extrapolated MHD Global View data,\textsuperscript{19} the MHD data used covered the period 1991–2007. This was done to remove the seasonal variations that tend to mask the outliers. The averaging periods used are the same for both ground and the scaled total column measurements, it covered the periods from August 2002 to October 2006. The plots of the final results showed major periods of anomaly in summer 2003 and summer 2004 in the FTIR data—as indicated by the arrows in Fig. 2b. The results were compared with the numbers of fires (hot spots) per month from 2002–2006, generated for the Northern Hemisphere (NH) with algorithm 1 of the night time data in the ATSR (Along Track Scanning Radiometer) World Fire Atlas.\textsuperscript{20} The comparisons showed that the enhancements are due to transported air masses that had been polluted by biomass burning products, Fig. 2c.

This is seen in the prolonged high biomass burning recorded in summer 2003 between June–September which reached the maximum in July of that year. Using backward trajectories, a closer look at summer 2004 events revealed similar
Applying the web trajectory service of British Atmospheric Data Centre (BADC),\textsuperscript{21,22} 10 days backward trajectories of the periods of significant enhancements, each reaching 800 hpa, 500 hpa and 200 hpa pressure levels were calculated. Since their tropospheric life-times are relatively longer than 10 days, the 10 days backward trajectories are capable of providing sufficient information on these molecules with better accuracy.\textsuperscript{23} The trajectories point to the fire activities (MODIS 10 days fire maps) in Portugal and Spain as the likely source of the pollutions in summer 2004, Fig. 2d. Similar backward trajectories were plotted for summer 2003 (not shown) and both confirmed that the enhanced pollutions in both summers were due to biomass burnings with possible contributions from smouldering fires and photochemical conversion of hydrocarbons that take some time after emission before it could be observed.

### 3.2.2. Comparison with model results of GEOS-chem.

The GEOS-Chem data used were produced from a global 3-dimensional (3D) model of tropospheric chemistry, driven by assimilated meteorological observations from Goddard Earth Observing System (GEOS) of NASA Global Modelling Assimilation Office.\textsuperscript{24} A general description of the model and its emission inventories are available in literatures.\textsuperscript{8,24} We compared the column average VMR of the FTIR C$_2$H$_6$ and CO data with the output of the model’s simulations for Bremen. The modelled seasonal variations are consistent with our observations for both gases; the model simulates correctly the seasonal phases and amplitudes of the concentrations of the two trace gases, Fig. 3.

### 4. Correlation

Further investigations were done by studying the correlations between C$_2$H$_6$ and C$_2$H$_2$, C$_2$H$_2$ and CO, and C$_2$H$_6$ and CO to see how well our results compared with others from different locations. In Fig. 4, the plots were made for burning periods (defined as June 2003–Sept. 2003 and July 2004–August 2004) and those without burning (i.e. the remaining periods within August 2002–October 2006). The definition is based on the observations seen in CO anomalies in which the burning periods correspond to the time of enhancements in the anomalies (shown with arrows in Fig. 2b). The correlation coefficients for the periods without burning between the respective pairs of trace gases are 0.95, 0.94 and 0.93 while their values for burning periods are 0.63, 0.48 and 0.43, Fig. 4. Also, their respective slopes for periods without burning are 2.64, $4.7 \times 10^{-3}$ and $13.0 \times 10^{-3}$ while 2.24, $1.1 \times 10^{-3}$ and $5.5 \times 10^{-3}$ are their respective values for burning periods (not shown). The ratio C$_2$H$_2$/CO is a good indicator of dynamical mixing and photochemistry because its value decreases with increased atmospheric processing as the air travels away from the source.\textsuperscript{6} Hence the lower slope obtained for C$_2$H$_2$/CO during the burning period revealed that the source of the pollutions are long-ranged transported materials. Thus the low correlations in burning periods are clear indications that local pollution plays minor roles in the background pollution in Bremen while the high correlations during the period without burning are pointing to the similarities in their sources and sinks.

These results agree well with those obtained at other sites where influence of biomass burnings had been observed. For instance, the correlation and slope obtained between C$_2$H$_6$ and CO are comparable with their respective values of 0.84 and $12.9 \times 10^{-3}$ estimated at the International Scientific Station of the Jungfraujoch, ISSJ (46.55°N, 8°E).\textsuperscript{7} The results are also
consistent with the correlation of 0.80 and slope $13.2 \times 10^{-3}$ got over Northern Japan [Rikubetsu (43.5°N, 143.8°E) and Moshiri (44.4°N, 142.3°E)] and with the 0.92 and $14.2 \times 10^{-3}$ observed in the northern mid-latitude observations at Kitt Peak (31.9°N, 111.6°W).25 Also there is good agreement with our results and the respective values of 0.91 and $5.7 \times 10^{-3}$ obtained as the correlation and slope between C$_2$H$_2$ and CO in the in situ aircraft measurements over the pacific region (25°N–48°N) during PEM-West B.26 No correlation was obtained between HCN and the other three molecules. Previous observation showed that the highest correlation coefficients and HCN/CO tropospheric columns slopes were measured during periods of intense burnings.1,10,25 In many previous studies, similarities had been observed in the seasonal cycles of these four molecules during biomass burning.6 Thus, the above observation might be due to significant contributions of fossil fuel combustion and other non-biomass burning related sources to the observed HCN and hence CO, C$_2$H$_2$ and C$_2$H$_6$ concentrations.

5. Conclusion

The column densities of C$_2$H$_2$, CO, C$_2$H$_6$ and HCN at Bremen were analysed and compared with in situ and model data. The comparison of column CO and C$_2$H$_6$ results with those from GEOS-Chem model revealed good agreements in their seasonal changes. Also, the MHD in situ CO data and FTIR agree in their seasonality, the elevated values recorded at MHD are most probably due to surface emissions while the FTIR data are lower seasonalities, the elevated values recorded at MHD are most possibly due to surface emissions while the FTIR data are lower because these data are average values obtained over the entire atmospheric columns. The high correlations obtained between C$_2$H$_2$, CO and C$_2$H$_6$ are consistent with their common origin and sink while the low values obtained during burning periods and between them and HCN are in support of low influence of local biomass burning pollutions. The results indicate that the background air in Bremen is relatively clean without much pollution from local industries. The fire plots and 10 days backward trajectories revealed that the observed enhancements in their tropospheric concentrations are due to pollutions from long-ranged transported biomass burning products. The study shows that the observation in Bremen can be used as representative for clean air.

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