CO_2 Source Attribution Improved by CO and N_2O in Analyses of Total-Column Solar-Occultation Data

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Abstract

Introduction

Data Sources:

TCCON data were obtained from the TCCON Data Archive, operated by the California Institute of Technology from the website at http://tccon.ipac.caltech.edu/.
We had subsequent communication with Nicholas Jones of the University of Wollongong regarding the instrument and site. We used the data available in April, 2012.

Procedure:

We sought to highlight particular source regions whose inflowing concentrations affected the TCCON site within the past few hours or days. Carbon dioxide has strong diel variations near the surface, and both CO_2 and CO have substantial variations by season of the year. We wished to filter the data to direct attention towards recent sources and transport, and just as importantly, to avoid, as possible, the attribution of correlations that were primarily repeating correlations in time. For example, seasonal variations can produce correlations between CO and CO_2 that are actually just due to the seasons themselves (preponderance of fixation or respiration).

Consequently, we worked with residuals containing CO2 and CO corrected for hour of day, day of year, and a secular trend. We used regressions that allowed these effects to be modeled

$$\mathrm{XCO2} = S_1(h_\mathrm{d}) + S_2(d_\mathrm{y}) + a \bullet (d_{2007}) + c$$
$$\mathrm{XCO} = S_3(h_\mathrm{d}) + S_4(d_\mathrm{y}) + b \bullet (d_{2007}) + d$$

where XCO2 and XCO are column CO2 and CO as mixing ratios to dry air, h_d is the hour of the local solar day, d_y is the day of year, and d_{2007} is the day count since the first day of 2007, the year in which the TCCON measurements began. The symbols S_1, S_2, S_3, S_4 refer to fitted (cyclic) spline functions in what is called an additive model. We used the residuals from these regression fits, XCO2 – $S_1(h_\mathrm{d}) + S_2(d_\mathrm{y}) + a \bullet (d_{2007}) + c$ regression

The use of additive models deserves a brief explanation. Oftentimes cos and sin of time variables like d_y are used in regressions, and this keeps the regression a linear regression, with advantages of uniqueness and easy computation. The S_i are spline functions which are iteratively estimated, but given any particular form, are treated as fixed functions in a type of linear regression, much as the form cos($d_\mathrm{y} - d_0$) would be treated in a regression where d_0 was iteratively estimated in a search for the best-fitting parameter d_0. The use of spline functions allows the simplest model to be estimated that is continuous and has continuous first and second derivatives. It is possible to specify cyclical behavior, i.e. smoothness at the year boundary or day boundary. It avoids the "ripple" properties of functions specified by polynomials or sines, The practice of additive modeling also allows an optimum estimation of the shape, given the pattern of scatter in the data, by generalized cross-validation or GCV. GCV is a systematized form of selective data denial (formulate with subset A and validate with subset B). Wood (2008) describes our approach. We used Wood's completely described package *mgcv* in the R language (`http://cran.r-project.org/web/packages/mgcv/index.html`), with spline determination set to "*bs=cc*" for cyclic behavior and "k = 4" to keep the annual and diel curves quite simple. The term $S_3(h_d)$ for CO was found to be inconsequential. (For other TCCON sites, particularly those with shorter data records, the S_2 and S_4 could be specified externally, e.g. by diagnostic global atmospheric composition models.)

Results and Interpretation

The results for the Wollongong site were strikingly different from other sites for which we made a brief investigation. An annotated plot of XCO vs XCO2 residuals is shown in Figure 1. High XCO2 occurred when XCO was high, a common feature in the TCCON datasets. However, there were many cases of high XCO2 with rather low XCO. This feature appeared in the basic XCO and XCO2 data; the use of residuals simply made the XCO-to-XCO2 relationship more clearly defined (e.g., a narrower ellipse around the straight red correlation line.

The high values of CO_2 without high CO are likely explained by influences of local industry, in particular the Bluescope Port Kembla Steelworks, whose proximity to the Wollongong FTS site is indicated in Figure 1. The broad ellipse indicates common urban emissions, with automobiles emitting both combustion CO and CO_2; autos are also co-located with other residential and business CO_2 sources. High amounts of CO are due to the proximity of cooler walls in small combustors. We have not been able to segregate such emissions as originating locally or from the much larger metropolitan area of Sydney, 80 km to the north. It is reasonable that the highest, correlated values come in the Sydney urban plume; occasional accumulation of local emissions under conditions of low mixing could also affect the columns of XCO and XCO2.

Wind data from the Wollongong FTS site should be available, but idiosyncratic difficulties in the data record prevent us from reporting wind analyses at this time.

Another feature shown in Figure 1 is the presence of very low XCO2 column measurements at moderate XCO values. These are attributable to situations of low tropopauses or substantial injections of stratospheric air above the FTS. The XCO column is much more sensitive to stratospheric air than XCO2 since CO can be reduced to low levels in the upper troposphere due to the CO+OH reaction, while CO_2 only declines in the stratosphere and responds to deeper circulations such as the Brewer-Dobson overturning. Our hypothesis is that XCO is controlled in the lower troposphere and held to relatively low mean values, whereas XCO2 is much more sensitive to tropopause-area variations. Using the variations shown on the graph to estimate deltas

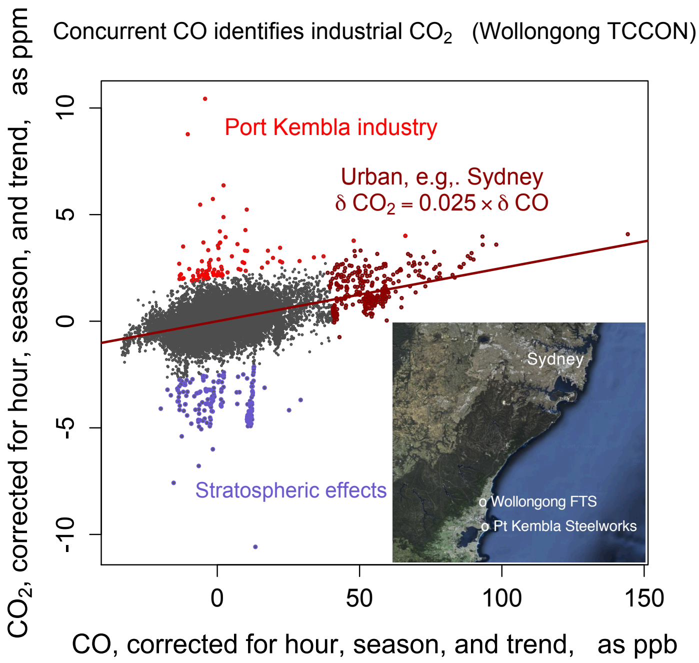

Figure 1. In this comparison of column CO2 to column CO at Wollongong, diel and seasonal cycles and secular multiyear trends have been removed. The regression line shows urban effects on CO2 ; urban CO reflects a mass combustion efficiency of 0.975. Industrial CO2 production is efficient and produces tiny CO effects, allowing the identification of plumes. The nearby Port Kembla Steel Plant is shown in the inset; the strongest urban effects are likely due to the Sydney plume, as a wind analysis also shows. Very low CO2 column at nominal CO column amounts confirm stratospheric (low tropopause) effects.

and the series-means XCO2 and XCO for the totals, *Δ*XCO2 / XCO2 = 5 ppm /~330 ppm ~ 1.3%, which would correspond to *Δ*XCO ~ 0.013*70 ~ 1 ppb. Indeed, that deviation is consistent with the very slight slope seen for *Δ*XCO / *Δ*XCO2 seen in the figure for measurements made at approximately the same time (e.g., the near-vertical linear features like the one seen at ~ 15 ppb residual CO). N_2O measured at the Wollongong TCCON site corroborates this effect: column XN2O also decreases when XCO2 does.

These results agree well from interpretations of the measurements made at the Cal Tech TCCON site (Wunch et al. 2009).

Wind Analysis (pending data clean-up)

Conclusions

References

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