Atmos. Chem. Phys. Discuss., 3, S1644–S1649, 2003
www.atmos-chem-phys.org/acpd/3/S1644/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "On the relationship between acetone and carbon monoxide in air masses of different origin" *by* M. de Reus et al.

M. de Reus et al.

Received and published: 2 October 2003

Reply to referee #1

1. We agree with the referee that the mixing ratios of CO and acetone are influenced by many factors and that it is, therefore, surprising that the observed linear relations are so similar at very different geographical locations. This is also the main reason why we wrote this paper. Up till now a single relation between acetone and CO has been used in box model calculations for the initialization of acetone mixing ratios, which is a too simple picture of the acetone-CO relation. We have shown that the linear correlation between acetone and CO can be used in model calculations, but that different relations have to be used for different air masses.

2. We agree with the referee that this is a very speculative conclusion. No measurements of the acetone concentration in surface water have been performed during

Full Screen / Esc
Print Version
Interactive Discussion
Discussion Paper

INDOEX and MINOS, so we cannot give any direct supporting evidence. However, model calculations support our findings. De Laat et al. [2001], simulated the acetone mixing ratios observed in the marine boundary layer during INDOEX using a global chemistry climate model. They had to include an oceanic source of acetone in order to simulate the observed acetone mixing ratios at low CO mixing ratios. At the same time they overestimate the acetone mixing ratios at CO mixing ratios exceeding 100 ppbv, indicating a missing acetone sink. In order to make any firm conclusions about the air-sea exchange of acetone a detailed analysis of surface water is necessary.

3. Enhanced OH mixing ratios in the marine boundary layer will lead to an enhanced oxidation of CO, acetone and hydrocarbons. Through the oxidation of hydrocarbons both CO and acetone will be formed again. Without using a box model with a detailed hydrocarbon chemistry scheme it is hard to determine what enhanced OH mixing ratios will do to the acetone-CO ratio. Since we do not have access to such an detailed boxmodel, we did not perform such calculations and focus on the description of the observations.

4. A detailed study of the origin and age of the air masses observed during INDOEX has been performed by de Gouw et al. [2001]. They determined the age of the pollution plumes observed during INDOEX using the acetylene/ethane and benzene/ethane ratios. The age of the air masses observed in the marine boundary layer over the Indian Ocean during INDOEX ranged between 4 and 15 days. In the free troposphere similar air mass ages were found since convection lifted the relative fresh pollution from the marine boundary layer to the middle free troposphere. Lelieveld et al. [2002] and Traub et al. [2003] describe the origin of the air masses observed over the Mediterranean region during MINOS. In the marine boundary layer anthropogenic pollution was observed originating from eastern and western Europe. In the free troposphere air masses originating from North America and Southeast Asia were observed. Salisbury et al. [2003] calculated the age of the air masses in the marine boundary layer using the toluene/benzene ratio from observations at the ground based station on Crete

ACPD

3, S1644–S1649, 2003

during the MINOS campaign and compared this with back trajectory calculations. They found that during the entire campaign the air mass age was below 30 hours. Since the aircraft performed its measurements north of the island of Crete, the air masses observed by the aircraft in the marine boundary layer have a maximum age of 30 hours. Scheeren et al. [2003] investigated the Southeast Asian air masses which dominated the free troposphere in the first half of the campaign. They determined a chemical age of these air masses of 7-15 days, based on the comparison of emission ratios from MINOS with emission ratios derived from INDOEX results and back trajectory calculations. The trajectory analysis also showed that North American pollution plumes were observed occasionally, which were lifted from below 700 hPa between 5 and 10 days prior to the measurements. Moreover, recent convective injection of European boundary layer air was observed during two flights. Fischer et al. [2002] subdivided the air masses observed in the free troposphere during STREAM98 in polar, midlatitude and (sub)tropical. They determined a chemical age of the polar and midlatitude air masses of 5-7 days, based on the C2H2/CO ratio. Trajectory analysis show that air masses originating from (sub)tropical latitudes were transported a few days before reaching the measurement area. Hence, the air masses observed in the free troposphere over the Indian Ocean, the Mediterranean Sea and the North American continent were influenced by anthropogenic pollution and had a chemical age between a few days and 15 days. Apparently, within 15 days the signature of the linear relation between acetone and CO does not change significantly. In the free troposphere, the lifetime of acetone is shorter as the CO lifetime, due to the photolysis of acetone. In order to keep the acetone-CO relation stable over a time period of 15 days, secondary production of acetone has to compensate for the loss of acetone, see also comment #2 in the reply to the second referee. The variability in the correlation plots can be caused by the different air mass ages, however based on the lifetime of acetone and CO alone, the variability should be much larger. The description of the air mass origin and age for the different campaigns has been included in section 3.

5. The background CO concentration, due to methane chemistry, in the atmosphere

ACPD

3, S1644–S1649, 2003

is about 60 ppbv. The background acetone concentration can, hence, be found by extrapolating the linear relation between acetone and CO to 60 ppbv CO, as is explained in section 5. The background acetone mixing ratio in the free troposphere during MINOS and STREAM98 is close to the background concentration of 500 ppt, which is observed in the northern hemisphere by Singh et al. [1995]. The higher acetone background concentration in the marine boundary layer can be explained by additional biogenic sources. These could also be of marine origin.

6. The words relatively clean are chosen to make clear that the anthropogenically influenced air mass has been processed or mixed with cleaner air, so that the CO mixing ratio has decreased substantially compared to fresh anthropogenic pollution. Hence, it is not a clean air mass.

7. We changed to acetone-CO relation.

Reply to referee #2

1. It would be out of the scope of this paper to perform a detailed model study. We focus on observations of acetone and CO during five airborne measurement campaigns. Note that global models tend to have problems in simulating acetone mixing ratios, which would make these studies very challenging.

2. Chemical aging alone does not necessarily produce a linear relation between acetone and CO, however, chemical aging of an air mass which already shows a linear relation will keep this relation. We calculated the change in the slope of the linear relation observed in the free troposphere during STREAM98, considering a lifetime for CO and acetone of 38 and 14 days, respectively. These lifetimes have been calculated based on the depletion of CO and acetone by reaction with OH, assuming an OH concentration of 1.7 * 106 molecules/cm3, and the destruction of acetone through photolysis. The OH reaction rates have been adopted from DeMore et al. [1997] and Wollenhaupt et al. [2000], the photolysis rates from Brühl and Crutzen [1989]. An exponential decay has been assumed using the lifetime as e-folding time. The results are

ACPD

3, S1644–S1649, 2003

shown in Figure 7 in the revised manuscript. The observed slope of the acetone-CO relation in the free troposphere during STREAM98 was 24.4 pptv acetone/ppbv CO. After 15 days this slope has decreased to 11.7 pptv acetone/ppbv and after 30 days to 6.3 pptv acetone/ppbv CO, which is close to the observed slope in the stratosphere. Note that only depletion of both gases is considered and no production or additional emission has been taken into account. The discussion about air mass aging has been added to section 5.

3. I agree with the reviewer that a correlation coefficient of 0.19 is not very convincing. The very low correlation coefficient for these air masses is due to the relatively short time period that the biomass burning plume was encountered, yielding a limited amount of data points. We changed this part of the text.

4. Due to the limited number of data points collected in the biomass burning plume, it is indeed hard to see a correlation between acetone and CO, which is also reflected by the low correlation coefficient. We would like to show that the outliers observed during CLAIRE represent air masses with a very different origin, resulting in very different acetone and CO mixing ratios and a different relation between the two gases. We do not make any conclusions based on this relation. Very high and very low CO and acetone mixing ratios have not been observed so often as moderate CO and acetone mixing ratios. This causes an uneven distribution of the data, which sometimes results in slopes which do not seem to fit to the upper and lower data points. Since moderate acetone and CO mixing ratios are observed more frequently in the atmosphere it is legal to weigh them more in the fit.

5. We added box and whisker plots to the Figures 1-5.

6. Detailed trajectory analyses for the measurement campaigns described in this paper have already been published. We added the most important findings to the text in section 3. See also comment #4 in the reply to the first referee.

7. The total uncertainty of the acetone and CO measurements have been added to

ACPD

3, S1644–S1649, 2003

section 6.

8. We removed the model results from Table 3 and section 4. The statement about the good correlation between acetone and CO is not only based on the measurement of one biomass burning plume during CLAIRE. The measurements during INDOEX were influenced by biomass burning as well.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 1017, 2003.