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Atmospheric Chemistry and Physics Discussions

Interactive comment on "New insights in the global cycle of acetonitrile: release from the ocean and dry deposition in the tropical savanna of Venezuela" *by* E. Sanhueza, et al.

Anonymous Referee #2

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This manuscript describes the measurement results of acetonitrile at a location in the tropical savanna. The authors observe a diurnal variation and explain it by invoking an ocean source and a surface deposition sink. These are surprising conclusions, as different authors have shown that acetonitrile can be lost by ocean uptake. Also, dry deposition has not been observed until now. Nevertheless, global observations of acetonitrile have been limited thus far, and surprises can certainly not be ruled out based on observations in other regions of the atmosphere. The measurement results reported in this manuscript are new and original and warrant publication. The discussion of the results is brief, however, and could be improved to strengthen the points made by the authors. I therefore recommend publication after taking the following points into account.

1. The authors have reduced their data to one plot, Figure 2, which shows the diurnal variation of acetonitrile and CO averaged over a three-week period. It certainly would not hurt to show the entire measurement series and/or the variation around the mean shown in Figure 2 (standard deviation and range). Also, the wind direction (and speed) are important parameters in the interpretation of the data, but other than the arrow indicating the prevailing wind direction in Figure 1, there is very little information about this in the manuscript. It would be good to show the wind direction along with the acetonitrile and CO data over the three-week measurement period. Also, some back-trajectory calculations would give the reader a general idea of the air mass origins.

2. The only indication for the existence of an ocean source is the enhanced daytime mixing ratio of acetonitrile observed throughout the measurement period, which was higher than observations in other regions summarized in Table 1. As global data for acetonitrile are still scarce, this evidence is rather indirect and therefore somewhat weak. Do the authors have evidence that background levels of acetonitrile should be lower than 210 pptv at the measurement location in Venezuela? Does the data set contain evidence that acetonitrile levels were lower when the sampled air masses had not moved over the Caribbean Sea? Such air masses may not have been observed, but from the limited information in the manuscript this is hard to find out (see point 1).

3. Two of the authors were involved with the LBA-Claire experiment in 1998, which involved airborne measurements of acetonitrile over Surinam in a similar region of the atmosphere as in this manuscript. During LBA-Claire the average mixing ratio of acetonitrile in the boundary layer was 190 pptv and the free troposphere 175 pptv (Crutzen et al., Atmos. Environ. 2000), which does not indicate a strong surface release. How do the authors reconcile these observations? Are there vertical profiles over the ocean from LBA-Claire that support the conclusion made in this paper about the existence of an ocean source?

4. A biogenic source of acetonitrile is dismissed because the temporal behavior of the acetonitrile mixing ratio is different from the profiles expected for isoprene and

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monoterpenes. This is not a very strong argument, as other diurnal patterns of biogenic emissions have been observed. For example, MacDonald and Fall, Atmos. Environ. 1993, observed a release of methanol before sunrise.

5. The conclusions about a surface deposition of acetonitrile are more convincing. It is possible, I assume, that the exchange is bi-directional: some of the acetonitrile that is lost to the vegetation during the night is released the next morning when the temperature increases?

Minor comments:

1. In section 2 the measurement period is said to be from September 24 to October 17, 1999. However, in section 4, a reference is made to data obtained on August 7 and 8.

2. Also in section 2, the manuscript mentions that no biomass burning was observed during the measurement period. What information is this statement based on?

3. In section 4, it is mentioned that no significant enhancements of acetonitrile were observed in air advected from nearby Calabozo. It would be of interest to put an upper limit on the emission ratio of acetonitrile vs. CO from anthropogenic sources in Venezuela. Holzinger reported a similar number for traffic emissions in Austria, but the vehicle fleet in Venezuela can be expected to be entirely different.

4. Some recent references that should be added include: A. Bange and Williams, Atmos. Environ. 2000, who suggested that acetonitrile in the ocean could be lost in biological processes, rather than simply dissolved as suggested in this manuscript. B. De Laat et al., JGR 2001, who showed that ocean uptake had to be included in a global model calculation to explain the measured acetonitrile concentrations over the tropical Indian Ocean. C. De Gouw et al., JGR 2003, who showed evidence of ocean uptake in the eastern Pacific Ocean, and suggested a connection with biological activity. D. A paper by Qinbin Li et al. will appear in JGR that explains acetonitrile observations

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in various worldwide locations using a global model that includes biomass burning as a source and ocean uptake as a sink. The paper includes a model prediction for Venezuela in April 2001 that is of interest for comparison with the present data set.

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