AGU PUBLICATIONS

Global Biogeochemical Cycles

Auxiliary Material for

Dimethyl Sulfide in the Amazon Rainforest

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The Auxiliary Material contains additional methodology and figures as described below.

1. Auxiliary Methodology

1.1 Branch emissions of DMS in a tropical rainforest mesocosm

The 27,000 m^3 tropical rainforest mesocosm at Biosphere 2 currently includes 91 species of tropical plants from 41 families, including 73 trees, under a flat-topped pyramidal glass enclosure operated as an open-flow system [Pegoraro et al., 2005]. Typical of neotropical forests, the trees are dominated by Fabaceae (pea family) and Arecaceae (palm family). Branch enclosure air temperature and PAR at branch height were continuously recorded. Eight 7-10 day measurement periods were made during 22 January to 14 April 2010. The following seven species were analyzed for DMS emissions using branch enclosures: *Mangifera indica L*., *Pterocarpus indicus* Wild., *Alpinia zerumbet* (Pers.) B.L. Burtt & R.M. Sm., *Hibiscus rosa-sinensis* L., *Inga vera* Wild., *Cissus sicyodes L.* Nicolson & C.E. Jarvis, and *Canna indica* L.

A fraction of the air entering and exiting a dynamic branch enclosure inside the tropical mesocosm were continuously pumped at ~1.0 l min^{-1} through heated (50 °C) Teflon tubing (PFA, ¼ in. O.D. x 60 m) into the adjacent laboratory for trace gas analysis. The two gas samples were sequentially analyzed for DMS mixing ratios by PTR-MS (each gas sample measured every hour). Branch DMS emission rates were calculated based on the flow rate through the enclosure (5 L min^{-1}), the mixing ratio difference between the air entering the enclosure and the air inside the enclosure, and the total leaf area inside the enclosure. The tubing was heated to minimize wall losses, but we did not account for potential loss of DMS to branch enclosure surfaces and/or tubing walls.

1.2 Gas Chromatography-Mass Spectrometry analysis of branch DMS emissions

Qualitative identification of DMS in the enclosure air from two of the plant species studied inside the Biosphere 2 rainforest mesocosm (*Hibiscus rosa – sinensi* and *Phytolacca dioica*) was performed using a thermal desorption gas chromatograph-mass spectrometer (TD-GC-MS). DMS was identified using a Series 2 air server connected to a Unity 2 thermal desorption system (MARKES International) interfaced with a 5975C series Gas Chromatograph/Electron Impact Mass Spectrometer with a triple-axis detector (Agilent Technologies). Air samples (1.5 L) entering and exiting the 5.0 L branch enclosure were preconcentrated on an internal sorbent tube (water management cold trap, MARKES International), held at 30 ºC (to avoid excess water collection) and dried by purging with dry carrier gas at 20 cm^3 min^{-1} (STP) for 20 min. During injection, the trap was heated to 300 ºC for three minutes while back flushing with

carrier gas at a flow of 6.5 cm^3 min^{-1} (STP). In order to improve peak shape and further reduce the amount of water introduced into the GC-MS, 5 cm^3 min^{-1} (STP) of this flow was vented through the split while the remaining 1.5 cm^3 min^{-1} (STP) was directed to the column (Agilent DB624 60 m x 0.32 mm x 1.8 µm), temperature programmed with an initial hold of 3 min at 40 ºC followed by an increase to 230 ºC at 6 ºC min^{-1}. The mass spectrometer was configured in scan mode (m/z 40-300) for trace analysis (15 X detector gain factor). The presence of DMS in the enclosure air was verified by comparison of the retention time (7.8 min) with that of an authentic standard and by comparison of the mass spectra with the standard and with the National Institute of Standards and Technology (NIST) database (**Fig. S5**).

1.3 Soil emissions of DMS using PTR-TOF-MS in laboratory incubation experiments

Re-wetted soil samples from the Amazon rainforest in Suriname were continuously dried in a laboratory incubation system [Behrendt et al., 2014]. The mixing ratio of DMS within the soil enclosure was monitored at high time resolution by a proton transfer reaction – time of flight – mass spectrometer (PTR-TOF-MS 8000, IONICON, Austria, see [Graus et al., 2010]). The post-processing of the data was performed according to standard procedures described elsewhere [Müller et al., 2010; Titzmann et al., 2010; Müller et al., 2011; Müller et al., 2013]. For PTR-TOF-MS calibration, a DMS compressed gas standard was used (Apel–Riemer Environmental, USA). In the dynamic chamber system a purging flow of 2.5 l min^{-1} hydrocarbon-free air was directed either through a reference chamber without soil or through a soil chamber by switching of valves. A previously described approach [Behrendt et al., 2014] was used to convert the mixing ratio of DMS into the net release rate of DMS, J_{DMS}, and the water vapor signal to gravimetric soil moisture (determined by a mass balance). While the soil sample was drying out, the soil temperature was sequentially switched between T_0=20°C and T_1=30°C to determine the temperature amplification factor, known as the Q_{10} value [Feig et al., 2008]. J_{DMS} was converted to a net potential flux of DMS, F_{lab}, by the use of the area of the soil chamber (~6.65 $x10^{-3}$ m^2).

2. Auxiliary figures

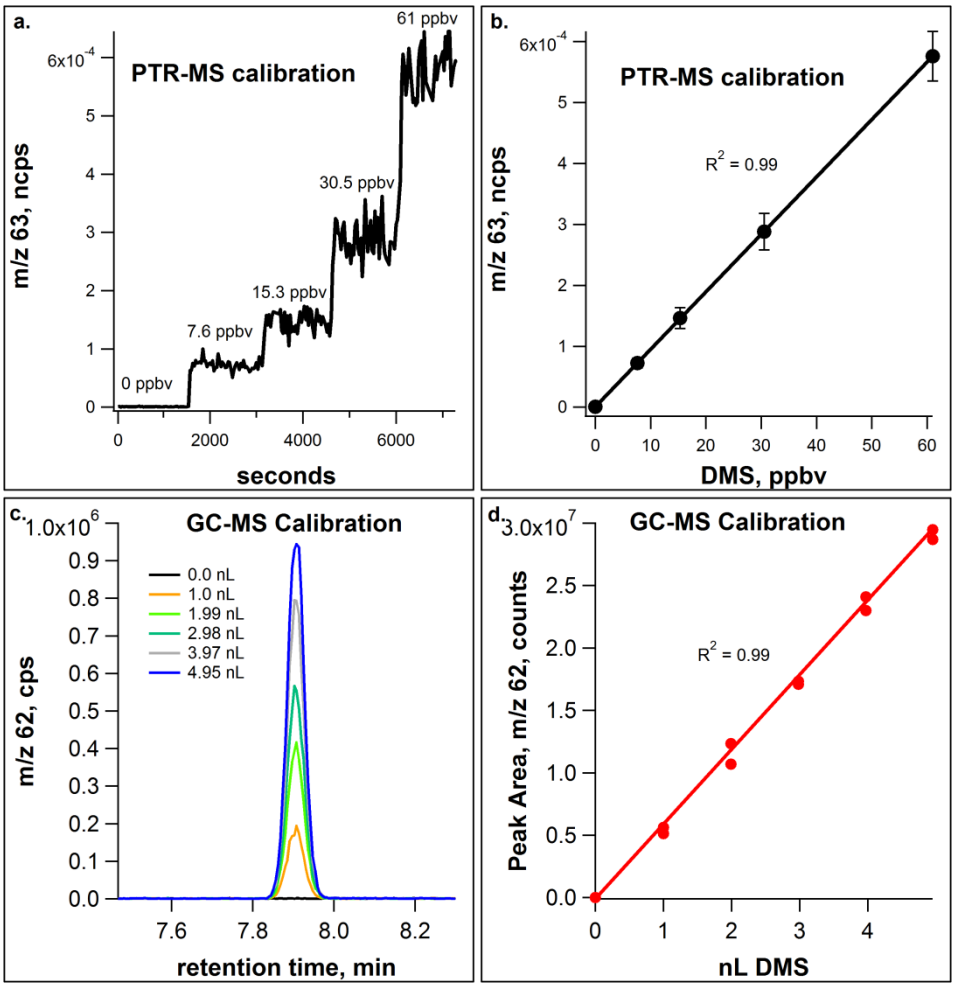

Figure A1: PTR-MS and GC-MS calibrations to DMS. (**a**) PTR-MS m/z 63 time series plot and (**b**) linear calibration curve showing high sensitivity and linearity to gas-phase DMS standards generated using the dynamic dilution of a liquid DMS standard. (**c**) GC-MS m/z 62 chromatograms and (**d**) linear calibration curve showing high sensitivity and linearity to gas-phase DMS standards generated by dynamic dilution of a compressed gas standard.

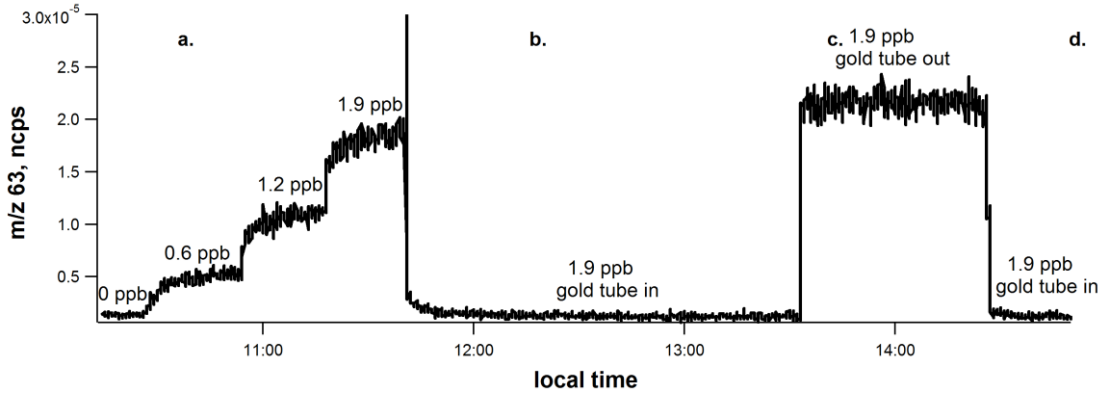

Figure A2: PTR-MS calibration to a DMS standard **a,c**) without and **b,d**) with a gold-wool tube in-line. Note the quantitative removal of DMS by placing the gold-wool tube in-line just prior to the PTR-MS inlet.

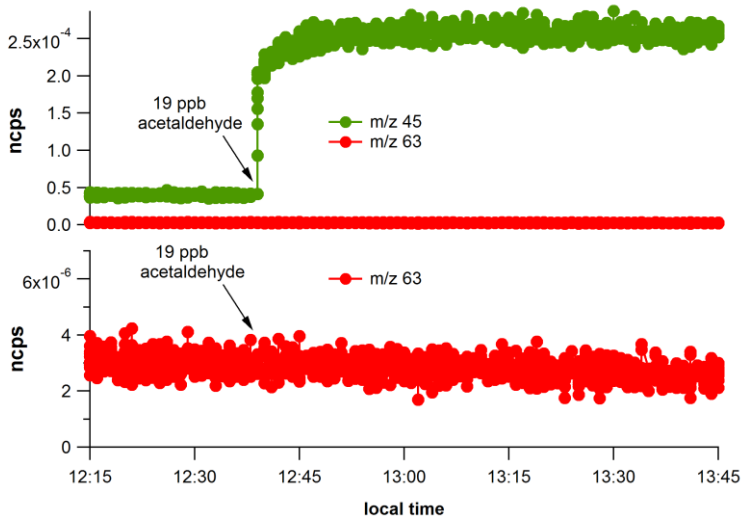

Figure A3: Analysis of potential humidity-dependent interference on the PTR-MS signal at m/z 63 (ncps) by a protonated acetaldehyde-water cluster. When 19.0 ppb acetaldehyde was added to air with a 20 ˚C dew point, a strong signal was observed at m/z 45 (ncps). However, the lack of signal at m/z 63 upon addition of acetaldehyde to the humidified air demonstrates the lack of significant acetaldehyde-water cluster formation.

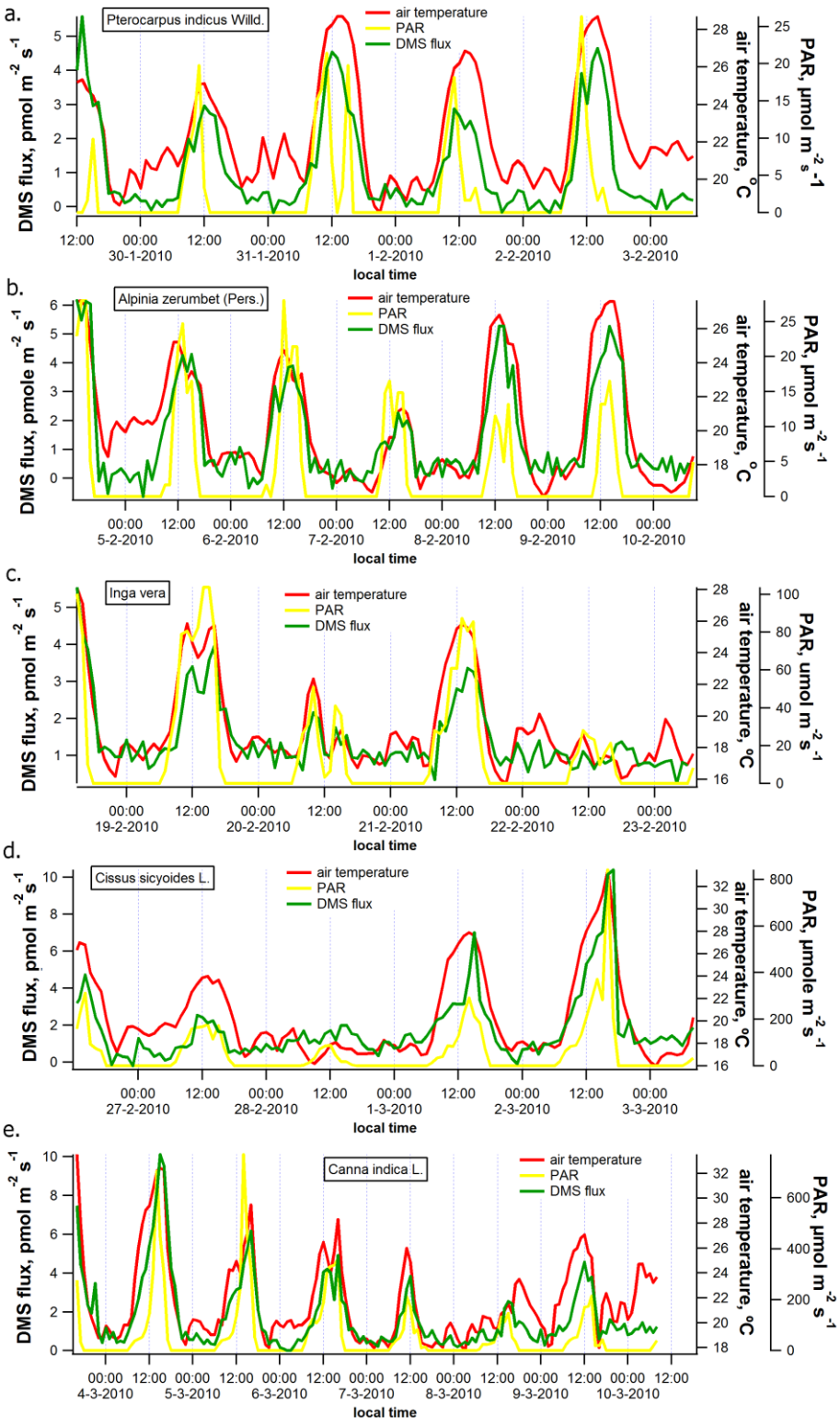

Figure A4: Time series plots of DMS emission rates from isolated branches from five additional tree species growing in the large tropical rainforest mesocosm in Arizona. Species shown include (a) *Pterocarpus indicus*, (b) *Alpinia zerumbet*, (c) *Inga Vera*, (d) *Cissus sicyodes*, and (e) *Canna indica*. Air temperature and photosynthetically active radiation (PAR) are also shown.

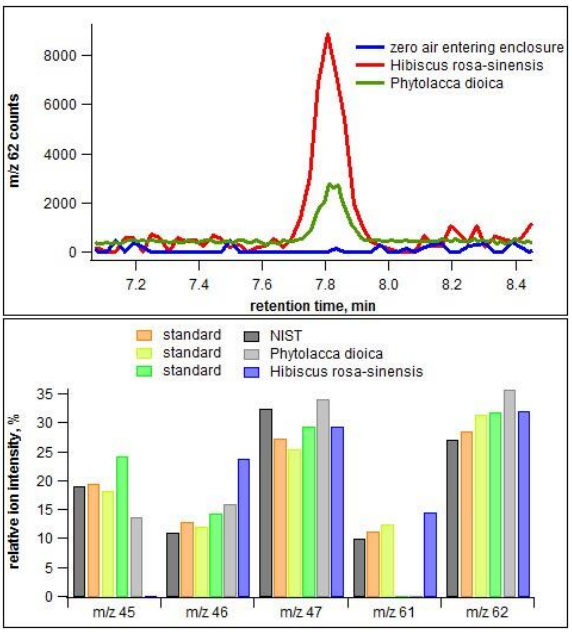

Figure A5: GC-MS chromatogram of branch enclosure air for two tropical plant species inside the rainforest mesocosm showing the presence of DMS (7.8 min retention time). Also shown are the relative ion intensities of the dominant DMS mass spectral fragments from the enclosure air samples together with the standard and NIST database.

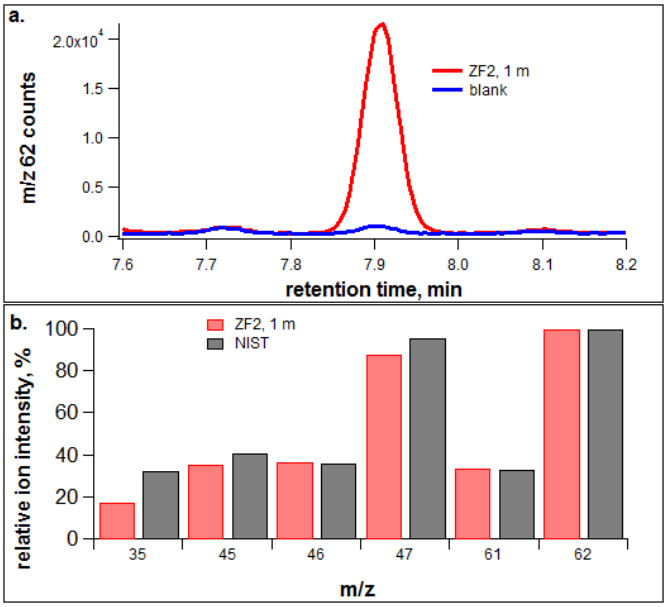

Figure A6: DMS in ambient air near the ground (1 m) at the ZF2 site in the central Amazon identified by GC-MS. (A) Selected ion GC-MS chromatogram of m/z 62 showing a peak at 7.9 min. (B) Relative ion intensity of the DMS mass spectral fragments extracted from the chromatogram at 7.9 min showing the presence of all major DMS ions reported in the NIST mass spectral database.

3. Auxiliary references

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