Amy M. Trowbridge, Ryan W. Daly, Detlev Helmig, Paul C. Stoy, and Russell K. Monson. **Herbivory and climate interact serially to control monoterpene emissions from pinyon pine forests.**

Appendix D. Methods describing volatile chemical analysis using thermal desorption.

Cartridge samples were analyzed for monoterpene emission rates within 7-21 days after sample collection by thermal desorption (Perkin-Elmer ATD400) GC-FID/MS (Hewlet-Packard 5890/5970, Wilmington, DE) following Helmig et al. (2004). The GC was fitted with a DB-1 column (30m x 0.320μm x 0.025μm, J & W Scientific, Folsom, CA) and compound separation was achieved through the following program: initial temperature of 40 °C held for 5 minutes with a ramp of 6 °C min^{-1} up to 200 °C and held for 5 minutes at this final temperature. A hydrogen carrier gas swept the analyte from the thermal desorber to the GC at a flow rate of 2.1 ml min-1, split between FID and MS detectors at a 4:1 split ratio. The instrument was calibrated with an n-alkane reference standard (NOAA, Boulder, CO) to determine a response factor (RF, peak area mL^{-1}$_{sample\ volume}$ ppbC^{-1}) that was used to calculate monoterpene concentrations. Individual compounds were identified by using authentic standards where available as well as the comparison of GC retention index (RI) and mass spectra scans to those reported by Adams (1989). Chromatograms were integrated using PeakSimple software (SRI Instruments, Menlo Park, CA). Emission rates were determined in the following manner. VOC mixing ratio (MR_{ppbV}) was calculated according to equation D.1:

$$MR_{[ppbV]} = \frac{PA}{V \cdot RF} \cdot \frac{N}{ECN} \qquad\qquad (D.1)$$

where *PA* is the integration peak area, *V* is the volume sampled, *RF* is the normalized per unit carbon calibrated GC-FID response factor, *N* is the number of carbons and *ECN* is the effective carbon number per compound. An emission rate in terms of µg ml^{-1} was then computed (Eq. D.2) taking into consideration molecular weight (*MW*) of the compound and accounting for standard temperature and pressure of the sample volume:

$$ER_{[\mu g\,ml^{-1}]} = \frac{MR}{1 \cdot 10^9} \cdot \frac{P}{R \cdot T} \cdot MW \qquad \text{(D.2)}$$

Finally, the observed emission rate (*ER*) as µg g$_{\text{dry weight}}^{-1}$ hr^{-1} value was realized after taking into consideration the diluting pure flow rate (*D*) feeding the enclosure and dry weight (*DW*) of the enclosed biomass (Eq. D.3).

$$ER_{[\mu g g^{-1} hr^{-1}]} = ER_{[\mu g ml^{-1}]} \cdot \frac{D}{DW} \qquad \text{(D.3)}$$

Basal emission rates were calculated following Guenther et al. (1993) (Eq. D.4), where *M* is monoterpene emission rate at temperature *T* (ºC), M_s is monoterpene emission rate at a standard temperature T_s (30 ºC), and *β* (ºC^{-1}) is an empirical coefficient, which was set to 0.09 following Guenther et al. (1993) due to the variability among emission factors resulting from seasonal variation and compound specificity.

$$M = M_s \cdot \exp[\beta(T - T_s)] \qquad \text{(D.4)}$$

Literature Cited

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