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A comparison of new measurements of total monoterpene flux with improved measurements of speciated monoterpene flux

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Abstract. Many monoterpenes have been identified in forest emissions using gas chromatography (GC). Until now, it has been impossible to determine whether all monoterpenes are appropriately measured using GC techniques. We used a proton transfer reaction mass spectrometer (PTR-MS) coupled with the eddy covariance (EC) technique to measure mixing ratios and fluxes of total monoterpenes above a ponderosa pine plantation. We compared PTR-MS-EC results with simultaneous measurements of eight speciated monoterpenes, β-pinene, α-pinene, 3-carene, d-limonene, β-phellandrene, α-terpinene, camphene, and terpinolene, made with an automated, in situ gas chromatograph with flame ionization detectors (GC-FID), coupled to a relaxed eddy accumulation system (REA). Monoterpene mixing ratios and fluxes measured by PTR-MS averaged 30±2.3% and 31±9.2% larger than by GC-FID, with larger mixing ratio discrepancies between the two techniques at night than during the day. Two unidentified peaks that correlated with β-pinene were resolved in the chromatograms and completely accounted for the daytime difference and reduced the nighttime mixing ratio difference to 20±2.9%. Measurements of total monoterpenes by PTR-MS-EC indicated that GC-FID-REA measured the common, longer-lived monoterpenes well, but that additional terpenes were emitted from the ecosystem that represented an important contribution to the total mixing ratio above the forest at night.

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