Nonmethane Hydrocarbon, Monocarboxylic Acid, and Low Molecular Weight Aldehyde and Ketone Emissions from Vegetation in Central New Mexico

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Direct emissions of nonmethane hydrocarbons, monocarboxylic acids, and low molecular weight carbonyl compounds were measured from vegetation typical to central New Mexico. These species included quaking aspen, cottonwood, Gambel oak, Douglas fir, Engelmann spruce, Rocky Mountain juniper, pinyon pine, and ponderosa pine. The hydrocarbon emissions from most of the coniferous trees were dominated by R\text{-}\text{pinene, myrcene, etc.} from deciduous trees as well as the spruce and fir trees showed isoprene emissions averaged 50–1660 ng g\(^{-1}\) h\(^{-1}\). Formaldehyde and acetaldehyde were the most common low molecular weight carbonyl compounds measured. The carbonyl emissions averaged 50–1660 ng g\(^{-1}\) h\(^{-1}\), depending on the compound and the trees species. Unlike the hydrocarbons, the carbonyl emissions displayed little correlation with enclosure temperature. Formic acid emissions averaged 15–920 ng g\(^{-1}\) h\(^{-1}\), and acetic acid emissions averaged 50–1300 ng g\(^{-1}\) h\(^{-1}\). As with the carbonyls, poor correlation was found between the acid emissions and the enclosure temperature. The deciduous trees were found to have average (mass-based) emissions of 98% hydrocarbons, 1% carbonyls, and 1% organic acids. The coniferous trees averaged 80%, 8%, and 12%, respectively.

Introduction

Emissions of reactive hydrocarbons from locally dominant vegetative species have been an area of growing interest in recent years. The impact of these ubiquitous, reactive compounds has been identified as an important constituent in regional and local atmospheric photochemical processes (1, 2). Much of the previous work has focused on the emission rates of olefinic species, including isoprene and monoterpenes (R\text{-}\text{pinene, R\text{-}\text{pinene, myrcene, etc.}}) from deciduous and coniferous trees (3–7). These data subsequently have been included in atmospheric models to estimate the production and reactions of secondary species such as ozone, organic acids, low molecular weight aldehydes and ketones, organonitrites, and other compounds for comparison with diurnal ambient measurements and to elucidate tropospheric photochemical behavior in areas of suspected significant biogenic impact (1, 8–10).

Many low molecular weight oxygenated compounds, such as formaldehyde, acetaldehyde, acetone, formic acid, and acetic acid, have been identified as key photochemical and acidic species, particularly in rural and remote environments. Relatively little work has been reported on the potential of vegetative emissions as direct sources of these important atmospheric species, although biogenic contributions of other species are often assumed to be significant. Indeed many modeling and apportionment studies assume ambient acids, and other carbonyls are derived primarily via photochemical production in conjunction with anthropogenic activities such as mobile sources and industrial combustion (11–13).

Few examinations of the vegetative, biogenic volatile organic carbon emissions have been made for trees in the southwestern United States. Several of the locally dominant tree species have been measured elsewhere, but not under field conditions typical of the arid southwest. The study reported herein describes field measurements of isoprene and monoterpene emissions from a wide range of southwest trees species using a dynamic enclosure technique. Additionally, as an equally important part of this study, emissions of organic acids and low molecular weight carboxyls were also examined.

Experimental Methods

Sampling Locations. During the summer of 1996, emissions of terpenic hydrocarbons, organic acids, aldehydes, and ketones were measured from eight tree species indigenous to New Mexico including quaking aspen (Populus tremuloides), cottonwood (Populus fremontii), Gambel oak (Quercus gambeli), Douglas fir (Pseudotsuga menziesii), Engelmann spruce (Picea engelmannii), Rocky Mountain juniper (Juniperus scopulorum), pinyon pine (Pinus edulis), and ponderosa pine (Pinus ponderosa). The samples were obtained from residential trees in Socorro, NM (1370 m elevation, 34.1° latitude, 106.9° longitude), and at various locations and elevations in the nearby Magdalena Mountains within the Cibola National Forest (33.9° latitude, 107.2° longitude). During May, samples were collected from juniper, ponderosa pine, pinyon pine, and cottonwood trees within the city limits of Socorro. This period was meteorologically characterized by unusually high temperatures (28.6 °C, average enclosure temperature) and a severe, sustained drought. During July and August, aspen, oak, Douglas fir, Engelmann spruce, and ponderosa pine trees were sampled in the Magdalena Mountains at elevations of 2130–3260 m. Cooler temperatures (18.5 °C, average enclosure temperature) and precipitation were common during this latter period. Finally, the same cottonwood tree previously sampled in May was re-examined in September (21.4 °C, average enclosure temperature), after significant summer precipitation.

Sample Collection and Analysis. A dynamic enclosure system was constructed using a 31.3 L (57 cm × 57 cm) Tedlar bag modified to slide over target branches and capable of being sealed around the branch with tape or rubber bands. Each tree was sampled over a 1–4 day period, with samples being collected nominally at 800, 1200, 1500, 1800, and 2400.
Compressed cylinder air, scrubbed via a series of desiccant and activated charcoal traps, was introduced at a rate of 12–13 L min⁻¹ on one side of the enclosure and withdrawn for sample analysis on the opposite side. Purified air was used as sweep air to ensure the compounds sampled were direct plant emissions and not brought in with the introduced air or formed via photochemical reactions. It was expected that the enclosure concentrations of the target species would be sufficiently above ambient levels to minimize any gradient emission effects. Furthermore, Kesselmeier et al. (14) have suggested that, for organic acids at least, the direction and the strength of the exchange is not or only weakly influenced by atmospheric concentrations. By maintaining a greater inlet sample flow rate than required by the various sampling systems, a positive pressure was obtained within the enclosure, slightly inflating the bag and minimizing leaf or needle damage. System flow rates were checked using mass flowmeters, and enclosure temperatures were monitored using a type K thermocouple. During nonsample periods, ambient air was swept through the enclosure to prevent excessive buildup of heat, moisture, and target gaseous species. After completion of each sampling session, the leaves/needles contained within the enclosure were recovered and oven dried (100 °C) for a minimum of 3 h until a constant weight was obtained.

Hydrocarbon samples were periodically collected by withdrawing whole air samples at a rate of about 370 mL min⁻¹ into 3.8 L (28.5 cm × 28.5 cm) Tedlar bags using a peristaltic pump. Prior to each use, the sample bags were triple rinsed with purified zero air and randomly checked for potential carryover. Once the samples were collected, the bags were stored at room temperature in the dark until subsequently analyzed at New Mexico Tech’s (NMT’s) Environmental Engineering Laboratory via GC/FID analysis, usually within 2 or 3 days. Stability studies were conducted and showed no significant hydrocarbon degradation for samples stored in the Tedlar bags under these conditions for periods up to 1 week (15). Measured volumes of sample (200–300 mL) were cryogenically preconcentrated into a stainless steel sample loop immersed in a liquid oxygen bath before being introduced onto the chromatographic column (DB-1; J&W Scientific). The column temperature was controlled via a profiling program that started at −20 °C for 3 min and then increased at 5 °C/min⁻¹ until a final temperature of 150 °C was reached. Peak identification was accomplished via retention time comparison with a specifically developed qualitative standard and quantified by FID response comparison with a neohexane external standard (200 ppb; Scott Specialty Gas). The lower detection limit for the target hydrocarbons as given by resolved chromatographic peaks was 0.5–1.0 ppb. Repeated analysis of the external standard (n = 53) showed repeatability within ±15% and a population standard deviation of 6.5%.

Organic acid species were collected via a mist chamber technique modified from Cofer et al. (16) and Andreae et al. (17), as described in Gaffney et al. (18). Sample air at 2–3 L min⁻¹ was pulled from the enclosure through a glass nebulizer (Devilbiss; model 40) containing 5–10 mL of distilled, deionized water for a period of 2 h around each of the nominal times previously mentioned. Samples were recovered by rinsing and diluting the nebulizer solution into dark, glass bottles to a total volume of 15 mL and sealed with Teflon-lined lids. Three drops of chloroform were added to each bottle to prevent microbial sample degradation. The bottles were then stored refrigerated until analyzed. Acid concentrations were determined at NMT’s Chemistry Laboratory by ion chromatography (Dionex 2000 system) using an Ionpac AS11-4mm analytical column with an AS11 guard column and a 2.5 mM potassium borate eluent. Quantification and identification were accomplished by comparison of detector response and retention to a series of diluted aqueous standards (sodium salts, 99.5%+ purity, Aldrich Chemical Co.). Standards were analyzed every six samples to verify the calibrations. Additionally, blank samples were taken once each day by setting up the sampling system as normal but immediately recovering the nebulizer rinse as described above without exposing the water to the enclosure environment. The acid detection limits, calculated from twice the deviation of the blanks, were 0.7 and 0.4 ppb for acetic and formic acids, respectively. Duplicate analysis was performed on 10% of the samples with the resulting error typically less than 10%.

Carbonyl samples were withdrawn from the enclosure at about 1.0 L min⁻¹ during the same time periods as the acid samples. Flow rates were controlled by a rotameter and calibrated using a mass flowmeter. Aldehydes and ketones were collected using 2,4-dinitrophenylhydrazine (DNPH)-coated Sep Pak C18 cartridges (Waters and Associates) as described by Zhou and Mopper (19) and Gaffney et al. (18). After exposure, the cartridges were recovered, wrapped with aluminum foil, and stored refrigerated in a clean, dark bottle until analyzed. The carbonyl hydrazones were eluted using HPLC-grade acetonitrile and analyzed by HPLC chromatography with UV detection. A 60:40 acetonitrile:water eluent was used to carry the sample through an Alltech C18U analytical column preceded by an Alltech C18U-5U guard column. Specifically prepared liquid standards were used for concentration determinations. Each day, as with the acids’ protocol, blank cartridges carried to and from the test site were processed in a similar manner as the sample cartridges. The carbonyl detection limits, calculated as above, were 0.8, 0.9, 1.5, 1.1, 0.4, and 1.6 ppb for formaldehyde, acetaldehyde, acetone, propionaldehyde, methacrolein, and methyl ethyl ketone, respectively. Duplicate analysis on 10% of the samples showed relative repeatability on the order of 15%.
In addition to the emission samples from the branch enclosures, concurrent ambient samples were also collected in the vicinity of the trees. The collection and analytical methodologies for the ambient samples were the same as for the enclosure samples, with the exception that samples were drawn directly from ambient air.

Results and Discussion

Terpenic Hydrocarbons. Six monoterpenes (α-pinene, camphene, β-pinene, myrcene, Δ^3-carene, and d-limonene) and one hemiterpene (isoprene) were identified as direct emissions from some or all of the examined trees species. It should be noted that several unidentified compounds were also observed on the individual chromatographs. As expected, the primary emissions from most the species belonging to the pine (Pinaceae) family were monoterpenes, with α-pinene being the most prevalent. In contrast, isoprene was the primary emission from the Engelmann spruce, also a member of the pine family. Other investigators have also shown significant isoprene emissions from spruce trees (7). The expected temperature dependence of the monoterpene emissions was observed for most of the dominant, identified compounds. For example, the mass rate of α-pinene emissions per unit mass of dried biomass (ng g⁻¹ h⁻¹) as compared to enclosure temperature can be seen in Figure 1. In general, average α-pinene emissions were on the order of 100–10 000 ng g⁻¹ h⁻¹. All of the monoterpene emission data were subsequently fitted to logarithmic algorithms (ln E = a + b (°C)) as described by Lamb et al. (20), which are shown as curves in Figure 1 and numerically in Table 1. The slope term for the major monoterpenes, defined as those with a correlation coefficient (r²) greater than or equal to 0.35, was consistent with those reported elsewhere (7, 21–23). Emissions of α-pinene from the Engelmann spruce showed no clear temperature dependency (r² < 0.01). Significant rains during the Engelmann measurements may have hindered reliable measurements.

Although α-pinene was dominant to most of the pine family, the remaining principal monoterpenes were different for each Pinaceae tree. Figure 2 shows the relative average occurrence, based on mass percentage, of each hydrocarbon emission from the tested trees. The majority of the identified...
Uncertainty Represents

Ponderosa pine emissions were predominantly characterized by \(\alpha\)-pinene (8%) and \(\Delta^3\)-carene (17%), with \(\beta\)-pinene accounting for only 7%.

Tree emissions measured later in the summer displayed greater temperature dependence than those measured in the spring (refer to Figure 1 and Table 1). It should be noted that although two different ponderosa pine trees were sampled during the early and late sample periods and that some natural tree variability is likely, the apparent seasonal trend mimics that of the single cottonwood that was examined during both periods. One likely factor influencing the early summer (hotter) measurements was the local meteorology of persistent drought and unusually warm temperatures that occurred throughout much of the southwestern United States from winter to early summer of 1996.

The deciduous species’ emissions were strongly dominated by isoprene, as was the previously mentioned Engelmann spruce. Also, as indicated above, the Douglas fir showed isoprene emissions on the same order as several of the monoterpenes. Figure 3 shows the approximate logarithmic relationship of emissions with temperature for the isoprene-emitting species. Derived equations can be found in Table 1. Although it is well-established that isoprene emissions are additionally light dependent (24), equipment limitations and the preliminary nature of this study precluded light measurements. The deciduous trees showed average isoprene emission rates in the range of \(100 - 100000\) ng g\(^{-1}\) h\(^{-1}\), reaching approximately 1 order of magnitude greater values than the measured monoterpenes rates discussed above. Of the isoprene emitters, the Douglas fir typically showed the lowest isoprene emission rate. The Engelmann spruce, as with the monoterpenes, showed little correlation between temperature and isoprene emissions (\(r^2 = 0.09\)).

**Low Molecular Weight Aldehyde and Ketones.** Formaldehyde (46%), acetaldehyde (23%), acetone (8%), propionaldehyde (10%), methacrolein (4%), and methyl ethyl ketone (9%) were in some or all of the emission samples. The percentages represent the overall average emissions distribution by mass. As shown, formaldehyde and acetaldehyde were the most common, collectively accounting for an average of approximately 70% of the measured vegetative aldehyde and ketone emissions. Formaldehyde emissions were typically larger than those of acetaldehyde. As can be seen in Table 2, these emissions averaged approximately 50–

**TABLE 2. Average Aldehyde, Ketone, and Organic Acid Emission Rates (ng g\(^{-1}\) h\(^{-1}\)) and Average Enclosure Temperature (Uncertainty Represents ±1 SD)**

<table>
<thead>
<tr>
<th>Tree Type</th>
<th>Formaldehyde</th>
<th>Acetaldehyde</th>
<th>Other Carbonyls</th>
<th>Formic Acid</th>
<th>Acetic Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aspen (Jul 30–Aug 2)</td>
<td>1658 ± 807</td>
<td>1122 ± 500</td>
<td>489 ± 38</td>
<td>916 ± 586</td>
<td>1275 ± 619</td>
</tr>
<tr>
<td>Cottonwood (May 29–31)</td>
<td>287 ± 103</td>
<td>64 ± 74</td>
<td>97 ± 199</td>
<td>203 ± 402</td>
<td>125 ± 246</td>
</tr>
<tr>
<td>Cottonwood (Sep 22–23)</td>
<td>1150 ± 574</td>
<td>54 ± 49</td>
<td>307 ± 48</td>
<td>363 ± 210</td>
<td>885 ± 386</td>
</tr>
<tr>
<td>Oak (Aug 21–25)</td>
<td>823 ± 356</td>
<td>49 ± 83</td>
<td>nd*</td>
<td>711 ± 445</td>
<td>1107 ± 590</td>
</tr>
<tr>
<td>Engelmann Spruce (Jul 16–20)</td>
<td>70 ± 33</td>
<td>111 ± 123</td>
<td>219 ± 54</td>
<td>16 ± 14</td>
<td>52 ± 80</td>
</tr>
<tr>
<td>Douglas Fir (Jul 22–25)</td>
<td>519 ± 347</td>
<td>588 ± 544</td>
<td>271 ± 24</td>
<td>260 ± 190</td>
<td>902 ± 1256</td>
</tr>
<tr>
<td>Juniper (May 8–10)</td>
<td>163 ± 79</td>
<td>106 ± 129</td>
<td>568 ± 752</td>
<td>23 ± 84</td>
<td>225 ± 234</td>
</tr>
<tr>
<td>Pinyon Pine (May 18–20)</td>
<td>258 ± 242</td>
<td>49 ± 41</td>
<td>73 ± 113</td>
<td>15 ± 13</td>
<td>310 ± 442</td>
</tr>
<tr>
<td>Ponderosa Pine (May 3)</td>
<td>289 ± 215</td>
<td>494 ± 197</td>
<td>451 ± 770</td>
<td>260 ± 132</td>
<td>179 ± 106</td>
</tr>
<tr>
<td>Ponderosa Pine (Aug 12–16)</td>
<td>668 ± 257</td>
<td>286 ± 181</td>
<td>510 ± 74</td>
<td>283 ± 88</td>
<td>354 ± 87</td>
</tr>
</tbody>
</table>

* nd, none detected.
1660 ng g⁻¹ h⁻¹, depending on the compound and the trees species. Kesselmeier et al. (25) reported similar magnitude of emissions of formaldehyde and acetaldehyde, normalized to 30 °C, for Mediterranean oak (Q. ilex) and Italian stone pine (P. pinea). Occasionally, methacrolein, a known isoprene oxidation product, was detected in both deciduous and coniferous emissions, but it averaged only 2.1% (based on mass) of the total aldehydes and ketones from the tree emissions in which it was detected.

In broad terms, the deciduous trees were found to have greater aldehyde and ketone emissions than the coniferous trees, with formaldehyde typically being the most dominant. This trend can be seen in Figure 4, which shows plots for formaldehyde and acetaldehyde emissions compared to enclosure temperature for the various tree species. As can be seen, the range of emissions was quite broad for most species. The deciduous species consistently showed greater formaldehyde emissions, while the dominance of formaldehyde or acetaldehyde varied among the coniferous trees. Kesselmeier et al. (25) reported acetaldehyde emissions as being greater than formaldehyde for both deciduous (Q. ilex) and a coniferous (P. pinea) species. As with the hydrocarbon emissions, it appears that the early season measurements were generally less in magnitude than the later measurements. This may again reflect the physiological state of the tree during drought stress conditions.

Unlike isoprene and the monoterpens, the measured aldehydes and ketones only occasionally displayed correlation between the natural log of the emission rate and enclosure temperature, suggesting the possibility of a different emissions mechanism. The average correlation coefficient for formaldehyde and temperature was 0.31, and for acetaldehyde and temperature, the average correlation coefficient was 0.27. Kesselmeier et al. (25) also noted no clear physiological dependence for the short-chain aldehyde emissions.

**Monocarboxylic Acids.** Formic and acetic acid emissions were detected from all measured species. Figure 5 shows the formic and acetic acids compared to enclosure temperature for each of the tested trees species. The C2 species (acetic acid) was nominally emitted in greater quantities than the C1 species (formic acid). The opposite was generally found for the aldehydes discussed above. Average emission rates can be found in Table 2 and comparisons with biogenic organic acid emissions reported by other investigators (14, 24–27) can be seen in Table 3. Individually, the highest acid emissions were from the aspen and the lowest were from the Engelmann spruce. As can be seen in Table 3 and Figure 5, the deciduous trees were typically found to have acidic emissions higher than the coniferous trees. Formic acid emissions averaged about 547 ng g⁻¹ h⁻¹ from the deciduous trees (excluding the May cottonwood) and 151 ng g⁻¹ h⁻¹ from the coniferous trees. Average acetic acid emissions were found to be 840 and 337 ng g⁻¹ h⁻¹ from the deciduous and coniferous trees, respectively.

Talbot et al. (26) quantified emissions of formic and acetic acids for trees from the Ducke Reserve in the Amazon region of Brazil using a static enclosure technique. Servant et al. (27) leached leaves using deionized water to estimate potential emission rates from trees in Congo’s Maymbe Forest. Kesselmeier et al. (14, 23) used a dynamic enclosure similar to the method of this study. The acid emission rates shown in Table 3 are compared on a dry weight basis as well as a leaf area basis whenever sufficient data were available. As can be seen in Table 3, the earlier investigators reported emission rates of similar magnitude but varying dominance.

**FIGURE 4.** Measured formaldehyde (○) and acetaldehyde (●) emission rates (ng g⁻¹ h⁻¹) from the tested tree species compared to enclosure temperature (°C).

**FIGURE 5.** Measured formic acid (○) and acetic acid (●) emission rates (ng g⁻¹ h⁻¹) from the tested tree species compared to enclosure temperature (°C).
Acids from the Tested Tree Species and the Average

TABLE 3. Comparison of Biogenic Formic and Acetic Acid Emission Rates with Other Investigators

<table>
<thead>
<tr>
<th>Species</th>
<th>Formic acid (ng g⁻¹ h⁻¹)</th>
<th>Acetic acid (ng g⁻¹ h⁻¹)</th>
<th>Kesselmeier et al. (14), B. pendula</th>
<th>Kesselmeier et al. (14), Q. ilex</th>
<th>Kesselmeier et al. (14), F. excelsior</th>
<th>Kesselmeier et al. (14), F. sylvatica</th>
<th>Kesselmeier et al. (14), Q. ilex</th>
<th>Kesselmeier et al. (14), (25) Q. ilex</th>
<th>Kesselmeier et al. (25), Q. ilex</th>
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</thead>
<tbody>
<tr>
<td>ponderosa pine (Aug)</td>
<td>6347</td>
<td>1464</td>
<td>21.4</td>
<td>28.5</td>
<td>151</td>
<td>4.1 × 10¹⁰</td>
<td>373</td>
<td>4.4 × 10⁹</td>
<td>21.4</td>
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<tr>
<td>ponderosa pine (May)</td>
<td>3482</td>
<td>247</td>
<td>27.8</td>
<td>3.6 × 10⁹</td>
<td>254</td>
<td>5.2 × 10⁹</td>
<td>96</td>
<td>1.5 × 10⁹</td>
<td>27.8</td>
</tr>
<tr>
<td>pinyon pine</td>
<td>11969</td>
<td>76</td>
<td>29.2</td>
<td>1.1</td>
<td>56</td>
<td>1.3 × 10⁹</td>
<td>25</td>
<td>3.9 × 10⁹</td>
<td>29.2</td>
</tr>
<tr>
<td>juniper</td>
<td>4040</td>
<td>167</td>
<td>34.5</td>
<td>112</td>
<td>16745</td>
<td>1512</td>
<td>1218</td>
<td>9.3 ≈ 34.5</td>
<td>34.5</td>
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<tr>
<td>oak</td>
<td>8868</td>
<td>594</td>
<td>14.9</td>
<td>1162</td>
<td>2790</td>
<td>400</td>
<td>112</td>
<td>71.1 ≈ 14.9</td>
<td>14.9</td>
</tr>
<tr>
<td>Engelmann spruce</td>
<td>33288</td>
<td>3269</td>
<td>19.2</td>
<td>1911</td>
<td>8311</td>
<td>1377</td>
<td>1818</td>
<td>112.2 ≈ 19.2</td>
<td>19.2</td>
</tr>
<tr>
<td>Douglas fir</td>
<td>38081</td>
<td>112</td>
<td>28.5</td>
<td>138</td>
<td>16745</td>
<td>1512</td>
<td>1218</td>
<td>88.8 ≈ 28.5</td>
<td>28.5</td>
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<td>cottonwood (May)</td>
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<td>34.5</td>
<td>1218</td>
<td>2790</td>
<td>400</td>
<td>112</td>
<td>71.1 ≈ 34.5</td>
<td>34.5</td>
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<tr>
<td>cottonwood (Sep)</td>
<td>8868</td>
<td>594</td>
<td>14.9</td>
<td>1162</td>
<td>2790</td>
<td>400</td>
<td>112</td>
<td>71.1 ≈ 14.9</td>
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<tr>
<td>deciduous</td>
<td>47592</td>
<td>922</td>
<td>24.2</td>
<td>1052</td>
<td>1052</td>
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<tr>
<td>coniferous</td>
<td>4040</td>
<td>167</td>
<td>34.5</td>
<td>112</td>
<td>2790</td>
<td>400</td>
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<td>71.1 ≈ 34.5</td>
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<tr>
<td>combined</td>
<td>47592</td>
<td>922</td>
<td>24.2</td>
<td>1052</td>
<td>1052</td>
<td>1052</td>
<td>1052</td>
<td>24.2</td>
<td>24.2</td>
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</tbody>
</table>

TABLE 4. Average Summed Emission Rates (ng g⁻¹ h⁻¹) for the Identified Terpenic Hydrocarbons, Carbonyls, and Organic Acids from the Tested Tree Species and the Average Enclosure Temperatures

<table>
<thead>
<tr>
<th>Compound</th>
<th>Hydrocarbons (ng g⁻¹ h⁻¹)</th>
<th>Carboxyls (ng g⁻¹ h⁻¹)</th>
<th>Organic Acids (ng g⁻¹ h⁻¹)</th>
<th>Temp avg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aspen</td>
<td>10974</td>
<td>1372</td>
<td>1177</td>
<td>24.3</td>
</tr>
<tr>
<td>Cottonwood (May)</td>
<td>6157</td>
<td>622</td>
<td>968</td>
<td>24.1</td>
</tr>
<tr>
<td>Cottonwood (Sep)</td>
<td>47592</td>
<td>922</td>
<td>1052</td>
<td>24.2</td>
</tr>
</tbody>
</table>

Comparison of early season and late season once again indicates higher emissions during the latter portion. Direct comparison of the two tree types measured during both periods (cottonwood and ponderosa pine) showed greater emissions during the cooler, wetter portion of the study (August–September). As with the aldehydes and ketones, the emissions of the measured organic acids showed poor correlation with temperature for most of the measured tree species (see Figure 5). The average correlation coefficients were found to be 0.17 and 0.16 for formic and acetic acids, respectively; once again indicating the apparent lack of temperature dependence on emission rate. The late summer cottonwood measurements were the exceptions with correlation coefficients of 0.73 for formic acid and 0.87 for acetic acid. Kesselmeier et al. (14, 23) found formic acid and acetic acid emissions closely related to plant transpiration and fit the emissions data to a light- and temperature-dependent relationship similar to the isoprene emission algorithm presented by Guenther et al. (28). Unfortunately, support (PAR) measurements necessary for determination of this process were not conducted during this study. However, it should be noted that emissions were observed during the nighttime samples, indicating that additional mechanisms may need to be examined. Interestingly, the average correlation coefficient for comparison of the formic acid emissions to those of acetic acid for the individual tree species was calculated to be 0.70, suggesting commonality in emission mechanism from the leaves.

Total Measured Emissions. As can be seen in Tables 4 and 5, on a mass compound per unit mass biomass basis, hydrocarbons (primarily isoprene from the deciduous species and α-pine for the coniferous trees) represented the bulk of the measured compounds. Total measured emissions averaged 110 000 ng g⁻¹ h⁻¹ for the deciduous trees and 6200 ng g⁻¹ h⁻¹ for the coniferous trees. The deciduous trees were found to have an average of ~98% of the measured emissions attributable to terpenic hydrocarbons, while the coniferous trees averaged 80%. It should be noted, however, that the lower percentages of aldehyde, ketone, and organic acid emissions from the deciduous trees do not reflect the relative mass of these compounds when compared to the coniferous tree emissions. The dominance of the aldehydes and ketones as compared to the organic acids also appeared to be split between deciduous and coniferous. Although the differences in average values were often slight, deciduous trees were generally found to have slightly greater emissions of the measured organic acids than the aldehydes and ketones. The opposite trend was typically noticed for the coniferous trees.

Table 5 also shows a comparison of the average mass distribution of the measured species for the emissions and concurrent ambient measurements. As can be seen, the mass ratios among the individual compound classes differed between the direct emissions and the ambient concentrations. The terpenic hydrocarbons represented the dominant directly emitted class (96%), while the aldehyde/ketone group was the largest in the ambient samples (54%). Since the sampling sites were located in rural and remote areas, the direct emissions closely related to plant transpiration and fit the emissions data to a light- and temperature-dependent relationship similar to the isoprene emission algorithm presented by Guenther et al. (28). Unfortunately, support (PAR) measurements necessary for determination of this process were not conducted during this study. However, it should be noted that emissions were observed during the nighttime samples, indicating that additional mechanisms may need to be examined. Interestingly, the average correlation coefficient for comparison of the formic acid emissions to those of acetic acid for the individual tree species was calculated to be 0.70, suggesting commonality in emission mechanism from the leaves.

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shift in dominance is believed to be a function of photochemical oxidation and transport.

Emissions of biogenic hydrocarbons are important precursors to many atmospheric reactions. The results of this study suggest direct vegetative sources for many of the low molecular weight oxygenated compounds previously thought to be produced primarily via atmospheric reactions or anthropogenic emissions. Guenther et al. (29) estimated the annual global flux of isoprene and monoterpenes to be 506 and 127 Tg of C, respectively. Using the mass ratios shown in Table 5, a first-order approximation of direct vegetative emissions of low molecular weight aldehydes, ketones, and organic acids can be derived. On the basis of these data, annual global vegetative emissions of the measured aldehydes and ketones are estimated to be 16 Tg, while the organic acid emissions are estimated to be approximately 20 Tg. Future studies of the photochemistry of tropospheric air impacted by vegetative emissions will need to include accurate emission estimates not only of the much studied hydrocarbons but also of formaldehyde, acetaldehyde, formic acid, acetic acid, and other oxygenated compounds.

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