Sources and sinks of formic, acetic, and pyruvic acids over central Amazonia: 2. Wet season

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Sources and Sinks of Formic, Acetic, and Pyruvic Acids
Over Central Amazonia

2. Wet Season

R. W. Talbot,1,2 M. O. Andreae,3,4 H. Berresheim,3,5 D. J. Jacob,6 and K. M. Beecher1

We have determined the gas phase concentrations of formic (HCOOH), acetic (CH3COOH), and pyruvic (CH3C(O)COOH) acids in the forest canopy, boundary layer, and free troposphere over the central Amazon Basin during the April–May segment of the 1987 wet season. At 150-m altitude in the boundary layer the daytime average concentrations were 450 ± 225, 340 ± 155, and 25 ± 15 ppt for HCOOH, CH3COOH, and CH3C(O)COOH, respectively. These values were fivefold lower than those observed in the 1985 dry season. Concentrations measured near canopy top were not significantly different from boundary layer values (P = 0.10), while concentrations in the lower canopy were significantly less. Concentrations in the free troposphere (5 km) were lower than in the boundary layer and averaged 170 ± 40, 210 ± 40, and 15 ± 15 ppt for HCOOH, CH3COOH, and CH3C(O)COOH, respectively. Fivefold enhancements of CH3C(O)COOH concentrations were observed in convective outflows at 5- to 6-km altitudes. Aerosol carbonylate concentrations were usually below our detection limit of 3–10 ppt. Preliminary branch enclosure measurements indicated significant direct emission of carbonylic acids by vegetation. A one-dimensional photochemical model for the canopy and the boundary layer was used to examine the contributions from various sources to the carbonylic acid budgets. Model results indicate that direct emissions from vegetation can account for most of the concentrations observed in the canopy. These emissions peak during the daytime hours, and 24-hour average upward fluxes at canopy top are 4.8 × 109, 3.7 × 108, and 2.8 × 107 molecules cm−2 s−1 for HCOOH, CH3COOH, and CH3C(O)COOH, respectively. However, direct emissions from vegetation can account for only a small fraction of the observed carbonylic acid concentrations in the boundary layer, suggesting a large contribution from atmospheric sources. The atmospheric reactions suggested in the literature as sources of carbonylic acids (gas phase decomposition of isoprene, CH3CO + peroxy, aqueous phase oxidation of CH2O) appear to be too slow to explain the observed concentrations. Other atmospheric reactions, so far unidentified, could make a major contribution to the carbonylic acid budgets.

1. INTRODUCTION

Precipitation acidity in remote regions of the world is typically dominated by HCOOH and CH3COOH [Galloway et al., 1982; Keene and Galloway, 1986]. Our measurements in central Amazonia, Brazil, during the 1985 dry season showed that these carbonylic acids were the principal contributors to rainwater acidity in that region [Andreae et al., 1988a]. Gas phase concentrations measured at canopy top averaged 1.6 ± 0.6 and 2.2 ± 1.0 parts per billion by volume (ppb) for HCOOH and CH3COOH, respectively [Andreae et al., 1988a]. Concentrations of carbonylates in the atmospheric aerosol were about 2 orders of magnitude lower. The highest concentrations of aerosol HCOO− and CH3COO− were associated with haze layers originating from biomass burning [Andreae et al., 1986b].

Keene and Galloway [1986] hypothesized that primary and secondary emissions from vegetation are responsible for the enhanced rainwater concentrations of HCOOH and CH3COOH observed over continents during the growing season. The strong seasonality of these species in the gas phase observed at a temperate site in eastern Virginia supports their hypothesis [Talbot et al., 1988]. Other sources of carbonylic acids include biomass burning [Talbot et al., 1988] (also, G. Helas et al., Measurements of organic acids in equatorial Africa during DECAFE 88, submitted to Journal of Geophysical Research, 1989; hereinafter referred to as submitted 1989) and possibly emissions from formicine ants [Graedel and Eisner, 1988]. Jacob and Wofsy [1988a] suggested that the oxidation of isoprene could provide a significant source of formic, methacrylic, and pyruvic acids over vegetated regions. Acetic acid is produced in the atmosphere by reactions of CH3COOH with HO2 and CH3O2 [Moortgat et al., 1989a, b], where CH3COOH can be supplied by atmospheric oxidation of biogenetic hydrocarbons or decomposition of peroxyacetyl nitrate (PAN) [Jacob and Wofsy, this issue]. Our dry season measurements of the diurnal behavior of HCOOH and CH3COOH within and just above the forest canopy in central Amazonia suggested that these acids have significant sources from both direct biogenic emissions and atmospheric reactions [Andreae et al., 1988a]. It has been suggested by Chameides and Davis [1983] that rapid aqueous phase oxidation of H2C(OH)2 by OH(aq) in clouds could be a major source of HCOOH in the remote troposphere. However, Jacob [1986] pointed out that cloud droplets can also be efficient sinks for HCOOH due to rapid oxidation of HCOO− by HO(aq), and for pH greater than five, clouds are not efficient HCOOH sources. Jacob and

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Wofsy [1988a] simulated the coupled gas and aqueous phase chemistry in clouds over the Amazon forest during the dry season and concluded that the aqueous phase was not a major source of HCOOH to mixed layer air. They also predicted that production of CH$_3$COOH by aqueous phase reactions in clouds is negligibly slow.

In this paper we report the results of our carboxylic acid measurements during the April–May segment of the 1987 wet season in central Amazonia. We utilize data obtained in the forest canopy, the planetary boundary layer (PBL), and free troposphere, combined with a photochemical model, to evaluate potential biogenic and atmospheric sources and sinks of HCOOH, CH$_3$COOH, and CH$_3$C(O)COOH over the Amazon forest. The role of HCOOH and CH$_3$COOH in wet season precipitation chemistry is discussed in a companion paper [Andreae et al., this issue (a)]. Here we focus on the gas phase carboxylic acid regime.

2. METHODS

2.1. Mist Chamber Technique

Gas phase concentrations of selected carboxylic acids were determined using the mist chamber technique. We have developed this technique and extensively tested and evaluated it in our laboratory. The mist chamber technique for measuring gaseous carboxylic acids appears to be one of the most reliable methods at this time [Keene et al., 1989]. The details of this sampling technique for carboxylic acids have been described by Talbot et al. [1988]. Briefly, the technique utilizes a mist of deionized water to efficiently strip soluble carboxylic species from the atmosphere and concentrate them in the aqueous phase. After sampling, the solution (≈10 mL) is withdrawn from the sampler, placed in a 15-mL amber linear polyethylene bottle, and CH$_3$Cl is added immediately to prevent biological degradation of the samples. Samples were usually analyzed the same day, and always within 24 hours after collection.

2.2. Ground-Based Sampling

Gaseous carboxylic acids were sampled from the micrometeorological tower located in the Duke Forest Reserve (2°56'S, 59°58'W) about 25 km north of Manaus in central Amazonas, Brazil. We obtained vertical profiles within and just above the forest canopy by sampling simultaneously at three heights above ground level: 12 or 19, 35, and 41 m. Our sampling configuration consisted of mist chamber samplers mounted on the tower, while the pumping and flow measurement devices were housed at the base of the tower in a wooden structure. Polyethylene tubing was used to connect the samplers to the vacuum source. Sampled air was drawn through about 2 m of 1-cm-diameter Teflon tubing, which extended horizontally out from the tower. We used 2-μm pore sized Zefluor Teflon filters (47 mm diameter) housed in Teflon inline holders to remove particulate matter from the sampled airstream. Tests in our laboratory showed that losses of HCOOH and CH$_3$COOH to the apparatus walls were negligible at levels of 300–500 parts per trillion by volume (ppt). Sample collection intervals were generally of 1-hour duration. Frequent interruptions in sampling were common due to intense tropical showers and associated electrical activity near the tower.

At the edge of a clearing at Duke Forest Reserve, we performed preliminary measurements of direct emission of carboxylic acids by Amazonia trees. We enclosed a portion of a tree branch in a 1-m$^{-3}$ fluorinated ethylene propylene (FEP) Teflon bag and determined the carboxylic acid average concentrations inside over a 10-min time interval (Figure 1). The selected branches were 2–3 m above ground level. One measurement was made per branch. Sampling began as soon as the branch was enclosed to minimize stress and possible perturbation of the emission rates. Although physical parameters such as temperature and humidity were not measured inside the enclosure, we believe that the conditions were not significantly different from ambient air. No condensation was observed on the interior surface of the Teflon bag. The bag was not completely sealed around the
branch. Instead, it was left open just enough at one end to allow ambient air to be easily pulled into the bag as we collected the sample at 8 L min⁻¹ from the center region of the bag. The measurements were conducted between 0900-1100 LT, when the trees were at their photosynthetic maxima as evidenced from CO₂ profiles through the canopy [Fan et al., this issue]. The ambient concentration of the carboxylic acids was monitored during the emission measurements with another sampler located about 10 m from the selected trees. Four different common tree species were surveyed before a severe tropical storm interrupted the measurements. Unfortunately, we were unable to obtain reliable information to correctly identify the actual tree species that we surveyed. We estimated the leaf surface area within the enclosure bag by counting the number of leaves and then measuring the dimensions of selected leaves.

2.3. Aircraft Sampling

Gas and particulate phase sampling of carboxylic acids was conducted aboard the NASA Electra research aircraft. The various flight scenarios are described elsewhere [Harrison et al., this issue]. The data reported here were obtained during missions designed to study the chemistry and vertical distribution of species in the low-to-middle troposphere associated with various scales of active convection. On one occasion, weather conditions permitted us to obtain data between Manaus and Belem located on the eastern coast of Amazonia.

For the gas phase, air was sampled using the mist chamber technique from a Teflon manifold (8 mm ID), which was continuously flushed at 50 L min⁻¹ with outside air. As with the ground-based collections, we used a Teflon filter to remove aerosols from the sampled airstream. An integrating mass flowmeter was utilized to determine sample air volumes. The overall uncertainty in atmospheric concentration is estimated to be 10%, comprised primarily of analytical and flow measurement errors.

The aerosol sampling system and procedures are described in detail in a companion paper [Talbot et al., this issue]. The atmospheric aerosol was segregated into fine (<1 μm) and coarse (≥1 μm) particle fractions using two sequential 90-mm-diameter filters mounted in polystyrene supports. Coarse mode particles were collected on a 8.0-μm pore sized Nuclepore filter, while a 2-μm nominal pore sized Zefluor Teflon filter retained the fine fraction. The sampling rate was about 175 standard liters per minute and was continuously adjusted to maintain isokinetic conditions. Filter samples were kept tightly sealed in polystyrene bags except during actual aerosol collection. One field blank was obtained for every three aerosol samples collected. Samples were extracted with water (Nuclepore) or a methanol-water sequence (Zefluor) and preserved with CH₂Cl₂ immediately after each aircraft mission. Chemical analysis was completed within 48 hours after sample collection. We estimate that the aerosol carboxylate concentrations have an uncertainty of 20%, based on propagation of the various errors associated with the measurement. Variation in filter blank levels is the largest component (12%) of the overall uncertainty.

2.4. Chemical Analysis

Carboxylic acid samples were analyzed by ion exchange chromatography using a Dionex HPIC-AS4 column and a weak bicarbonate eluent (0.45 mmol L⁻¹ NaHCO₃). We confirmed these results, especially for CH₃COOH, by reanalyzing selected samples by Donnan exclusion chromatography utilizing a Dionex HPIC-AS1 column with a 1 mmol L⁻¹ HCl eluent. The results from both chromatographic techniques agreed within 10%, and usually 5%. Aqueous standards of the acids were prepared from their sodium salts (Fluka), with CHCl₃ (Aldrich, gold label) added to prevent microbial decomposition. Blanks were handled and analyzed in identical format as samples.

3. Results and Discussion

3.1. Distribution in Atmosphere

Over Amazon Forest

The mean atmospheric concentrations of gaseous HCOOH, CH₃COOH, and CH₂C(O)COOH at 150-m altitude in the boundary layer were 430 ± 225, 340 ± 155, and 25 ± 15 ppt (N = 27), respectively. These concentrations are threefold lower for HCOOH, fivefold for CH₃COOH, and sevenfold for CH₂C(O)COOH from the levels that we observed during the 1985 dry season. Gaseous carboxylic acid concentrations in the boundary layer were highly variable and strongly influenced by precipitation events [Andreue et al., this issue (a)].

The frequency distributions of HCOOH, CH₃COOH, and CH₂C(O)COOH concentrations at 150-m altitude in the boundary layer over central Amazonia are shown in Figure 2. For CH₃COOH, 93% of the data were in the 100-500 ppt range. In contrast, HCOOH and CH₂C(O)COOH concentrations were highly variable within the ranges 100-1000 and 5-60 ppt, respectively. In 10 of the 27 boundary layer samples collected at 150 m, the CH₂C(O)COOH concentration was below our detection limit of about 5 ppt. The variability in these data cannot be attributed to diel periodicities, as the majority of the measurements were performed around midday. The highest concentrations of carboxylic acids were observed during mission 16 (April 29), when the atmosphere over central Amazonia was strongly influenced by inflow of northern hemispheric air [Talbot et al., this issue].

The concentrations of HCOOH, CH₃COOH, and CH₂C(O)COOH in the free troposphere were much less variable than in the boundary layer. We observed at 5 km a mean concentration (ppt) of 170 ± 40 for HCOOH, 210 ± 40 for CH₃COOH, and 15 ± 15 for CH₂C(O)COOH (N = 15). Despite frequent precipitation in the boundary layer, HCOOH was enriched there 2.5-fold over free tropospheric air. The same was true for CH₃COOH and CH₂C(O)COOH, but the enhancement was less, averaging only 1.6-fold. These relationships indicate that the Amazonia biosphere may be a source of atmospheric carboxylic acids.

Measurements of gaseous HCOOH in cross-basin flights illustrate the strong continental source for this species. Unfortunately, CH₃COOH concentrations are not available for these flights due to a contamination problem. The distribution of HCOOH in the boundary layer across Amazonia eastward to the Atlantic Ocean is shown in Figure 3. The mean value for all data collected in the Manaus region during our wet season study period is also shown. The cross-basin flights were flown on April 23 (eastward legs) and April 24 (westward legs). The concentration of HCOOH decreased
were usually below our detection limit of 5–10 ppt. On one occasion we observed elevated levels of these species in the particulate phase. This enhancement occurred during mission 16 (April 29), when we observed a large influx of soil dust into the central Amazon Basin. We have hypothesized that this material originated in Africa and possibly represented a mixture of Saharan dust and biomass-burning products [Talbot et al., this issue]. Acetate was particularly enhanced on April 29, reaching a concentration of 30 ppt. However, its gas phase concentration on that day was also much higher (730 ppt). The low concentrations in the aerosol relative to the gas phase are consistent with our observations for the dry season, where aerosol carboxylate concentrations in the boundary layer were around 25 ppt compared with gas phase concentrations of 1500 ppt [Andreae et al., 1988a]. Similar phase partitioning of these carboxylic acids has been observed in the atmosphere over temperate regions of North America and over marine areas [Andreae et al., 1987; Talbot et al., 1988].

3.2. Distribution Through Forest Canopy and Vegetation Emissions

Recent measurements of HCOOH and CH$_3$COOH in the gas phase and precipitation at temperate and tropical continental sites have led to the hypothesis that vegetation may be the dominant source of these acids [Keene and Galloway, 1986; Talbot et al., 1988; Andreae et al., 1988a]. We determined the vertical distribution of gaseous HCOOH, CH$_3$COOH, and CH$_3$C(O)COOH through the forest canopy to gain insight on potential vegetative sources. In Figure 4, representative profiles through the canopy are shown for four different days (April 28 and 30, May 2 and 5). The highest concentrations of HCOOH, CH$_3$COOH, and CH$_3$C(O)COOH consistently occurred at our uppermost sampling height (41 m), about 10 m above the mean canopy top. The lowest concentrations of these carboxylic acids were at ground level (1.5 m). The concentrations within and above the canopy show a daily temporal trend of rapid increase from early morning to midafternoon and then a decrease beginning around 1500 LT. To illustrate this daily pattern better, we show data from the 41-m location as a function of time in Figure 5. We obtained data through the night on one occasion, but the data were compromised by apparent pollution from nearby Manaus. Concentrations of NO measured by the Harvard group on that night showed intermittent high values believed to reflect transport of fresh anthropogenic emissions to our sampling site [Bakwin et al., this issue]. The carboxylic acid concentrations increased by a factor of 2 during this time period. These data have been omitted from our analysis here, since various anthropogenic activities are known to be sources of atmospheric HCOOH and CH$_3$COOH [Talbot et al., 1988].

The observed diurnal behavior of the carboxylic acids suggest a daytime source followed by removal from the atmosphere during the evening and nighttime. We observed a similar diurnal signal for these acids during the dry season in Amazonia [Andreae et al., 1988a] and at a site in eastern Virginia [Talbot et al., 1988]. The near-surface diurnal cycle in atmospheric carboxylic acids is strikingly similar to that observed for isoprene in Amazonia [Rasmussen and Khalil, 1988]. This similarity and the known vegetative source for isoprene point to the biosphere as a potential source of
atmospheric HCOOH, CH₃COOH, and CH₃C(O)COOH. The pronounced enhancement of these species in daytime boundary layer air is most likely related to biogenic emissions or atmospheric photochemical processes. In the absence of precipitation, removal of carboxylic species from the atmosphere during the daytime is probably primarily by dry deposition to the forest canopy, as known chemical loss mechanisms are too slow [Jacob and Wofsy, 1988a].

At the very end of our wet season study period, we obtained some preliminary data on direct emission of carboxylic acids from Amazonian trees. The estimated direct emission rates of HCOOH, CH₃COOH, and CH₃C(O)COOH are shown in Table 1. We observed rapid enhancement over ambient levels inside the enclosure bags within 10 min which are attributed to direct emissions from the tree leaves. We interpret these measurements as representing net vegetative direct emissions to the atmosphere; the instantaneous fluxes were not determined, and deposition back to the leaf surface could have occurred during the sampling interval. Concentrations of HCOOH and CH₃COOH as high as 7000 ppt were measured in the bag, while ambient levels were 400–600 ppt. Surprisingly, the same was found for CH₃C(O)COOH, where the ambient level was about 35 ppt compared with 100–1000 ppt inside the bag. Among the trees surveyed, we found an order of magnitude variation in the emission rates of the various carboxylic acids. The mean emission fluxes in mmol m⁻² min⁻¹ were 0.66, 1.4, and 0.14 for HCOOH, CH₃COOH, and CH₃C(O)COOH, respectively.

There appeared to be no relationship between tree species in the emission of various acids, as the ratios HCOOH/CH₃COOH and HCOOH/CH₃C(O)COOH varied 40- and 35-fold, respectively. The ratio determined from the mean emission flux of each acid (HCOOH/CH₃COOH = 1.1 and HCOOH/CH₃C(O)COOH = 16) is similar to values that we observed in and above the forest canopy. However, direct comparison with observed atmospheric concentration ratios is difficult because the acids have different lifetimes. Our measurements indicate that direct emissions of HCOOH, CH₃COOH, and CH₃C(O)COOH from trees are a source of these species to the atmosphere over the Amazon Basin. In section 4 of this paper we compare this primary biogenic source to various secondary sources.

### 3.3. Vertical Gradients and Relationships in the Gas Phase

To gain further insight on sources and sinks of carboxylic acids in the atmosphere over the Amazon forest, we examined the vertical gradients in concentration and the interspecies relationships. We calculated the mean concentrations of HCOOH, CH₃COOH, and CH₃C(O)COOH for five altitude ranges and present this summary in Table 2. Only concentrations measured over the central Amazon Basin were included in the aircraft-based boundary layer data. The carboxylic acid concentrations measured both in and above the canopy are not significantly different (at P = 0.10 level) from the aircraft-based boundary layer measurements. However, the concentrations observed under the canopy (1.5 m) are significantly lower (P = 0.10) than those higher up in the canopy and boundary layer. The low concentrations under the canopy indicate that ground-based emissions of carboxylic acids (e.g., from soil or ants) must be small relative to canopy emissions (e.g., from vegetation) and atmospheric production. However, it is not obvious from Tables 1 and 2 how canopy emissions compare with atmospheric production. The lack of a significant concentration gradient between the canopy top and the boundary layer (150–2000 m) seems difficult to explain on the basis of canopy emissions only, since the rapid removal of carboxylic acids by wet deposition should preclude the mixing of canopy emissions over such a deep layer. The model calculations presented in section 4 suggest that atmospheric production may provide the principal source of carboxylic acids in the boundary layer over the Amazon forest.

We examined our data for CH₃C(O)COOH in more detail to look for possible direct effects of convection. Pyruvic acid photolyzes in the daytime (lifetime of a few hours), so that its distribution may give insights into the rates of vertical transport. On two occasions, we sampled during flights...
where the aircraft flew in a triangular pattern at both 0.15- and 4.5-km altitude as a convective system moved through the enclosed area. The flight path intercepted potential cloud draft inflow and outflow regions. The concentration of CH$_3$C(O)COOH at 4.5 km during these flights was about 50 ppt, the same as it was in the boundary layer (Figure 6). The mean concentration of CH$_3$C(O)COOH in the free troposphere, with data for missions 7 and 20 omitted, was 9 ± 5 ppt. We thus observed fivefold enhancement in CH$_3$C(O)COOH concentration at 4.5 km during missions 7 and 20 compared with the average concentration observed for all other missions. The concentration of HCOOH was also enhanced at 4.5 km during mission 7 (435 ppt compared with 170 ± 40 ppt), but not during mission 20 (195 ppt). No enhancement at 4.5 km was observed for CH$_3$COOH during either mission ($P = 0.05$). The data for CH$_3$C(O)COOH support the idea that rapid convective transport plays a role in determining the vertical distribution of species in the atmosphere over the Amazon forest during the wet season. Examination of the vertical distribution of
correlated linearly, especially just above the forest canopy. We used the reduced major axis (RMA) method to derive the relationship between the carboxyl species [Miller and Kahn, 1962]. The results of this analysis are summarized in Table 3. There is a progressive increase in the value of the ratio HCOOH/CH$_3$COOH going from in the canopy to just above it and upward into the boundary layer. This trend suggests a proportionately larger source of HCOOH compared with CH$_3$COOH in boundary layer air. Although there appears to be little correlation between HCOOH and CH$_3$COOH in free tropospheric air, the dynamic range in concentration variation is confined to 120–260 ppt. With such limited variation in concentration, it is not possible to reliably ascertain the relationship HCOOH/CH$_3$COOH for these data.

The RMA analysis for HCOOH and CH$_3$C(O)COOH showed the same slope in the canopy and boundary layer. However, in boundary layer air the $r^2$ value was very low, indicating little correlation there between HCOOH and CH$_3$C(O)COOH concentrations. In addition, the value of the ratio HCOOH/CH$_3$C(O)COOH just above the forest canopy (14) was much less than a photochemical source from isoprene decomposition over Amazonia should produce (i.e., 25–50) [Jacob and Wofsy, 1988a, b]. The direct source of CH$_3$C(O)COOH from Amazonia trees is a likely cause for this result.

4. Modeling of Carboxylic Acid Concentrations Over the Amazon Forest

We use the photochemical model of Jacob and Wofsy [this issue] to estimate the contributions from various sources to the carboxylic acid concentrations over the Amazon forest. The model was developed to simulate the atmospheric composition observed during the Amazon Boundary Layer Experiment (ABLE 2B); it includes a detailed gas phase photochemical mechanism, and a one-dimensional representation of vertical transport within the canopy and in the boundary layer (up to 2000 m). Simulations of observations for O$_3$, NO, PAN, NO$_y$, and sulfur species suggest that the model provides a reasonable representation of chemistry and vertical transport in the boundary layer over the forest [Jacob and Wofsy, this issue; Andreae et al., this issue (b)]. Carboxylic acids in the model are emitted directly by vegetation and are also produced by a number of atmospheric reactions. Ground-based emissions from soils or ants are assumed negligible (cf. section 3.3). Sinks for carboxylic acids include wet and dry deposition, reaction with OH, and photolysis (for CH$_3$C(O)COOH).

Atmospheric sources of HCOOH in the model include the ozonolysis reactions of isoprene, methacrolein, and methylnitroethene; the latter reaction is also a source of CH$_3$C(O)COOH [Jacob and Wofsy, 1988a, b]. In clouds, aqueous phase oxidation of CH$_3$O provides an additional source of HCOOH [Chameides, 1984]. Production of HCOOH by the CH$_3$O + HO$_2$ reaction is negligible [cf. Jacob and Wofsy, 1988a]. Acetic acid is produced in the model by the reactions CH$_3$CO$_3$ + HO$_2$ and CH$_3$CO$_3$ + CH$_3$O$_2$ [Moortgat et al., 1989a, b], where the CH$_3$CO$_3$ radicals are supplied by atmospheric decomposition of isoprene and acetaldehyde. Aqueous phase sources of CH$_3$COOH in cloud (oxidation of acetaldehyde, hydrolysis of peroxyacetic acid) are negligibly slow [Jacob and Wofsy, 1988a].

Fig. 5. Diurnal variation of HCOOH, CH$_3$COOH, and CH$_3$C(O)COOH in the gas phase above the terra firme forest canopy at Dukke Forest Reserve. Data correspond to measurements performed at 41-m altitude on (a) April 30, (b) May 2, and (c) May 5 (see Figure 4).

CH$_3$C(O)COOH over Amazonia, with the free tropospheric values for missions 7 and 20 removed, shows that its boundary layer concentration was on the average significantly higher than in the free troposphere ($P = 0.10$). It appears that the vertical gradients in CH$_3$C(O)COOH and HCOOH are indeed very similar.

The relationship between the various carboxylic acids provides clues to their sources and sinks. We examined the relationships HCOOH/CH$_3$COOH and HCOOH/CH$_3$C(O)COOH at various heights in the atmosphere over Amazonia (Figures 7 and 8). At all altitudes in the boundary layer, HCOOH and CH$_3$COOH concentrations appear to be
TABLE 1. Measurements of Net Direct Emissions of Carboxylic Acids by Amazonian Trees

<table>
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<tr>
<th>Area per Leaf*, cm²</th>
<th>Full Sun%,</th>
<th>Emission Flux‡</th>
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<tr>
<td></td>
<td>HFO</td>
<td>HAC</td>
</tr>
<tr>
<td>30</td>
<td>100</td>
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<td>140</td>
<td>50</td>
<td>0.14</td>
</tr>
<tr>
<td>700</td>
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<td>0.20</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td>0.66</td>
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</table>

Measurements were performed between 0900 and 1100 LT on May 6, 1987, in terra firma forest at Ducke Forest Reserve. Each line entry corresponds to a different tree species. HFO, formic acid; HAC, acetic acid; and HPY, pyruvic acid. Represents net flux, i.e., instantaneous flux minus deposition during measurement interval (see text).

*Represents one side only.
†Indicates percentage of measurement interval where vegetation was exposed to direct solar irradiation. Cumulus were constantly building throughout the morning and intermittently blocked direct solar radiation.
‡Flux is expressed in nanomoles per meter squared of leaf per minute.

Vegetative emissions of carboxylic acids in the model are assumed to vary with temperature and light intensity, in the same way as isoprene emission [Jacob and Wofsy, this issue]. The emission fluxes are scaled to the isoprene emission flux, with scaling factors (6% for HCOOH, 5% for CH₃COOH, and 0.3% for CH₃C(O)COOH) adjusted to provide a good simulation of the observed midday concentrations of each acid at canopy top. Emission is balanced partly by dry deposition to the leaves, which is simulated using a multilevel resistance-in-series scheme [Meyers and Baldocchi, 1988]. At night the forest is a slow sink for carboxylic acids, due to deposition at the cuticular surfaces of leaves (a cuticular resistance of 200 s cm⁻¹ per cm² of leaf is assumed). In addition to this dry deposition sink the carboxylic acids are also removed from the boundary layer by wet deposition, with a time constant of 1 day [Andreae et al., this issue (a)].

The results presented here are taken from the standard model calculation of Jacob and Wofsy [this issue], which is discussed in detail in that paper. The simulation was conducted over three diurnal cycles, starting from observed mean free troposphere concentrations (Table 2) as initial conditions. This initialization is intended to simulate the passage of a major meteorological disturbance, when air from the free troposphere is rapidly mixed with the PBL [Scala et al., this issue]. It is assumed that relatively undisturbed conditions follow the initial disturbance and persist for the duration of the model simulation. By model day 3 the concentrations of carboxylic acids have approached a steady state due to the short time constant for wet deposition; our presentation will focus on results from model day 3. Aqueous phase reactions in cloud are not included in the model calculation but are considered separately in sensitivity calculations discussed below.

Simulated vertical fluxes of carboxylic acids at canopy top are shown in Figure 9 as a function of time of day. The 24-hour average fluxes are 4.4 × 10⁻⁹ molecules cm⁻² s⁻¹ for HCOOH, 3.7 × 10⁻⁹ molecules cm⁻² s⁻¹ for CH₃COOH, and 2.8 × 10⁻⁸ molecules cm⁻² s⁻¹ for CH₃C(O)COOH. These values may be compared with the emission rates measured in the branch enclosures (Table 1). Assuming that the leaves sampled in the enclosures were representative of the forest vegetation, and assuming a canopy leaf index of 7 [Fan et al., this issue], then the mean emission fluxes given in Table 2 correspond to total canopy fluxes of 4.6 × 10⁻⁹ molecules cm⁻² s⁻¹ for HCOOH, 9.8 × 10⁻⁹ molecules cm⁻² s⁻¹ for CH₃COOH, and 9.8 × 10⁻⁸ molecules cm⁻² s⁻¹ for CH₃C(O)COOH. This extrapolation of the enclosure data may be somewhat biased because the measurements were taken at 0900–1100 LT, and near the edge of a clearing; the leaves were therefore exposed to higher-than-average sunshine. Overall, and considering the scatter in the data, the emission fluxes simulated by the model may be viewed as reasonably consistent with the branch enclosure measurements.

The simulated concentrations within the canopy (Figure

TABLE 2. Summary of Gas Phase Carboxylic Acids Over the Central Amazon Basin

<table>
<thead>
<tr>
<th>Region</th>
<th>Mean ± σ, ppt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Formic</td>
</tr>
<tr>
<td>Free troposphere</td>
<td></td>
</tr>
<tr>
<td>3–5 km</td>
<td>170 ± 40</td>
</tr>
<tr>
<td>Boundary layer</td>
<td>430 ± 225</td>
</tr>
<tr>
<td>0.15–2 km</td>
<td></td>
</tr>
<tr>
<td>Above canopy 35–41 m</td>
<td>510 ± 150</td>
</tr>
<tr>
<td>In canopy 12–19 m</td>
<td>295 ± 120</td>
</tr>
<tr>
<td>Under Canopy 1.5 m</td>
<td>190 ± 45</td>
</tr>
</tbody>
</table>

Measurements associated with forest canopy were performed from the 45-m micrometeorological tower located at Ducke Forest Reserve. N represents the number of observations.
Fig. 6. Mean concentration of CH₃C(O)COOH (see text) under the canopy, in boundary layer air, and in the free troposphere (solid circles). Open symbols represent the concentrations observed near convective cells during missions 7 and 20.

10) are reasonably consistent with observed values (Figures 4 and 5), but this result reflects largely the adjustment of the vegetative emission fluxes in the model. In contrast, the predicted concentrations in the boundary layer (Figure 11) are significantly lower than observed. The 24-hour average concentrations in the model boundary layer (30–2000 m) are 156, 153, and 5 ppt for HCOOH, CH₃COOH, and CH₃C(O)COOH, respectively (Table 4), while the mean observed values for the altitude range 150–2000 m are 430, 340, and 25 ppt (Table 2). Although most of the observations were made in the daytime, the diurnal variation of concentrations in the model is small (Figure 11), so that the timing of the observations could not account for the difference with model results.

A likely explanation for the discrepancies between model and observations is that important sources of carboxylic acids in the boundary layer are missing from the model. We advance this explanation because the sources and sinks regulating the concentrations in the model (Table 4) appear to be relatively well constrained. Wet deposition, which is the principal sink for HCOOH and CH₃COOH, is constrained by the observed rainfall fluxes [Andreea et al., this issue (a)]. Vegetative emissions are constrained by the observed concentrations at canopy top, and by the canopy ventilation rates which are specified in the model on the basis of data for O₃, CO₂, and ²²²Rn concentrations and fluxes [Jacob and Wofsy, this issue]. Production of HCOOH and CH₃C(O)COOH by ozonolysis of isoprene, methylvinylketone, and methacrolein could be underpredicted by probably no more than a factor of 2, reflecting the uncertainty on the fate of the Criegee biradical intermediates [Atkinson and Lloyd, 1984]. Finally, the rates of CH₃COOH production by the reactions CH₃CO₃ + CH₃O₂ and CH₃CO₃ + HO₂ should be fairly reliable, since the concentrations of these peroxy radicals show little sensitivity to model conditions [Jacob and Wofsy, this issue].

The possibility of HCOOH production by aqueous phase oxidation of CH₂O in cloud was examined in a sensitivity calculation which assumed instantaneous formation of a nonprecipitating cloud at 800-m altitude at noon, and simu-

Fig. 7. Relationship between HCOOH and CH₃COOH in the gas phase at various altitudes over the Amazon forest: (a) free troposphere 3–5 km, (b) boundary layer 0.15–2 km, (c) just above forest canopy 35–41 m, and (d) directly within forest canopy 12–19 m. RMA regression lines are also shown.
TABLE 3. Results of RMA Regression Analysis

<table>
<thead>
<tr>
<th>Region</th>
<th>Formic Versus Acetic</th>
<th>Formic Versus Pyruvic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Slope</td>
<td>Intercept</td>
</tr>
<tr>
<td>Boundary layer</td>
<td>1.4</td>
<td>-52</td>
</tr>
<tr>
<td>0.15–2 km</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Above canopy</td>
<td>1.2</td>
<td>+9.2</td>
</tr>
<tr>
<td>35–41 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In canopy</td>
<td>0.94</td>
<td>-19</td>
</tr>
<tr>
<td>12–19 m</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

lated the chemical evolution of this cloud over a 1-hour period with the cloud chemistry model of Jacob [1986]. The cloud was assumed monodisperse (droplet radius 10 μm), with a constant liquid water content (1 g m⁻³) and a constant pH. The efficiency of HCOOH aqueous phase production is expected to be strongly pH dependent [Jacob, 1986]. We find that at pH 5 (the mean rainwater pH observed during ABLE 2B), the cloud is a net sink of HCOOH due to rapid aqueous phase oxidation of HCOO⁻ by OH(aq). Total (gas phase) + (aqueous phase) concentrations of HCOOH decrease from 131 ppt before cloud formation to 74 ppt 1 hour after cloud formation. At pH 4 the cloud becomes a net source of HCOOH, but after 1 hour of cloud the concentration has risen to only 154 ppt. We conclude that aqueous phase oxidation of CH₂O cannot provide a significant source of HCOOH over the Amazon forest.

The missing sources of carboxylic acids in the model could possibly represent long-range transport of material exogenous to the Amazon Basin. In particular, the high concentrations observed in mission 16 were associated with recent influx of air from Africa (cf. section 3). Very high concentrations of carboxylic acids (i.e., ppb levels) have been observed in biomass-burning plumes advected from Africa to the tropical Atlantic (G. Helas et al., submitted, 1989). Ubiquitous pollution from sources outside the basin have been invoked to explain the observed concentrations of NO₃⁻ [Bakwin et al., this issue] and aerosol species [Talbot et al., this issue] observed during ABLE 2B, and it seems reason-

Fig. 8. Relationship between HCOOH and CH₂C(O)COOH in the gas phase at various altitudes over the Amazon forest: (a) free troposphere 3–5 km, (b) boundary layer 0.15–2 km, (c) just above forest canopy 35–41 m, and (d) directly within forest canopy 12–19 m. RMA regression lines are also shown.

Fig. 9. Simulated vertical fluxes at canopy top, as a function of time of day, of HCOOH (solid line), CH₂COOH (dashed line), and CH₂C(O)COOH (dash-dot line). Positive values indicate upward fluxes.
able to postulate that such exogenous sources could have ubiquitously affected the carboxylic acid budgets as well.

It is possible that unknown chemical sources of carboxylic acids may be missing from the model. Our results indicate that peroxo-peroxy reactions involving CH$_2$CO$_3$ [Moortgat et al., 1999a, b] provide a substantial source of CH$_3$COOH to the atmosphere (Table 4); other peroxo-peroxy reactions involving higher (>C$_1$) peroxy or peroxacyl radicals could provide additional sources of carboxylic acids, but no kinetic data are available. The atmosphere over the Amazon forest would be particularly conducive to peroxo-peroxy reactions because of the low concentration of NO, which hinders the consumption of peroxy radicals by NO. Hydroxy-RO$_2$ radicals produced from the isoprene + OH reaction are expected to be abundant over the forest [Jacob and Wofsy, this issue], but the atmospheric reactivity of these radicals under low-NO$_x$ conditions is essentially unknown.

Finally, microbial production of carboxylic acids in cloud droplets must be considered as a possible atmospheric source. Herlihy et al. [1987] observed high concentrations of bacteria in rain samples collected in Charlottesville, Virginia, and suggested that these bacteria were principally of vegetative origin. Production of carboxylic acids by vegeta-

**TABLE 4. Simulated Budgets of Carboxylic Acids in the Boundary Layer (30–2000 m)**

<table>
<thead>
<tr>
<th>Source and Sinks</th>
<th>Formic</th>
<th>Acetic</th>
<th>Pyruvic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration, ppt</td>
<td>156</td>
<td>153</td>
<td>5.0</td>
</tr>
<tr>
<td>Sources and sinks, ppt d$^{-1}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vegetative emissions</td>
<td>+88</td>
<td>+73</td>
<td>+5.5</td>
</tr>
<tr>
<td>Ventilation (at 2000 m)</td>
<td>+4</td>
<td>+7</td>
<td>+3.8</td>
</tr>
<tr>
<td>Isoprene + O$_3$</td>
<td>+47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl/vinylketone + O$_3$</td>
<td>+10</td>
<td></td>
<td>+9.9</td>
</tr>
<tr>
<td>Methacrolein + O$_3$</td>
<td>+1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_2$CO$_3$ + HO$_2$</td>
<td></td>
<td>+35</td>
<td></td>
</tr>
<tr>
<td>CH$_2$CO$_3$ + CH$_3$O$_2$</td>
<td></td>
<td>+39</td>
<td></td>
</tr>
<tr>
<td>Wet deposition</td>
<td>-156</td>
<td>-153</td>
<td>-5.0</td>
</tr>
<tr>
<td>HCOOH + OH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_2$C(O)COOH + hv</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Accumulation, ppt d$^{-1}$</td>
<td>-7</td>
<td>+1</td>
<td>+0.7</td>
</tr>
</tbody>
</table>

Values are 24-hour mean model values averaged over the boundary layer air column (30–2000 m).
tive microbes has been extensively documented [e.g., Schmidt, 1986; Rozycki and Strzelczyk, 1986], but the possibility of such production in atmospheric cloud droplets remains a matter of speculation. Bacterial activity in cloud droplets could actually provide a sink for carboxylic acids instead of a source; in particular, bacteria observed in rain samples were found to utilize efficiently HCOO\(^-\) and CH\(_3\)COO\(^-\), although this utilization did not begin until after an incubation period of a few days [Herlihy et al., 1987].

The atmospheric concentrations of HCOOH and CH\(_3\)COOH observed in the wet season were a factor of 3–5 lower than those observed in the dry season ABLE 2A experiment [Andreae et al., 1988a]. This difference can be explained largely by the longer atmospheric lifetimes of carboxylic acids against wet deposition in the dry season. Rainfall at Manaus varies by a factor of 4 between the dry and wet seasons [Kousky and Kagan, 1981], and this factor could account for the observed variations in HCOOH and CH\(_3\)COOH concentrations. The ABLE 2A model calculations of Jacob and Wofsy [1988a] suggest that HCOOH production from ozonolysis of olefins could have contributed only 15–50% of the HCOOH concentrations observed in the dry season; we find in the wet season that this contribution is even less because O\(_3\) concentrations are about a factor of 2 lower [Browell et al., this issue]. Sources of CH\(_3\)COOH were not included in the model of Jacob and Wofsy [1988a], but more recent model simulations of the ABLE 2A data by Madronich and Calvert [1990] indicate that peroxy-peroxy reactions involving CH\(_2\)CO\(_2\)H could have been important contributors to the observed CH\(_3\)COOH concentrations. As in the wet season, it seems logical to speculate that other peroxy-peroxy radical reactions (involving \(>C_1\) radicals) may have been important sources of carboxylic acids in the dry season. Biomass burning, which is widespread in Amazonia and the savannah areas to the south during the dry season [Andreae et al., 1988b] could have supplied an important additional source [Talbot et al., 1988].

5. CONCLUSIONS

In this paper we have presented a likely scenario of the gas phase carboxylic acid regime during the April–May segment of the 1987 wet season in central Amazonia. We utilized data obtained within the forest canopy, the PBL, and free troposphere, in combination with a photochemical model to evaluate potential biogenic and atmospheric sources and sinks of HCOOH, CH\(_3\)COOH, and CH\(_3\)C(O)COOH. The distribution of HCOOH in the boundary layer from the Atlantic Ocean westward to central Amazonia shows a strong continental source for this species. Despite frequent precipitation over central Amazonia, HCOOH was enhanced by a factor of 2.5 in the boundary layer compared with the free troposphere. Concentrations of carbonylate ions in the atmospheric aerosol were usually below our detection limit of 5–10 ppt.

The diurnal cycles of HCOOH, CH\(_3\)COOH, and CH\(_3\)C(O)COOH just above the forest canopy showed a rapid increase in concentration from early morning to midafternoon, followed by a decrease beginning around 1500 LT. This behavior suggests daytime biogenic and photochemical production followed by deposition to vegetation at night.

We used a one-dimensional photochemical model to estimate the contributions from various sources to the observed concentrations of carboxylic acids. Direct emissions from vegetation can account for most of the observed concentrations within the canopy and just above it. Concentrations in the boundary layer are much higher than would be expected from direct emissions, suggesting an important source from secondary production. However, we find that the atmospheric reactions considered in the model (decomposition of isoprene, CH\(_3\)CO\(_2\) + peroxy, aqueous phase oxidation of CH\(_2\)O) are too slow to account for the observed concentrations. Unknown atmospheric reactions (possibly interactions between organic peroxy radicals) appear to dominate the budget of carboxylic acids over Amazonia.

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