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Influence of biomass combustion emissions on the distribution of acidic trace gases over the southern Pacific basin during austral springtime

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Influence of biomass combustion emissions on the distribution of acidic trace gases over the southern Pacific basin during austral springtime


Abstract. This paper describes the large-scale distributions of HNO₃, HCOOH, and CH₃COOH over the central and South Pacific basins during the Pacific Exploratory Mission-Tropics (PEM-Tropics) in austral springtime. Because of the remoteness of this region from continental areas, low part per trillion by volume (pptv) mixing ratios of acidic gases were anticipated to be pervasive over the South Pacific basin. However, at altitudes of 2-12 km over the South Pacific, air parcels were encountered frequently with significantly enhanced mixing ratios (up to 1200 pptv) of acidic gases. Most of these air parcels were centered in the 3-7 km altitude range and occurred within the 15°-65°S latitudinal band. The acidic gases exhibited an overall general correlation with CH₃Cl, PAN, and O₃, suggestive of photochemical and biomass burning sources. There was no correlation or trend of acidic gases with common industrial tracer compounds (e.g., C₂Cl₄ or CH₃CCl₃). The emission compositions sampled over the South Pacific basin were relatively aged exhibiting C₂H₂/CO ratios in the range of 0.2-2.2 pptv/ppbv. The relationships between acidic gases and this ratio were similar to what was observed in aged air parcels (i.e., >3-5 days since they were over a continental area) over the western North Pacific during the Pacific Exploratory Mission-West Phases A and B. In the South Pacific marine boundary layer a median C₂H₂/CO ratio of 0.6 suggested that this region was generally not influenced by direct inputs of biomass combustion emissions. Here we observed the lowest mixing ratios of acidic gases, with median values of 14 pptv for HNO₃, 19 pptv for HCOOH, and 18 pptv for CH₃COOH. These values were coincident with low mixing ratios of NOₓ (<10 pptv), CO (<20 parts per billion by volume (ppbv)), O₃ (<20 ppbv), and long-lived hydrocarbons (e.g., C₂H₆ <300 pptv). Overall, the PEM-Tropics data suggest an important influence of aged biomass combustion emissions on the distributions of acidic gases over the South Pacific basin in austral springtime.

1. Introduction

Acidic gases are important participants in tropospheric chemical processes. They are major end products of oxidative cycles, with wet and dry removal of HNO₃ and H₂SO₄ from the atmosphere. Principal sinks include NOₓ recycling, photolysis, precipitation, and aqueous phase OH oxidation. In remote regions the principal sinks for tropospheric NOₓ (NO + NO₂) and SO₂ are precipitation [Keene et al., 1983; Andreae et al., 1988, 1990], and possibly soils [Kawamura et al., 1985; Talbot et al., 1988, 1990]. Vegetation [Keene and Galloway, 1986; Talbot et al., 1988, 1990] and possibly oceans [Sanhueza and Andreae, 1991; Talbot et al., 1995]. Formic acid is also a major sink for OH radicals in cloudwater [Jacob, 1986].

Formic acid may be produced by aqueous phase OH oxidation of hydrated formaldehyde (H₂C(OH)₂) in cloudwater and subsequently provides an important source of gas phase HCOOH in the troposphere [Chameides and Davis, 1983; Jacob, 1986]. Aqueous phase production mechanisms for CH₃COOH appear to be quite slow and probably are a negligible source of this species to the troposphere [Jacob and WoJy, 1988]. The major sources of HCOOH and CH₃COOH to the global troposphere appear to be emissions from combustion [Kawamura et al., 1985; Talbot et al., 1988, 1992; Lefer et al., 1994], vegetation [Keene and Galloway, 1986; Talbot et al., 1988, 1990], and possibly soils [Sanhueza and Andreae, 1991; Talbot et al., 1995]. Permutation reactions of peroxy radicals have been proposed as potentially important sources of carboxylic acids [Madronich and Calvert, 1990; Madronich et al., 1990], but recent measurements at a continental site indicate that this pathway may be relatively unimportant [Talbot et al., 1995].

There are potentially numerous production mechanisms for HNO₃ in the troposphere including, NO₂ + OH, recycling of reactive nitrogen reservoir species, and evaporation of NO₃⁻ in aerosol and aqueous phases [Roberts, 1995]. Many of these processes are thought to very slow in the upper tropical troposphere due to low O₃ mixing ratios and cold temperatures retaining most of the reactive nitrogen in the form of NO during the daytime [Folkins et al., 1995].

Measurements conducted in winter 1992 at 10-12 km altitude between Tahiti and California showed an abrupt decrease in the mixing ratios of O₃ and NOₓ (i.e., the sum of reactive nitrogen species) at the southern edge of the Intertropical Convergence Zone.
NOy is not surprising. In fact, low mixing ratios would be expected to be pervasive over the South Pacific basin for most tropospheric trace species, including acidic gases.

In this paper we present the large-scale distributions of HNO₃, HCOOH, and CH₂COOH over the central and South Pacific basins during the NASA Global Tropospheric Experiment/Pacific Exploratory Mission-Tropics (GTE/PEM-Tropics) in September/October 1996. Objectives of PEM-Tropics included obtaining baseline data for important tropospheric gases, evaluating the oxidizing capacity of the troposphere and factors influencing it, and improving our understanding of the natural sulfur cycle over the South Pacific basin.

The first part of this paper focuses on the distributions of acidic gases in the 2-12 km altitude range which were apparently heavily impacted by aged biomass combustion emissions. Supporting evidence for this source is provided by coincident distributions of selected hydrocarbon compounds. The distribution of acidic gases is examined in the marine boundary layer and overlying transition region in the second part of this paper. Here there was little evidence for a direct influence of biomass combustion inputs on the chemistry, in stark contrast to the middle and upper troposphere.

Overall, the PEM-Tropics measurements provide unique information of the chemistry of this extensive remote region during austral springtime.

2. Experimental Methods

2.1. Study Area

The PEM-Tropics airborne expedition was conducted using the NASA Ames DC-8 research aircraft. Transit and intensive site science missions composed 18 flights, averaging 8-10 hours in duration and covering the altitude range of 0.3 to 12.5 km. The base of operations for these missions progressed as follows: (1) Tahiti (three missions), (2) Easter Island (two missions), (3) Tahiti (one mission), (4) New Zealand (one mission), and (5) Fiji (three missions). The data used in this paper were obtained in the geographic grid approximately bounded by 60°N-75°S latitude and 165°E-105°W longitude. Data obtained on transit flights (eight missions) were also utilized in this paper. A geographic map of the study region is shown in several companion papers (e.g., Gregory et al., this issue; Hoell et al., this issue).

The overall scientific rationale and description of individual aircraft missions is described in the PEM-Tropics overview paper [Hoell et al., this issue]. The features of the large-scale meteorological regime and associated air mass trajectory analyses for the September-October 1996 time period are presented by Fuehrberg et al. [this issue].

2.2. Sampling and Analytical Methodology

Acidic gases were subsampled from a high-volume (500-1500 standard liters per minute (sLpm)) flow of ambient air using the mist chamber technique [Talbot et al., 1988, 1990, 1997a]. The subsample flow rate was always <10% of the primary manifold total flow. Sample collection intervals were typically 4 min in the boundary layer, 6 min at 2.9 km altitude, and 8 min above 9 km altitude, reflecting decreased pumping rates in the middle and upper troposphere. The inlet manifold consisted of a 0.9 m length of 41 mm ID glass coated stainless steel pipe. The pipe extended from the DC-8 fuselage to provide a 90° orientation to the ambient air streamline flow. To facilitate pumping of the high-volume manifold flow, a diffuser was mounted over the end of the inlet pipe parallel to the DC-8 fuselage. This device provided a "shroud" effect, slowing the flow of ambient air through it slightly below the true air speed of the DC-8 and adding 50-100 hPa of pressurization to the sampling manifold. This effectively eliminated the reverse venturi effect (~40 hPa) on the sampling manifold. An additional feature of the diffuser was a curved step around the manifold pipe which provided the streamline effects of a backward facing inlet. Its function was to facilitate exclusion of aerosol particles greater than ~2 μm in diameter from the sampling manifold. Aerosols smaller than this were removed from the sampled air stream using a 1μm pore-sized Zefluor teflon filter that was readily changeable every 5-10 min to minimize aerosol loading on the filter and gas/aerosol phase partitioning from ambient conditions.

In addition to the features described above, the inlet manifold was equipped with the capability for conducting a standard addition of HNO₃ into the manifold ambient air stream. This spike was added ~10 cm downstream inside the manifold pipe through a 6.5 mm OD glass coated stainless steel tube mounted perpendicular to the air flow. This tube was ~20 mm long and maintained at 40°C to facilitate passing of calibration gas through it. Through a tee, this injection length of tubing was connected to about 1.5 m of heated tubing that was directly linked to the perm oven output. This design effectively tested the passing efficiency of the entire manifold system, which was indistinguishable from 100 ± 1.5%. The calibration system for HNO₃ consisted of a permeation oven held at 50°C and a dilution flow of ultra zero air (1.5 sLpm) which swept the oven outflow to either a nylon filter for output quantification or the sampling manifold for standard addition on ambient air. The heated tubing through which the HNO₃ stream passed was kept equilibrated by a flow design that allowed the calibration gas to constantly pass to the point of injection into the manifold flow before being dumped to waste through a return line. The mixing ratio of HNO₃ in the 1.5 sLpm flow was typically 200 parts per billion by volume (ppbv). This spike was then diluted several hundred times by the high flow rate of ambient air in the sampling manifold, producing standard additions of 100-1200 pptv. Previously we have studied the passing efficiency of carboxylic acids through our inlet manifold, and found it to be ≥95% [Talbot et al., 1992]. Thus we focused our attention on HNO₃ due to its importance to the reactive nitrogen cycle and tropospheric chemistry.

The permeation oven output of HNO₃ was monitored on the ground and in the air in near-real time. We fabricated a new calibration system for PEM-Tropics which maintained the permeation tube to 50.0 ± 0.1°C and 1850 ± 1 hPa pressure at all altitudes. The permeation source was constant to ± 8.5% over the course of the expedition, with no equilibration time required at any altitude, even with rapid changes such as during spiral maneuvers. This new design utilized upstream pressure control (i.e., before the permeation tube) so that there were no fittings, valves, or flow/pressure controllers in-line between the tube and the injection point into our sampling manifold. The flow through the oven varied from 20-25 cm³ min⁻¹ depending on the ambient pressure and was diluted into the 1.5 sLpm flow described above. Standard additions were conducted with and without a teflon filter in-line to verify that the filter did not influence the passing efficiency of the sampling manifold.

Computer controlled syringe pumps were used to move sample solutions in and out of the mist chamber samplers and our sample containers. This essentially provided a closed system of liquid handling which greatly simplified contamination control. The concentrations of acidic gases in our samples were quantified using...
a custom built dual ion chromatography system equipped with a computer interface for data acquisition. The system was composed primarily of Dionex components with the detectors and flow system thermostated to 40°C. Eluants were constantly purged with He gas. Nitric acid was measured using a fast anion column while the carboxylic acids were determined using an AS4 column. Concentrator columns and electronic suppression was used in both chromatography systems. Calibration curves generated on the ground and in the air agreed within ±2%. We thus were able to determine atmospheric mixing ratios of acidic gases in near-real time.

In addition to data for acidic gases, we present selected information on several important trace gases including ozone (O₃), carbon monoxide (CO), ethyne (C₂H₂), perchloroethylene (C₂C₁₄), and peroxyacetyl nitrate (PAN). Aerosol NO₃ was measured on bulk filter samples collected with a forward facing isokinetic probe housed in a shroud to ensure isoaxial flow [Dibb et al., 1996a]. Ninety millimeter diameter 2 μm pore-sized Zefluor teflon filters were used as the collection substrate. Specific details regarding the measurement of various other species used in this paper are presented in companion papers [Blake et al., this issue; Dibb et al., this issue; Gregory et al., this issue; Vay et al., this issue]. The measurements of these species were averaged to provide mean values that corresponded directly to the acidic gas sampling times. This merged data product was generated at Harvard University, and it is used exclusively in this paper.

### 3. Results

In the data presented in this paper, obvious stratospherically impacted values have been removed based on coincident measurements of O₃, CO, dew point, and selected hydrocarbons and halocarbons. This amounted to removing a total of about 25 data points obtained on three different flights.

The large-scale latitudinal distribution of acidic gases over the central and South Pacific basins is presented in Figure 1. It is evident from these distributions that numerous air parcels were encountered between 15° and 60°S latitude which contained large mixing ratios of acidic gases. The northern border of the impacted Pacific troposphere appears to be controlled by the presence and location of the South Pacific Convergence Zone (SPCZ) [Gregory et al., this issue]. Nitric acid mixing ratios, for example, typically decreased by a factor of 2-5 in crossing the SPCZ region from south to north. This trend was also apparent in other trace gases such as CO, C₂H₂, C₆H₆, O₃, and PAN [Gregory et al., this issue]. Thus polluted air parcels appeared to be present south of the SPCZ with the carboxylic acids exhibiting values 2-3 times greater in the central Pacific region. In the middle troposphere the mixing ratios of acidic gases showed the largest values in the western and central regions. This is consistent with the generally westerly flow of air at these altitudes over the South Pacific basin, implying that the least processed air parcels would be found in these regions [Fuelberg et al., this issue]. Most of the plumes that we sampled were, in fact, encountered over the western and central Pacific areas. The eastern Pacific regions were dominated by relatively “clean” air parcels. This longitudinal difference seemingly reflects chemical and physical losses of acidic gases as air parcels transverse the Pacific basin in a westerly flow regime.

Mixing ratios of acidic gases over the South Pacific were generally less than 200 pptv but approached or exceeded 1000 pptv in some air parcels. These air parcels (i.e., plumes) were observed mainly between 2 and 7 km altitude (Figures 2a-2c). Because of the strong trade wind inversion over this region, the marine boundary layer exhibited very small mixing ratios of acidic gases. The inversion appeared to be a very effective barrier to downward mixing of acidic gases from aloft. Indeed, the most processed (i.e., aging and mixing influences) air parcels were sampled in the marine boundary layer. This feature of the data is illustrated using the ratio C₂H₂/CO which had a median value of 0.6 below 1 km altitude but showed significantly larger values in the rest of the tropospheric column (Figure 3). Values of this ratio less than 1.0 are typical of photochemically aged and well mixed (diluted) air parcels [Smyth et al., 1998; Talbot et al., 1997b].

As an example of the detailed vertical structure over the South Pacific selected data from a slow spiral (80 m min⁻¹) conducted east of Fiji is shown in Figure 4. An apparent combustion plume was sampled near 5 km, with corresponding large increases in HNO₃, C₂H₂, and C₂H₂/CO but not C₂Cl₄. Notice the very rapid vertical changes in the mixing ratios and generally good correspondence between HNO₃ and C₂H₂. While the plumes with large mixing ratios of many trace gases clearly stand out, the PEM-Tropics data in general support the idea that much of the tropospheric column from 2-10 km altitude was fumigated with varying degrees of combustion emissions. The smooth shape of the vertical distribution of C₂Cl₄ is typical of what was observed over the South Pacific (Figure 1), and it suggests minimal influence on the chemistry from industrial emissions. The distribution of CH₃CCl₃ and other halocarbons also supports this ascertain (N. Blake, personal communication, 1998).

To provide a detailed description of the distribution of acidic gases over the central and South Pacific basins, this information is presented in a regional summary format (Table 1) consistent with that used in companion papers [Gregory et al., this issue; Dibb et al., this issue]. Information on the distribution of many other trace gases can be found in these papers, so it is not duplicated here. The regional breakdown was developed to provide data summaries that correspond to logical latitudinal and longitudinal areas (e.g., the ITCZ, and the eastern, central, and western Pacific basins). In some regions the sampling was quite sparse, so interregional comparisons need to be conducted with caution. On the basis of the vertical measurement density of acidic gases, the data were broken into four altitude bins: (1) the marine boundary layer (<1 km), (2) the transition or cloud layer (1-2 km), (3) the middle (2-8 km), and (4) upper (8-12 km) troposphere.

As shown in the large-scale vertical distributions (Table 1 and Figure 2), the smallest mixing ratios of acidic gases were found in the marine boundary layer. Here median mixing ratios were 14 pptv for HNO₃, 19 pptv for HCOOH, and 18 pptv for CH₃COOH. The very small mixing ratios of HNO₃ are consistent with the observed NO₃ values of only a few or sub (i.e, <1) pptv in the boundary layer (Georgia Institute of Technology NO₃ data are available from the Distributed Active Archive Center (DAAC) at NASA Langley Research Center, Hampton, Virginia). There was no significant regional difference in the mixing ratio of HNO₃ in the marine boundary layer, but the carboxylic acids exhibited values 2-3 times larger in the central Pacific region. In the middle troposphere the mixing ratios of acidic gases showed the largest values in the western and central regions. This is consistent with the generally westerly flow of air at these altitudes over the South Pacific basin, implying that the least processed air parcels would be found in these regions [Fuelberg et al., this issue]. Most of the plumes that we sampled were, in fact, encountered over the western and central Pacific areas. The eastern Pacific regions were dominated by relatively “clean” air parcels. This longitudinal difference seemingly reflects chemical and physical losses of acidic gases as air parcels transverse the Pacific basin in a westerly flow regime.

The mixing ratios of the carboxylic acids HCOOH and CH₃COOH are generally found to be highly correlated in the gas and liquid phases in the troposphere [Keene and Galloway, 1986]. On continental areas the ratio HCOOH/CH₃COOH usually has a value near 2.0 with a correlation coefficient between these two species near 0.9 [Keene and Galloway, 1986; Talbot et al., 1988]. Although we observed linear correlations between HCOOH and CH₃COOH over the Pacific basin (Figures 5a and 5b), they were less robust than what we observed during the Pacific Exploratory Mission-West Phases A and B (PEM-West A and B) [Talbot et al.,]
In some of the plumes, HCOOH was highly enhanced with regard to CH$_3$COOH, and the ratio HCOOH/CH$_3$COOH had values as large as 5.0 (plume median equal to 1.6). This suggests the possibility of substantial photochemical production of HCOOH compared to CH$_3$COOH (or more efficient loss of CH$_3$COOH) in some of the plumes that we sampled over the South Pacific. This point is further explored in later sections of this paper.

4. Discussion

4.1. Altitude Range of 2-12 km

The large-scale impact of pollution over much of the western and central Pacific basins is a significant feature of the PEM-Tropics data set. Backward trajectories indicate that many of the air parcels we sampled had not been over continental areas for 10-20 days [Fuelberg et al., this issue]. This is consistent with the chemical measurements which suggest that the air parcels were photochemically aged and physically processed for a week or two since the last injection of combustion emissions. Many of the trajectories follow a path that implies that the last continental areas that the air parcels passed over were Brazil and Africa. Since biomass burning occurs on both of these continental areas during austral spring [Cahoon et al., 1992], this is likely to be a major source of combustion emissions over the Pacific basin at this time of year.

Methyl chloride is a reasonably good chemical tracer of biomass burning emissions [Blake et al., 1996]. The relationship between
Figure 2. Vertical distribution of acidic gases over the central and southern Pacific basins. These distributions show that plume encounters with enhanced mixing ratios of acidic gases commonly occurred in the 3-7 km altitude region.

The mixing ratios of CH$_3$Cl and acidic gases is depicted in Figure 6. These plots indicate a general relationship between acidic gases and CH$_3$Cl ($r^2 = 0.4$). The enhancements of CH$_3$Cl in the plumes are small due to the significant dilution these well aged air parcels have undergone. Plots of C$_2$H$_2$ and C$_2$H$_6$ versus CH$_3$Cl (not shown) show similar relationships to those in Figure 6, again reflecting the substantial processing of the air parcels over the Indian and Pacific basins.

One feature of the plumes is the absence of enhancements in aerosol or aerosol associated species [Dibb et al., this issue], even for ammonium which is released in large quantities from biomass combustion [Lobert et al., 1991]. This indicates that the air parcels over the Pacific basin have been effectively scavenged by clouds and precipitation. It also suggests, since most acidic gases are highly water-soluble, that their large mixing ratios in some of the plumes may be due to photochemical production since the last scavenging event. Evidence for a photochemical source of acidic gases is provided in Figures 7 and 8, where the relationships between these species and O$_3$ and PAN are presented. As with CH$_3$Cl, the trends are only general ($r^2$ near 0.4) but suggestive of photochemical production of acidic gases. The break in the relationships at <5 pptv of PAN is presumably due to thermal decomposition of PAN to NO$_x$ at lower altitudes [Roberts, 1995]. The data corresponding to <5 pptv PAN was obtained in the 2-4 km altitude band where air temperatures were typically 280-285°K.

Plotting an individual species as a function of the ratio C$_2$H$_2$/CO gives insight on the effect of air parcel processing on its mixing ratio. These relationships for acidic gases are shown in Figure 9. It is evident that the relationship is much tighter for the carboxylic acids compared to HNO$_3$, but it is unclear as to why this is the case.
Clearly, the largest mixing ratios of acidic gases were contained in the least processed air parcels ($C_2H_2/CO > 1$). On the basis of the correlations shown in this paper, it follows that these same air parcels also contained the largest mixing ratios of $CH_3Cl$, $O_3$, and PAN. It appears that the chemical composition of these air parcels reflects photochemical activity of biomass burning emissions aged over a minimum of a one week time frame. This is based largely on the absence of reactive hydrocarbons (i.e., $C_4$ and higher) in these air parcels. It appears that mixing processes (i.e., dilution) are responsible for much of the variation in individual species mixing ratios and inter-relationships between various compounds. Thus, air parcels can be quite photochemically aged with significant mixing ratios of secondary species but still appear much younger (e.g., $C_2H_2/CO > 1$) due to less mixing with background air.

To examine the potential combustion source of $HNO_3$, only mixing ratios greater than 100 pptv are plotted versus CO and $C_2H_2$ (Figure 10). Only in a few plumes does there appear to be a direct relationship between $HNO_3$ and CO or $C_2H_2$. The largest mixing ratios of $HNO_3$ occurred at relatively low values of CO and $C_2H_2$ and correspond to a $C_2H_2/CO$ ratio near 1 (Figure 9). In general, there was very substantial amounts of $HNO_3$ in air parcels with CO of 50-100 ppbv and $C_2H_2 < 150$ pptv. Together these results point to significant photochemical production of $HNO_3$ (since the last scavenging event) during long-range transport of air parcels over the South Pacific. Similar arguments can be made for photochemical generation of carboxylic acids in these air parcels, especially $HCOOH$. Previous measurements of the ratio $HCOOH/CH_3COOH$ in biomass burning plumes transported long distances in the middle troposphere show values of 1.5-3 [Helas et al., 1992; Lefer et al., 1994; Dibb et al., 1996b].

Additional modeling studies are needed to enhance our understanding of photochemical processes occurring within plumes over the South Pacific basin. Limited insight as to whether we observed loss of $CH_3COOH$ in these plumes can be gleaned by examination of the $CH_3COOH$ and $CH_3OH$ data. Plotting various subsets of these data obtained over the South Pacific (not shown) revealed no correspondence between the two species, as would be expected if $CH_3COOH$ were a significant decomposition source of $CH_3OOH$.

**Figure 3.** Vertical distribution of the ratio $C_2H_2/CO$ over the central and southern Pacific basins.

**Figure 4.** Vertical distribution of selected trace gases during a slow spiral conducted during mission 17 just east of Fiji.
Table 1. Regional Summary of Acidic Gases Over the Central and Pacific Basins

<table>
<thead>
<tr>
<th>Altitude, km</th>
<th>HNO₃, pptv</th>
<th>HCOOH, pptv</th>
<th>CH₃COOH, pptv</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 1</td>
<td>13 ± 8.5 (10)</td>
<td>45 ± 18 (30)</td>
<td>55 ± 23 (60)</td>
<td>17</td>
</tr>
<tr>
<td>1-2</td>
<td>46 ± 10 (50)</td>
<td>39 ± 30 (30)</td>
<td>44 ± 35 (36)</td>
<td>6</td>
</tr>
<tr>
<td>2-8</td>
<td>87 ± 43 (83)</td>
<td>72 ± 49 (55)</td>
<td>72 ± 45 (59)</td>
<td>42</td>
</tr>
<tr>
<td>8-12</td>
<td>63 ± 53 (42)</td>
<td>55 ± 26 (52)</td>
<td>54 ± 30 (55)</td>
<td>29</td>
</tr>
</tbody>
</table>

0°-15° N, 120°-170° W

| < 1          | 20 ± 11 (15) | 35 ± 30 (27) | 34 ± 23 (20) | 19 |
| 1-2          | 52 ± 14 (49) | 33 ± 24 (18) | 36 ± 26 (22) | 10 |
| 2-8          | 67 ± 35 (51) | 31 ± 14 (33) | 33 ± 14 (35) | 31 |
| 8-12         | 150 ± 107 (107) | 27 ± 26 (14) | 23 ± 19 (13) | 16 |

0°-35° S, 120°-170° W

| < 1          | 18 ± 10 (17) | 66 ± 216 (23) | 84 ± 293 (27) | 40 |
| 1-2          | 32 ± 14 (30) | 44 ± 20 (43) | 43 ± 345 (39) | 21 |
| 2-8          | 139 ± 145 (84) | 124 ± 181 (49) | 84 ± 81 (54) | 192 |
| 8-12         | 63 ± 63 (37) | 61 ± 54 (46) | 56 ± 46 (41) | 122 |

0°-35° S, > 170° W

| < 1          | 15 ± 7.7 (13) | 18 ± 7.4 (17) | 17 ± 8.1 (15) | 12 |
| 1-2          | 40 ± 3.0 (40) | 50 ± 5.0 (50) | 46 ± 8.5 (46) | 2  |
| 2-8          | 160 ± 124 (97) | 71 ± 54 (47) | 84 ± 70 (53) | 46 |
| 8-12         | 100 ± 61 (81) | 66 ± 32 (52) | 92 ± 27 (94) | 19 |

0°-35° S, 80°-120° W

| < 1          | 13 ± 7.1 (14) | 18 ± 5.9 (18) | 16 ± 13 (18) | 27 |
| 1-2          | 28 ± 8.2 (30) | 33 ± 8.5 (32) | 67 ± 47 (47) | 5  |
| 2-8          | 43 ± 37 (31) | 43 ± 28 (36) | 52 ± 43 (36) | 50 |
| 8-12         | 45 ± 30 (45) | 54 ± 41 (39) | 42 ± 26 (43) | 28 |

35°-72° S, > 170° W

| < 1          | 14 ± 4.6 (14) | 11 ± 4.1 (10) | 13 ± 3.9 (12) | 23 |
| 1-2          | 25 ± 9.9 (28) | 38 ± 26 (33) | 29 ± 16 (26) | 13 |
| 2-8          | 180 ± 262 (80) | 162 ± 176 (90) | 114 ± 12 (57) | 70 |
| 8-12         | 54 ± 71 (25) | 54 ± 39 (40) | 45 ± 25 (37) | 23 |

35°-72° S, 80°-120° W

| < 1          | 12 ± 2.3 (11) | 16 ± 4.4 (18) | 18 ± 4.6 (19) | 7  |
| 1-2          | 31 ± NA (31) | 22 ± NA (22) | 20 ± NA (20) | 1  |
| 2-8          | 26 ± 16 (23) | 35 ± 19 (36) | 33 ± 18 (36) | 16 |
| 8-12         | 38 ± 60 (9.0) | 18 ± 5.0 (19) | 16 ± 4.8 (17) | 5  |

Values are stated as mean ± one standard deviation (median). N represents the number of data in altitude bin. NA means not applicable.

Figure 5. Relationship between mixing ratios of HCOOH and CH₃COOH over the central and southern Pacific basins; (a) <2 km and (b) 2-12 km altitude.
burning plumes, there is clearly much uncertainty surrounding the production and decomposition of carboxylic acids in such air parcels.

4.2 Altitude Range of 1-2 km

The altitude band <2 km was broken into the marine boundary layer (<1 km) and the transition or cloud layer from 1-2 km. The mixing ratio of acidic gases in these two layers are shown as a function of latitude in Figures 11a-11c. Nitric acid mixing ratios were smaller at <1 km compared to 1-2 km altitude, except for the most southerly data where they were about equal. There does not

\[ HNO_3 = 10.0 \times CH_3CI - 26 \]

\[ HCOOH = 12.0 \times CH_3CI - 31 \]

\[ CH_3COOH = 9.0 \times CH_3Cl - 23 \]

\[ HNO_3 = 1.2 \times O_3 - 0.25 \]

\[ CH_3COOH = 0.84 \times O_3 + 0.30 \]

\[ HCOOH = 1.0 \times O_3 + 0.02 \]

\[ CH_3COOH = 0.84 \times O_3 + 0.30 \]

Figure 6. Relationships between mixing ratios of acidic gases and CH3Cl in the altitude range 2-12 km. The $r^2$ values for these correlations were =0.35. Particularly for HCOOH and CH3COOH, there is a general trend of enhanced mixing ratios at the largest values of CH3Cl. These correlations potentially indicate an important biomass burning source for acidic gases over the South Pacific basin. Note that the abscissas are also a logarithmic scale, ranging from 500 to 650 pptv.

[Madronich and Calvert, 1990]. This result appears to support a significant photochemical source of HCOOH rather than a predominance of decomposition of CH3COOH in aged biomass burning plumes over the South Pacific. We can not rule out, however, some photochemical production of CH3COOH as well. Because of potentially complex (and unknown) chemistry in these biomass

Figure 7. Relationships between mixing ratios of acidic gases and $O_3$ in the altitude range 2-12 km. The $r^2$ values for these correlations were =0.40. These general correlations potentially indicate a photochemical source for HCOOH and CH3COOH.
Figure 8. Relationships between mixing ratios of acidic gases and PAN in the altitude range 2-12 km. The $r^2$ values for these correlations were 0.40. These general correlations potentially indicate a photochemical source for HCOOH and CH$_3$COOH. Mixing ratios of PAN below 5 pptv were observed in the altitude range 2-4 km, where thermal decomposition of PAN was apparently significant.

The mixing ratios of carboxylic acids in the marine boundary layer over the South Pacific were about an order of magnitude less than those previously determined from shipboard sampling in the central North Pacific region [Ariander et al., 1990]. This probably is due to the remoteness of the South Pacific basin from continental areas and restricted downward mixing across the trade wind inversion. Formic and acetic acid did not exhibit a difference in their mixing ratios between the marine boundary and transition layers. In the marine boundary layer they had the largest mixing ratios north of the ITCZ. This may reflect the closer proximity of
Figure 10. Mixing ratio of HNO₃ as a function of CO and C₂H₂ for HNO₃ >100 pptv.

Figure 11. Latitudinal distribution of acidic gases in the marine boundary layer (<1 km) and the overlying transition layer (1-2 km). The solid lines represent a plot of the median mixing ratio value as a function of latitude.
continental areas to this region leading to enhanced primary or secondary production of these species. One difference between the vertical distribution of HNO₃ and the carboxylic acids in the two surface layers is the similarity of the mixing ratios of HCOOH and CH₃COOH in these two altitude bands but not those of HNO₃. This observation may be explained by more extensive uptake of HNO₃ onto sea salt aerosols compared to the carboxylic acids. Detailed gas phase, cloud droplet, and aerosol measurements over the remote oceans are needed to better understand this issue.

5. Conclusion

The distribution of acidic gases over the South Pacific basin in austral springtime appears to be strongly influenced by emissions from biomass burning, most likely occurring in Africa and Brazil. Owing to the generally westerly flow of air over this area in the middle and upper troposphere, elevated mixing ratios of acidic gases and the presence of pollution plumes were concentrated in the western and central South Pacific. The eastern Pacific basin was relatively “clean” presumably due to chemical and physical removal of these species during the long transit across the South Pacific.

The enhanced mixing ratios of acidic gases in pollution plumes were coincident with relatively low mixing ratios of the combustion tracers CO and C₂H₄. This observation and their general correlations with O₃ and PAN suggest that the mixing ratios of acidic gases may have been sustained by photochemical production in the pollution plumes. Most likely this generation of acidic gases occurred after the last scavenging event the air parcels encountered since other soluble species such as aerosols were not enhanced in these same plumes. The PEM-Tropics data document the hemispheric-scale pollution of the southern troposphere by biomass burning in austral springtime. The impact of these emissions on the chemistry of the southern hemisphere troposphere appears to be much greater than previously recognized.

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