

The biogeochemical cycling of formic and acetic acids through the troposphere: an overview of current understanding

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ABSTRACT

Despite remaining uncertainties, a general picture of the biogeochemical cycling of HCOOH and CH₃COOH is beginning to emerge. These acids are ubiquitous vapor- and aqueous-phase constituents of the global troposphere, contributing significant fractions of the natural acidity in precipitation and cloudwater, particularly in continental regions of the tropics and subtropics. The similarity of concentrations in remote and impacted regions indicates that anthropogenic emissions of carboxylic acids or precursors are probably not important sources over broad geographic areas. In continental regions, seasonally varying emissions of acids and hydrocarbon precursors from vegetation are thought to represent major sources for both acids. In marine areas, the seasonality of wet deposition and apparent lack of transport from continents support the hypothesis of a marine biogenic source. Ratios of total (aqueous + vapor) concentrations of HCOOH versus CH₃COOH in clouds vary as a function of H⁺. This observation is consistent with the hypothesis of a pH-dependent aqueous-phase source and sink for HCOOH in clouds which may act to stabilize aqueous-phase ratios against shifts in solution H⁺. Large diel periodicities in the concentrations of vapor-phase species over continents, together with a lack of evidence for long-distance transport, suggest that HCOOH and CH₃COOH experience short atmospheric lifetimes of several hours to a few (at most) days. Because they are important controllers of free acidity and represent a potentially large sink for aqueous-phase OH radicals, the cycling of the carboxylic acids is expected to interact directly and indirectly in the chemical cycling of other atmospheric constituents.

1. Introduction

Eriksson (1960) first suggested more than a quarter century ago that organic compounds may contribute significantly to the ionic composition of precipitation. This astute speculation was verified in the early 1980s when advances in sampling and analytical techniques revealed that formic acid (HCOOH) and acetic acid (CH₃COOH) were major vapor- (Dawson et al., 1980) and aqueous- (Keene et al., 1983) phase constituents of the troposphere. These early observations stimulated research into the distributions and chemical cycling of carboxylic acids resulting in a large number of measurements and related hypotheses concerning atmospheric sources, transformations, and sinks (e.g.

see Chameides and Davis, 1983; Graedel et al., 1986; Keene and Galloway, 1986; Andreae et al., 1988; Jacob and Wofsy, 1988; Talbot et al., 1988 among others).

During August 1987, results from the majority of current research efforts in this area were presented in the special session on Organic Acids and Related Compounds in the Atmosphere, at the Sixth International Symposium of the Commission on Atmospheric Chemistry and Global Pollution (CACGP) in Peterborough, Canada. Many of these presentations are summarized in the companion papers in this special issue of *Tellus*. By way of introduction, we present in this paper a general overview of the field with special emphasis on aqueous-phase measurements in precipitation and cloud water.

These measurements will be related to various hypotheses concerning the cycling of HCOOH and CH₃COOH through the troposphere, and potential interactions with the cycling of other atmospheric constituents will be discussed.

2. Methods

The chemical data evaluated in this paper were generated by the Global Precipitation Chemistry Project (GPCP), the Western Atlantic Ocean Experiment (WATOX), the MAP3S Project, and the Mountain Cloud Chemistry Project (MCCP). Detailed descriptions of the collection protocols and analytical procedures for the GPCP and WATOX are given by Galloway et al. (1982) and Keene et al. (1983), and those for MAP3S are given by Dana (1980). Precipitation was sampled by event in scrupulously washed polyethylene collectors. Cloud water was collected from non-precipitating clouds using a passive device (Falconer and Falconer, 1980) mounted on a tower which extended approximately 3 m above the canopy at the top of the Shaver Hollow watershed in the Shenandoah National Park (SNP), Virginia. Samples were collected on an hourly basis during cloud events, but collections were stopped during periods of precipitation. Immediately after collection, all samples of precipitation and cloud water were treated with CHCl₃ to prevent the loss of organic acids resulting from microbial transformation (Keene et al., 1983; Herlihy et al., 1987), and were subsequently sent to the University of Virginia for chemical analysis. Total aqueous HCOOH_{T,aq} (HCOO⁻ + HCOOH_{aq}) and CH₃COOH_{T,aq} (CH₃COO⁻ + CH₃COOH_{aq}) were measured by ion exclusion chromatography (ICE); Cl⁻, NO₃⁻, and SO₄²⁻ by ion chromatography (IC); NH₄⁺ by automated wet chemistry; Ca²⁺, Mg²⁺, Na⁺, and K⁺ by atomic absorption spectroscopy; and H⁺ with a combination electrode. Dissociated and undissociated fractions of aqueous-phase HCOOH_{T,aq} and CH₃COOH_{T,aq} were calculated using standard thermodynamic relationships and pK_A's of 3.75 and 4.76, respectively (Keene and Galloway, 1984). Equilibrium vapor-phase concentrations of HCOOH_g and CH₃COOH_g in clouds were derived from measured aqueous-phase concentrations using Henry's Law con-

stants of 5.6×10^3 M/atm and 8.8×10^3 M/atm, respectively (Keene and Galloway, 1986).

3. Results and discussion

3.1. Data base

The collection periods and numbers of precipitation samples included in this study are summarized in Table 1. In past reports (e.g. Keene and Galloway, 1986), we evaluated only samples with sufficient volume for analysis of all major chemical constituents. While this restriction allowed the assessment of overall data quality through reviews of ion balances, it did result in a slight bias toward larger volume events and a potential related bias in the chemistry of the resulting data subset. Data for samples with ion imbalances exceeding $\pm 25\%$ or ± 5.0 $\mu\text{eq/l}$ were removed from these earlier data sets. In many samples, however, particularly those from marine regions, HCOO⁻ and CH₃COO⁻ made only minor contributions to the total ionic strength of the samples, and as such, this ion imbalance criterion was not a very useful indicator for the data quality of carboxylic anions. Standard additions and replicates reveal that the measurements of HCOOH_{T,aq} and CH₃COOH_{T,aq} are unbiased and precise to approximately $\pm 7\%$ or ± 0.5 $\mu\text{mol/l}$ (Keene et al., 1983). Based on the above reasoning, we chose to interpret in this report all measurements of carboxylic acids, including those for small volume samples with incomplete analyses, and those for the approximately 3% of samples with ion imbalances which exceeded the stated criterion. This procedure substantially increased the numbers of observations for several of the smaller data sets, particularly those for oceanic cruises which generated predominately low volume samples.

3.2. Spatial and temporal distributions

3.2.1. Precipitation. The arithmetic or volume-weighted mean (VWM) concentrations of H⁺, HCOOH_{T,aq}, and CH₃COOH_{T,aq} measured in precipitation from sixteen widely spaced continental and marine locations are depicted in Fig. 1. These results are presented in order of approximate latitude, although there are some overlaps associated with data from oceanic cruises. The

Table 1. Collection periods and numbers of precipitation samples comprising data base evaluated in this study

Location	Latitude/ longitude	Sampling period (ddmmyy)	Collected (Event Only)	Analyzed for H ⁺ and carboxylic anions*
<i>Continental</i>				
Lago Colado,	3° 15' S	10 Sep, 1982–6 Feb, 1983	4	4
Amazonia, Brazil	60° 34' W	22 Apr, 1987–26 Apr, 1987	3	1
Katherine, Northern Territory, Australia	14° 28' S 132° 18' E	18 Nov, 1980–6 Feb, 1987	271	220
Lijiang, Yunnan Province, China	27° 10' W 100° 7' E	2 Jun, 1987–3 Aug, 1987	10	10
Charlottesville, Virginia, USA	38° 2' N 78° 33' W	25 Apr, 1983–7 May, 1987	158	142
Torres del Paine, Southern Chile	51° 10' S 72° 58' W	23 Mar, 1984–9 Sep, 1986	46	44
Poker Flat, Central Alaska, USA	67° 7' N 147° 29' W	3 May, 1982–22 Sep, 1982	14	14
<i>Marine</i>				
Central Atlantic, NOAA Researcher	16°–29° N 63°–77° W	19 Apr, 1985–29 Jan, 1986	16	11
Mauna Loa, Hawaii	19° 32' N 155° 35' W	9 May, 1983–22 May, 1987	57	57
High Point, Bermuda	32° 19' N 64° 45' W	10 Mar, 1983–18 May, 1984	90	90
North Atlantic, Knorr	18°–48° N 18°–70° W	19 Apr, 1984–5 May, 1984	11	8
North Pacific, NOAA Discoverer	1°–51° N 151°W–178°E	10 Apr, 1982–30 Jun, 1982	25	16
Cape Point, South Africa	34° 22' S 18° 31' E	26 Aug, 1983–25 Sep, 1986	69	69
90 Mile Beach, New Zealand	34° 31' S 172° 42' E	24 Jun, 1983–24 Jul, 1983	8	8
Amsterdam Island, Indian Ocean	37° 47' S 77° 31' E	12 Sep, 1981–14 Jun, 1986	133	133
Adrigole, Ireland	51° 41' N 9° 45' W	8 Nov, 1984–20 Oct, 1986	174	174
Antarctica, Polar Duke	54°–65° S 60°–67° W	23 Mar, 1986–27 Apr, 1986	17	11

* Data for samples collected at land based sites which did not have corresponding precipitation gauge readings were excluded from the analyses.

small numbers of observations and related inadequate temporal coverage for many data sets (Table 1) limits resolution in identifying latitudinal trends. It does appear, however, that on average, carboxylic acids exhibit highest concentrations and make the greatest proportionate contributions to free acidity in continental precipitation from tropical (central Brazil) and subtropical (north-central Australia) regions. VWM concentrations in continental precipitation

from more temperate and sub-arctic regions were significantly lower (Fig. 1). Results for marine precipitation do not provide evidence for a distinct latitudinal gradient in carboxylic acids over the oceans.

The high concentrations of free acidity in precipitation from central Virginia (Fig. 1) is but one obvious example of the influence of upwind anthropogenic emissions on regional atmospheric chemistry in eastern North America (also see

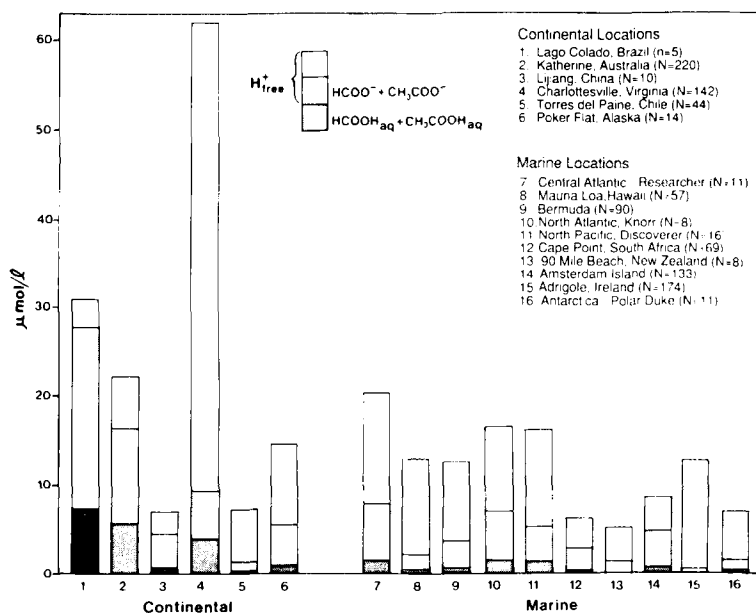


Fig. 1. Comparison between the concentrations of H^+ and dissociated and undissociated carboxylic acids in precipitation collected at 16 continental and marine locations. Data for land based sites correspond to volume-weighted averages and those for ship board collections (numbers 7, 10, 11, and 16) represent arithmetic averages.

Galloway et al., 1984 among others). Corresponding enrichments in $HCOOH_{T,aq}$ and $CH_3COOH_{T,aq}$ were not evident in the data (Fig. 1). As discussed by Keene and Galloway (1986), the absolute and relative magnitudes of $HCOOH_{T,aq}$ and $CH_3COOH_{T,aq}$ in precipitation from central Virginia during growing seasons is similar to that at a remote terrestrial site in Australia (also see Likens et al., 1987). This evidence supports the hypothesis that carboxylic acids in precipitation over predominately rural areas within industrialized regions originate primarily from natural sources.

Marked seasonal cycles in the concentrations of organic acids were evident in the larger data sets. The interpretation of trends in concentration data can, however, be complicated by potential dilution effects resulting from systematic spatial or temporal variation in associated water deposition (e.g., Galloway et al., 1989). To minimize such influences, seasonal relationships were assessed with per-event depositions. The monthly medians and distributions for per-event depositions of $HCOOH_{T,aq}$ and $CH_3COOH_{T,aq}$ in precipitation from central Virginia reveal a dis-

tinct seasonal cycle (Fig. 2). Although the following discussion focuses primarily on medians, similar seasonal cycles are also evident in mean monthly depositions. During the late autumn and winter months (October through February), similar amounts of $HCOOH_{T,aq}$ and $CH_3COOH_{T,aq}$ were deposited via precipitation, and rates of wet deposition were generally low relative to warmer months. March appears to be a transition month with generally higher deposition rates for both acids. During spring and summer (April through August), median deposition rates of $HCOOH_{T,aq}$ and $CH_3COOH_{T,aq}$ were greater than those observed during autumn and winter by factors of approximately 4 and 2, respectively. This suggests that although source strengths for both acids increase during the warmer period, sources for $HCOOH$ are disproportionately greater than those for CH_3COOH . Like March, September appears to be a transition month between the warm and cold seasons.

Similar seasonal cycles in the monthly VWM concentrations of $HCOOH_{T,aq}$ and $CH_3COOH_{T,aq}$ in precipitation from Virginia have been

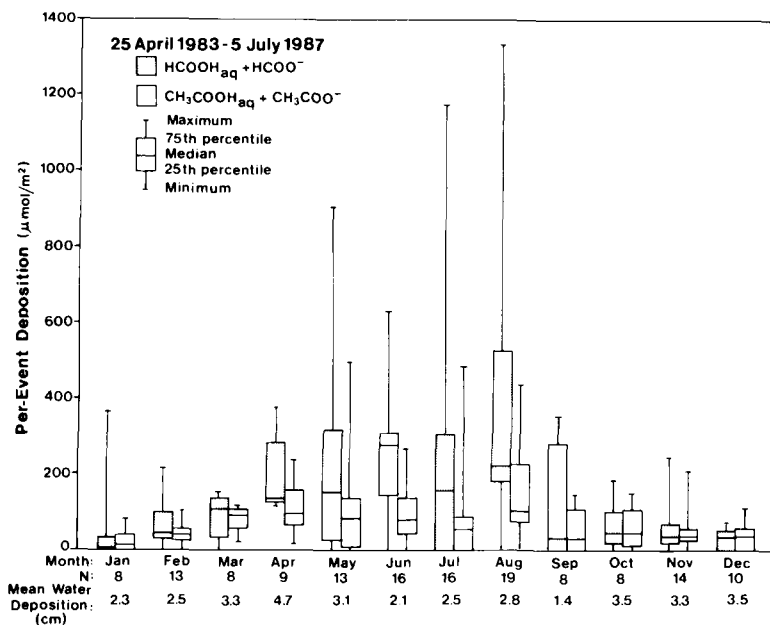


Fig. 2. Distributions for monthly per-event depositions of $\text{HCOOH}_{\text{Taq}}$ (on left) and $\text{CH}_3\text{COOH}_{\text{Taq}}$ (on right) measured at the MAP3S site near Charlottesville, Virginia.

previously reported (Keene and Galloway, 1986; Talbot et al., 1988). Keene and Galloway (1986) assessed a number of factors including solar radiation, storm types, air mass source region, and amount of precipitation which might have contributed to a seasonal cycle in concentrations. Such factors could not, however, account for major features of the observed trends. We agree with the interpretations of previous reports that the higher concentrations (and resulting depositions) during the warmer months originate primarily with biogenic emissions from terrestrial vegetation. Both direct emissions and emissions of hydrocarbon precursors such as isoprene may be important (Jacob and Wofsy, 1988).

Seasonal cycles in event depositions were also observed at Amsterdam Island, a remote marine location in the southern Indian Ocean (Fig. 3). Median values for both acids were generally lowest from late summer through winter (March through September) increasing by approximately a factor of 2 during the spring through mid-summer (October through February). This trend of lower depositions in the winter and higher in the summer is similar to trends in the concentrations of non-sea-salt (nss) SO_4^{2-} in precipitation at

the site (e.g. see Galloway and Gaudry, 1984). Andreae (1986) suggested that some marine biogenic dimethyl sulfide (DMS) may be oxidized to SO_2 by a mechanism which generates formaldehyde (HCHO) as a by-product. If the HCHO was subsequently oxidized to HCOOH (e.g., see Chemeides and Davis, 1983), there could be a direct link between the cycling of HCOOH and sulfur compounds. Such a mechanism does not, however, generate CH_3COOH , and as such cannot account for the observed correlations between $\text{HCOOH}_{\text{Taq}}$ and $\text{CH}_3\text{COOH}_{\text{Taq}}$ in precipitation at the site (see Keene and Galloway, 1986). Alternatively, the observed cycle in depositions could be explained by an independent biogenic source which varies seasonally. G. R. Harvey and R. F. Lang (personal communication) have suggested that carboxylic acids might originate with olefins that are emitted by marine microbiota, volatilized to the atmosphere and subsequently photooxidized.

The highest rates of deposition were observed during the early spring (September and October) and summer (January through March) when the greatest marine biological activity is expected (Fig. 3). Such high depositions were not

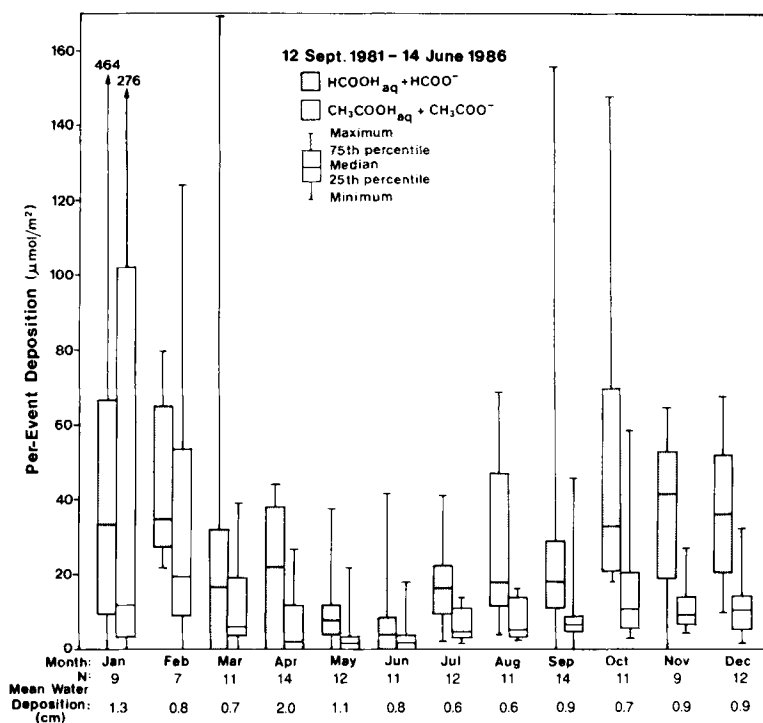


Fig. 3. Distributions for monthly per-event depositions of $\text{HCOOH}_{\text{Taq}}$ (on left) and $\text{CH}_3\text{COOH}_{\text{Taq}}$ (on right) measured on Amsterdam Island in the southern Indian Ocean.

measured during autumn and winter months. Phytoplankton blooms tend to be episodic and of short duration. If such blooms generated high concentrations of precursor hydrocarbons, then episodic and highly variable concentrations of carboxylic acids in the atmosphere might be expected during the seasons when such conditions exist. The observed seasonal pattern of extreme values is therefore consistent with the hypothesis of a marine biogenic source for carboxylic acids in precipitation at the site.

It is unlikely that the seasonal cycle of depositions is associated with the long distance transport of terrestrial material. Amsterdam Island is approximately 5000 km from southern Africa, the nearest continental land mass, and transit time for air parcels from Africa to the site are typically 3 to 6 days (J. Moody, personal communication). The high concentrations and rapid cycling of sea-salt aerosol over the mid-latitude southern oceans (Erickson et al., 1986) should contribute to rapid deposition and short atmospheric lifetimes of acidic gases over this marine region. In addition,

Galloway et al. (1989) found little evidence for the transport of significant quantities of HCOOH and CH_3COOH from North America to Bermuda, a distance over the ocean of only ~ 1000 km. There were no significant differences between the medians and distributions for per-event depositions of $\text{HCOOH}_{\text{Taq}}$ on Bermuda associated with southeastern (SE) and northwestern (NW) trajectories (Fig. 4). This is in contrast to the factor of two difference between SE and NW storms for the cumulative deposition of nss SO_4^{2-} resulting from the transport of anthropogenic sulfur from North America to Bermuda. These data suggest that HCOOH and CH_3COOH have short atmospheric lifetimes over the ocean relative to H_2SO_4 and its precursors. Like Amsterdam Island, the highest event depositions of $\text{HCOOH}_{\text{Taq}}$ from both sectors were typically observed during the spring and early summer. These observations support the hypothesis of a significant seasonally varying source for HCOOH and CH_3COOH in the marine atmosphere.

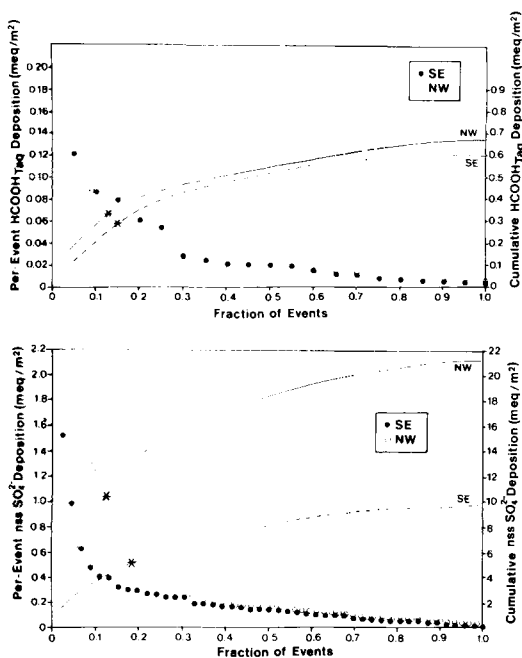


Fig. 4. Per-event (points) and cumulative (lines) depositions of $\text{HCOOH}_{\text{Taq}}$ and SO_4^- as a function of fraction of events for precipitation collected on Bermuda. Data are shown for storms associated with SE and NW trajectories. Stars indicate 50% of cumulative deposition.

The concentrations of $\text{HCOOH}_{\text{Taq}}$ and $\text{CH}_3\text{COOH}_{\text{Taq}}$ in precipitation are typically highly correlated both at a given site and between sites (e.g. see Keene and Galloway, 1986). For example, the arithmetic average or VWM concentrations of $\text{HCOOH}_{\text{Taq}}$ and $\text{CH}_3\text{COOH}_{\text{Taq}}$ for data sets described in Table 1 are plotted in Fig. 5. The reduced major axis procedure was used to calculate a linear regression. Results yielded a significant linear relationship between the two with a slope of 2.25, an intercept of 0.13 and a correlation coefficient of 0.90. Such high correlations led Keene and Galloway (1986) to speculate that HCOOH and CH_3COOH may originate with a common source or be controlled by a common reactant. The fact that these ratios were fairly constant over a wide range of pH also suggested some type of mechanistic control over the proportionality between $\text{HCOOH}_{\text{Taq}}$ and $\text{CH}_3\text{COOH}_{\text{Taq}}$. In the following section we will assess such a mechanism.

3.2.2. Cloud water. The concentrations of $\text{HCOOH}_{\text{Taq}}$ and $\text{CH}_3\text{COOH}_{\text{Taq}}$ in cloud water have been measured at a wide variety of continental and marine locations worldwide (e.g., see Jacob et al., 1986; Noller et al., 1986; Weathers et al., 1986; 1988). In general, similar concentrations were found in impacted and remote regions supporting the hypothesis that carboxylic acids in rural areas originate primarily from natural sources. $\text{HCOOH}_{\text{Taq}}$ and $\text{CH}_3\text{COOH}_{\text{Taq}}$ contribute significantly to the acidity of remote clouds, but because of high levels of strong mineral acids, carboxylic acids have only a minor influence on the acid-base chemistry of clouds in regions impacted by anthropogenic emissions.

Weathers et al. (1988) noted that like precipitation the ratios of $\text{HCOOH}_{\text{Taq}}$ and $\text{CH}_3\text{COOH}_{\text{Taq}}$ were similar in cloud water over a wide (factor of 20) range in the concentration of H^+ . If the aqueous and vapour phases within clouds are in thermodynamic equilibrium, then higher concentrations of total HCOOH_T ($\text{HCOOH}_{\text{Taq}} + \text{HCOOH}_g$) relative to total CH_3COOH_T ($\text{CH}_3\text{COOH}_{\text{Taq}} + \text{CH}_3\text{COOH}_g$) must exist in more acidic clouds to maintain these fairly constant ratios of aqueous-phase species. This relationship can be illustrated with a simplified example (Fig. 6). For this calculation, the mean aqueous-phase ratio of $\text{HCOOH}_{\text{Taq}}$ to $\text{CH}_3\text{COOH}_{\text{Taq}}$ (1.8 nmol/nmol) observed by Weathers et al. (1988) was held constant over the reported range in H^+ (42.7 to 851. $\mu\text{eq/l}$). Vapor-phase concentrations were estimated, as described in the Methods section, by assuming equilibrium with the aqueous phase. The assumption of equilibrium between phases within clouds is supported by the fact that the time required for mass exchange (seconds) is typically much less than the lifetime of cloud droplets (minutes) (Munger et al., 1989). Direct measurements of liquid water content (LWC) were not available and therefore a representative value of 0.5 g/SCM was assumed (Jacob, 1986). It is evident that under equilibrium conditions, HCOOH_T must increase relative to CH_3COOH_T as a function of H^+ to maintain constant ratios of $\text{HCOOH}_{\text{Taq}}$ to $\text{CH}_3\text{COOH}_{\text{Taq}}$ in cloud water.

One mechanism which might explain this phenomenon is the pH-dependent aqueous-phase source for HCOOH first hypothesized by

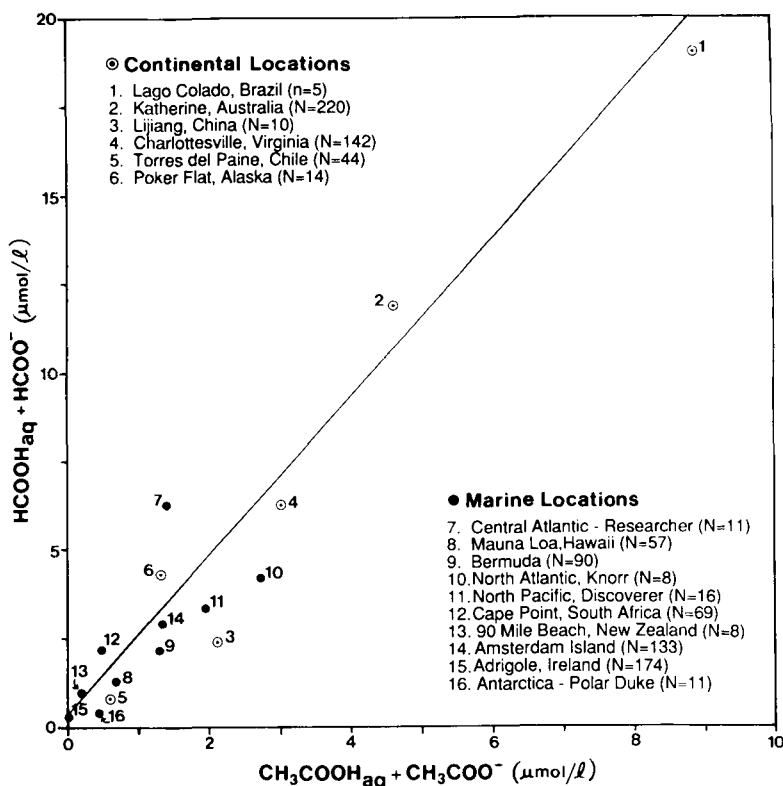


Fig. 5. The concentrations of $\text{HCOOH}_{\text{Taq}}$ versus $\text{CH}_3\text{COOH}_{\text{Taq}}$ in precipitation collected at 16 continental and marine locations. The RMA regression line is depicted (see discussion in text).

Chameides and Davis (1983). Modeling investigations of this mechanism indicate that HCOOH_T within clouds should increase as H^+ increases (e.g. Jacob, 1986), but no pH-dependent controls for the concentrations of CH_3COOH_T are known (Jacob and Wofsy, 1988). If CH_3COOH_T does not vary as a function of H^+ , then it follows from the previous discussion that such a mechanism could stabilize to some degree the ratios of $\text{HCOOH}_{\text{Taq}}$ to $\text{CH}_3\text{COOH}_{\text{Taq}}$ against variations in solution H^+ .

To investigate this mechanism in more detail, we measured time series of $\text{HCOOH}_{\text{Taq}}$, $\text{CH}_3\text{COOH}_{\text{Taq}}$ and H^+ in cloud water collected by the MCCP in SNP, Virginia (Fig. 7). Direct measurements of LWC were not available during the sampling period, and therefore the total amounts of HCOOH_T and CH_3COOH_T in the clouds were calculated for a range of representative values (1 g/SCM, 0.5 g/SCM, and 0.1

g/SCM) (e.g. Jacob, 1986). In the range of measured pH's and for all assumed LWC's, the majority of HCOOH_T and CH_3COOH_T in the clouds existed as vapor. As such, similar relationships between HCOOH_T , CH_3COOH_T and H^+ were calculated at all LWC's, and therefore the lack of direct measurements of LWC was not a critical constraint in this analysis. The ratios of HCOOH_T to CH_3COOH_T at an assumed LWC of 0.5 g/SCM are plotted against measured cloud water H^+ in Fig. 8. It is evident that as H^+ increased, the amount of HCOOH_T in the sampled clouds generally increased relative to CH_3COOH_T . There is some scatter in the relationship and not every pair or group of data strictly adhere to the overall trend. This scatter likely reflects uncertainties in the actual LWC, analytical uncertainties, as yet undescribed chemical reactions in the cloud water, and undoubtedly other factors. The overall pattern is,

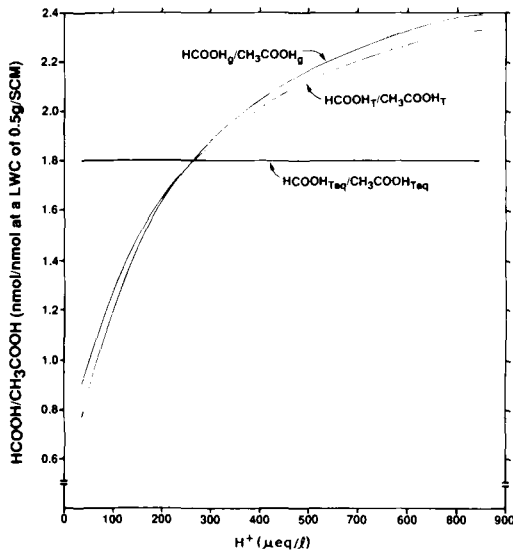


Fig. 6. Relative variability in the ratios of HCOOH_g to CH_3COOH_g and of HCOOH_T to CH_3COOH_T for a constant ratio of HCOOH_{Taq} to $\text{CH}_3\text{COOH}_{Taq}$ over an observed range in cloud water H^+ . A LWC of 0.5 g/SCM was assumed for the calculations.

however, consistent with that expected for the hypothesized aqueous-phase mechanism. Such a mechanism may contribute to the observed stability in aqueous-phase ratios of HCOOH_{Taq} to $\text{CH}_3\text{COOH}_{Taq}$ over wide ranges in the concentrations of solution H^+ .

3.2.3. *Gases and aerosols.* Relative to the extensive data base of aqueous phase observations, few measurements of carboxylic acids in the vapor and particulate phases have been published. This is due in part to the lack of verified sampling methodologies for these atmospheric constituents as evidenced by a recent intercomparison which found significant bias between many currently deployed measurement systems (Keene et al., 1986). Subsequent experimentation revealed that alkaline sampling media for vapor were subject to significant positive artifacts possibly related to reactions of gaseous aldehydes subsequent to collection (R. W. Talbot and M. O. Andreae, personal communication). Mist chambers (Cofer et al., 1985) appear to be free of any identifiable arti-

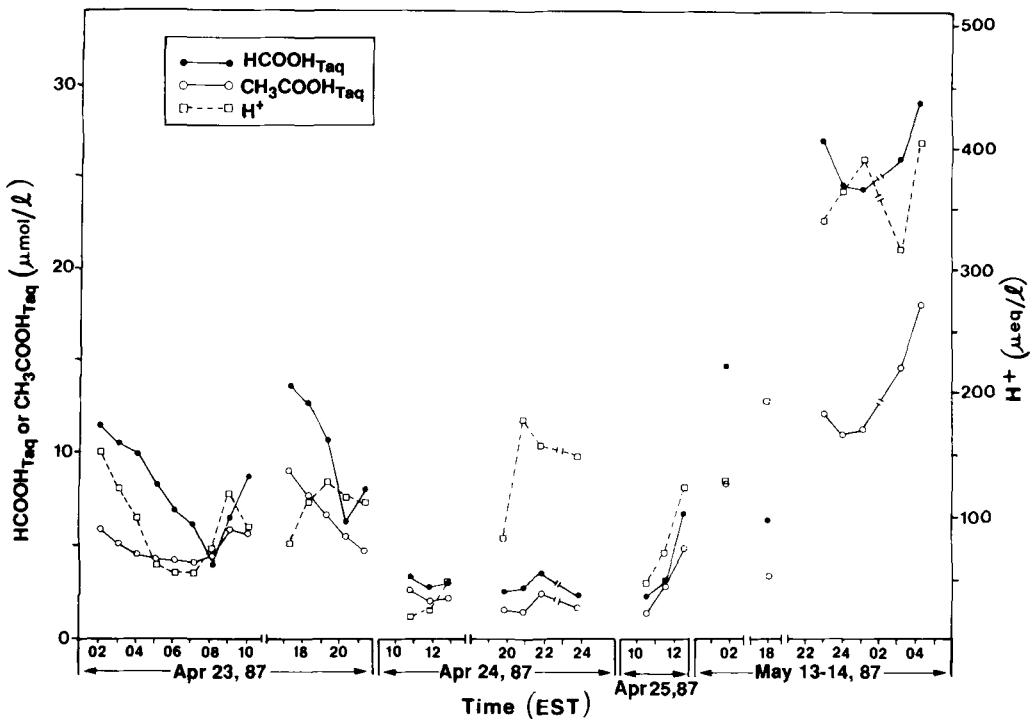


Fig. 7. The concentrations of H^+ , HCOOH_{Taq} and $\text{CH}_3\text{COOH}_{Taq}$ measured in cloud water collected in the Shenandoah National Park, Virginia.

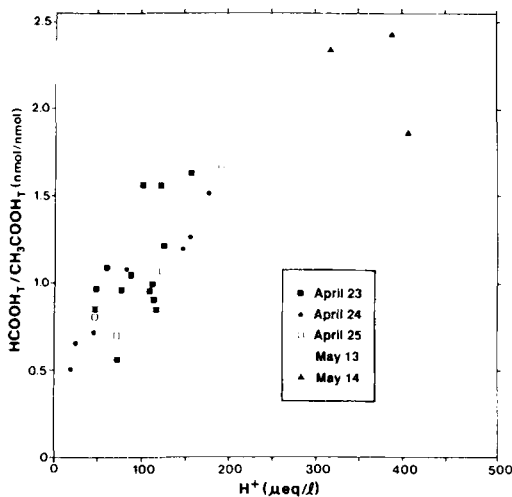


Fig. 8. Ratios of HCOOH_T to CH_3COOH_T plotted as a function of H^+ for samples of cloud water collected in the Shenandoah National Park, Virginia. A LWC of 0.5 g/SCM was assumed for the calculations.

facts (e.g. see Talbot et al., 1988) and the following assessment will be limited to data generated by that method of collection.

Significant bias was also found in measurements of particulate-phase concentrations during the above intercomparison. Particulate filters from the different systems were stored under different conditions and for different amounts of times between collection and analysis. Keene et al. (1986) speculated that this may have given rise to different rates of biological transformation on the different sets of filters leading to the observed artifacts, but additional experimentation is needed to rigorously test this speculation. In general, particulate-phase concentrations are one to two orders of magnitude lower than corresponding vapor-phase concentrations, and therefore, in terms of biogeochemical cycling, appear to be relatively unimportant in most areas. Possible exceptions include polar regions where extreme temperatures can result in higher fractions of carboxylic acids in the condensed phase (Li and Winchester, 1986).

Vapor-phase concentrations of HCOOH_g and CH_3COOH_g vary over both diel and seasonal cycles. Diel periodicities, which have been observed in both the Amazonia region of Brazil

(Andreae et al., 1988) and in Virginia (Keene et al., 1986; Talbot et al., 1988), are typically associated with increasing concentrations during the daytime followed by falling concentrations at night. Mean daily concentrations range from less than one to several ppbv's and vary by factors of 2 to 10 over 24-h periods. Modeling investigations suggest that these diel cycles at the surface are associated with diurnal vegetative sources of acids or precursors coupled with rapid dry deposition and nocturnal ventilation (Jacob and Wofsy, 1988). The mixing down of air from aloft which is enriched in HCOOH_g and CH_3COOH_g relative to the depleted surface layer may also contribute to rapid increases in concentrations observed during the early morning hours.

Seasonal cycles in the concentrations of vapor-phase HCOOH_g and CH_3COOH_g (Talbot et al., 1988) are similar to those observed for precipitation. Highest levels were measured during the spring and summer with lower levels during the remainder of the year. Like precipitation, the ratios of HCOOH_g to CH_3COOH_g were higher during the warmer months relative to the rest of the year, and the two acids were also significantly correlated.

3.3. Biogeochemical cycling

Despite many remaining uncertainties, a general picture of the biogeochemical cycling of HCOOH and CH_3COOH through the troposphere is beginning to emerge. Vertical profiles of carboxylic acids through the canopy of a tropical rainforest in Brazil suggest that in remote continental areas direct emissions of CH_3COOH_g from vegetation or soils may represent major atmospheric sources (Andreae et al., 1988). An important source for HCOOH in Brazil appears to be secondary production from the photo-oxidation of isoprene (Jacob and Wofsy, 1988). Additional sources for HCOOH , possibly associated with emissions from Formicine ants (Graedel and Eisner, 1988) or direct emissions from vegetation or soils, are needed to balance model predictions with field observations. HCOOH is, however, an important atmospheric constituent in continental regions such as central Alaska (Figs. 1, 5) where isoprene-emitting vegetation (Lamb et al., 1985) is not found in abundance. In terms of sources for HCOOH , the relative importance of other precursor hydrocar-

bons or of direct emissions is therefore expected to vary spatially from region to region.

Substantial amounts of HCOOH may be processed through clouds in many regions of the world. Depending on the relative importance of heterogeneous versus homogeneous processes, aqueous-phase reactions may, as previously described, have a significant influence on the absolute and relative magnitudes of HCOOH and CH₃COOH in the atmosphere. Modeling investigations suggest that aqueous-phase reactions have only a minor effect on total atmospheric HCOOH in Brazil (Jacob and Wofsy, 1988), but little information is available to make such an assessment for other continental regions.

Large diel periodicities in vapor-phase concentrations suggest that carboxylic acids are rapidly produced during the day and lost at night. The lack of an obvious chemical mechanism to explain the observed nighttime depletions has led a number of investigators to speculate that dry deposition, possibly enhanced by dissolution into surface dews, may be the most important sink for these acids (Andreae et al., 1988; Jacob and Wofsy, 1988; Talbot et al., 1988). This apparent rapid cycling indicates that the atmospheric lifetimes of HCOOH and CH₃COOH should be on the order of several hours to a few (at most) days. Such short lifetimes are consistent with the hypothesized surface source, the high solubilities predicted by Henry's Law constants, and the lack of evidence for significant long distance transport (Keene and Galloway, 1986; Galloway et al., 1989).

Evidence based on direct measurements (Norton; 1985; Talbot et al., 1988) and on indirect estimates (Keene and Galloway, 1984) suggest that anthropogenic activities may represent important local sources for carboxylic acids, especially CH₃COOH. Relative to remote regions, however, obvious enrichments in the concentrations of HCOOH_{T,aq} and CH₃COOH_{T,aq} are not evident in precipitation and cloud water from rural locations in eastern North America (Keene and Galloway, 1986; Weathers et al., 1988). This suggests that carboxylic acids originating with anthropogenic processes are deposited near sources and, in contrast to sulfur and nitrogen species, are not transported long distances. HCOOH and CH₃COOH in the atmosphere over predominately rural areas of

North America appear to originate primarily from seasonally varying natural sources.

The cycling of carboxylic acids through the marine atmosphere is less well understood, but available evidence on seasonality and transport (see Precipitation section) supports the hypothesis of a seasonally varying biogenic source. Such a source is consistent with biogenic precursors such as alpha-olefins which are emitted by marine microorganisms, volatilized to the atmosphere, and subsequently photooxidized. Major sinks are expected to be a combination of wet deposition, the direct deposition of vapor, and the scavenging of vapor by sea-salt aerosol and its subsequent dry deposition to the surface. The relative importance of these processes will vary temporally and spatially as a function of precipitation frequency, wind velocity and related concentrations of sea-salt aerosol, and undoubtedly other factors.

3.4. Interactions with other chemical cycles

Although no direct evidence exists, the chemical cycles of carboxylic acids are expected to interact directly and indirectly with those of other atmospheric constituents. As major sources of acidity in remote precipitation and cloud water, HCOOH and CH₃COOH will control in part the rates of pH-dependent chemical reactions and the phase partitioning of species with pH-dependent solubilities (Prospero et al., 1985). In addition, aqueous-phase reactions involving HCOOH may represent an important sink for in-cloud concentrations of OH radicals (Jacob, 1986), thereby potentially influencing the oxidative state of the troposphere. The chemical cycling of carboxylic acids must, therefore, be understood to explain transformations involving numerous other atmospheric constituents, particularly in the remote troposphere.

3.5. Future research needs

It is evident from the preceding discussion that much of our current knowledge concerning the biogeochemical cycling of HCOOH and CH₃COOH is based on inferences drawn from measurements of aqueous-phase concentrations and from modeling investigations. The lack of verified sampling methodologies for vapor-phase species has hindered past field investigations, and several data sets have not been reported in

the literature because of questions concerning data quality. With some notable exceptions (e.g. Andreae et al., 1988), few field experiments involving multi-phase measurements of carboxylic acids and potential precursors have been carried out, and fluxes from hypothesized sources have not been measured directly.

With the knowledge gained over the past few years, we are now in a position to plan and carry out mechanistic investigations of processes involved in the emissions, chemical transformations, transport, and deposition of these potentially important atmospheric constituents. The following list details major areas of uncertainty that should be investigated to advance our understanding.

- Source strength of HCOOH from formicine ants.
- Identity and magnitude of marine biogenic sources.
- Relative importance of homogeneous versus heterogeneous chemical transformations.
- Magnitude and regional importance of anthropogenic sources.
- Rates of dry deposition.
- Importance of long distance transport.
- Interactions with other chemical cycles.

We view the resolution of these issues as a challenge to all investigators involved in this area of atmospheric research.

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