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Surface Wetness as an Unexpected Control on Forest Exchange of Volatile Organic Acids

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Abstract We report bidirectional exchange of volatile acids, including isocyanic and alkanoic acids, over a pine forest across multiple seasons. The exchange velocity of these acids is well correlated with dew point depression, suggesting an equilibrium-driven continuum of flux. Wetness on forest surfaces impacts the vertical exchange of gases, and we suggest that water films and droplets drive equilibrium partitioning, with acids being solvated in surface wetness and released through evaporation. Despite their volatility, these acids partition into neutral-to-alkaline aqueous films, consistent with reported dew pH. This relationship between exchange velocity and dew point depression holds for a wetter mixed forest, but not a very dry orchard. Dew point depression is an excellent indicator of acid fluxes so long as the canopy is occasionally wetted.

Plain Language Summary Volatile, water-soluble organic acids are exchanged between ecosystems and the atmosphere, but the processes underlying that exchange are poorly understood. We present evidence that water films and droplets on ecosystem surfaces uptake atmospheric organic acids by an equilibrium solvation process. As solar radiation warms ecosystem surfaces, surface wetness evaporates releasing absorbed acids into the gas phase. Uptake by surface wetness can cause net canopy-scale organic acid deposition. Organic acids released by evaporating surface wetness can cause net canopy-scale emissions.

1. Introduction

The exchange of reactive trace gases between ecosystems and the atmosphere drives the source of much atmospheric organic carbon. However, trace gas fluxes from the biosphere can be bidirectional (Gabriel et al., 1999; Millet et al., 2018; Niinemets et al., 2014; Park et al., 2013), and deposition processes from the atmosphere to ecosystems are important sinks of many air pollutants including ozone (Clifton et al., 2020) and oxidized organic precursors for secondary organic aerosol (Knote et al., 2015). Measurement challenges coupled to the complexity of interpreting flux observations when multiple sources, sinks, and in-canopy chemistry are occurring mean that the processes driving bidirectional organic gas fluxes remain poorly understood. Here we investigate a set of volatile organic acid flux observations and the role of surface wetness in controlling biosphere-atmosphere exchange.

Leaf wetness includes both water films and larger drops of water (i.e., dew) and can either enhance or inhibit plant-atmosphere gas exchange. The diffusion of CO_2 through water is 10^4 times slower than air, and wet leaves damage photosynthesis (Ishibashi & Terashima, 1995). The impact of leaf wetness on photosynthesis depends on plant type and leaf wettability, which depends on the hydrophobicity of leaf surfaces. For example, with increasing water coverage, photosynthesis decreased in wettable bean plants, but increased in non-wettable pea plants (Hanba et al., 2004). However, this observation is not universal: morning dew reduced net ecosystem exchange of CO_2 over a nonwettable ponderosa pine plantation compared with dry mornings (Misson et al., 2005). Surface wetness also controls the cuticular resistance of leaves to NH_3 deposition as a function of layer or droplet thickness and acidity. Generally, wetness increases NH_3 uptake (Massad et al., 2010) although alkaline water films suppress NH_3 deposition (Walker et al., 2013). Leaf wetness can increase, decrease, or make no significant change to ozone deposition measured over a variety of forested
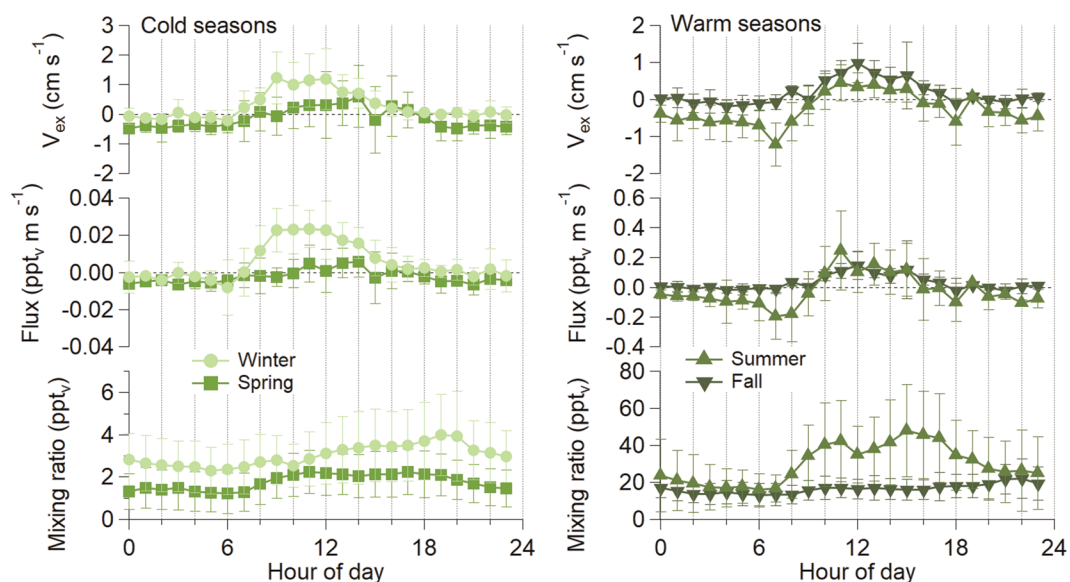
Figure 1. Diel time series of HNCO mixing ratio (ppt_v; lower panels), flux (ppt_v m s^{-1}; middle panels), and exchange velocity (cm s^{-1}; upper panels) for each season. Markers represent hourly averages; whiskers are standard deviations.

and agricultural canopies (Massman, 2004). Overall, the role of surface wetness in controlling trace gas fluxes is inconsistent in the literature and poorly understood.

Due to their water solubility and high volatility, volatile organic acids are well suited to probe the influence of leaf wetness on bidirectional gas exchange. Fluxes of organic acids are poorly understood, with multiple studies observing unexplained upward fluxes of formic acid from forests (Alwe et al., 2019; Fulgham et al., 2019; Nguyen et al., 2015; Schobesberger et al., 2016). We previously reported persistent upward fluxes of formic, butyric, propionic, methacrylic, valeric, and heptanoic acids at Manitou Experimental Forest (Fulgham et al., 2019). Even after considering in-canopy oxidation of monoterpenes, these data suggested a missing source—or overestimated sink—of formic acid.

Here we use observations from multiple field sites to explore leaf wetness and bidirectional fluxes of HNCO and other volatile acids.

2. Materials and Methods

2.1. Primary Site Description

Manitou Experimental Forest Observatory (MEFO) is a semiarid coniferous forest in Colorado. The ~16 m tall canopy is sparse and almost exclusively ponderosa pine (*Pinus ponderosa*). Most annual precipitation is snowfall during winter and spring, although transient afternoon summer rainstorms occur. The site is well characterized (Fulgham et al., 2019; Karl et al., 2014; Kaser et al., 2013; Ortega et al., 2014; Pryor et al., 2013; Rhew et al., 2017). Our work was part of the Seasonal Particles in Forests Flux studY (SPiFFY), which spanned four seasonally representative campaigns in 2016: winter (1 February to 1 March), spring (15 April to 15 May), summer (15 July to 15 August), and fall (1 October to 1 November).

2.2. MEFO Flux Measurements

We quantify volatile organic acids, including formic (HCOOH), propionic ($C_3H_6O_2$), methacrylic ($C_4H_6O_2$), butyric ($C_4H_8O_2$), valeric ($C_5H_{10}O_2$), heptanoic ($C_7H_{14}O_2$), and isocyanic (HNCO) acids, with a Time-of-Flight Chemical Ionization Mass Spectrometer (CIMS; Tofwerk AG and Aerodyne Research, Inc.) using acetate reagent ions. Fulgham et al. (2019) details the instrument operation and online calibrations. As the CIMS was calibrated online for HCOOH, we used previous measurements of the relative sensitivity of HCOOH to HNCO taken on the same instrument to quantify HNCO (Link et al., 2016; Mattila et al., 2018). Supporting information Table S1 summarizes calibration sensitivities.
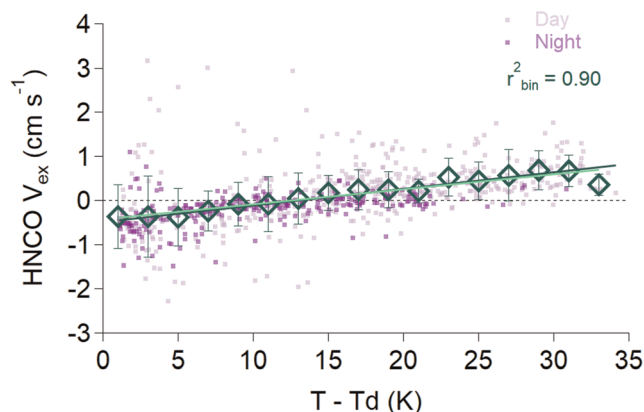
Figure 2. The exchange velocity (V_{ex}) of HNCO increases linearly with dew point depression (T-T_d). All data from MEFO that met eddy covariance filtering criteria are in dots; dark green, open diamonds show averages of 20 evenly spaced T-T_d bins with corresponding standard deviation. Dots are colored according to incident solar radiation (dark dots <10 nmol photons $m^{-2} s^{-1}$; light dots ≥10 nmol photons $m^{-2} s^{-1}$). Least squares linear regression fits the data $\left[V_{ex}^{bin} = (-0.42 \pm 0.06) + (0.034 \pm 0.003) \times T - T_d \right]$. The r^2 is 0.25 for all data and 0.90 for the binned data.

We measured the vertical exchange of acids from the 30 m MEFO tower using the eddy covariance technique (Fulgham et al., 2019) (section S1).

3. HNCO

Atmospherically relevant HNCO concentrations (≥1 ppb_v) are likely toxic to human health (Roberts et al., 2011). Combustion is a primary source (Jathar et al., 2017; Link et al., 2016; Roberts et al., 2014), while oxidation of amides is a secondary source of HNCO (Barnes et al., 2010). Due to the low reactivity of HNCO with atmospheric oxidants, wet and dry deposition are thought to be key removal processes. Dry deposition is expected to occur at a similar rate to formic acid and formaldehyde, resulting in lifetimes of weeks over land (Young et al., 2012). HNCO at MEFO ranges from 1–50 ppt_v, comparable to summertime background concentrations elsewhere (Leslie et al., 2019). Diel trends (Figure 1) are consistent with organic acids at the site (Fulgham et al., 2019), suggesting photochemical sources.

Surprisingly, HNCO fluxes suggest persistent upward midday exchange during all seasons. Net deposition occurs at night during spring and summer (Figure 1). Bidirectional HNCO exchange is unexpected—there are no combustion sources within the flux footprint at MEFO. We filtered data for spikes in carbon monoxide concentration to exclude periods influenced by local biomass burning. Unlike the other acids, plants are not sources of HNCO, and HNCO emissions were not observed during summer 2016 branch enclosure studies at MEFO.

Although photochemistry is an important source of the other acids, secondary production from in-canopy amide oxidation sufficient to produce the observed upward daytime exchange would have to produce a concentration gradient with higher HNCO levels in the canopy than above the sensor height. Amines are precursors for amides and thus HNCO, but amine levels at clean continental sites are typically low, on the order of <1–100 ppt (Ge et al., 2011; Sipilä et al., 2015; VandenBoer et al., 2011). There is no evidence for an adequately strong emission source of amines or amides within the flux footprint. Amine levels are significantly lower than ammonia; Hrdina et al. (2019) reported in-canopy ammonia <1.5 ppb_v at Manitou. For these low levels of amides to produce enough HNCO to account for the observed upward flux, in-canopy oxidation would have to occur rapidly (residence time for air in forest canopies is typically <10 min; lifetime for oxidation of formamide is ~2 days given 1.5×10^6 molecules OH cm^{-3}) and to a greater extent than secondary production above the canopy. Amines require multiple oxidation steps to form HNCO and are unlikely to produce the observed exchange. Thus, we find no plausible explanation in the literature for the observed upward HNCO flux.

Here we hypothesize that water films and droplets on ecosystem surfaces can mediate equilibrium partitioning of volatile acids. Under wet conditions, these acids tend to partition to wet ecosystem surfaces inducing a downward flux, while under dry conditions, water films or droplets dry out and release acids to the atmosphere, thereby causing an upward flux. While simple solubility suggests that these volatile acids would dominantly remain in the gas phase, dew is often more alkaline than natural water, or water equilibrated with ambient CO_2 (dew pH > pKa for these acids) (Lekouch et al., 2010; Muselli et al., 2002; Takeuchi et al., 2002; Xu et al., 2015). The subsequent acid-base equilibria will enhance partitioning from the atmosphere to the aqueous phase, as will additional hydrolysis chemistry or reactions.

4. Evidence for Partitioning to Surface Wetness

4.1. V_{ex} Depends Linearly on Dew Point Depression

Dew point depression (T-T_d) is the difference between the air temperature and dew point temperature at a given height and describes the amount of water vapor in the air relative to saturation. Large T-T_d values
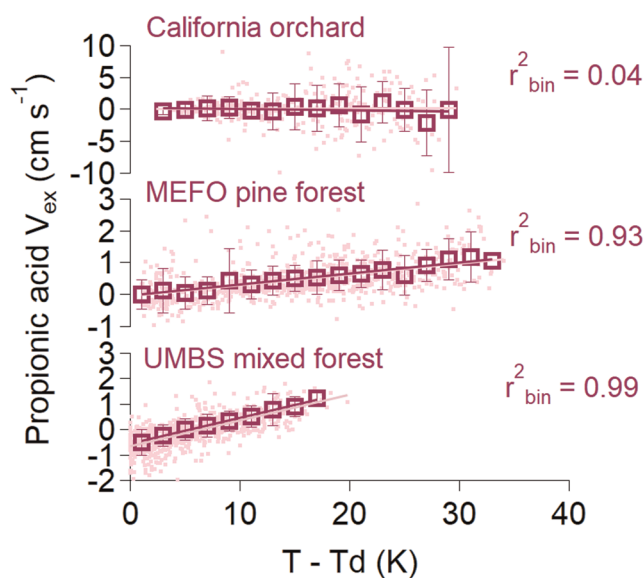
Figure 3. Propionic acid exchange velocity (V_{ex}) linearly correlates with dew point depression ($T-T_d$) at the MEFO pine forest and UMBS mixed forest, but not the very dry California orchard. V_{ex} are averaged into 2°C bins for all sites. Fit equations are in Table S2. The r^2 (all-data/binned) are 0.00/0.04 for the California orchard, 0.18/0.93 for the MEFO pine forest, and 0.47/0.99 for the UMBS mixed forest.

indicate drier air, and air parcels with small $T-T_d$ values are closer to saturated. For example, at dew point (i.e., $T-T_d = 0$ K) an air parcel is saturated with water vapor (relative humidity (RH) = 100%), whereas a $T-T_d$ of 30 K indicates that the air would have to be cooled by 30 K for water to condense.

The V_{ex} of HNCO linearly increases as a function of dew point depression with a strong correlation ($r^2 = 0.90$ for binned data; Figure 2). This tight correlation is consistent with a dependence on surface wetness. Condensation of water vapor onto cool canopy surfaces and interception of rainfall both cause surface wetness (Monteith, 1957). Ecosystem surface temperatures are generally close to air temperature at night, but slightly cooler due to radiative release of energy, and higher than air temperature when surfaces receive direct sunlight. Since $T-T_d$ follows a diel trend with low nighttime values and high daytime values (Figure 2), dew point depression calculated with air temperature captures the dependence of acid exchange on $T-T_d$. High relative humidity causes water to adsorb onto canopy surfaces and form water films and droplets. Even at low RH (<20%), water can adsorb to a variety of surfaces (e.g., mica, metals, metallic oxides, and carbonates) to form submonolayer-to-multilayer films (Ewing, 2006; Freund et al., 1999; Verdaguer et al., 2006). At lower RH, isolated water clusters on surfaces are highly ordered, but films of water molecules cluster more like bulk liquid water at higher RH (Rubasinghege & Grassian, 2013). Thus, we expect water to condense on canopy surfaces when environmental conditions are near dew point (i.e., low $T-T_d$)—and that these conditions cause net HNCO uptake and negative V_{ex}. During the afternoon, environmental conditions move away from the dew point (i.e., $T-T_d$ increases) and aqueous HNCO then partitions out of evaporating wetness, causing HNCO emission and positive V_{ex}. Intriguingly, Figure 2 shows an x axis crossover at high $T-T_d$ suggesting that even once surface wetness evaporates there may be an emission flux. We hypothesize that surface wetness facilitates organic acid uptake into the leaf/soil matrix, a process that provides a reservoir that enables continued emissions even after surface wetness has fully evaporated, at least for a short period of time (hours to days). For example, studies have observed that solutes diffuse into epistomatal spaces from surface wetness adjacent to leaf stomata (Burkhardt et al., 2012; Burkhardt & Hunsche, 2013; Eichert et al., 2008; Fernández & Eichert, 2009). If organic acids similarly diffuse from surface wetness into leaf water, we expect leaf water to continue to release organic acids from stomatal pores as part of transpiration flux even after surface wetness evaporates.

Using established metrics for ecosystem surface wetness (Altimir et al., 2006), we find seasonal variation in wetness. Spring is the wettest season, followed by summer. Despite the lack of precipitation during fall, high RH enabled some wet periods in the fall. In contrast, winter was completely dry. Figure S1 shows that correlations between HNCO V_{ex} and dew point depression are strongest in spring ($r^2 = 0.87$) and summer ($r^2 = 0.94$) but disappear completely during winter ($r^2 = 0.01$), consistent with negligible surface wetness as predicted from precipitation data and ambient RH.

To investigate the ubiquity of this surface phenomenon, we compare volatile organic acid fluxes from the dry pine forest of MEFO to a humid continental, mixed canopy forest in Michigan (UMBS) (Alwe et al., 2019) and a Mediterranean-to-semiarid California orange orchard (Fares et al., 2012; Park et al., 2013). The same linear relationship between exchange velocity and dew point depression for volatile organic acids occurs at the MEFO pine forest and the UMBS mixed forest, but not the California orange orchard (Figures S2–S4). Figure 3 shows propionic acid as an example of the general trends. Like the MEFO seasonal data, these observations are consistent with observed dew point depression ranges (Figure S5) and predicted ecosystem surface wetness (Altimir et al., 2006). The California site was consistently dry with no wet periods based on precipitation and RH criteria versus MEFO (31% wet periods) and the UMBS forest (81% wet periods). In situ leaf wetness sensors measured no surface wetness during summer 2010 at the California orchard.
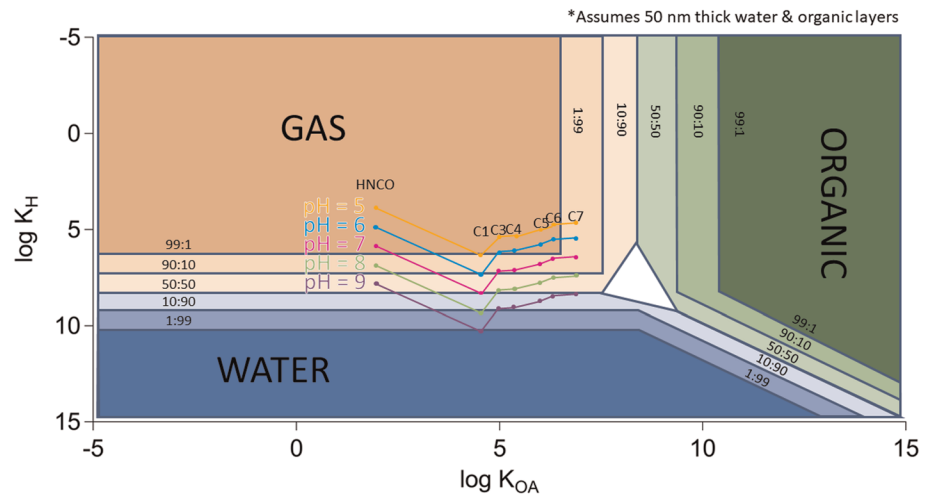
Figure 4. Partitioning plots estimate the volatile organic acid phase distribution at MEFO. HNCO and six short-chain alkanoic acids (C1 formic acid, C3 propionic acid, etc.) are highlighted by text markers and predicted to be primarily in the gas phase given the corresponding Henry's law constants (K_H). Accounting for weak-acid equilibria increased partitioning to the aqueous phase with higher pH. pH isopleths are connected to guide the eye. Equilibria are calculated at standard temperature and pressure.

The T-T_d dependence for other acids are consistent with formic acid at the wet sites. The slopes for formic acid exchange velocity versus dew point depression agree for MEFO (0.14 ± 0.01 cm s^{-1} K^{-1}) and UMBS (0.15 ± 0.01 cm s^{-1} K^{-1}) (Table S2, Figures S2–S4). The intercepts do not: -0.37 ± 0.2 cm s^{-1} (MEFO) versus -0.83 ± 0.1 cm s^{-1} (UMBS).

4.2. Organic Acids in Aqueous Phase

Partitioning space plots act as phase maps in which water-air equilibrium constants (K_{wa}; Henry's law) are logarithmically plotted against octanol-air equilibrium constants (K_{oa}). Partitioning space plots have been used to predict phase partitioning for surface films, particles, and clouds (Lei & Wania, 2004; Wang et al., 2015, 2020; Wania et al., 2015), and we employ them here to investigate the potential for organic acid uptake and loss from surface wetness. Figure 4 assumes three phases are in equilibrium: gas, aqueous film, and water-insoluble organic matter film. The fraction in each phase is

$$Frac_{gas} = \left(1 + K_{oa} \times \frac{V_{org}}{V_{gas}} + K_{wa} \times \frac{V_w}{V_{gas}}\right)^{-1}, \tag{1}$$

$$Frac_{water} = \left(1 + \frac{1}{K_{wa} \times \frac{V_w}{V_{gas}}} + \frac{K_{oa}}{K_{wa}} \times \frac{V_{org}}{V_w}\right)^{-1}, \tag{2}$$

$$Frac_{organic} = \left(1 + \frac{1}{K_{oa} \times \frac{V_{org}}{V_{gas}}} + \frac{K_w}{K_{oa}} \times \frac{V_w}{V_{org}}\right)^{-1}. \tag{3}$$

V represents the volume occupied by the gas phase (V_{gas}), water film (V_w), and organic film (V_{org}). To estimate volumetric phase ratios, we assume films are evenly distributed, and that V_{gas} is much larger than the other phases. We estimate film thicknesses of 50 nm (X_w and X_{org}) and a surface area to volume ratio of 0.0713 m^{-1}, or the sum of the average fetch area and leaf area divided by the product of the fetch area and measurement height (section S2).

Intrinsic Henry's law constants imply that organic acids are predominantly in the gas phase. However, weak acids additionally partitioning to the aqueous phase as described by effective Henry's law constants (K_{eff}):

$$K_{eff} = K_{wa} \times \left(1 + 10^{pH - pKa}\right). \tag{4}$$

The pH of dew in forests ranges between 3.2 and 8.2 (Okochi et al., 1996; Polkowska et al., 2008; Richards, 2004; Wentworth et al., 2016). At pH 8.2, ≥20% of the alkanoic acids reside in the aqueous phase, suggesting a mechanism to enhance organic acid deposition to ecosystem wetness. Additional aqueous chemistry or biology could further enhance the K_{eff} and partitioning; for example, microbes digest organic acids in precipitation over the course of months (Keene & Galloway, 1984).

Aqueous partitioning depends on film thickness, with more acid uptake occurring over thicker water films. This simple analysis assumes uniform water films, but ecosystem wetness is likely inhomogeneous. Microscopic water films over ecosystem surfaces are typically <1 μm with macroscopic droplets <100 μm (Burkhardt & Hunsche, 2013), but droplets of 1 mm have been observed (Hughes & Brimblecombe, 1994). For example, given a 1 μm water film at pH 7, over 90% of formic acid is in the aqueous phase at equilibrium. This dependence of partitioning on film thickness provides a mechanism for the continuum of exchange velocity dependence on dew point depression in Figures 2 and 3. If surface wetness and the effective ecosystem water film thickness depends linearly on dew point depression ($T-T_d$), then we would predict the observed linear shift from uptake and negative V_{ex} to emission and positive V_{ex}—as long as aqueous reactions are reversible. One open question is how long an ecosystem must dry out before this relationship breaks down (i.e., how many days without surface wetness are needed for MEFO and UMBS to resemble the California orchard?). Mineral dust may also become an important sink in absence of precipitation.

This hypothesis of fluxes driven by equilibrium-driven partitioning to the aqueous phase suggests that the slopes (or intercepts) of Figure 2 should trend with solubility. However, we find no clear relationships between the observed slopes and solubility or related parameters, reflecting the complexity of additional aqueous reactions and salt formation in ambient water films. Figure 3 shows that slope and intercept differences can also manifest for the same compound between sites, potentially due to differences in water film pH or structure (and thickness) of surface wetness on different leaf types.

In contrast to the alkanoic acids, simple weak acid equilibria suggest that HNCO will remain dominantly in the gas phase. However, HNCO hydrolyzes through multiple pathways including reaction with aqueous ammonia (Borduas et al., 2016; Leslie et al., 2019; Roberts & Liu, 2019) that are not considered by Equation 4—thus, leading to an overestimate of the gas phase fraction. However, some of these reactions are permanent sinks for HNCO and could not lead to equilibrium partitioning back out of surface wetness.

Temperature influences gas-water partitioning. The K_{wa} of HNCO is particularly temperature sensitive (Roberts & Liu, 2019). For example, a temperature range of −10–30°C implies a range of 21–3.0% for the aqueous HNCO fraction (pH 8). Figure S6 shows this effect of temperature on HNCO aqueous solubility. While dew point depression does not linearly depend on temperature, there is evidence for a role of temperature in influencing observed concentration and fluxes of organic acids (Fulgham et al., 2019).

4.3. Solvation: Wet Versus Dry

Observed gas-phase concentrations of all the volatile acids described herein increased exponentially with temperature at MEFO (Figure S7). Calculating observed enthalpies of solvation (ΔH_{obs}) and comparing them with literature values ($\Delta H_{solvation}$) (Figure S9) provides further evidence for the role of gas-water partitioning in controlling biosphere-atmosphere exchange. The van't Hoff equation describes solvation equilibria:

$$\ln(r_g) = \frac{\Delta H_{obs}}{RT} + \left\{ \ln(r_{aq}) - \frac{\Delta S}{R} \right\}, \tag{5}$$

where r_g is volumetric mixing ratio of the acid in the gas phase, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the air temperature (K), r_{aq} is the volumetric mixing ratio of the acid in the aqueous phase, and ΔS is the solvation entropy (J/K). Figure S8 plots the natural logarithm of gas phase HNCO mixing ratio against inverse temperature, with the slope providing ΔH_{obs} in kJ mol^{-1}. Wet and dry periods at MEFO yield distinct enthalpies, which we plot against literature values for $\Delta H_{solvation}$ (Roberts & Liu, 2019; Sander, 2015) in Figure S9. Observed enthalpies agree with literature values during dry periods but become more enthalpically favorable during wet periods. This observation is consistent

with the hypothesis that under wet conditions, volatile acids may be taken up in the forest by alkaline solutions and/or undergo additional reactions that enhance the solubility of the acid, such as hydrolysis. Under dry conditions, little acid uptake will occur, and instead shrinking water films would force reversible partitioning to the gas phase. Conversely, a modified van't Hoff plot for isoprene, which exhibits temperature and light dependent emissions but is insoluble in water, shows no significant difference between the dry/wet regressions (Figure S10)—further supporting our hypothesized role for air-water partitioning in the case of organic acids.

5. Conclusions

Phase partitioning between surface wetness and the atmosphere may drive the bidirectional flux of acids between forests and the atmosphere. Water films or droplets can take up molecules, driving downward deposition fluxes, while drying out and shrinking of water films will cause emission of acids. Additional aqueous reactions or changes in pH with wetness may enhance or suppress this partitioning. We hypothesize that dew point depression is a proxy for surface wetness, but that different plant morphologies and leaf chemistry may influence differences in the slope and intercept at different sites.

HNCO fluxes show strong and significant diel trends, but once averaged over the entire annual data set, cumulative HNCO fluxes fall within the measurement uncertainty (cumulative flux of $+6.6$ ppq$_v$ m s^{-1}, average uncertainty for all SPiFFY measurements is ± 15 ppq$_v$ m s^{-1} following Finkelstein & Sims, 2001). The five alkanoic acids exhibit net annual emission at MEFO, implying a net ecosystem source—either directly to the aqueous phase from plant exudates, or through alternative processes in the gas or aerosol phases that preserve the observed continuum between exchange velocity and dew point depression.

The dependence of exchange velocity on dew point depression appears consistent across sites, so long as adequate leaf wetness is available. We investigated the potential applicability of the relationship in Figure 3 to describe organic acid fluxes and found that previously described observations of upward formic acid fluxes at Hyytiälä follow the UMBS relationship, which explains 56% of the variance for diel averages in formic acid flux.

Field and laboratory studies to investigate links between ecosystem wetness, dew point depression, and gas exchange over wet leaves are essential to understanding atmospheric lifetime not just for weak acids, but also for weak bases and other water-soluble pollutants such as inorganic mercury. Reversible and/or irreversible equilibrium partitioning to surface wetness are known to impact NH_3 and O_3 biosphere-atmosphere exchange (Massad et al., 2010; Massman, 2004; Walker et al., 2013). Here we suggest that surface wetness also impacts organic acid exchange. These observations suggest that "dry deposition" is not a simple process driven merely by ecosystem surface area. The pH of ecosystem wetness remains unclear but likely influences the exchange of weak acids and bases. Despite being weak acids, organic acids contribute an increasing fraction of precipitation acidity as atmospheric SO_2 and NO_x concentrations decrease (Vet et al., 2014). Our work suggests an additional mechanism that mediates atmospheric acid uptake to ecosystem surfaces.

Data Availability Statement

MEFO data are available at http://manitou.acom.ucar.edu and otherwise from authors upon request.

Conflict of Interest

The authors report no conflicts of interest.

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