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Emission of formic and acetic acids from two Colorado soils

Anne Mielnik, Michael Link, James Mattila, S. Ryan Fulgham and Delphine K. Farmer *

A 'missing source' of atmospheric formic acid is consistently observed during model-measurement comparisons, and evidence from multiple environments suggests a near-surface source. Soil emissions are considered to be a small formic acid source, but estimates are based on a single study from a tropical site. Here, we investigate soil emissions of organic acids from two soils – a ponderosa pine forest (Manitou Experimental Forest Observatory), and a managed lawn (Colorado State University) using a laboratory chamber. Both soils are a source of formic and acetic acids. Under ambient conditions, formic acid emissions are 0.11 (pine forest) and 0.15 (lawn) nmol m^{-2} s^{-1}, and acetic acid emissions are 0.05 (pine forest) and 0.71 (lawn) nmol m^{-2} s^{-1}. Only acetic acid emissions from the forest site correlate with CO_2 fluxes, but all formic and acetic acid emissions increase exponentially with temperature. Increasing soil moisture only enhances acetic acid emissions from the forest. Considering this temperature and moisture dependence, we hypothesize that while equilibrium partitioning may contribute to the forest emissions, organic acid emissions from the lawn are likely driven by microbial activity. Lactic acid was emitted from both soils, but not quantified. The observed formic acid emissions are higher than previous measurements, but still low enough that soils are unlikely the 'missing source' of atmospheric organic acids, although the variability in the soil source is substantial. We contrast observations to previous parameterizations used in models, and present recommendations for modified parameterizations for formic and acetic acid emission.

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Environmental significance

Organic acids are ubiquitous in the atmosphere, and impact ozone formation, ecosystem acidification and the atmospheric organic carbon budget. However, models typically underestimate even the simplest organic acid–formic acid. Direct emission of organic acids from soils are a possible atmospheric source, but are poorly constrained by a single study. Here, we investigate soil emissions of formic and acetic acid from soils, and find that emissions increase with temperature. Precipitation effects are more complex. Overall, we find that soils remain a small source of formic acid to the global atmosphere.

1. Introduction

Organic acids are molecules with a carboxylic acid group (RC(O)OH), and are substantial components of the non-methane hydrocarbon (NMHC) budget in the atmosphere. Organic acids are estimated to account for ~25% of the NMHC molecules[1] and thus contribute to tropospheric ozone production,[2] while less volatile organic acids are estimated to account for 10–50% (average of 28%) of molecules in Northern Hemisphere secondary organic aerosol,[3] thereby impacting aqueous-phase chemistry and cloud albedo effects.[4,5] Organic acids have also been measured in precipitation, accounting for up to 60% of rain acidity in remote areas and 30% in industrial regions.[6–8] However, the sources and sinks of organic acids to the atmosphere remain poorly understood. Organic acids have direct sources, including fossil fuel and biofuel combustion,[9] biomass burning,[10] formicine ants,[11] and plants,[12] but are predominantly produced in the atmosphere *via* secondary chemistry, mostly from NMHC precursors.[13] Oxidation of biogenic volatile organic compound precursors are substantial sources of atmospheric organic acids, including formic and acetic acid.[4,14–16]

Formic and acetic acids are the most abundant atmospheric organic acids, and provide interesting case studies for investigating atmospheric organic acid sources and sinks.[1] For example, boundary layer mixing ratios of formic acid are consistently two to three times greater than what can be accounted for by known production and loss pathways, indicating missing sources or overestimated sinks in atmospheric chemistry models.[13,15,16] Tropospheric oxidation of NMHCs and near-surface sources of formic acid from ecosystem emissions

Department of Chemistry, Colorado State University, Fort Collins, CO 80523, USA. E-mail: delphine.farmer@colostate.edu

and/or their subsequent chemistry have been raised as possible sources.[13,15–17] In a recent study over a boreal pine forest, Schobesberger *et al.* invoke a near-surface source of formic acid with similar light and temperature dependences to other biogenic NMHCs to explain the observed upward formic acid fluxes.[17] However, the exact source of these emissions (plants *versus* soils *versus* in-canopy chemistry) remains unknown.

Detailed studies of direct ecosystem emissions of organic acids are limited. Ground-level vegetation and soils can be significant sources (and sinks) of NMHCs,[17–20] although only one published study has directly measured soil emissions of organic acids.[21] In that work, Sanhueza and Andreae found that soils from a scrub-grass savanna emit formic and acetic acid in a diurnal cycle, with average daily emissions of 0.14 nmol m^{-2} s^{-1} and 0.07 nmol m^{-2} s^{-1}, respectively.[21] The authors also observed increased formic and acetic acid emissions after a simulated rainfall event, suggesting that microorganisms in the soil produce the organic acids. Inclusion of these soil emissions consistently fails to account for the 'missing source' of formic acid.[13,16] However, soil chemistry and microbial activity varies widely by soil type and ecotype, and the lack of additional measurements has limited generalizations about the role of soils in atmospheric organic acid budgets. Further, Sanhueza and Andreae noted that their measurements were taken after an extended dry period, with the savanna soils at 1% soil moisture.

Soil sources of atmospheric organic acids likely include root exudates, microbial activity and the biotic and abiotic degradation of organic material, such as leaf litter.[16,19,22] In the rhizosphere, bacteria have been isolated that produce lactic acid, along with CO_2 and acetate, *via* fermentation processes[23,24] or biodegradation.[25,26] In aerobic conditions, some bacteria produce organic acids by oxidation processes; specifically, formic acid from methane[27] or acetic acid from sugars and alcohols.[28] In addition, lactic and acetic acids are products of glucose catabolism.[23] Larger, lower volatility organic acids such as pyruvic acid are also products of cellular respiration, yet may be released from soils less frequently than formic and acetic acid due to differing vapor pressures and octanol–air partitioning coefficients.[29] Organic acids with low octanol–air partitioning coefficients, such as formic and acetic acid, are more likely to partition from soils into the atmosphere.

Here, we use laboratory studies to examine emissions of formic acid and acetic acids from two Colorado soils: a ponderosa pine forest and a managed urban lawn. We investigate the dependence of organic acid emissions on temperature and soil moisture, and compare the results to previous findings.

2. Field sites & soil properties

We investigate soil emissions from two sites: the Manitou Experimental Forest Observatory (MEFO) (39.1006° N, 105.0942° W; elevation 2347 m) near Woodland Park, CO and the Colorado State University (CSU) campus in Fort Collins, CO (40.5734° N, 105.0865° W; elevation 1525 m).

MEFO is a 6760 hectare ponderosa pine plantation southwest of Denver in the Colorado Front Range and is described in detail elsewhere.[30] MEFO includes ponderosa pine, Douglas fir, and mixed conifer trees. The median tree age at the time of sampling in 2018 was ~59 years.[30] The climate at MEFO is representative of the arid West, maintaining average daily temperatures of −2 °C in January and 19 °C in July with light precipitation. The mean annual rainfall at MEFO is 432 mm, with 50% occurring during summer thunderstorms. Soils at this site are typically slightly alkaline (pH = 7.4) and maintain a sandy clay loam texture.

The CSU sampling site is a lawn adjacent to the chemistry building. The CSU campus grounds include over 4500 trees and 80 flower beds, containing annuals, perennials, shrubs, or a combination of three. The lawn is Kentucky bluegrass, which is watered most days, either manually or by natural precipitation. The managed soils at CSU are high in phosphorous and potassium as the grounds are fertilized with urea formaldehyde every fall.

The Colorado State University Water, Soil, and Plant Testing Lab measured soil pH (deionized water paste) and soil texture (hydrometer method with a sodium hexametaphosphate dispersing solution) for all samples, along with total nitrogen and total carbon using a carbon–nitrogen furnace (TruSpec CN, Leco) (Table 1). Total organic carbon (TOC) is the difference between total carbon and carbonate carbon (as measured following sulfuric acid reaction with the soil). We also measured soil moisture content gravimetrically by heating soil subsamples in an oven at 105 °C for 24 hours and attributing the mass loss to water. Both CSU and MEFO soils are sandy clay loams (CSU: 63% sand, 16% silt, and 21% clay; MEFO: 50% sand, 19% silt, and 31% clay) with total N content <0.3%. TOC of CSU soils is twice as high as MEFO soils. The soil chemistry at MEFO is less acidic and lower in TOC than a previous study, likely due to a different sampling time and location within the MEFO site.[31] The gravimetric moisture content of CSU samples is consistent across sample collections (16.2%) and usually higher than the collected MEFO soil samples, which range from 3.7% to 16.3%, although a majority of samples fall below 5%.

3. Methods

We analyze soil emissions in the laboratory on samples collected in May and June 2018 from the upper 5 cm of soil, beneath the litter layer. Soils were transported to the laboratory in 500 mL high-density polyethylene containers on ice and stored in the refrigerator prior to analysis, typically within 14 days of collection.

To measure soil emissions, we place ~10 g of soil in a temperature-controlled small glass chamber under constant flow into the headspace (*i.e.* dynamic chamber) and measure trace gases from the headspace flow out of the chamber (Fig. 1). This sampler is similar in setup to previous laboratory studies of soil and leaf litter emissions of reactive trace gases.[32,33] The sample chamber is a 210 mL glass pressure tube (Model 8648-33, AceGlass) sealed with a polytetrafluoroethylene NPT fitting equipped with inlet and outlet ports (1/8″ i.d., Swagelok). A mass flow controller (MFC) (Model #: M100B01858CR1BV, MKS) ensures a constant flow of ultrahigh purity zero air (UZA, Airgas)

Table 1 Physio-chemical properties of CSU and MEFO soils. Moisture content values are displayed as mean (range), as determined periodically with unperturbed samples

Sample site	Moisture content (%)	pH	TOC(%)	Total N(%)	Soil texture
CSU	16.2 (14.9 to 18.5)	5.2	1.68	0.11	Sandy clay loam
MEFO	8.3 (3.7 to 16.3)	7.4	3.38	0.26	Sandy clay loam

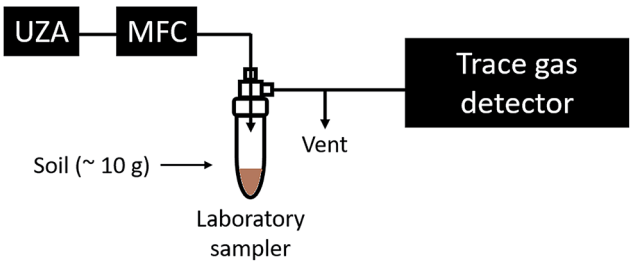

Fig. 1 Diagram of the dynamic laboratory soil chamber setup. A constant flow of zero air (UZA, flow of 2.0 LPM) enters the temperature-controlled laboratory sampler and is subsequently analyzed by trace gas detectors, either a CO_2 analyzer (flow of 1.0 LPM) or organic acid detector (flow of 1.9 LPM) with overflow air released into the room *via* a vent (0.1–1.0 LPM).

in the sample chamber, typically 2.0 liters per minute (LPM). The outflow air is sub-sampled continuously for trace gas concentrations (total flow of 1.0–1.9 LPM), with overflow air released into the room. In this study, we measure CO_2 with an infrared gas analyzer (LICOR LI-840A CO_2/H_2O gas analyzer; flow rate of 1.0 LPM) and organic acids with an Aerodyne high-resolution time-of-flight chemical ionization mass spectrometer (HR-ToF-CIMS; flow rate of 1.9 LPM, described below). Prior to each experiment, we send UZA through the empty chamber setup (*i.e.* no soil) for at least one hour to measure the system background. Inflow UZA contains near-zero levels of organic acids, with measured background mixing ratios of 0.02 ppb_v and 0.08 ppb_v for formic and acetic acid, respectively. Once soil is added, we wait 30 minutes before applying perturbations to the system to ensure that the system has stabilized and the air is flushed through the sample lines. This time ensures that the tubing and reactor have reached gas–surface equilibrium.[34] Previous studies in our laboratory have demonstrated that losses of formic and acetic acid to the walls of this system are negligible. However, we acknowledge that losses of less volatile species on the walls of the tubing and chamber can be substantial.

3.1 Trace gas measurements

We detect gas-phase organic acids using HR-ToF-CIMS (Tofwerk AG and Aerodyne Research, Inc.) coupled to iodide reagent ions. Iodide ions form clusters with water ($I\cdot H_2O^-$), which subsequently participate in ligand-exchange reactions to form adducts with the analyte ($I\cdot M^-$).[35,36] We generate the iodide reagent ions by passing ultrahigh purity N_2 over a methyl iodide permeation device and through a Polonium-210 ionizer (NRD). These ions enter the ion-molecule reaction chamber and interact with sampled headspace air, thus ionizing organic acids, which are then transferred through a series of ion optics to the TOF mass analyzer (Tofwerk AG; $m/\Delta m \sim 4000$). The system is sensitive to a broad array of organic and inorganic acids, although we only report quantified emissions from formic and acetic acids as other acids were not observed above background – with the exception of lactic acid, for which the long surface-air equilibration time and low volatility prevented quantitative flux measurements. Instrument sensitivity to formic acid (CH(O)OH) during experiments ranges from (5.1–26) $\times$ 10^2 normalized counts per second per parts per billion by volume (ncps ppb_v^{-1}), as determined by multi-point calibrations with a CH(O)OH permeation device (Dynacal) over a range of 0 to 9 ppb_v. We use a cross-calibration method[37] to quantify acetic acid ($C_2H_3(O)OH$), assuming the ratio of formic to acetic acid sensitivity remained constant throughout experiments, given that mass spectrometer voltage settings were unchanged. For example, instrument sensitivity was 5.50 $\times$ 10^2 ncps ppb_v for acetic acid and 22 $\times$ 10^2 ncps ppb_v for formic acid. The detection limits for acetic and formic acid were 0.091 and 0.023 ppb_v, respectively.

Organic acid mixing ratios are converted to soil organic acid fluxes following Gray *et al.*[18] (eqn (1)):

$$F = \frac{C \times Q \times P}{R \times A \times T} \quad (1)$$

where F is the flux rate in nmol m^{-2} s^{-1}, C is the measured organic acid mixing-ratio in nmol mol^{-1} (1 nmol mol^{-1} = 1 ppb_v), Q is the flow rate through the chamber in L s^{-1}, P is atmospheric pressure in bar, R is the gas constant (0.083145 L bar K^{-1} mol^{-1}), A is the cross-sectional area of the laboratory sampler in m2, and T is soil temperature in K. Background mixing ratios are subtracted from measured organic acid signals to quantify soil emissions. Positive fluxes indicate emission from the soil to the atmosphere, while negative fluxes would indicate deposition from the atmosphere to the soil.

In addition to organic acids, we measure CO_2 emissions from the outflow of the laboratory chamber using the LI840-A infrared gas analyzer, which we calibrate by two-span calibrations using UZA (Airgas) and compressed CO_2 (CP Grade 99.5%, Matheson Co.), ranging from 0 to 48 ppm_v. Observed CO_2 mixing ratios are converted to fluxes in μmol C m^{-2} s^{-1} using eqn (1) (note: 1 ppm_v = 1 μmol mol^{-1}).[18]

3.2 Laboratory perturbation experiments

We conduct two sets of perturbation experiments to investigate trace gas emissions from soil, varying soil temperature and

moisture content. Temperature experiments involve varying temperature on soil samples with constant, ambient soil moisture content (Manitou: 4.00%, CSU: 16.2%). Each sample experiences variable temperatures (0°, 21°, and 35 °C) in a single experiment. Initially, soils are held at laboratory room temperature (21 °C) for 30 minutes without perturbation. The soil chamber is then thermally perturbed in a continuous, non-specific order. For example, we attain a temperature of 0 °C by submerging the laboratory sampler in an ice-water bath for 30 minutes. To reach 35 °C, the soil chamber is wrapped in silicone rubber heating tape (Omega Engineering, Inc.) coupled to a PID temperature controller (CN76000, Omega Engineering, Inc.) and set at 35 °C for 30 minutes. Soil temperatures measured ±1 °C of 21 °C during laboratory room temperature experiments and within ±4 °C of the 35° and 0 °C set points during perturbations.

To examine the effects of soil moisture content on trace gas emissions, we simulate a precipitation event by applying 1.00 mL of distilled water using a micropipette to 10 g of an unperturbed sample. This provides soil moisture contents of 12% and 23% for MEFO and CSU samples, respectively. Soil samples typically dry out in the chamber and back to ambient levels within 2 hours of simulated precipitation events. At this point, we add an additional 3.00 mL of distilled water to the laboratory sampler. With this, soil samples reached 25% and 34% moisture contents for respective samples. We sample the headspace for CO_2 and organic acids separately throughout perturbation experiments.

4. Results and discussion

4.1 CO_2 emissions

While the focus of this work is on organic acid emissions, we also measured soil CO_2 emissions, which provide a useful benchmark regarding the health and behavior of the soils during the laboratory perturbation studies. Overall, soil CO_2 emissions were consistent with expected behavior. Soils are known sources of CO_2 from soil respiration, *i.e.* the production of CO_2 by biotic processes involving root exudates or soil microorganisms, and less commonly, the abiotic oxidation of organic compounds in soil.[38,39] CO_2 emissions from forest floors are expected to increase with temperature and soil moisture content, with reduced emissions at the highest and lowest water-holding capacities (~100% and 20%, respectively).[40] Previous studies indicate that up to 84% of the spatial variation in such emissions are explained by biotic factors, including: fine root biomass, microbial biomass, and nutrient availability (*e.g.* total N, TOC, and magnesium).[39] However, temporal variation of soil CO_2 effluxes is best explained by physical factors (*e.g.* soil temperature and moisture content), most significantly in soils with moisture contents exceeding 19%.[39,41] In fact, soil temperature is the single best predictor of soil respiration rates, though precipitation also plays an important role.[41] However, soil CO_2 emissions also display high spatial and temporal variability due to microbial composition, land management, and climate conditions, and can vary by soil type and region.[39]

In unperturbed conditions (*i.e.* under constant temperature of 21 °C and ambient soil moisture conditions), the average CO_2 flux is 0.04 ± 0.34 μmol C m^{-2} s^{-1} from MEFO soils and 2.89 ± 0.08 μmol C m^{-2} s^{-1} from CSU soils (Table 2). In general, CO_2 fluxes from CSU soils are 7× greater than from MEFO (p = 0.031), consistent with the acidic soil pH and higher TOC at CSU. CO_2 emissions determined from our chamber measurements are similar, but slightly lower than previous studies of soil CO_2 emissions in similar regions. For example, summertime soil CO_2 effluxes from a ponderosa pine forest in Oregon, USA (mean annual soil moisture of 14–15%) ranged from 1.0 to 6.5 μmol C m^{-2} s^{-1}, with 70% of measurements falling between 2.0 and 3.0 μmol C m^{-2} s^{-1}.[42] In a ponderosa pine forest in northern California, USA, soil CO_2 effluxes of 4.43 and 3.12 μmol C m^{-2} s^{-1} have been reported during the growing and non-growing seasons, with mean gravimetric moisture contents of 19.57% and 10.21%, respectively.[39] In a Jack pine forest in eastern Ontario, soil CO_2 fluxes display a seasonal variation, increasing with temperature, and range from 0.385 to 0.481 μmol C m^{-2} s^{-1}.[43] Here, Weber observed decreased rainfall (433 mm from May to November, with 11 mm of precipitation in July, which falls 65 mm short of the 30 year average), which may have contributed to low CO_2 effluxes. We hypothesize that the slightly lower CO_2 effluxes measured from MEFO soils are due to the extraordinarily low rainfall during the study period, resulting in low soil moisture content and thus slower soil respiration.

Previous studies have also found increased CO_2 effluxes from managed soils compared to natural ecosystems. In northern Colorado, urban soil emissions range from <6.9 to 11.6 μmol C m^{-2} s^{-1}. These emissions increase with temperature, with no effect from precipitation events.[44] Soil CO_2 effluxes in Phoenix, AZ range from 0.471 to 13.6 μmol C m^{-2} s^{-1}, with the lowest emissions from unmanaged desert soils that lack C sequestration (TOC 0.2–0.5%). In the same region, managed lawns (*e.g.* golf courses and agricultural areas) displayed the highest CO_2 effluxes, likely due to increased TOC (up to 2%) and increased moisture content from watering events.[45] While the soil CO_2 efflux measurements from the CSU lawns taken in this study are lower than these previous studies of managed Colorado sites, the values are consistent with the soil moisture and TOC. The temperature dependence of CO_2 fluxes is consistent with previous studies, providing validation of the experimental setup. Emissions of CO_2 from soil typically follow an exponential relationship (eqn (2)),[38,42]

$$E_s = Ae^{(BT_s)} \quad (2)$$

where E_s is the soil CO_2 efflux in μmol C m^{-2} s^{-1}, T_s is soil temperature in °C and A (μmol C m^{-2} s^{-1}) and B are fit parameters. A previous study at a Ponderosa pine forest found fit parameters of A = 1.216 μmol C m^{-2} s^{-1} and B = 0.059,[42] which are consistent with the CSU data (r^2 = 0.83 for CSU data *versus* the literature fit) and provide some confidence in our perturbation approach. The CSU soils showed a greater sensitivity in CO_2 emission to temperature than the MEFO soils, consistent with their higher soil moisture content. Xu and Qi

Table 2 Trace gases emissions from MEFO and CSU soils. Soil effluxes are reported as means ± standard error determined from 3 replicate experiments for each perturbation. Positive numbers indicate emission from the soil. Italicized lines indicate unperturbed conditions. * denotes experiments in which measurements were not obtained

Soil temperature (°C)	Moisture content (%)	CO_2 (μmol C m^{-2} s^{-1})	Formic acid (nmol m^{-2} s^{-1})	Acetic acid (nmol m^{-2} s^{-1})
Ponderosa pine forest (MEFO)				
0	4.0	*	0.01 ± 0.04	0.05 ± 0.01
21	*4.0*	*0.04 ± 0.34*	*0.11 ± 0.02*	*0.05 ± 0.01*
	12.1	0.40 ± 0.94	0.07 ± 0.04	0.17 ± 0.04
	24.7	0.4 ± 1.0	0.12 ± 0.04	0.33 ± 0.05
35	4.0	0.2 ± 1.9	0.13 ± 0.06	*
Managed lawn (CSU)				
0	16.2	1.3 ± 0.7	0.06 ± 0.05	0.54 ± 0.04
21	*16.2*	*2.83 ± 0.07*	*0.15 ± 0.03*	*0.71 ± 0.04*
	22.7	1.9 ± 0.2	0.17 ± 0.05	0.82 ± 0.06
	34.1	0.73 ± 0.49	0.15 ± 0.05	1.1 ± 0.1
35	16.2	3.9 ± 0.3	0.16 ± 0.05	1.2 ± 0.1

also observed that soil respiration rates are less sensitive to temperature changes in moisture contents below 14%. Further, increasing moisture content suppressed soil CO_2 effluxes from CSU, but had no significant effect on MEFO soils. Previous studies have found that while CO_2 emissions increase after simulated precipitation events, gravimetric moisture content is a poor predictor of soil CO_2 effluxes.[39] Overall, our laboratory flux measurements provide CO_2 emission fluxes that are consistent with previous field measurements.

4.2 Organic acid emissions

Soils can be a source of both formic and acetic acid. In unperturbed conditions, soil formic acid effluxes are 0.11 ± 0.02 and 0.15 ± 0.03 nmol m^{-2} s^{-1} from MEFO and CSU, respectively, while soil acetic acid effluxes are 0.05 ± 0.01 (MEFO) and 0.71 ± 0.04 nmol m^{-2} s^{-1} (CSU).

There are few measurements to which we can compare these observations, but daily average emissions from an Amazon savanna under dry conditions (soil moisture < 1%), are 0.14 nmol m^{-2} s^{-1} for formic acid and 0.07 nmol m^{-2} s^{-1} acetic acid.[21] We hypothesize that the substantially lower organic acid emissions from the dry savanna site are due to the low soil moisture – the soil pH of this site was 4.6, TOC was 2.1%, total N was 0.075–0.13%, and the soil was a sandy clay loam. In other words, while more acidic, the site was not dissimilar from MEFO. However, the authors themselves suggested soil moisture played a role in organic acid emission, with enhanced fluxes after wetting the soils. These comparisons suggest that recent papers that have used the Amazonian measurements to estimate the contribution of soils to global or local formic acid budgets are reasonable, but that soil as a source of acetic acid may be underestimated.

The higher organic acid fluxes from CSU could be due to chemical (*e.g.* lower soil pH) or microbial factors (*e.g.* more productive population or more rapid activity). The temperature-dependence of organic acid fluxes is consistent with either a chemical source driven by soil-air partitioning, or a microbial source. However, increases in soil moisture are well known to increase soil microbial activity.[20]

First, we consider soil-air partitioning as the cause of observed organic acid emissions. CSU soils are more acidic than MEFO soils, and may be more likely to emit organic acids to the atmosphere than the MEFO soils. If the pKa of an organic acid is greater than the pH of an aqueous medium, then much of the organic acid exists in the neutral protonated form (HA), and would be more likely to partition to the gas phase. The pKa of formic acid is 3.75 and acetic acid is 4.75, suggesting that the acids are dominantly deprotonated and dominantly exist in an aqueous equilibrium – although soils are notoriously heterogeneous, and the bulk soil pH may not represent complex conditions within the soil structure. To further quantify the role, we follow the approach laid out by Mungall *et al.* and consider that the gas-phase partial pressure (C_g) can be derived from the effective Henry's Law constant (K^*_H), hydrogen ion concentration, aqueous-phase equilibrium coefficient (K_A), and concentration of conjugate base in soil aqueous media (C_s):[46]

$$K^*_H = K_H\left(1 + \frac{K_A}{[H^+]}\right) \quad (3)$$

$$K^*_H = \frac{C_s}{C_g} \quad (4)$$

$$C_g = \frac{C_s}{K^*_H} \quad (5)$$

Given that the Henry's law constants of formic and acetic acids are 88 and 40 mol m^{-3} Pa^{-1} at room temperature,[47] suggesting increased formic acid in the aqueous phase, and that formate in North American forest soils can be on the order of 4–10 μmol L^{-1} (and 4–50 μmol L^{-1} for acetate),[48] we calculate room-temperature gas-phase mixing ratios for formic acid of 0.1–0.3 ppt_v for MEFO soils (20–50 for ppt_v for CSU) (ppt_v; parts per trillion by volume). We note that these concentrations are substantially lower than reported summer concentrations in the

region (2–3 ppb_v for the front range;[49] 1.5 ppb_v in Manitou). This is a similar observation as Mungall *et al.*'s work in the high Arctic, where large and highly variable atmospheric mixing ratios of formic and acetic acids were observed despite conditions in which physical equilibrium disfavors the re-volatilization of organic acids.[46] Thus, soil-partitioning-driven emissions are not the dominant source of atmospheric formic acid concentrations in the region. We calculate the predicted temperature dependence from aqueous-gas partitioning, and find that gas-phase formic acid should increase by 11× between 273 and 308 K (975% for MEFO) while acetic acid should increase by 14×. These predicted increases are consistent with the MEFO formic acid data (increase of 13×, or 1200% from 273 to 308 K), but are not similar to the observed CSU data, nor the MEFO acetic acid data (Fig. 2, Table 2). Thus, while we cannot rule out partitioning between the aqueous soil and the atmosphere as the sole source of formic acid at MEFO, the temperature-dependence of the acetic acid emissions from both MEFO and CSU and formic acid emissions from CSU are not consistent with partitioning-only processes, even considering the large uncertainties in soil formate and acetate concentrations. Microbial sources are thus more likely culprits of acetic acid emission, and the CSU soil system.

In ambient conditions at Manitou, we observe greater emissions of formic acid than acetic acid, but note that at higher soil moisture or temperature, acetic acid dominates. Acetic acid emissions are consistently larger than formic acid under all conditions at CSU. Interestingly, formic acid is far less sensitive to soil moisture than acetic acid, again suggesting that the mechanisms for emission are different between the two organic acids, and are not driven solely by a chemical equilibrium between the soil and air.

Previous studies have found increased near-surface VOC emissions following precipitation events,[19,20,46] and we expected increased organic acid emissions following addition of water. However, while increasing soil moisture in the precipitation experiments has no or negative effects on CO_2 fluxes, it enhances acetic acid emissions from both sites and formic acid emissions from the Manitou samples – but has no effect on the formic acid emissions from CSU (Fig. 3). In an Amazon forest, soil acetic acid emissions increased by 3 to 4× after a simulated precipitation event, while formic acid emissions were suppressed or within the uncertainty of the measurement.[21] However, the authors also observed increased formic acid emissions two hours after the simulated precipitation event, which was not observed during these experiments, even after many hours. The difference in soil moisture effects between soils (and across organic acids) highlights the challenge in extrapolating emissions from one soil type to others – the underlying sources and controls on organic acid emissions clearly vary.

However, emissions of formic, acetic, and lactic acids consistently increase with temperature. The one previous study of soil organic acid fluxes explained diurnal variation in formic and acetic acids with an exponential relationship, modified slightly from eqn (1):

$$E_s = A e^{((B \times T_s)^{-1})} \quad (6)$$

where E_s is soil formic acid emission in nmol m^{-2} s^{-1}, T_s is soil temperature in °C, and A and B are constants. Paulot *et al.* fit the Sanhueza and Andreae data to find an A of 1.7×10^{-3} nmol m^{-2} s^{-1} for formic acid and 2.5×10^{-3} nmol m^{-2} s^{-1} for acetic acid, and a B of 0.119 (formic acid) and 0.091 (acetic acid).[16] This fit would underestimate the observed fluxes for ambient soil moisture conditions at MEFO and CSU by 10–20× for formic acid and up to 120× for acetic acid fluxes. For example, using this fit (coupled to a more advanced algorithm accounting for pulsing effects following rainfall), Paulot *et al.* suggest that un-

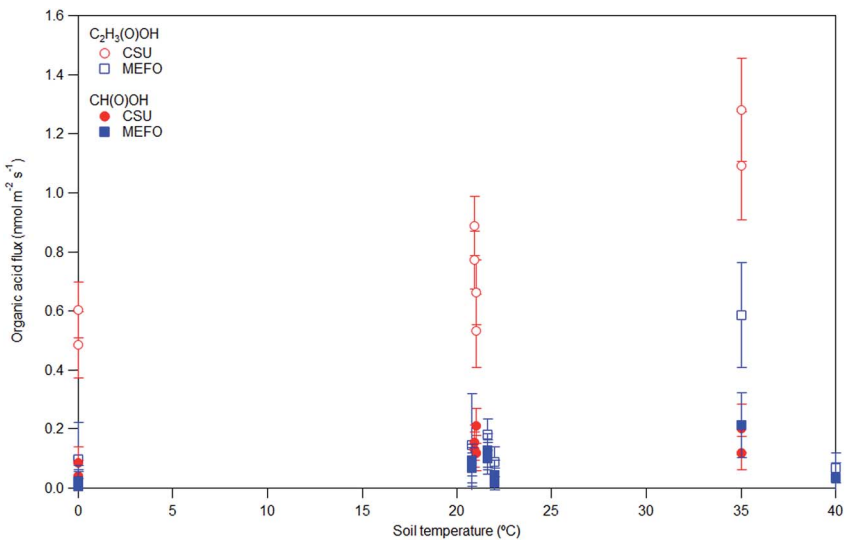

Fig. 2 Organic acid fluxes of formic (closed) and acetic (open) acids from soils collected at Manitou Experiment Forest (blue; squares) and CSU (red; circles). All temperature perturbations experiments were conducted at ambient moisture. Each marker represents a single experiment, while error bars represent the standard error for each experiment.

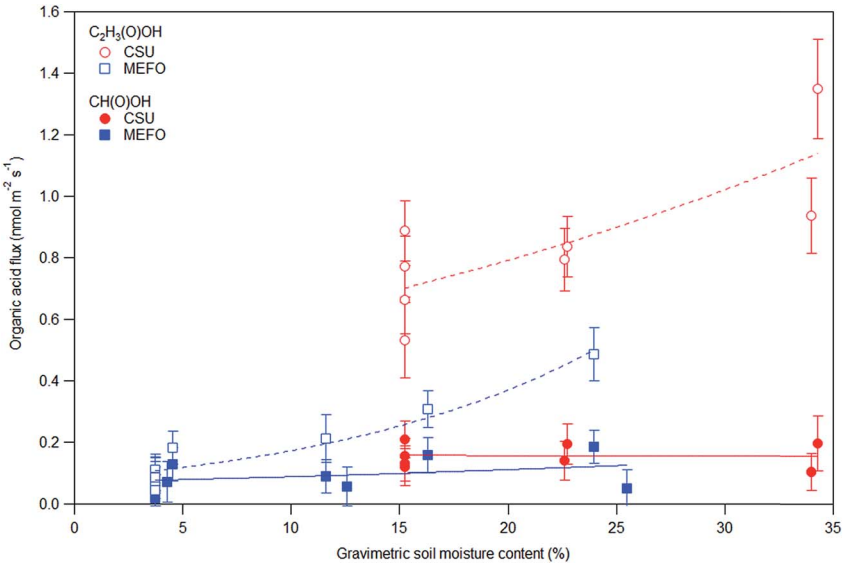

Fig. 3 Organic acid fluxes of formic (closed) and acetic (open) acids from soils collected at Manitou Experiment Forest (blue; squares) and CSU (red; circles) as a function of gravimetric soil moisture at 21 °C. Each marker represents a single experiment, while error bars represent the standard error for each experiment.

wetted coniferous forests emit 0.005 nmol formic acid m^{-2} s^{-1} and 0.003 nmol acetic acid m^{-2} s^{-1}, which are potentially underestimates by over an order of magnitude when compared to data in Table 2.[16] Fitting our data independently, we find an A of 0.11 ± 0.08 (MEFO) and 0.24 ± 0.07 (CSU) nmol m^{-2} s^{-1} and a B of 0.028 ± 0.023 (MEFO) and 0.020 ± 0.011 (CSU) for formic acid. In contrast, for acetic acid we find an A of 0.15 ± 0.16 (MEFO) and 1.2 ± 0.2 (CSU) nmol m^{-2} s^{-1} and a B of 0.04 ± 0.03 (MEFO) and 0.026 ± 0.007 (CSU). We can consider the A factor to represent a basal emission rate for the soils and B to represent the temperature sensitivity, making it clear that emissions from Manitou are more temperature sensitive than emissions from CSU, possibly due to different microbial populations that respond to environmental perturbations in different ways – or to the greater importance of chemical equilibria relative to microbial processes.

Based on the strong dependence of formic acid on temperature, and the lack of conclusive evidence on soil moisture effects on formic acid emission, we recommend parameterization of formic acid according to eqn (6), with the appropriate A and B for temperate forest or managed lawn ecosystems. We note that the nutrient dynamics and microbiology of Ponderosa pine and managed lawn soils are very different, and provide one indication of the dynamic range in organic acid fluxes that are likely found in terrestrial ecosystems. However, acetic acid is more complicated with its dual moisture and temperature dependence. Compiling the average data from Table 2, we determine the best fit for the combined MEFO and CSU data according to eqn (7):

$$E_{AA} = A e^{((B\times T_s)^{-1})} e^{((C\times\theta)^{-1})} \quad (7)$$

where A is a compiled basal emission rate of 0.4 (±0.4) nmol m^{-2} s^{-1}, B is a temperature sensitivity of 0.065 (±0.026) $°C^{-1}$ and C is the soil moisture sensitivity of 4.8 (±2.2). θ is the soil moisture on a scale of 0–1 (*i.e.* 16% is 0.16). This fit captures 55% of the variance in the MEFO and CSU acetic acid flux data, and is clearly limited by the variability across sites, which is not considered in eqn (7). Additional measurements are required to more rigorously understand how the acetic acid flux varies across soil and types, and if wetting events cause 'pulsing' of organic acid emissions in the same way as for NO_x.[50] While the Sanhueza and Andreae data suggest pulsing may occur, those soils were very dry (1% soil moisture), and our experiments did not provide strong evidence for such behavior.

We observe little correlation between CO_2 and formic acid fluxes ($r^2 < 0.2$). The only observed correlation with CO_2 and acetic acid was found in the MEFO samples ($r^2 = 0.58$). This is interesting as CO_2, lactic and acetic acid are products of the same microbial processes (*e.g.* glucose catabolism and the pentose phosphate pathway).[23] Thus, while all observed organic acid and CO_2 emissions from soil increased exponentially with temperature, the rate of increase was very different across molecules, consistent with different controlling processes behind the emission of each molecule.

The measurements described herein were conducted using air with very low atmospheric organic acid concentrations, and thus ignore the potential of soil microbes to consume organic acids. While Ramirez *et al.* suggest that soil microbes catabolize VOCs from leaf litter and the surrounding canopy in an enzymatically-driven reaction that increases with ambient levels of VOCs,[51] our analysis suggests little contribution of equilibrium-driven soil-air partitioning and changing atmospheric organic acid concentrations is not likely to have a substantial effect. Compensation points have been observed at atmospherically relevant concentrations for some species (*e.g.* CO, NO_x under specific circumstances), but not for others

(*e.g.* CH_4).[52] Considering this limitation in experimental design, the soil formic and acetic acid fluxes presented herein represent an upper bound for soil emissions, consistent with the conclusion that soils are not substantial sources of organic acids to the atmosphere.

4.3 Lactic acid

At ambient temperature and above, both soils are sources of not only formic and acetic acids, but also lactic acid. Due to the challenge in calibrating for sticky organic acids and substantial wall losses and time required to reach equilibrium between tubing and chamber surfaces with air, we are unable to quantify lactic acid effluxes, but instead qualitatively note a soil source of this compound that increases with temperature (Fig. 4). This is perhaps unsurprising as lactic acid is a known bacterial emission, produced as an end product of glucose catabolism and fermentation[23] or, less commonly, the biodegradation of polyacetic acid.[25,26] In addition, organic acids, including citric, malic, and oxalic acids, are released from the rhizosphere into soils under nutrient and oxygen stress, mobilizing minerals, such as iron and phosphorous, to reduce phytotoxicity and promote plant growth.[22] However, emissions of these organic acids were not observed here, possibly due to low oxygen availability or inadequate soil pH – or to wall losses in the chamber setup. In addition, the Henry's law constants of these acids are much higher than those of detected organic acids (citric $= 3.0 \times 10^{16}$, oxalic $= 6.1 \times 10^{6}$, and malic $= 2.7 \times 10^{8}$) and thus are less likely to partition to the gas phase.[47] Lactic acid emissions are higher from CSU than from MEFO, likely due to the acidity of these soils and the availability of phosphorus from active management and fertilizer application, as lactic acid bacteria utilize the pentose phosphate pathway to produce lactic acid, CO_2, and acetate.[23]

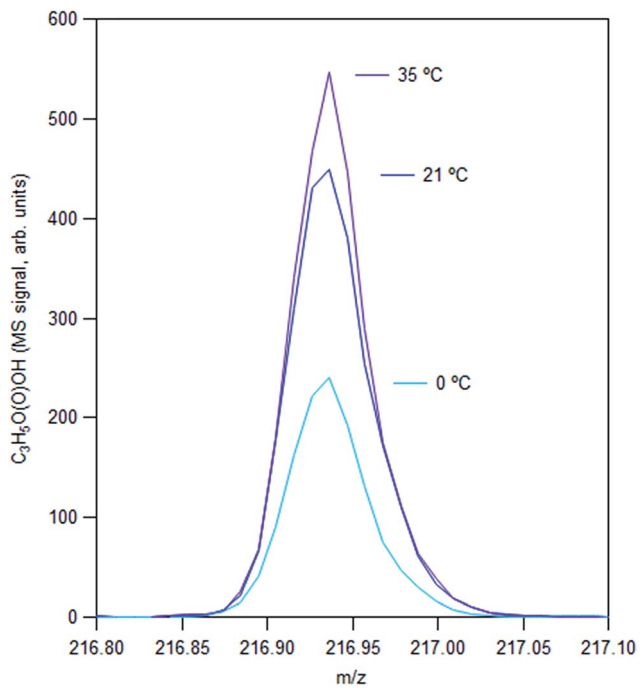

Fig. 4 MS signals for lactic acid from soils collected at CSU at 0 °C (light blue), 21 °C (dark blue), and 35 °C (purple) in a single temperature perturbation experiment. Lactic emissions from both CSU and MEFO increased with soil temperature.

5. Conclusions

Soils are a clear source of organic acids, though the processes and magnitude of these emissions vary by soil location and environmental conditions. Soil organic acid emissions increase exponentially with temperature, with greater temperature sensitivity observed for acetic acid. Some increases in emissions with soil moisture are observed under specific environmental conditions. While the exact microbial and/or chemical controls on these soil emissions remain poorly constrained, coupling these results with the one set of previous soil emissions estimates for formic and acetic acids suggest that ambient soil formic acid emissions do not vary substantially from the previous measurements, and that soils retain their minor role as a global atmospheric formic acid source and are unlikely the 'missing source' needed to rectify widely observed model-measurement discrepancies for atmospheric formic acid. However, extrapolating acetic acid emissions from the single Amazon study to other ecosystems may result in underestimates by a factor of two. Finally, soils are an atmospheric source of lactic acid, although further investigation is required to quantify this source.

Conflicts of interest

There are no conflicts to declare.

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