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Advances in research on the sources, distribution, and isotopic tracing of low molecular weight monocarboxylic acids in the atmosphere

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Low molecular weight (C_1–C_{10}) monocarboxylic acids constitute one of the most abundant classes of atmospheric organic compounds. They occur ubiquitously in the gas, particle, and aqueous phases and exert significant influences on atmospheric acidity, radiative forcing, and the global carbon and water cycles. Stimulated by the severe acid rain crisis in the 1980s, research on the geochemical processes of atmospheric monocarboxylic acids advanced rapidly but declined over the past two decades following the effective control of acid rain. However, in recent years, the global implementation of emission reduction policies has substantially altered aerosol composition and properties, potentially leading to changes in the gas-particle partitioning behaviour and environmental fate of monocarboxylic acids. This paper provides a comprehensive review of the sampling and analytical techniques, sources and sinks, and global distribution patterns of monocarboxylic acids in the atmosphere and precipitation, and further discusses the application prospects of dual-carbon isotope ($\delta^{13}C$–$\Delta^{14}C$) techniques. By integrating these aspects, this study aims to provide a theoretical foundation for revitalizing and deepening research on the geochemical processes of atmospheric monocarboxylic acids.

Environmental significance

Low molecular weight (C_1–C_{10}) monocarboxylic acids are among the most ubiquitous organic compounds in the atmosphere and play a critical role in regulating aerosol acidity, cloud condensation processes, and the atmospheric carbon cycle. Their environmental behaviour is increasingly shaped by contemporary changes in aerosol chemical composition and particle acidity. This review systematically synthesizes recent advances in their sources, distribution, and gas-particle partitioning patterns, and highlights the emerging potential of dual-carbon isotope ($\delta^{13}C$–$\Delta^{14}C$) techniques for tracing their origins and transformation pathways. By integrating chemical and isotopic perspectives, this work provides an updated framework for reassessing the roles of low molecular weight monocarboxylic acids in air quality, atmospheric chemistry, and climate forcing.

1. Introduction

Low molecular weight (C_1–C_{10}) monocarboxylic acids (LMW monoacids) are widely distributed throughout the troposphere, occurring in gaseous, particulate, and aqueous phases (*e.g.*, clouds, fog, and precipitation), with formic acid (C_1) and acetic acid (C_2) being the most abundant species.[1,2] They play significant roles in atmospheric chemical processes, global climate effects, and ecosystem functions (Fig. 1).[3–5] To date, extensive research has been conducted on LMW monoacids across a wide range of environments, including forests,[6–8] marine,[9–11] urban,[12,13] and rural regions.[14–16]

LMW monoacids are major contributors to atmospheric acidity. Due to their widespread sources and relatively low chemical reactivity, they persist in the global atmosphere and readily dissolve in cloud, rain, and fog droplets, where they dissociate to release H^+ ions, thereby directly enhancing aqueous phase acidity.[17] In remote regions, organic acids make a particularly significant contribution to atmospheric acidity because of the low concentrations of anthropogenic strong inorganic acids (*e.g.*, sulfuric and nitric acids) and the limited availability of alkaline neutralizing agents such as ammonia and mineral dust particles. In the West African savanna, formic and acetic acids contribute approximately 56% of the total acidity,[18] whereas in the Amazon rainforest, they account for over 90% of rainwater acidity.[19] In contrast, the contribution of formic and acetic acids to rainwater acidity in urban and peri-urban areas varies considerably, ranging from 3% to 45%.[20–22] Wet deposition studies in Cuba reported that formic and acetic acids accounted for 20–45% of total acidity in rural areas, compared with only 10–20% in urban sites.[23] In coastal cities of

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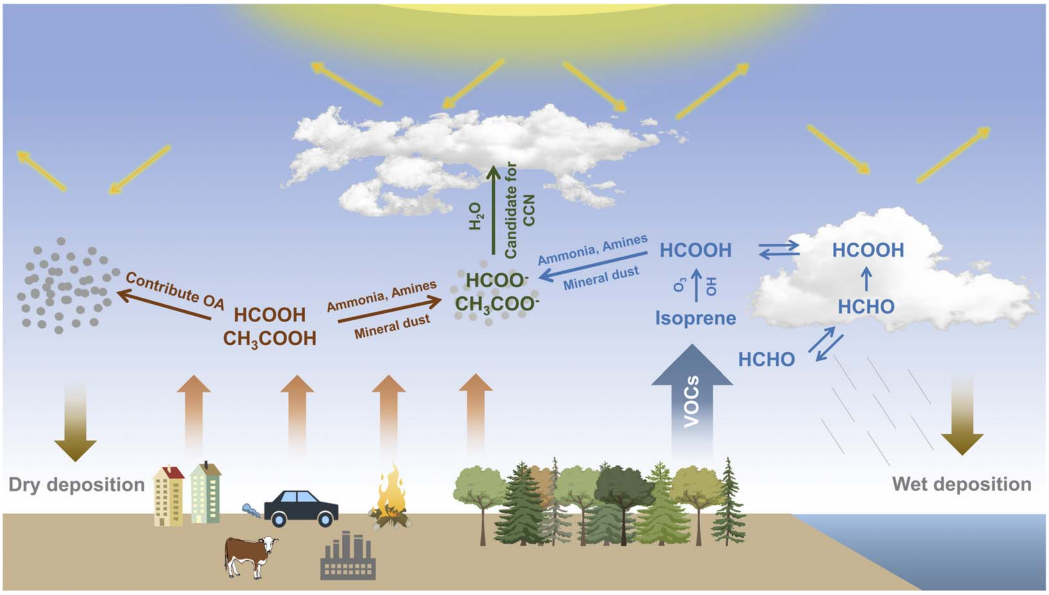

Fig. 1 Schematic illustration of the sources, sinks, and climatic impacts of LMW monoacids. OA, organic aerosol; CCN, cloud condensation nuclei; VOCs, volatile organic compounds.

south-eastern China, such as Xiamen and Shenzhen, organic acids contributed less than 5% to the free acidity of rainwater.[24,25] Most studies on the role of monoacids in atmospheric acidity were conducted in the late twentieth century, when acid rain was a major global concern. As acid rain has been effectively mitigated, research attention has gradually shifted toward the climatic implications of monoacids.

LMW monoacids also play an important role in cloud condensation nuclei (CCN) activity.[4,26] Although their relatively high vapor pressures favour their presence in the gas-phase, these acids can also partition into the particulate phase, especially into submicron particles, through heterogeneous adsorption onto organic aerosol surfaces or neutralization reactions with basic substances such as ammonia, amines, or mineral dust to form stable salts.[21,27] Monoacids and their salts have high water solubility and surface activity. These properties enable them to modify aerosol hygroscopicity and reduce the critical supersaturation, thereby enhancing CCN activation efficiency.[28–30] Several studies have observed a strong positive correlation between water-soluble organic carbon concentration and CCN number concentration, underscoring the important role of monoacids in cloud droplet formation.[31,32] Recent observations during heat waves further highlight the growing importance of organic acids in new particle formation and their potential implications for CCN production.[33] The particle-phase fraction (F_p) of formic and acetic acids has increased significantly in recent years, reaching 30–50%, whereas their F_p values were only about 2% in studies conducted before 2000.[15,16] This increase may further enhance the influence of monoacids on cloud microphysical processes, modify cloud radiative properties, and ultimately affect Earth's energy balance and global climate.

In addition, LMW monoacids are significant components of the global carbon cycle. Paulot *et al.*[34] estimated the global annual emissions of formic and acetic acids to be approximately 1200 and 1400 Gmol per year, respectively, with 74% of formic acid and 67% of acetic acid originating from the atmospheric oxidation of biogenic volatile organic compounds (BVOCs). These organic acids are removed from the atmosphere through dry and wet deposition, serving as important carbon sources for both terrestrial and aquatic ecosystems.[1] Among them, formic and acetic acids exhibit high bioavailability (~90%) and account for 30% of the total bioavailable dissolved organic carbon in rainwater.[35,36] Notably, the atmospheric lifetimes of formic and acetic acids can reach several days,[37] enabling their long-range transport on a global scale and linking the oceanic and terrestrial carbon cycles.

Driven by two key factors, the concentrations and geochemical behaviours of LMW monoacids are undergoing significant transformations. First, BVOC emissions have increased sharply in response to global warming,[38–40] providing abundant precursors for the atmospheric formation of LMW monoacids. The increase in vegetation coverage has further accelerated the nationwide growth of BVOC emissions. It is estimated that between 1981 and 2018, total BVOC emissions in China increased by 58.66%, with an average growth rate of 96.64 Gg per year.[41] Second, the implementation of global air pollution control policies has led to profound changes in the atmospheric chemical composition and aerosol properties. Substantial reductions in SO_2 and NO_x emissions have been observed worldwide.[42–45] In China, SO_2 and NO_x emissions decreased by 70% and 28%, respectively, between 2013 and 2020.[46] Global agriculture NH_3 emissions increased by 78% between 1980 and 2018.[47] These changes have influenced the geochemical behaviours of LMW monoacids. On the one hand, the mass fraction of inorganic aerosols has declined, while organic aerosols have gradually become the dominant component of fine particulate matter, accounting for up to 50%.[48–50] This compositional shift enhances the heterogeneous adsorption of gaseous organic acids onto organic aerosol surfaces, thereby increasing their partitioning into the particle-phase. On the other hand, with the substantial reduction in SO_2 emissions, ammonium nitrate has surpassed ammonium sulfate to become the dominant component of inorganic aerosols in the atmosphere. Nitrate-rich particles exhibit stronger hygroscopicity, leading to increased aerosol liquid water content (ALWC) and, consequently, alterations in aerosol pH.[51,52]

In summary, our understanding of the geochemical processes of LMW monoacids remains shaped by the research focus of the late twentieth century, when acid rain was a major environmental issue. Over the past two decades, substantial changes in aerosol composition and acidity have likely altered the environmental fate and climatic impacts of these compounds. This review synthesizes recent advances in sampling and analytical methods for LMW monoacids, summarizes their sources and sinks, and evaluates the application of dual-carbon isotope techniques. It further highlights key challenges and perspectives for future studies. The purpose of this study is to provide new insights into the environmental behaviours and global significance of LMW monoacids.

2. Sampling methods and analytical techniques for LMW monoacids in the atmosphere and precipitation

2.1 Sampling methods

Various sampling methods have been developed for collecting gaseous LMW organic acids, each designed according to their physicochemical properties such as acidity, water solubility, and polarity. These techniques capture gaseous organic acids through adsorption or chemical reaction. The most widely used approach is the neutralization reaction, in which alkaline filters are prepared by impregnating neutral filters with alkaline solutions to efficiently trap acidic gases.[15,53,54] Common alkaline reagents include KOH and $Ca(OH)_2$. Other studies have used KOH-coated annular denuders or tubes,[55] as well as glass beads coated with $Sr(OH)_2$,[56] for the collection of gaseous organic acids. In the wet adsorption method, ambient air is drawn through a mist chamber or scrubber at a low flow rate (less than 10 L min^{-1}), where water-soluble gases are efficiently absorbed by mist droplets.[57] Andreae *et al.*[7] applied this method to collect gaseous organic acids and investigate formic and acetic acid characteristics in the Amazon Basin during the dry season. Solid sorbent methods use adsorption tubes packed with materials such as silica gel or activated charcoal. For example, Dremetsika *et al.*[58] collected organic acids from display cases and cabinets at the Athens Museum using silica gel tubes for active sampling (50 mL min^{-1} for 3 h) and charcoal passive samplers for 24 h.

Ambient air is passed through a neutral filter to remove particulate matter during the sampling of gaseous organic acids. Fig. 2 illustrates a two-stage filter sampler consisting of two sampling stages, a flowmeter, and a pump. The upper stage holds a neutral filter for collecting particulate organic acids, while the lower stage contains a KOH-impregnated filter for capturing gaseous organic acids.

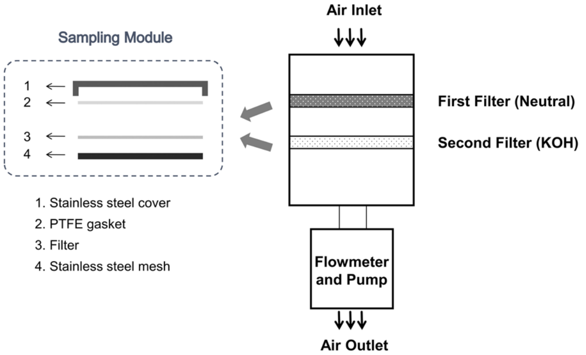

Fig. 2 Schematic diagram of a two-stage sampler for gas- and particle-phase organic acids, designed based on Kawamura.[2,53]

Compared with the various methods used for gaseous organic acids, the sampling of particulate matter and dry or wet deposition is more standardized and well established. Total suspended particles (TSP), $PM_{2.5}$ and PM_{10} are typically collected using medium- or high-volume samplers equipped with different upper size cuts.[59] For dry deposition, automated dry deposition plates are employed to capture dust particles efficiently.[60,61] The sampling period typically ranges from one week to one month. Wet deposition is generally collected using automatic precipitation samplers equipped with sensors that open the lid at the onset of precipitation and close it afterward to avoid contamination by dry deposition. Researchers can select suitable sampling instruments and procedures based on specific study objectives.

2.2 Analytical techniques

Different pretreatment procedures are required for LMW organic acid samples collected by various methods. Filter and dry deposition samples are extracted ultrasonically. The extracts are then passed through PTFE filters to remove particulates. In contrast, wet deposition samples and absorbent solutions from the annular denuders require only a filtration step.

For offline analysis, several techniques can be employed, including ion chromatography (IC), liquid chromatography (LC), and capillary electrophoresis (CE). Among these, IC is the most commonly used.[16,54,62,63] Due to the limited sensitivity of conductivity detectors, IC can accurately quantify formic and acetic acids, which are present at relatively high concentrations. When high-performance ion or ion-exclusion chromatography columns are used, propionic acid (C_3) can also be detected.[64,65] However, IC is unsuitable for determining butyric acid (C_4) or longer-chain monoacids. LC is mainly used for the determination of formic and acetic acids, with dilute phosphoric acid or potassium phosphate solutions as the mobile phase for separating target compounds.[58,66] CE provides high separation efficiency and rapid analysis. It was widely used for environmental analysis in the early 2000s.[67,68] However, it is now more commonly applied in biological and food fields.[69,70] Because of its limited analytical precision, CE is generally used only for the quantification of C_1–C_3.[71]

To improve chromatographic accuracy and analytical sensitivity, derivatization can be performed on the samples. Before derivatization, the samples should be evaporated to dryness, typically using a combination of a rotary evaporator and nitrogen blowdown. The resulting derivatives are then analysed using LC or gas chromatography (GC). Pentafluorobenzyl bromide and α,*p*-dibromoacetophenone are commonly used as derivatization reagents in LC analysis, in which an acetonitrile-water mobile phase is employed.[72–74] Compared with LC, GC provides higher resolution and sensitivity. It enables the determination of a homologous series of C_1–C_{10} monoacids and allows effective separation of their isomers. In 1976, Galloway *et al.* first applied gas chromatography-mass spectrometry (GC-MS) with the benzyl ester derivatization technique to detect volatile organic acids in rainwater collected in New York. The identified LMW monoacids included C_1–C_4 species.[75] In 1984, Kawamura and Kaplan developed the *p*-bromophenacyl ester derivatization technique for the determination of C_1–C_{10} monoacids, which significantly reduced the evaporative loss of small-molecule esters.[76] Since then, this method has been widely applied to various types of samples, including rainwater, air, aerosols, and snow.[8,15,27] Fig. 3 shows representative GC-MS chromatograms of *p*-bromophenacyl ester derivatives of LMW monoacids in a standard solution and a rainwater sample.

3. Sources and sinks of LMW monoacids in the atmosphere

Sources of LMW monoacids include primary anthropogenic emissions, primary biogenic emissions, and secondary formation. Among the primary anthropogenic sources, biomass burning and motor vehicle exhaust are the dominant contributors. Laboratory burning experiments and field observations have shown that direct emissions of LMW monoacids increase substantially during intensive biomass burning periods.[15,62,63,77] LMW monoacid concentrations in vehicle exhaust can be up to 17 times higher than those in ambient air, with acetic acid being the predominant species.[53,77,78] Other primary anthropogenic sources include plastic burning, industrial activities, waste incineration, and animal excreta.[79] Overall, primary anthropogenic emissions are largely confined to urban regions and contribute only a small fraction of the global flux of LMW monoacids. Based on the detailed global budget analysis by Paulot *et al.*, primary anthropogenic emissions, including fossil fuel, biofuel and biomass burning, and cattle, are estimated to contribute 6.7% and 24.4% to the global sources of formic acid and acetic acid, respectively.[80] Primary biogenic emissions arise mainly from vegetation and animals, soil, and microbial metabolism.[37,81–84] Field observations and model simulations consistently indicate that LMW monoacid concentrations in forests show a vertical gradient that decreases from the surface upward. These findings confirm the contribution of vegetation and microbial activity to monoacid emissions.[85–87] Seasonal variations of LMW monoacid concentrations in air and precipitation further emphasize the importance of biogenic emissions, as formic and acetic acid levels increase markedly during the growing season.[20,88,89]

Secondary formation from various organic precursors in the gaseous and aqueous phases is a dominant source of LMW monoacids compared with primary emissions. Estimates based on emission inventories and chemical transport models have indicated that secondary formation accounts for approximately 85% of atmospheric formic acid and 70% of acetic acid globally.[80] The ozonolysis of alkenes is a major gas-phase source. In

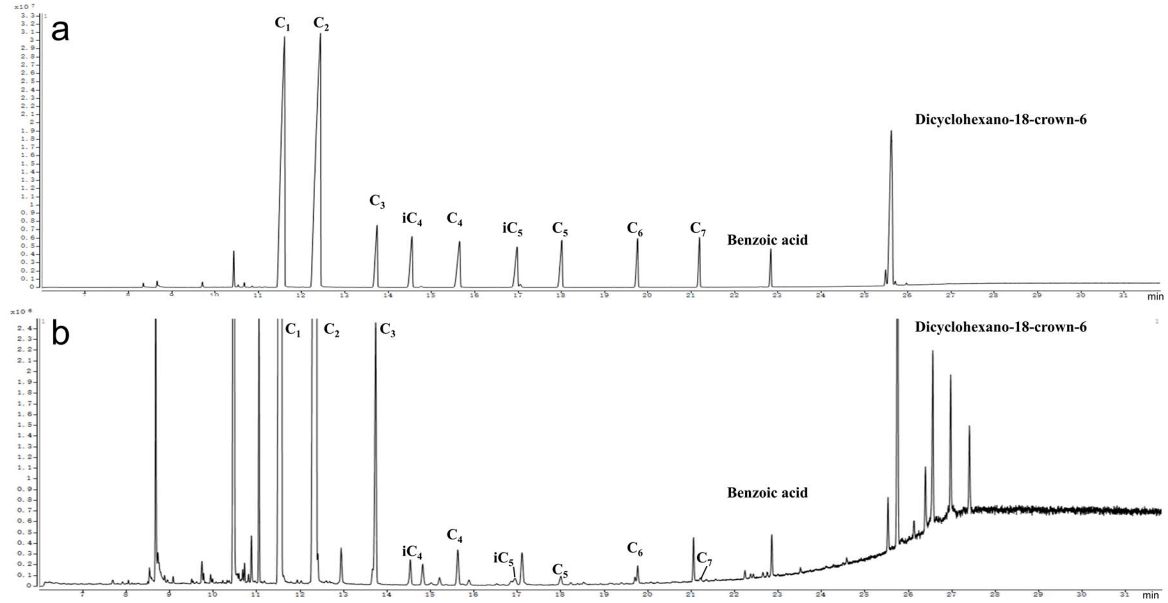

Fig. 3 Chromatograms of (a) a mixture standard and (b) a rainwater sample for LMW monoacids. Monoacids were analysed using an Agilent 7890A GC coupled to an Agilent 5975C MSD and were separated on a DS-5MS fused silica capillary column (30 m × 0.25 mm × 0.25 μm). The GC oven temperature program started at 60 °C, held for 2 min, then increased to 185 °C at 15 °C min^{-1} and held for 6 min, followed by an increased to 290 °C at 10 °C min^{-1}, held for 5 min. The rainwater sample was collected in Guangzhou in November 2024.

this process, electrophilic addition of O_3 to the unsaturated carbon-carbon bond produces Criegee intermediates, which subsequently isomerize to form carboxylic acids.[1,90] Laboratory studies have confirmed that ozonolysis of isoprene, which is predominantly emitted by vegetation, generates C_1–C_5 monoacids, with formic acid as the major product.[2] Reactions of peroxy acyl radicals with HO_2 and other peroxyl radicals also constitute an important pathway, particularly under low-NO_x conditions such as those in forested regions and the marine boundary layer. This pathway plays a key role in acetic acid formation.[91,92] In the aqueous phase, cloud and fog droplets act as reaction media. The oxidation of dissolved formaldehyde by hydroxyl radicals is a major source of formic acid, and the efficiency of this reaction is strongly influenced by pH.[93,94] Under acidic conditions, cloud water acts as a source, allowing formic acid to volatilize back to the gas-phase. Under neutral conditions, however, cloud water behaves as a sink, where formic acid remains as formate and undergoes further oxidation and degradation.

Despite incorporating known emissions and chemical formation pathways, global-scale chemical models still substantially underestimate the ambient levels of formic and acetic acids.[95,96] Model-simulated concentrations reach only about 15% and 65% of measured values, respectively.[97] These discrepancies point to missing or underestimated sources as well as incomplete chemical mechanisms. In recent years, several new formation pathways and sources of LMW monoacids have been proposed.

One emerging pathway involves the aging of aerosols. Jiang *et al.* demonstrated that photochemical ageing of aerosols, driven by heterogeneous reactions involving ozone and nitrate photolysis, contributes significantly to the production of atmospheric formic acid. Incorporating this pathway into models increased the net formic acid production rate by approximately threefold.[98] Biomass burning plumes appear to be particularly important environments for such aerosol aging processes. Chen *et al.* found that formic acid concentrations in the remote atmosphere correlate with black carbon and hydrogen cyanide (a biomass burning tracer), indicating significant missing production pathways within aging fire plumes.[99] Recent mechanistic studies have begun to elucidate the underlying chemistry. Liu *et al.* identified that the reaction of carbonyl peroxy radicals with HO_2 radicals under cool-flame conditions represents a previously missing source of organic acids.[100] Furthermore, Zhang *et al.* showed that multiphase oxidation of levoglucosan by hydroxyl radicals efficiently produces gaseous formic acid with molar yields of 22–66%.[101] Aqueous-phase chemistry has also emerged as a critical pathway. Franco *et al.* proposed a new cloud-mediated mechanism for formic acid production, which increased predicted atmospheric columns by a factor of 2–4 and largely reconciled the long-standing discrepancy between model simulations and satellite observations.[5] Beyond the pathways discussed above, additional sources and reaction pathways are still under active investigation, underscoring the need for further experimental and modelling efforts.[102–105]

Dry and wet deposition are considered the primary sinks of formic and acetic acids.[1,80] Photochemical oxidation, aqueous-phase reactions, in-cloud processes, and biodegradation act as their secondary sinks.[90,106,107] The wet deposition rate of monoacids is strongly influenced by both the amount and frequency of rainfall, leading to pronounced seasonal variations. For example, in Anshun City, Guizhou Province, China, the summer wet deposition fluxes of formic and acetic acids (0.37 and 0.56 mmol m^{-2} day^{-1}, respectively) were substantially higher than the winter fluxes (0.13 and 0.063 mmol m^{-2} day^{-1}).[20] Dry deposition velocities depend on meteorological conditions and surface characteristics, and a value of 1 cm s^{-1} is commonly assumed for both acids in deposition estimates.[1,108,109] The relative importance of dry and wet deposition varies seasonally. In the Venezuelan savanna, removal of formic and acetic acids occurred almost entirely through dry deposition during the dry season, with fluxes of 0.028 and 0.017 mmol m^{-2} day^{-1}, respectively. During the wet season, however, wet deposition becomes the dominant sink, with wet deposition fluxes of formic and acetic acids (0.033 and 0.019 mmol m^{-2} day^{-1}) approximately doubling their corresponding dry deposition fluxes (0.020 and 0.011 mmol m^{-2} day^{-1}).[108]

4. Concentrations and gas-particle partitioning characteristics of LMW monoacids in the atmosphere

The molecular distribution of LMW monoacids is dominated by formic and acetic acids, whereas C_3–C_{10} monoacids typically occur at concentrations one to two orders of magnitude lower. Given their high atmospheric abundance and significant climatic impact, formic and acetic acids have been the primary focus of observational and mechanistic studies. Their concentrations, seasonal and diurnal variability, and responses to episodic events have been extensively documented across diverse environmental settings worldwide. Tables 1 and 2 and Fig. 4 summarize reported atmospheric concentrations of gas- and particle-phase formic and acetic acids over the past 45 years. For consistency, all gas-phase data are converted to mass concentrations (1 ppbv = 1.88 μg m^{-3} for formic acid; 1 ppbv = 2.45 μg m^{-3} for acetic acid, at 25 °C and 1 atm).

4.1 Gaseous phase concentrations

As shown in Table 1, gaseous formic and acetic acid concentrations vary considerably worldwide, ranging from 0.05 to 20 μg m^{-3} and displaying pronounced spatial variability. In contrast, the concentration ratio of formic to acetic acid (C_1/C_2) remains relatively stable, typically within 0.2–2, with no clear spatial pattern. In urban sites, gaseous formic and acetic acids generally occur at concentrations of 1–5 μg m^{-3}. Exceptionally high formic and acetic acid levels of 17.48 μg m^{-3} and 10.15 μg m^{-3} were reported in Uniontown and Boston (USA) during 1990–1991.[55] Comparable high concentrations of formic (14.29 μg m^{-3}) and acetic acid (12.81 μg m^{-3}) were also observed in Baoding, China.[110] In suburban, mountainous, and other remote regions, concentrations are generally below 2 μg m^{-3}.

Table 1 Summary of reported gas-phase formic and acetic acid concentrations ($\mu g\ m^{-3}$)

Location	Type	Date	Formic acid	Acetic acid	C_1/C_2	References
London, UK	Urban	Jan–Feb 2012	2.44	—	—	Bannan *et al.*[113]
		Jul–Aug 2012	1.18			
Los Angeles, USA	Urban	Jul–Sep 1984	0.12–5.56	0.70–9.56	—	Kawamura *et al.*[53]
Uniontown, USA	Urban	Jun–Aug 1990	17.48 ± 15.79	9.31 ± 6.37	1.87	Lawrence *et al.*[55]
Boston, USA	Urban	Jul–Sep 1991	10.15 ± 6.02	5.39 ± 2.70	1.88	
Los Angeles, USA	Urban	May–Jun 2010	3.01	—	—	Liu *et al.*[12]
Atlanta, USA	Urban	Aug–Sep 2010	4.32			Fu *et al.*[118]
Los Angeles, USA	Urban	Sep 1993	—	16.17 ± 0.91	—	Nolte *et al.*[119]
Pasadena, USA	Urban	May–Jun 2010	3.76 ± 1.88	—	—	Bao *et al.*[35]
Uinta Basin, USA	Oil & gas region	Jan–Feb 2013	4.32 ± 2.44			Yuan *et al.*[117]
Shenzhen, China	Urban	Oct 2022–Mar 2023	3.1	—	—	Lu *et al.*[120]
		Apr–Sep 2023	2.5			
Nanjing, China	Urban	Dec 2021	2.68 ± 1.43	5.01 ± 2.29	0.53	Wu *et al.*[121]
		Daytime	3.13 ± 1.55	5.50 ± 2.40	0.57	
		Nighttime	2.20 ± 1.13	4.50 ± 2.10	0.49	
Zhengzhou, China	Urban	Oct–Nov 2019	5.98 ± 2.52	6.18 ± 3.09	0.97	Yang *et al.*[122]
Shenzhen, China	Urban	Aug–Sep 2016	2.27 ± 1.64	4.12 ± 4.09	0.55	Zhu *et al.*[123]
Baoding, China	Urban	Jun–Jul 2014	14.29	12.81	1.12	Han *et al.*[110]
Rome, Italy	Suburban	Jan 1986	0.1–1.8	0.5–5.5	—	Brocco *et al.*[54]
Mt. Tai, China	Mountain	2–5 Jun 2006	1.57	3.96	0.40	Mochizuki *et al.*[15]
		23–25 Jun 2006	0.89	1.27	0.70	
Mt. Tianjing, China	Mountain	Oct–Nov 2020	1.67 ± 1.58	2.32 ± 1.67	0.72	Guo *et al.*[116]
Alert, Canada	Suburban	Jun–Jul 2016	2.31	2.77	0.83	Mungall *et al.*[124]
Mont Blanc, France	Mountain	Sep 2004	0.64	0.83	0.77	Preunkert *et al.*[125]
Melpitz, Germany	Suburban	Oct 2016–Nov 2017	0.13	0.45	0.29	Stieger *et al.*[126]
Hampton, USA	Suburban	Sep 1985, Mar–Sep 1986	3.55 ± 2.32	3.21 ± 2.23	1.11	Talbot *et al.*[77]
Hampton, USA	Suburban	Oct 1985–Feb 1986	1.31 ± 0.76	1.72 ± 0.92	0.76	Andreae *et al.*[7]
The northern Congo	Suburban	Feb 1989	4.03 ± 2.37	3.23 ± 1.72	1.24	Helas *et al.*[65]
Socorro, USA	Suburban	Jun–Aug 1997	1.32 ± 1.69	6.62 ± 9.31	0.20	Villanueva-Fierro *et al.*[127]
Magdalena mountains, USA	Mountain	Jun–Aug 1997	1.13 ± 0.94	4.17 ± 4.9	0.27	
Yorkville, Georgia	Suburban	Sep–Oct 2016	2.15 ± 0.16	1.86 ± 1.34	1.16	Chen *et al.*[128]
Dianshan lake, China	Suburban	Jun–Dec 2017	3.91 ± 3.55	—		Xu *et al.*[129]
		Nov 2020	1.13 ± 0.79	0.81 ± 0.45	1.10	Yao *et al.*[16]
		Nov 2020–Jan 2021	1.30 ± 1.02	0.94 ± 0.74	1.38	
Hokkaido, Japan	Forest	Jun–Jul 2010	0.95	0.53	1.79	Mochizuki *et al.*[8]
Mayombe, Congo	Rainforest	Jun–Sep 1987	0.53	2.43	0.22	Servant *et al.*[82]
Amazon region	Rainforest	Jul–Aug 1985	3.01 ± 1.13	5.39 ± 2.45	0.56	Andreae *et al.*[7]
The northern Congo	Rainforest	Feb 1988	0.46 ± 0.49	0.44 ± 0.69	1.05	Helas *et al.*[65]
Brazil	Rainforest	Sep–Dec 2010	1.50–6.39	3.675–14.7	—	Jardine *et al.*[37]
		Oct 2010–Jan 2011	1.13–2.56	0.245–4.165		
Hong Kong, China	Coastal	Aug–Oct 2021	1.09 ± 1.00	—	—	Jiang *et al.*[98]
Shenzhen, China	Coastal	Jun–Jul 2016	1.26	1.4	0.9	Han *et al.*[110]
Dumont d'Urville, Antarctica	Coastal	Jan 1997–Oct 2002	0.11–0.58	0.12–1.71	—	Legrand *et al.*[114]
South pacific	Marine	Apr–Jul 1988	0.41 ± 0.24	0.69 ± 0.44	0.59	Arlander *et al.*[10]
North indian ocean	Marine	Apr–Jul 1989	1.41 ± 0.45	1.69 ± 0.66	0.83	
South indian ocean	Marine	Apr–Jul 1990	0.36 ± 0.32	0.71 ± 0.39	0.51	
Subarctic north pacific	Marine	30 Jul—9 Aug 2008	0.057 ± 0.075	0.14 ± 0.082	0.41	Miyazaki *et al.*[11]
		9–19 Aug 2008	0.053 ± 0.073	0.10 ± 0.042	0.53	
Atlantic ocean	Marine	Oct–Nov 1996	0.84 ± 0.34	0.71 ± 0.37	1.18	Baboukas *et al.*[130]
Japanese coast	Marine	Jul 1991	1.37 ± 1.03	0.85 ± 0.98	1.61	Morikami *et al.*[112]
East China sea	Marine	Sep 1991	1.30 ± 0.83	1.05 ± 0.78	1.24	
South China sea	Marine	Aug 1991	1.54 ± 0.83	1.00 ± 0.54	1.54	
Arabian sea	Marine	Aug 1991	0.82 ± 0.49	0.64 ± 0.42	1.28	

However, in tropical rainforest regions, concentrations can reach approximately 5 $\mu g\ m^{-3}$ due to strong biogenic emissions. Satellite observations further identify tropical rainforests and boreal forests (*e.g.*, Siberia and North America) as global hotspots of formic acid.[111] Over oceanic and coastal areas, gas-phase concentrations of formic and acetic acid are generally low (0.05–1.5 $\mu g\ m^{-3}$). However, shipborne observations along the transect from Japan to the Persian Gulf have revealed substantially elevated concentrations. Over the South China Sea, formic acid concentrations averaged 3.85 ± 1.62 $\mu g\ m^{-3}$, and even higher levels of 15.26 ± 8.40 $\mu g\ m^{-3}$ were measured over the Strait of Malacca. These enhancements reflect the influence of ship emissions as well as the long-range transport of monoacids and their precursors from Southeast Asia.[112]

Table 2 Summary of reported particle-phase formic and acetic acid concentrations (μg m^{-3})

Location	Type	Date	Size	Formic acid	Acetic acid	C_1/C_2	References
Los Angeles, USA	Urban	May–Jun 2010	$PM_{2.5}$	0.049	—	—	Liu *et al.*[12]
Atlanta, USA	Urban	Aug–Sep 2010	$PM_{2.5}$	0.039	—	—	
Chiang Mai, Thailand	Urban	Feb–Apr 2010 (PM_{10}Event)	PM_{10}	0.12 ± 0.089	0.42 ± 0.33	0.29	Tsai *et al.*[87]
		Feb–Apr 2010	PM_{10}	0.058 ± 0.038	0.34 ± 0.27	0.17	
Chiang Mai, Thailand	Industrial	Feb–Apr 2010 (PM_{10} event)	PM_{10}	0.052 ± 0.025	0.46 ± 0.31	0.11	
		Feb–Apr 2010	PM_{10}	0.052 ± 0.035	0.49 ± 0.39	0.11	
Agra, India	Semi-urban	Apr 2014–Aug 2015	$PM_{2.5}$	0.35 ± 0.19	0.33 ± 0.21	1.06	Verma *et al.*[63]
			PM_{10}	0.34 ± 0.18	0.39 ± 0.22	0.87	
Albany	Urban	2018	$PM_{2.5}$	0.23	0.44	0.52	Tripathy *et al.*[135]
Beijing, China	Urban	2002–2003	$PM_{2.5}$	0.11 ± 0.08	0.08 ± 0.22	1.38	Wang *et al.*[132]
			PM_{10}	0.15 ± 0.10	0.08 ± 0.11	1.88	
Nanjing, China	Urban	Dec 2021	TSP	0.38 ± 0.16	0.37 ± 0.21	1.03	Wu *et al.*[121]
Nanchang, China	Urban	Dec 2018–Aug 2019	$PM_{2.5}$	0.31	0.20	1.55	Zhang *et al.*[133]
Shijiazhuang, China	Urban	Sep–Oct 2017	$PM_{2.5}$	0.12	0.13	0.92	Lv *et al.*[136]
Zhengzhou, China	Urban	Oct–Nov 2020	$PM_{2.5}$	0.19 ± 0.1	0.05 ± 0.04	3.80	Yang *et al.*[122]
Kunming, China	Urban	Sep–Oct 2017	$PM_{2.5}$	0.10 ± 0.05	0.11 ± 0.05	0.91	Guo *et al.*[137]
Nanning, China	Urban	Sep–Oct 2017	$PM_{2.5}$	0.10 ± 0.06	0.10 ± 0.07	1.00	Guo *et al.*[137]
Jinan, China	Urban	Dec 2016–Feb 2017	$PM_{2.5}$	0.20 ± 0.08	0.41 ± 0.18	0.49	Tang *et al.*[138]
Dianshan lake, China	Suburban	Jun–Dec 2017	$PM_{2.5}$	0.45 ± 0.24	—	—	Xu *et al.*[129]
		Nov 2020	$PM_{2.5}$	0.41 ± 0.12	0.41 ± 0.12	0.98	Yao *et al.*[16]
		Nov 2020–Jan 2021	PM_{10}	0.62 ± 0.35	0.54 ± 0.16	1.15	
Mount Tai, China	Mountain	2–5 Jun 2006	TSP	1.41	1.12	1.26	Mochizuki *et al.*[15]
		23–25 Jun 2006	TSP	0.88	0.76	1.16	
Melpitz, Germany	Suburban	Oct 2016–Nov 2017	PM_{10}	0.031	0.021	1.48	Stieger *et al.*[126]
Hampton, USA	Suburban	Sep 1985–Dec 1986	$PM_{2.5}$	0.028 ± 0.028	0.022 ± 0.020	1.27	Talbot *et al.*[77]
Yorkville, Georgia	Suburban	Sep–Oct 2016	PM_1	0.05 ± 0.026	0.064 ± 0.025	0.78	Chen *et al.*[128]
Taiwan, China	Forest	Nov 2009	$PM_{2.5}$	0.022 ± 0.010	0.26 ± 0.11	0.85	Tsai *et al.*[87]
			$PM_{2.5-10}$	0.0073 ± 0.0050	0.050 ± 0.029	0.15	
Hokkaido, Japan	Forest	Jun–Jul 2010	TSP	0.071	0.10	0.71	Mochizuki *et al.*[8]
Amazon region	Rainforest	Jul–Aug 1985	PM_1	0.046 ± 0.023	0.050 ± 0.030	0.92	Andreae *et al.*[7]
Northern Bay of Bengal	Marine	Dec 2008–Jan 2009	$PM_{2.5}$	0.028	0.032	0.88	Boreddy *et al.*[27]
Southern Bay of Bengal	Marine	Dec 2008–Jan 2009	$PM_{2.5}$	0.021	0.025	0.84	
Subarctic north pacific	Marine	30 Jul–9 Aug 2008	TSP	0.0032 ± 0.0046	0.011 ± 0.010	0.29	Miyazaki *et al.*[11]
		9–19 Aug 2008	TSP	0.0015 ± 0.0020	0.0047 ± 0.0072	0.32	
Atlantic ocean	Marine	Oct–Nov 1996	$PM_{2.1}$	0.061 ± 0.074	0.17 ± 0.12	0.36	Baboukas *et al.*[130]
Arctic	Polar	Mar–May 1986	TSP	0.24 ± 0.032	0.74 ± 0.13	0.32	Li *et al.*[139]
		Mar–May 1987	PM_1	0.11 ± 0.023	0.17 ± 0.03	0.65	
		Mar–May 1988	$PM_{>1}$	0.13 ± 0.018	0.52 ± 0.13	0.25	

Concentrations of formic and acetic acids exhibit pronounced seasonal and diurnal variability. Seasonally, their concentrations are highest in summer and during the plant growing season, underscoring the importance of secondary formation from BVOCs.[77,113,114] Diurnal variations are also evident, with daytime concentrations generally exceeding nighttime levels and peaking between 10 : 00 and 18 : 00 when solar radiation is strongest. This trend reflects the significant influence of photochemical aging on monoacid formation.[115] Gas-phase monoacid concentrations are also influenced by episodic events such as biomass burning, haze pollution, photochemical smog, and high-ozone episodes. At the summit of Mount Tai, formic and acetic acid concentrations during more field-burning influenced periods were approximately two and three times higher, respectively, than those measured during less field-burning influenced periods.[15] Similar patterns have been observed in the Amazon Basin, where dry-season concentrations exceed those in the wet season due to more frequent biomass burning.[37] Ozone is another key factor regulating monoacid levels because it participates in major atmospheric photochemical reactions. Formic and acetic acid levels typically exhibit a positive correlation with those of ozone.[98,116] During high-ozone episodes, formic acid concentrations reached 8.12 μg m^{-3}, compared with 2.67 μg m^{-3} during low-ozone periods.[117]

4.2 Particulate and aqueous phases concentrations

Atmospheric concentrations of aerosol formic and acetic acids show substantial spatial variability. In urban sites, concentrations typically range from 0.05 to 0.5 μg m^{-3}, with similar levels reported in suburban and mountainous regions. However, concentrations of both acids can exceed 1 μg m^{-3} during periods influenced by intensive biomass burning. In contrast, much lower concentrations are generally observed in forest and marine aerosols, where formic acid ranges from 0.002 to 0.2 μg m^{-3} and acetic acid from 0.002 to 0.7 μg m^{-3}.

Due to its lower vapor pressure and higher pK_a value,[66] acetic acid is less volatile and partitions more readily into the particulate phase than formic acid. Consequently, particle-phase C_1/C_2 ratios in remote regions such as forests and oceans are

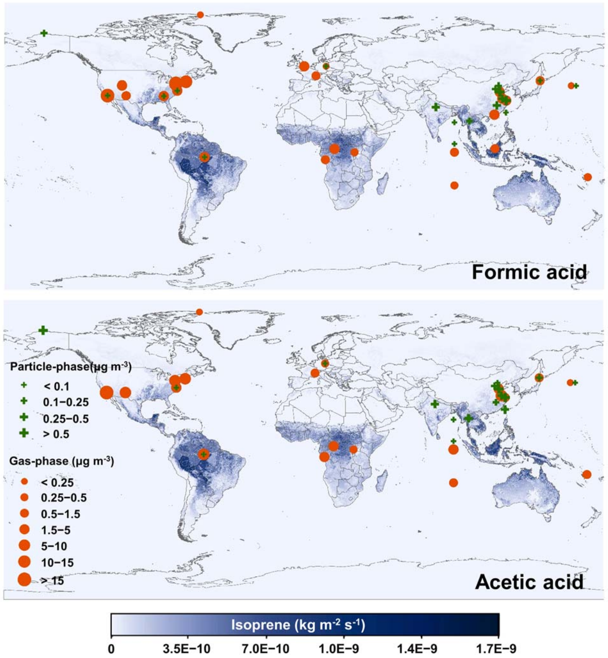

Fig. 4 Global distribution of reported gas- and particle-phase concentrations (μg m^{-3}) of formic and acetic acids. More specific concentration data are shown in Tables 1 and 2. The 2022 annual isoprene emissions data are downloaded from https://eccad.sedoo.fr/.

typically less than 1 (Table 2). In urban and suburban areas, however, particulate formic acid concentrations often exceed those of acetic acid ($C_1/C_2 > 1$). This contrasting pattern can be attributed to several factors. First, the stronger acidity of formic acid promotes its dissociation and subsequent neutralization by alkaline aerosol components, enhancing its partitioning into particles. Second, aqueous-phase oxidation of dissolved formaldehyde, which has substantial anthropogenic contributions, can directly generate formic acid within aerosols, further increasing its relative abundance.[131] In contrast to the gas-phase, particle-phase concentrations of formic and acetic acids are generally higher in autumn and winter than in spring and summer, reflecting both increased anthropogenic emissions during winter and enhanced partitioning into particles at lower temperatures.[63,132,133] The diurnal variations are relatively weak, with daytime concentrations usually slightly higher than nighttime levels. This pattern is influenced by daytime photochemical production and emissions from sources such as vehicle exhaust.[126,129] Enhanced daytime photochemical oxidation of BVOCs elevates gas-phase monoacid concentrations, which in turn promotes greater partitioning into aerosols. Regional differences in diurnal patterns have also been reported. In a deciduous broadleaf forest in northern Japan, nighttime particulate monoacid concentrations exceeded daytime levels. The elevated nighttime levels may be associated with a shallower planetary boundary layer, which allows pollutant accumulation near the ground surface.[8] These contrasting patterns highlight the combined influence of biogenic emissions, anthropogenic activities, and meteorological conditions on the temporal variability of particle-phase organic acids.

The concentration characteristics of LMW monoacids in wet deposition have been widely investigated. In rainwater, formic and acetic acid concentrations range from 0.1 to 20 μmol L^{-1}, and C_1/C_2 ratios fall between 0.4 and 4 (Table 3), with no evident spatial variation across regions. Seasonal variations, however, differ among regions. In Guizhou Province, formic and acetic acid concentrations were lower during the growing season than during the non-growing season, largely due to the strong dilution effect of frequent rainfall.[20] In contrast, a wet deposition study in Spain reported higher formic and acetic acid concentrations during the growing season, reflecting the dominance of biogenic emissions.[22] In addition to rainfall, clouds, fog, and snow also represent important forms of wet deposition. Comparative measurements of cloud/fog water and rainwater in locations such as Los Angeles (USA), Mount Lu, and Taiwan consistently show that cloud and fog water contain higher concentrations of formic and acetic acids than rainwater. This enrichment reflects the efficient scavenging of gas- and particle-phase LMW monoacids by cloud droplets.[14,76,87] In mountain and polar regions, formic and acetic acid concentrations in snow are typically below 1 μmol L^{-1}. At Mount Tateyama in Japan, Mochizuki *et al.* analysed the vertical distribution of organic acids in snow pit samples. By investigating the correlations between the sum of formic and acetic acids and inorganic ions (*e.g.*, Ca^{2+}, SO_4^{2-}, NO_3^-), they demonstrated the influence of long-range transport of continental pollutants and dust on high-altitude environments.[134]

4.3 Gas-particle partitioning characteristics

LMW monoacids are important products of atmospheric photochemical reactions and therefore play a key role in secondary organic aerosol formation *via* gas-particle partitioning. The partitioning behaviour of organic acids is controlled by three major factors. First, the physicochemical properties of the compounds are essential. Monoacids with lower saturation vapor pressures tend to partition more readily into the particulate phase.[6] Second, the chemical composition of aerosols affects their partitioning. High aerosol liquid water content (ALWC), together with abundant alkaline components, such as ammonia, amines, and alkali metal ions, enhances the uptake of organic acids into particles and facilitates the formation of organic acid salts.[149] Third, meteorological conditions also exert substantial influence. Temperature and humidity affect both the physicochemical properties of monoacids and the composition of aerosols. ALWC increases with relative humidity, while the saturation vapor pressure of organic acids decreases exponentially as temperature decreases.[150–152] The particle-phase fraction (F_p), defined as the ratio of the particle-phase concentration to the total concentration, is a key parameter for quantifying gas-particle partitioning. Fig. 5 presents the temporal variations of F_p values for formic and acetic acids ($F_{p,C1}$, $F_{p,C2}$) reported from various sites around the world.

In the Amazon rainforest and in suburban Hampton in the United States, $F_{p,C1}$ and $F_{p,C2}$ values were both reported to be below 2%, based on studies conducted around 1985.[7,77] In contrast, gas-particle partitioning measurements from the same

Table 3 Summary of reported aqueous-phase formic and acetic acid concentrations (μmol L^{-1})

Location	Type	Date	Sample	Formic acid	Acetic acid	C$_1$/C$_2$	References
Xiamen, China	Urban	Aug 2018–Aug 2019	Rainwater	0.4 ± 0.4	0.2 ± 0.3	2	Bao *et al.*[35]
São Paulo, Brazil	Urban	Feb–Oct 2000	Rainwater	17.0	8.9	1.91	Fornaro *et al.*[78]
Los Angeles, USA	Urban	Winter 1982, spring–Summer 1983	Rainwater	2.28–10.2	2.70–87.6	0.84	Kawamura *et al.*[76]
		Jun 1983	Fog	91.5	42.8	2.14	
Los Angeles, USA	Urban	1981–1984	Rainwater	6.5	5.6	1.16	Kawamura *et al.*[140]
North Carolina, USA	Urban	Oct 2007, Mar 2009	Rainwater	5.6	2.6	2.15	Willey *et al.*[89]
Abidjan, Africa	Urban	2019–2020	Rainwater	6.8 ± 1.55	5.3 ± 2.48	1.28	Kassamba-Diaby *et al.*[141]
Korhogo, Africa	Urban	2019–2020	Rainwater	9.97 ± 1.75	5.61 ± 0.24	1.78	
Fujian, China	Urban	Jun–Jul 1990	Rainwater	5.67	1.46	3.88	Yu *et al.*[21]
Guizhou, China	Urban	Jun 2007–Jun 2008	Rainwater	8.77	6.93	1.27	Zhang *et al.*[20]
Shanghai, China	Urban	Aug 2020–May 2021	Rainwater	13.54	8.32	1.63	Xie *et al.*[142]
California, USA	Mixed	Spring 1982–Winter 1983	Rainwater	0.88–15.85	1.23–13.45	—	Kawamura *et al.*[13]
			Snow	0.18–0.62	0.37–0.52		
Rome, Italy	Suburban	Jan–Feb 1986	Rainwater	2.17–24.12	nd–38.47	—	Brocco *et al.*[54]
Northwest Spain	Suburban	Aug 1996–Aug 1997	Rainwater	11.9 ± 22.7	11.6 ± 18.8	1.03	Peña *et al.*[22]
		Aug–Sep 1996, Apr–Aug 1997		12.7	15.4	0.82	
		Oct 1996–Mar 1997		2.8	3.0	0.93	
Lamto, Africa	Suburban	2019–2020	Rainwater	11.51 ± 3.10	6.64 ± 2.17	1.73	Kassamba-Diaby *et al.*[141]
Mount lu, China	Mountain	Aug–Sep 2011	Cloud	14.8	6.7	2.21	Sun *et al.*[14]
		Mar–May 2012	Cloud	8.1	4.04	2.00	
		Aug–Sep 2011	Rainwater	12.6	5.22	2.41	
		Mar–May 2012	Rainwater	9.6	5.7	1.68	
North Carolina, USA	Coastal	Sep 1996–May 1998	Rainwater	9.9	7.3	1.36	Avery *et al.*[143]
Amazon region	Rainforest	Jul–Aug 1985	Rainwater	17.9	5.7	3.14	Andreae *et al.*[7]
Taiwan, China	Forest	Nov 2009	Rainwater	2.73 ± 1.72	6.83 ± 3.99	0.36	Tsai *et al.*[87]
			Fog	5.61 ± 3.15	15.53 ± 11.09	0.40	
Tateyama Murododaira, Japan	Mountain	Apr 2008	Snow	27.7 ng g^{-1}	34.8 ng g^{-1}	0.80	Kawamura *et al.*[144]
Tateyama Murododaira, Japan	Mountain	Apr 2018	Snow	85.7 ng g^{-1}	125 ng g^{-1}	0.69	Mochizuki *et al.*[134]
Siberia	Permafrost	2010–2015	Snow	0.89	1.02	0.87	Makarov[145]
Alps, France	Mountain	Jan–Feb 1990–1991	Snow	0.31 ± 0.14	0.20 ± 0.12	1.55	Maupetit *et al.*[146]
		Mar–Apr 1990–1991	Snow	0.91 ± 0.64	0.38 ± 0.19	0.39	
Alaska, USA	Polar	Mar–Apr 1989	Snow	0.21–0.56	0.31–4.71	—	Li *et al.*[147]
Antarctic ice Cap	Polar	2008	Snow	bDL–0.07	bDL–0.72	—	Samui *et al.*[148]
Antarctic ice Shelf	Polar	2012	Snow	bDL–0.18	bDL–0.25		

period in California showed higher levels, with $F_{p,C1}$ ranging from 2–10% and $F_{p,C2}$ ranging from 10–20%.[153] This spatial variability is largely attributed to the higher abundance of ammonium salts in urban aerosols. These salts are formed from precursors emitted by intensive traffic and agricultural activities, which enhance the partitioning of organic acids into particles. Since the early 2000s, many studies have documented a marked increase in $F_{p,C1}$ and $F_{p,C2}$ values. In September 2002, an online analysis of air and PM_{10} samples in Zurich reported $F_{p,C1}$ and $F_{p,C2}$ values as high as 40% and 20%, respectively.[131] Similar values were observed in Melpitz, Germany, where $F_{p,C1}$ and $F_{p,C2}$ reached 37% and 26%.[126] In 2006, air samples collected at Mount Tai in China during more field-burning influenced period showed even higher values, with $F_{p,C1}$ up to 50% and $F_{p,C2}$ up to 40%.[15] At Dianshan Lake in Shanghai, two studies using an *in situ* gas and aerosol composition monitor investigated the gas-particle partitioning of formic acid from June to December 2017 and in November 2020. The corresponding $F_{p,C1}$ values were 12.5% and 30.2%, respectively.[16,129]

Such high F_p values of monoacids cannot be accurately predicted by thermodynamic equilibrium models based on Raoult's law and Henry's law constants. This discrepancy largely reflects the fact that chemical processes occurring in the real atmosphere are often simplified or omitted in these models, including the formation of organic acid salts and aqueous-phase reactions.[126,154] Unlike physical absorption, organic salt formation is an irreversible chemical process that converts volatile organic acids into low-volatility ionic species, thereby effectively locking them into the particle phase. For instance, Mochizuki *et al.* attributed the high F_p values of formic and acetic acids observed at Mount Tai to organic salt formation driven by excess cations (*e.g.*, K^+, Ca^{2+}, NH_4^+) and potentially amines, which efficiently neutralize gaseous acids and promote their retention in the particle phase.[15] Another often overlooked pathway is aqueous-phase chemistry within aerosols.[155] Bates *et al.* demonstrated that aqueous oxidation of isoprene-derived secondary organic aerosol (*e.g.*, 2-methyltetrols and their organosulfates) can produce formic and acetic acids in high

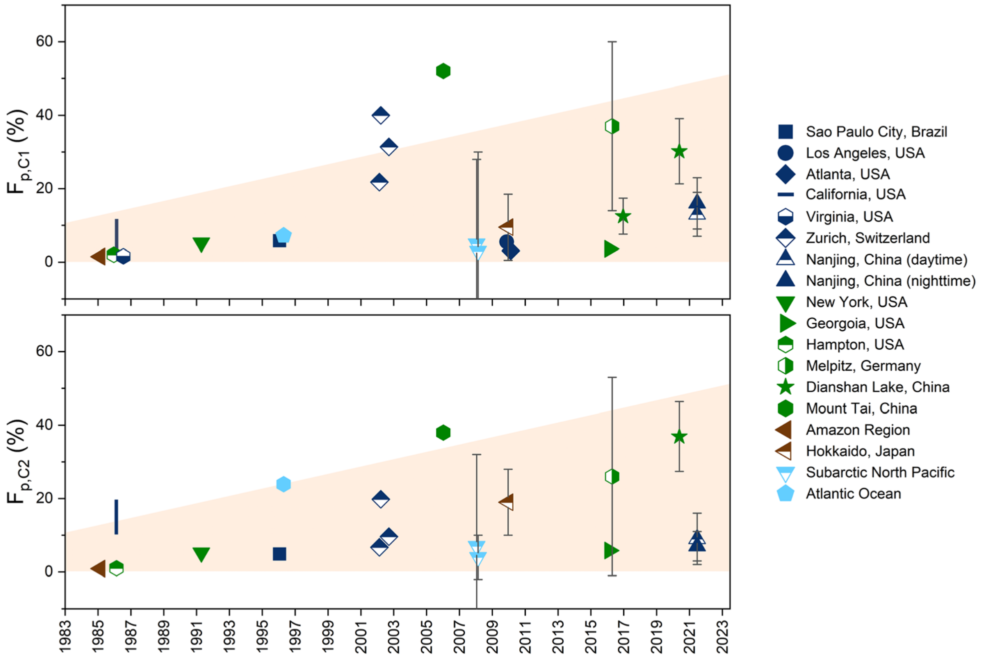

Fig. 5 Global temporal trends in particle-phase fractions (F_p) of formic and acetic acids. Colours denote site types: dark blue for urban, green for suburban/mountainous, brown for forests/rainforests, and light blue for marine sites. The orange-shaded region highlights the envelope encompassing most reported F_p ranges. Data from California are shown as ranges (straight line). Data compiled from ref. 7,8,11,12,15,16,77,121,126,129–131,153,154,164–166.

yields.[102] Furthermore, recent studies suggest that under intense photochemical conditions, gaseous organic acids may directly contribute to particle formation through intermolecular self-assembly, providing an additional non-equilibrium pathway for their transfer to the particle phase.[33] In addition, dimerization of monoacids in aqueous particles may also influence their phase distribution by modifying their effective volatility and chemical reactivity.[154,156,157]

These chemical processes are strongly modulated by aerosol acidity, which controls the neutralization capacity of particles and thereby regulates organic salt formation and aqueous-phase reactions. LMW monoacids tend to partition more favourably into aerosol particles with low acidity. Long-term aerosol acidity is governed by the relative abundances of atmospheric alkaline species (*e.g.*, NH_3, crustal cations) and acidic components (*e.g.*, SO_2, NO_x).[158] Over recent decades, widespread reductions in SO_2 and NO_x emissions have decreased the availability of strong acids, whereas NH_3 emissions have remained largely unregulated and even have increased in many regions.[42–45,47,159,160] This imbalance has driven a gradual increase in aerosol pH and enhanced the capacity of particles to neutralize acidic gases.

Global modelling studies have confirmed this trend. Karydis *et al.* examined the global distribution and evolution of aerosol acidity over the past 50 years (1970–2020).[161] Their results showed a substantial increase in aerosol pH across Europe and North America, driven primarily by reduced SO_2 and NO_x emissions and increased NH_3 emissions. In China, long-term measurements at Zhengzhou showed aerosol pH increasing by approximately 0.1 per year during 2011–2019, accelerating to 0.21 per year in 2019–2022.[162] Wang *et al.* simulated winter trends in the North China Plain and projected that aerosol pH will continue to rise until at least 2030, and until 2060 in the southern part of the region, due to the multiphase buffering of the NH_3/NH_4^+ system.[163]

In response to these changing atmospheric conditions, LMW monoacids increasingly partition into the particulate phase, reflecting their geochemical response to changes in aerosol acidity and composition worldwide. This emerging trend highlights the need to consider monoacids in the particulate phase and suggests that they may play an important role in enhancing CCN formation.

5. Current research on compound specific stable and radiocarbon isotopic tracing of LMW monoacids

5.1 Compound specific stable carbon isotopes

Compound-specific stable carbon isotope ($\delta^{13}C$) analysis (CSIA) is a powerful tool for tracing the sources of organic pollutants, as different emission sources exhibit distinct isotopic signatures.[167,168] Due to the kinetic isotope effect, the lighter isotope (^{12}C) is more reactive and becomes relatively enriched in the products, whereas the heavier isotope (^{13}C) is depleted during atmospheric reactions.[169,170] Therefore, CSIA also provides valuable insights into key atmospheric chemical processes of organic carbon species. The application of CSIA for LMW monoacids requires two essential steps, namely the isolation of individual compounds and the determination of their $\delta^{13}C$ values. Compound separation is typically achieved by GC, HPLC, or IC, and $\delta^{13}C$ values are subsequently determined by isotope ratio mass spectrometry (IRMS).

In 1995, Sakugawa and Kaplan isolated formic and acetic acids from rainwater in Los Angeles using ion-exclusion chromatography (ICE).[171] Both acids were then oxidized to CO_2 at 600 °C with cupric oxide as the catalyst, and the resulting CO_2 was analysed by IRMS. This work provided the first $\delta^{13}C$ values of individual formic and acetic acids, with mean values of $-30.13‰$ and $-20.51‰$, respectively. By comparing these isotopic signatures with those of fossil-fuel and biogenic sources, the authors inferred that formic acid originated from both primary emissions and secondary formation, whereas acetic acid was dominated by primary emissions. Fisseha *et al.* conducted a similar investigation in Zurich during both winter and summer.[169] In their methods, formic and acetic acids were separated by IC and then converted to CO_2 *via* wet oxidation prior to IRMS analysis. Correlation analysis between $\delta^{13}C$ values of these acids and ozone concentrations also indicated that formic acid was influenced by secondary formation in addition to primary emissions, while acetic acid was derived predominantly from primary sources.

The separation and $\delta^{13}C$ analysis of individual formic and acetic acids have also been attempted using HPLC-IRMS. However, the application of this approach to ambient samples is constrained by detection limits and matrix interferences. For instance, Tagami and Uchida developed an online HPLC-IRMS method for $\delta^{13}C$ analysis of formic and acetic acids in aqueous solutions, but the method required a relatively high minimum carbon concentration of 0.4 mmol L^{-1} for reliable detection.[172] Lang *et al.* used HPLC with a C_{18} column to separate these acids from seawater, followed by off-line wet oxidation and IRMS analysis. Despite its innovation, this method still faced challenges, including incomplete separation of formic acid from the initial salt peak in concentrated seawater samples, as well as significant and variable procedural blanks, particularly for acetate, which complicate accurate isotopic measurements.[173]

Lee *et al.* developed an analysis technique using needle trap and GC-IRMS for compound-specific $\delta^{13}C$ analysis of LMW monoacids. In this approach, air samples are collected by pumping air through the NeedlEx. Organic acids in precipitation are liberated by acidification, purged with helium, and then trapped in the NeedlEx (Fig. 6a).[174] No statistically significant isotope fractionation was observed during the trapping and desorption process. Detection limits are 4.3 mmol L^{-1} for formic acid and 1.7 mmol L^{-1} for acetic acid, with an analytical uncertainty of ~0.5‰.[175] Applying this technique to air samples collected in urban and suburban Guiyang and above a forest canopy, Lee *et al.* found that the $\delta^{13}C$ signatures indicate that primary biogenic emissions constitute a major source of formic and acetic acids in the lower troposphere, second only to the photochemical transformation of biogenic precursors. These findings highlight the prominent role of biogenic emissions even in regions influenced by anthropogenic activities.[176]

Overall, compound-specific $\delta^{13}C$ analysis of LMW monoacids remains at an early developmental stage, with only a limited number of studies published to date. Each existing analytical approach exhibits notable limitations. As shown in Fig. 7, reported $\delta^{13}C$ values of formic acid range from $-30.1‰$ to $-23.2‰$, while those of acetic acid range from $-29.3‰$ to $-20.51‰$. Considerable discrepancies exist among studies, particularly between the two rainwater datasets from Anholt (Denmark) and Los Angeles (USA). These differences likely arise from variations in sources and atmospheric processing, as well as from underlying methodological uncertainties. Inadequate compound purity during separation and incomplete oxidation to CO_2 can both compromise the accuracy of the isotope ratio measurements. For IC-IRMS analysis, $\delta^{13}C$ analysis requires offline processing after chromatographic separation, which

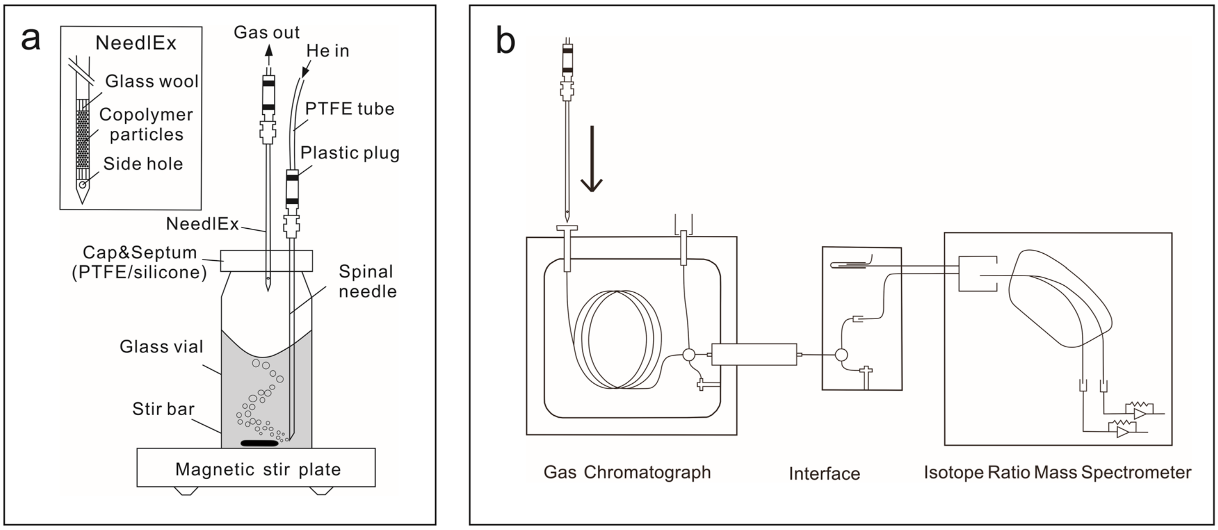

Fig. 6 Schematic diagram of (a) trapping organic acids from aqueous solutions onto the NeedlEx and (b) introducing NeedlEx into the GC-IRMS system. Fig. 6a is reproduced from Lee *et al.*[175] with permission from Wiley, copyright 2013; Fig. 6b is adapted from Sessions[177] with permission from Elsevier, copyright 2006.

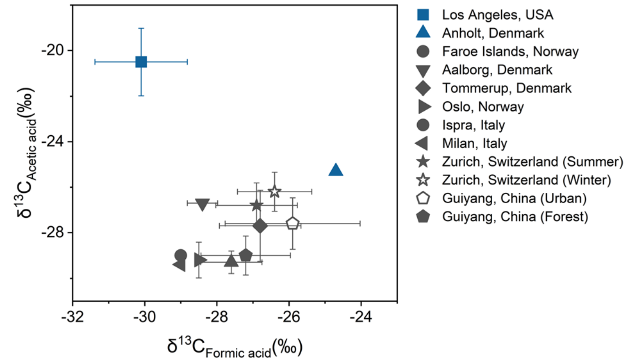

Fig. 7 Reported compound-specific stable carbon isotope ($\delta^{13}C$) values of formic and acetic acids. Blue points represent rainwater samples, and grey points represent air samples. Data are compiled from Sakugawa *et al.*,[171] Glasius *et al.*,[178] Fisseha *et al.*,[169] and Lee *et al.*[176]

introduces risks of sample loss, contamination, and isotopic fractionation.

The NeedlEx SPME-GC-IRMS technique enables online separation and measurement, but concentration quantification remains difficult because the trapping efficiency of the NeedlEx cannot be reliably assessed. Current HPLC-IRMS methods face challenges, including incomplete separation of formic acid from the initial salt peak and relatively high procedural blanks for acetic acid. Although derivatization can improve chromatographic behaviour of LMW monoacids, derivatization-based GC-IRMS analysis for these compounds remains largely unexplored. Since the derivatization process introduces extraneous carbon atoms, careful evaluation of mass balance correction and potential isotopic fractionation during the reaction would be required. Given these challenges, source apportionment based solely on $\delta^{13}C$ analysis remains limited.

5.2 Compound specific radiocarbon isotopes

Radiocarbon (^{14}C) in fossil fuels has completely decayed over geological timescales, meaning that fossil-derived carbon contains no detectable ^{14}C. In contrast, modern biogenic carbon remains in equilibrium with the contemporary atmospheric ^{14}C level.[179] This fundamental distinction enables quantitative apportionment of fossil *versus* biogenic contributions to atmospheric organic species through $\Delta^{14}C$ measurements.[180–182] In 1993, Johnson and Dawson reported the first compound-specific ^{14}C measurements of formic acid.[183] The modern carbon fractions ranged from 81.6% to 100%. In their method, formic acid was selectively oxidized to CO_2 by reaction with mercuric chloride. The resulting CO_2 was then cryogenically trapped and converted into solid graphite targets for ^{14}C analysis. Building on this selective oxidation procedure, Glasius *et al.* isolated acetic acid *via* vacuum distillation and conducted a systematic analysis of ^{14}C in formic and acetic acids from air and precipitation across Europe.[178] Their results showed substantial fossil contributions in urban atmospheres (35–45%), with markedly lower contributions in suburban environments (4–21%) and negligible contributions in marine air. These studies demonstrated the feasibility of isolating individual monoacids for ^{14}C analysis using selective oxidation-based approaches. However, the procedures were complex and struggled to ensure sufficient compound purity. Due to these limitations, no major methodological advances for compound-specific ^{14}C analysis of monoacids appeared in the following two decades. Lang *et al.* attempted to apply HPLC separation combined with wet oxidation to determine dual-carbon isotopes of formic and acetic acids in seawater.[173] However, their work was limited to spiked seawater samples. The complex matrix and low ambient concentrations prevented application to ambient samples.

More recently, Xu *et al.* established a validated method for compound-specific ^{14}C analysis of dicarboxylic acids using preparative capillary gas chromatography (PCGC), enabling precise ^{14}C analysis of molecules such as oxalic acid in aerosols.[184,185] Given the favourable chromatographic behaviour of derivatized monoacids on GC, PCGC shows strong potential for isolating individual LMW monoacids. This approach may provide a promising route for developing compound-specific ^{14}C analysis methods for monoacids in the future.

Unlike $\delta^{13}C$ analysis, which mainly provides qualitative insights into source and process information, $\Delta^{14}C$ measurements offer a direct quantitative constraint on fossil *versus* modern carbon fractions. The combined application of $\delta^{13}C$ and $\Delta^{14}C$ therefore provides complementary constraints that improve the robustness of source apportionment and enhance our understanding of atmospheric processing.[186]

6. Conclusions and perspectives

Over the past several decades, significant progress has been made in understanding the environmental fate of LMW monoacids in the atmosphere. Global field observations have characterized their concentrations and gas-particle partitioning patterns. Laboratory studies have elucidated a range of multiphase reaction mechanisms. Moreover, the emerging application of compound-specific dual-carbon isotope ($\delta^{13}C$ and $\Delta^{14}C$) techniques has enabled preliminary quantitative source apportionment and provided new insights into their atmospheric processes. Despite these advances, several key challenges remain:

(1) Lack of standardized sampling and analytical methods. Current approaches for sampling and analysing LMW monoacids vary widely, and no unified protocol exists. Systematic evaluation and comparison of these methods are needed to improve the consistency and comparability of published datasets.

(2) Insufficient understanding of C_3–C_{10} monoacids. Most studies have focused on the more abundant formic and acetic acids, leaving C_3–C_{10} monoacids poorly characterized. Species such as isobutyric acid and lactic acid may serve as important molecular markers for identifying emission sources and atmospheric processes.

(3) Large uncertainties in source apportionment. Incomplete understanding of secondary formation mechanisms and missing biogenic sources of LMW monoacids lead to

substantial discrepancies among satellite observations, model simulations, and field measurements.

(4) Limitations in compound-specific dual-carbon isotope techniques. Although δ^{13}C and Δ^{14}C signatures hold great potential for tracing sources and atmospheric processes of monoacids, analytical methods remain underdeveloped. A major challenge lies in isolating individual monoacids with sufficient purity for accurate isotope analysis.

(5) Limited understanding of the contribution of LMW monoacids to CCN formation. With increasing global BVOC emissions, changing aerosol acidity, and increasing organic aerosol fractions, the particle-phase fraction of monoacids is expected to increase. Their potential contribution to CCN formation by particulate monoacids and the associated climate effects therefore requires rigorous evaluation.

To advance the understanding of the LMW monoacid geochemistry, future research should prioritize several key areas. First, field observations should be expanded and strengthened. Systematic, long-term monitoring across more globally representative regions is needed to better characterize the spatiotemporal variations and gas-particle partitioning of LMW monoacids. These measurements will provide critical constraints for model simulations, thereby improving climate impact assessments. Second, methodological development is essential to overcome key technical challenges in δ^{13}C and Δ^{14}C analysis of LMW monoacids in ambient samples. Progress can be achieved by optimizing sample pretreatment and selecting chromatographic columns that minimize interferences from initial salt peaks and procedural blanks. Such optimizations could enable preparative HPLC/IC techniques for Δ^{14}C analysis of formic and acetic acids in ambient samples. Additionally, derivatization can substantially improve the chromatographic behaviour of LMW monoacids on GC, making GC-IRMS and PCGC techniques for dual-carbon isotope analysis theoretically feasible and highly promising. Third, greater attention should be devoted to the climatic impacts of LMW monoacids. Key questions include their size distribution, their potential contribution to CCN, and their influence on ALWC. Addressing these issues is essential for clarifying how LMW monoacids modify cloud microphysical properties and thus indirectly affect climate.

Author contributions

Lingxiao Lu: data curation, formal analysis, investigation, validation, visualization, writing – original draft. Buqing Xu: conceptualization, investigation, methodology, project administration, supervision, validation, writing – review & editing. Gan Zhang: investigation, project administration, supervision, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

All data used in this study are publicly available and can be accessed through the references cited in this manuscript.

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