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10.1029/2026JG009767

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Volatile Organic Compounds in Rainwater: A New Frontier in Atmosphere–Biosphere Interactions

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Abstract Rainwater is a key vector of atmospheric deposition, linking the atmosphere with terrestrial and aquatic ecosystems. While the inorganic chemistry of precipitation (dominated by sulfate, nitrate, ammonium, and trace metals) has been extensively studied, organic compounds in rainwater have received less attention, and Volatile Organic Compounds (VOCs) in particular have been practically overlooked. Recent methodological advances have revealed that a diverse suite of VOCs can be detected in rainwater along with VOC-derived compounds, challenging the long-held assumption that wet deposition plays a negligible role in VOC cycling. Although wet deposition is generally thought to be a minor atmospheric sink for VOCs (∼13.3% of total VOC emissions), rainborne VOCs are chemically reactive and biologically labile, such that even small quantities may exert disproportionate effects on soil microbial activity, plants, short-term biogeochemical cycling, and water chemistry at local to regional scales. This article combines a synthesis of the current state of knowledge on rainborne VOCs and VOCs-derived compounds with a particular focus on VOC occurrence, sources, partitioning, and transformation processes, with a forward-looking perspective on the potential significance of rainborne VOCs for carbon cycling and atmosphere–biosphere interactions. We identify major gaps in observations, analytical capability, and modeling frameworks that limit quantitative understanding of VOC wet deposition and its ecological significance. Finally, we outline priority research directions, including improved sampling strategies, advanced analytical techniques, and integration into Earth system models. Together, these advances are needed to reassess the role of precipitation not only as a passive sink for atmospheric pollutants, but as an active driver of ecosystem functioning and Earth system processes in a changing climate.

Plain Language Summary Rain connects the atmosphere to the land and oceans by washing chemicals out of the air and delivering them to ecosystems. For decades, scientists have focused on inorganic substances in rainwater, such as nitrate and sulfate, because of their links to acid rain and nutrient pollution. Much less attention has been paid to organic compounds, especially volatile organic compounds (VOCs), which are emitted by plants, microbes, and human activities. New analytical tools now show that VOCs are present in rainwater more often than previously thought. Even assuming that rain may remove only a small fraction of VOCs from the atmosphere (∼13.3% of total VOC emissions), these compounds are highly reactive and easily used by microbes. This means that small amounts delivered by rain could influence soil and water chemistry, microbial activity, plants, and short-term carbon cycling, particularly at local scales. However, we still lack basic information on how much VOCs rain delivers, how they may change rain chemistry, and what they do once they reach ecosystems. This document highlights why measuring VOCs in rainwater is important now, identifies key knowledge gaps, and explains how improved monitoring, experiments, and models could transform our understanding of rain as an active player in the Earth system, especially under climate change.

Key Points:

- Rainwater is an active vector of VOC cycling and atmosphere–biosphere exchange
- Rainborne VOCs may exert disproportionate biogeochemical impacts despite small fluxes
- VOCs in rainwater represent a major unresolved gap in Earth system understanding

Supporting Information:

Supporting Information may be found in the online version of this article.

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Citation:
Yáñez-Serrano, A. M., Moreno, T., Izquierdo, M., Pey, J., Seco, R., Alastuey, A., & Peñuelas, J. (2026). Volatile organic compounds in rainwater: A new frontier in atmosphere–biosphere interactions. *Journal of Geophysical Research: Biogeosciences*, *131*, e2026JG009767. https://doi.org/10.1029/2026JG009767

Received 30 JAN 2026
Accepted 15 AUG 2026

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1. Introduction

Volatile organic compounds (VOCs) are central regulators of atmosphere–biosphere interactions because they link biological activity, atmospheric oxidation chemistry, aerosol formation, and carbon cycling. VOCs are commonly defined operationally based on their volatility, with one widely used criterion corresponding to a vapor pressure >10 Pa at 25°C; however, no single volatility threshold universally separates VOCs from semi volatile organic compounds (SVOCs). Atmospheric organic compounds instead occur along a continuous volatility spectrum, and compounds near the VOC/SVOC boundary may be classified differently depending on the

Funding acquisition: Ana M. Yáñez-Serrano, Teresa Moreno, Maria Izquierdo, Roger Seco, Andrés Alastuey, Josep Peñuelas
Investigation: Ana M. Yáñez-Serrano, Teresa Moreno, Maria Izquierdo, Jorge Pey, Roger Seco, Andrés Alastuey, Josep Peñuelas
Methodology: Ana M. Yáñez-Serrano, Maria Izquierdo, Jorge Pey, Roger Seco, Josep Peñuelas
Project administration: Ana M. Yáñez-Serrano, Teresa Moreno, Andrés Alastuey, Josep Peñuelas
Resources: Ana M. Yáñez-Serrano, Teresa Moreno, Maria Izquierdo, Jorge Pey, Roger Seco, Andrés Alastuey, Josep Peñuelas
Software: Ana M. Yáñez-Serrano, Maria Izquierdo
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Visualization: Ana M. Yáñez-Serrano, Maria Izquierdo, Roger Seco, Josep Peñuelas
Writing – original draft: Ana M. Yáñez-Serrano, Teresa Moreno, Maria Izquierdo, Jorge Pey, Roger Seco, Andrés Alastuey, Josep Peñuelas
Writing – review & editing: Ana M. Yáñez-Serrano, Teresa Moreno, Maria Izquierdo, Jorge Pey, Roger Seco, Andrés Alastuey, Josep Peñuelas

framework used. In this review, VOCs represent the volatile end of this continuum and the starting point for tracking atmospheric organic carbon into lower-volatility oxidation products and dissolved or particulate organic matter. VOCs can partition into atmospheric aqueous phases, including cloud and rain droplets (Franco et al., 2021). Their emissions are dominated globally by biogenic sources (including vegetation, microbes, fungi, algae, and animals) whose magnitude and composition vary with biotic and abiotic drivers (Šimpraga et al., 2019; Yáñez-Serrano et al., 2020). Anthropogenic activities such as traffic, industry, solvent use, and biomass burning additionally contribute with substantial regional and local inputs. Together, these sources emit approximately 800 Tg C yr^{-1} of VOCs globally (Sfendla et al., 2026). Once emitted, VOCs undergo atmospheric oxidation that can generate secondary organic aerosols (SOA) and cloud condensation nuclei (CCN) or progress toward complete oxidation to CO_2 (Figure 1). Through these processes, VOCs strongly influence biological signaling and defense, atmospheric oxidation capacity, aerosol formation, radiative balance, water quality, and human health despite their trace concentrations (Kulmala et al., 2013; Laothawornkitkul et al., 2009; Manisalidis et al., 2020; Pöschl et al., 2010).

VOCs are removed from the atmosphere through chemical oxidation as well as wet and dry deposition. Dry deposition transfers gases and particles to terrestrial and aquatic surfaces through turbulent transport, molecular diffusion, gravitational settling, and surface uptake processes that depend strongly on land-surface characteristics and atmospheric conditions. In contrast, wet deposition scavenges atmospheric constituents into cloud, rain, snow, or fog water, linking atmospheric processing with aqueous-phase chemistry and ecosystem delivery (Franco et al., 2021; Seinfeld & Pandis, 2006; Willey et al., 2000). Despite extensive work on atmospheric VOC chemistry, the role of rainwater as a sink, transformation medium, and ecosystem transfer pathway for VOCs and VOC-derived carbon remains poorly constrained. Wet deposition is recognized as an important atmospheric carbon sink, yet its magnitude and controls remain poorly understood (Iavorivska et al., 2016; Jurado et al., 2008). In particular, neither wet nor dry deposition of gas-phase VOCs has been robustly quantified at the global scale, despite their potential importance as ecosystem carbon fluxes (Iavorivska et al., 2016; Liggio et al., 2025). These removal pathways remain inadequately characterized due to the chemical diversity of VOCs, their wide range of solubilities and reactivities, and the scarcity of observational data, compounded by limitations in conventional measurement techniques.

Rainwater composition reflects the combined effects of gas–particle partitioning, aqueous-phase reactions, and aerosol scavenging. Although many rainwater organic acids are formed through atmospheric oxidation and in situ aqueous processing, some environments, notably tropical regions such as the Amazon, also receive direct emissions of certain organic acids as primary VOCs (Andreae et al., 1988). Similarly, rainwater contains organic material originating from primary aerosol, biological particles, soil and vegetation, and other sources that need not result from VOC oxidation. Atmospheric organic carbon therefore exists along a continuum from volatile emissions to progressively more oxidized and lower-volatility products that partition into atmospheric particles and aqueous phases, alongside primary organic material that can enter atmospheric waters directly. These materials are ultimately transferred to terrestrial and aquatic ecosystems through wet deposition. Understanding these processes is essential not only for constraining atmospheric chemistry, but also for evaluating impacts on carbon cycling, ecosystem functioning, water quality, and climate-relevant feedbacks.

This review synthesizes the current state of knowledge on rainborne VOCs and VOC-derived compounds, with particular emphasis on their occurrence, sources, partitioning behavior, and transformation processes in atmospheric aqueous phases. Beyond summarizing existing observations, the review adopts a forward-looking perspective on the potential significance of rainborne VOCs for carbon cycling and atmosphere–biosphere interactions. We further identify major limitations in observations, analytical capabilities, and modeling frameworks that currently hinder quantitative assessment of VOC wet deposition and its ecological significance, and highlight priority research directions needed to advance the field.

Throughout this review, VOCs are defined as gas-phase organic compounds that can partition into atmospheric aqueous phases such as cloud and rain droplets. Following dissolution, these compounds may undergo rapid aqueous-phase reactions, including oxidation, hydration, and oligomerization, producing more oxygenated and less volatile products. Atmospheric processing therefore generates a continuum spanning parent VOCs, intermediate oxidation products, SVOCs and dissolved or particulate organic matter. Here, the term "VOC-derived" specifically refers to organic compounds or carbon whose formation or atmospheric processing can be linked to the oxidation or chemical transformation of VOC precursors. This distinction is important because not all organic

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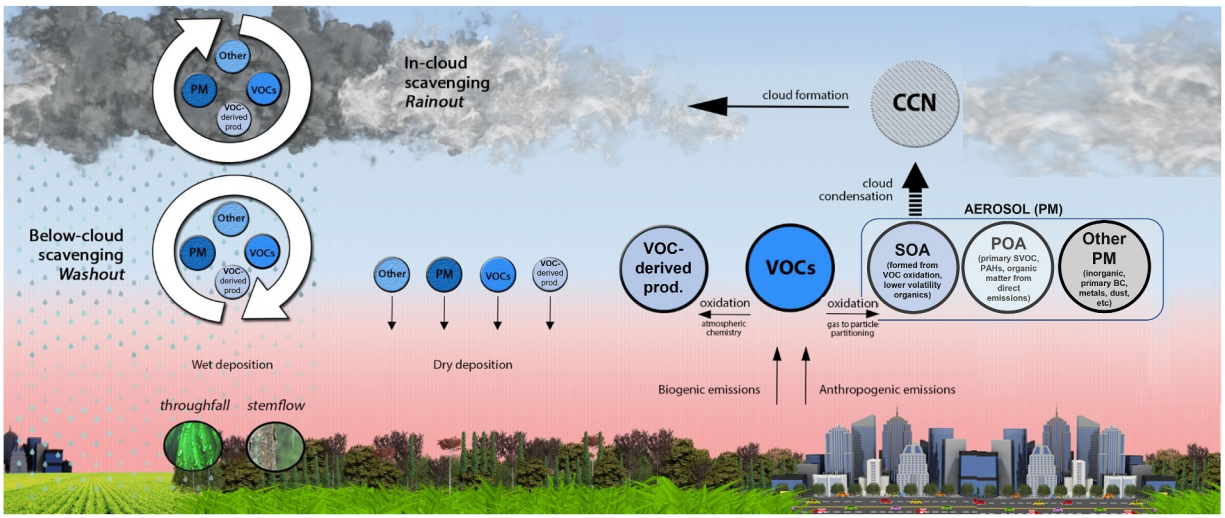

Figure 1. Cycle of VOC dry and wet deposition. VOCs stands for volatile organic compounds; PM for particulate matter; SOA for secondary organic aerosol; POA for primary organic aerosol; SVOC for semi-volatile organic compounds; and CCN for cloud condensation nuclei.

material present in cloud water or rainwater is necessarily VOC-derived: primary organic aerosol, directly emitted organic acids, biological material, and soil- or dust-associated organic matter may enter atmospheric waters without first being formed through VOC oxidation. We therefore adopt a broader "VOC-derived carbon" framework to trace carbon originating from volatile emissions through atmospheric transformation, partitioning, aqueous processing, and eventual wet deposition, while recognizing that rainwater contains a broader organic carbon pool that also includes primary and externally derived organic material.

Accordingly, we distinguish throughout the manuscript between (a) parent VOCs in the gas phase (e.g., isoprene, BTEX, methanol, and terpenes), (b) VOC-derived products formed through gas- and aqueous-phase chemistry (e.g., carbonyls, organic acids, and organosulfates), and (c) other dissolved and particulate organic matter incorporated into cloud water and rainwater through direct emission, gas–particle partitioning, aerosol scavenging, or multiphase atmospheric processing. This framework also recognizes the continuous transition between VOCs and lower-volatility compounds: compounds such as naphthalene occur near the VOC/SVOC boundary, while higher-molecular-weight PAHs are more appropriately considered SVOCs and are predominantly associated with the particulate phase. Thus, the use of "VOC-derived carbon" does not imply that all organic carbon in rainwater originates from VOC oxidation, but rather provides a framework for tracing the contribution and fate of carbon originating from volatile atmospheric emissions within the broader rainwater organic carbon pool.

Following this framework, the review addresses four key questions: (a) what determines the chemical composition and acidity of rainwater; (b) how VOCs are transferred, partitioned, and transformed within atmospheric aqueous phases; (c) what ecological and biogeochemical consequences arise from VOC wet deposition; and (d) what methodological limitations and knowledge gaps currently impede quantitative understanding of these processes. Finally, we outline future priorities, including improved sampling strategies, advanced analytical approaches, and integration of VOC wet-deposition processes into atmospheric chemistry and Earth system models. By structuring the discussion along the pathway from atmospheric emissions to ecosystem impacts continuum, we aim to provide a coherent framework linking atmospheric chemistry, wet deposition, carbon cycling, and Earth system processes.

2. Wet Deposition

Wet deposition is a major atmospheric removal pathway for gases and particles, transferring pollutants from the atmosphere to the Earth's surface via precipitation. In addition to its role in atmospheric cleansing, wet deposition represents a key pathway linking atmospheric processing with the delivery of chemical species to terrestrial and aquatic ecosystems (Seinfeld & Pandis, 2006; Willey et al., 2000). Wet deposition occurs primarily through two mechanisms: in-cloud scavenging (rainout) and below-cloud scavenging (washout) (Seinfeld & Pandis, 2006).

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These processes differ in their microphysical pathways and in their effectiveness across chemical species and meteorological conditions.

In-cloud scavenging or rainout occurs during cloud formation when water vapor condenses onto aerosol particles acting as CCN, forming cloud droplets that subsequently grow into precipitation. During this process, particles are incorporated into droplets through nucleation scavenging and collision–coalescence, while gases dissolve into the aqueous phase according to their solubility and ambient concentrations (Ervens, 2015; Garrett et al., 2006; MacDonald et al., 2018).

Below-cloud scavenging, *or washout*, refers to the removal of gases and particles below the cloud base by falling precipitation. As raindrops descend, particles are captured by impaction and diffusion, while gases dissolve into droplets through mass transfer governed by their solubility and ambient concentrations (MacDonald et al., 2018). Washout efficiency depends strongly on particle size, gas solubility, and precipitation intensity (Gong et al., 2011).

The relative importance of rainout and washout is controlled by the vertical distribution of atmospheric constituents, their physicochemical properties, and meteorological conditions such as cloud dynamics and rainfall intensity (Ervens, 2015; MacDonald et al., 2018). Together, these processes govern the transfer of atmospheric constituents into precipitation, linking atmospheric composition with surface deposition and ecosystem exposure.

3. Chemical Composition and Acidity of Rainwater

Rainwater is a chemically complex medium containing not only water but a wide range of dissolved gases, particulate matter, organic compounds, trace metals, and microorganisms, all of which influence its physicochemical properties and environmental impacts (Willey et al., 2000). The chemical composition of precipitation reflects the integrated effects of atmospheric processes occurring before and during precipitation, including gas–particle partitioning, cloud microphysics, in-cloud transformations, and below-cloud scavenging (Kulshrestha et al., 1999; Sakihama et al., 2008).

Although aerosol particles, cloud droplets, fog water, and rainwater are chemically connected through multiphase atmospheric processing, they represent distinct physicochemical environments. Aerosol particles exhibit high solute concentrations and long atmospheric residence times that favor heterogeneous and interfacial reactions. Cloud droplets act as transient aqueous microreactors where rapid oxidation, hydration, and oligomerization reactions occur. In contrast, rainwater integrates both in-cloud chemistry and below-cloud scavenging, reflecting a combination of local emissions and long-range atmospheric transport (Roy et al., 2016). Consequently, precipitation chemistry provides valuable insights into regional pollution sources, atmospheric processing, and large-scale transport patterns (Bhuyan et al., 2020; Keresztesi et al., 2020; Roy et al., 2016).

3.1. Inorganic Composition of Rainwater

Rainwater contains a broad suite inorganic of substances derived from both natural and anthropogenic sources. Major ionic constituents include cations (K^+, Na^+, NH_4^+, Mg^{2+}, Ca^{2+}, H_3O^+) and anions (OH^-, Cl^-, NO_2^-, NO_3^-, SO_3^{2-}, SO_4^{2-}, PO_4^{3-}), together with trace metals and metalloids such as Cd, Cu, Fe, Ni, Pb, Mn, Se, and Zn (Àvila & Rodà, 2012; Polkowska et al., 2011; Roy et al., 2016). Natural inputs include sea-salt aerosols and mineral dust, whereas anthropogenic contributions arise from fossil fuel combustion, traffic emissions, road dust resuspension, biomass burning, shipping and ore mining and processing among many other industrial activities (Rivera-Rivera et al., 2020).

Regional differences in inorganic composition reflect source proximity and atmospheric transport pathways. For instance, remote regions such as Antarctica exhibit low concentrations due to minimal anthropogenic influence, whereas industrialized regions in Asia show elevated levels of sulfate, nitrate, and ammonium (Polkowska et al., 2011). The origin of air masses strongly influences rainwater chemistry (Kulshrestha et al., 1999): mineral dust from Saharan intrusions enriches precipitation in Ca^{2+} and Mg^{2+}, while air masses influenced by industrial emissions produce sulfate- and nitrate-rich, more acidic precipitation (Àvila & Rodà, 2012; Keresztesi et al., 2019).

Trace elements in rainwater exhibit strong variability depending on emission sources, transport history, and precipitation characteristics. Their solubility is closely linked to acidity, generally increasing under low-pH conditions due to enhanced dissolution of metal-bearing particles. As a result, elements such as Cd, Cr, Cu,

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Ni, Pb, V, and Zn are more readily mobilized during long-range atmospheric transport in acidified cloud and rainwater (Cheng et al., 2021; Hsu et al., 2010; Jickells et al., 2016).

The relative concentrations and ratios of inorganic species are widely used as tracers of emission sources, nutrient inputs, acidification processes, and regional deposition patterns, providing insight into atmospheric processing and the influence of natural and anthropogenic activities on precipitation chemistry. These chemical signatures also reflect underlying physicochemical conditions that influence aqueous-phase kinetics, radical chemistry, VOC solubility and partitioning, and the efficiency of organic carbon transfer from the atmosphere to terrestrial and aquatic ecosystems.

3.2. Organic Composition of Rainwater: Total Organic Carbon (TOC)

Rainwater contains a diverse mixture of organic compounds collectively termed dissolved organic matter (DOM), whose carbon component is operationally quantified as dissolved organic carbon (DOC), which plays a central role in its chemical reactivity and environmental impact. Total organic carbon (TOC) integrates contributions from in-cloud chemical processing, below-cloud scavenging, organic matter cycling, microbial activity and both local and long-range atmospheric transport (Bhuyan et al., 2020; Sakihama et al., 2008).

Atmospheric organic carbon spans a continuum from VOCs and SVOCs to low-volatility oxidation products and particulate organic matter. In precipitation, TOC is operationally divided into particulate organic carbon (POC), and DOC, also referred to as water-soluble organic carbon (WSOC), commonly defined as the fraction passing through a 0.45 μm membrane filter (Iavorivska et al., 2016). These operational definitions do not strictly correspond to atmospheric volatility classes, multiphase processing and aerosol scavenging as these processes introduce complexity.

DOC concentrations in rainwater vary globally over more than two orders of magnitude, typically ranging from ∼0.1 to ∼10 mg C L^{-1} (Guillemette et al., 2023; Siudek et al., 2015). This variability is strongly influenced by precipitation amount, emission intensity, and atmospheric processing, and highlights the importance of dissolved organic carbon as a major component of the atmospheric carbon cycle. In precipitation, DOC concentrations can equal or even exceed the combined concentrations of nitric and sulfuric acids, underscoring the substantial but often overlooked contribution of organic carbon to rainwater chemistry (Willey et al., 2000). Rainwater and cloud water DOC influences rainwater acidity, photochemistry, visibility, trace-metal complexation, cloud albedo, and nutrient delivery to ecosystems (Facchini et al., 1999; Seitzinger et al., 2003; Seitzinger & Sanders, 1999).

Spatial gradients in rainwater DOC are well pronounced. Deposition fluxes in Africa, and Central and South America (32–101 kg C ha^{-1} yr^{-1}) are up to 7 times higher than in North America, Europe, or Asia (14–17 kg C ha^{-1} yr^{-1}), due to higher precipitation in tropical latitudes (∼1,700 mm yr^{-1} vs. 800 mm yr^{-1} in temperate regions). DOC deposition is primarily driven by rainfall amount when annual precipitation is >1,400 mm yr^{-1}. Below this rainfall threshold, emission intensity plays an equally important role (Cao et al., 2025). Furthermore, temporal trends in DOC show regional variability. In a number of long-term data sets, DOC concentrations exhibit little change over decadal scales despite shifts in land-use practices, such as the partial phase-out of sugarcane burning in Brazil; in these tropical regions, ongoing biomass burning remains the dominant DOC source, exceeding fossil fuel and natural biogenic contributions (Godoy-Silva et al., 2017). Elsewhere, rising DOC has been linked to warmer temperatures (Freeman et al., 2001), fossil-fuel combustion (Cao et al., 2025; Liptzin et al., 2022), changes in hydrology (Tranvik & Jansson, 2002), increases in atmospheric CO_2 (Freeman et al., 2004), and declines in acid deposition (Driscoll et al., 2003; Liptzin et al., 2022; Skjelkvåle et al., 2005). For instance, in China, decreases in DOC deposition since ∼2010 reflect declines in OC and VOC emissions (Cao et al., 2025).

Global estimates of DOC wet deposition further illustrate the significance of DOC but also reveal substantial uncertainties. Early assessments suggested an average flux of ∼430 Tg C yr^{-1} based on a limited number of observation sites (Willey et al., 2000). Subsequent studies, incorporating broader spatial coverage including tropical and urban regions, revised this estimate upward to ∼658 Tg C yr^{-1} (Iavorivska et al., 2016), while more recent syntheses based on an expanded data set of 172 observations (1985–2024) suggest intermediate values around ∼460 Tg C yr^{-1} (Cao et al., 2025). These estimates remain considerably higher than those predicted by global models (Safieddine & Heald, 2017), reflecting persistent discrepancies driven by uneven spatial coverage and the historical underrepresentation of key regions such as the tropics and China (Cao et al., 2025).

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3.2.1. Chemical Composition

The molecular composition of cloud and rainwater DOM is highly complex, as revealed by advanced techniques such as Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS), which detect hundreds to thousands of distinct molecular formulae, including oxygenated compounds, organosulfates, and oligomeric species (Altieri et al., 2009b). However, because FT-ICR-MS provides molecular formula information rather than direct compound-specific identification or quantification, these results primarily illustrate non-target characterization of DOM composition. This complexity reflects the diverse origins and multiphase processing of atmospheric organic matter, with atmospheric oxidation further increasing DOM structural diversity and oxidation state.

Broadly, cloud and rainwater DOC comprises several major classes of compounds:

- *Volatile and semi-volatile organic compounds (VOCs and SVOCs)* encompass both primary emissions and secondary oxidation products and form a chemically continuous spectrum from highly water-soluble oxygenated species to hydrophobic semi-volatile compounds associated with aerosols and colloidal organic matter. These compounds contribute substantially to DOC and influence rainwater acidity, redox chemistry, and overall reactivity.
- *Nitrogen-containing organic compounds*, including amino acids and protein-like substances, typically account for approximately 2%–20% of DOC (Willey et al., 2000, 2006). These compounds are linked to biological sources such as plants, algae, microorganisms, and aerosols (Milne & Zika, 1993). Fluorescence-based studies have identified tyrosine-like (TYLIS), tryptophan-like (TRYLIS), and protein-like substances (PRLIS), further highlighting the importance of biological inputs to rainwater DOM (Li et al., 2026; Liptzin et al., 2022; Muller et al., 2008). Furthermore, Total Organic Nitrogen (TON) and Dissolved Organic Nitrogen (DON) are also commonly monitored together with DOC (Gioda et al., 2008).
- *Carbohydrates and polyols*, derived from primary biological emissions or secondary organic aerosol (SOA) formation pathways, are also present in rainwater and cloud water and contribute to the labile fraction of dissolved organic matter (Bianco, Pailler, et al., 2025; Willey et al., 2000).
- *Humic-like substances (HULIS)* represent a major macromolecular fraction of DOC. These compounds are structurally similar to aquatic humic substances but are primarily formed through atmospheric oxidation processes. HULIS play an important role in metal complexation, radical chemistry, and cloud microphysics (Graber & Rudich, 2006; Kiss et al., 2003), and have been described in the literature as atmospheric humic matter, macromolecular compounds, or polycarboxylic acids (Gelencsér et al., 2000; Varga et al., 2001; Zappoli et al., 1999).
- In addition, rainwater contains a wide range of *anthropogenic semi-volatile and persistent organic pollutants (POP)*, including currently used pesticides (CUPs) such as triazines, chloroacetamides, neonicotinoids, and pyrethroids, as well as legacy contaminants such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), per- and polyfluoroalkyl substances (PFAS), and organophosphate esters (OPEs). These compounds are typically present at trace concentrations but are globally distributed due to efficient long-range atmospheric transport and wet deposition. Many exhibit enhanced apparent solubility in rainwater, often exceeding Henry's law predictions due to interfacial processes and association with organic matter (Bianco, Nibert, et al., 2025; Casas et al., 2021; Cousins et al., 2022; Décuq et al., 2022; Dias et al., 2025; Gray et al., 2022; Levsen et al., 1993; Putri et al., 2025; Ruggirello et al., 2010; Wu et al., 2025).

Despite advances in analytical techniques, a substantial fraction of DOC remains chemically unresolved, reflecting the complexity of multiphase atmospheric organic chemistry (Dominutti et al., 2022; Herckes et al., 2013).

3.2.2. Microbial Communities and Biological Contribution

Rainwater and cloud water host a range of microbial communities, including bacteria, cyanobacteria, and microalgae, that contribute to the multiphase processing of atmospheric organic matter and influence chemical composition. Although microbial abundances in rainwater are relatively low (10^2–10^5 cells mL^{-1}) compared to cloud water and are far below those in aquatic systems (Guillemette et al., 2023; Joyce et al., 2019; Péguilhan et al., 2021), many taxa remain viable and metabolically active (even at very low organic matter conditions). These microorganisms are capable of degrading trace dissolved organics, including low-molecular-weight carboxylic acids in rainwater (Guillemette et al., 2023; Kawamura & Kaplan, 1990) and in cloud-water (Vaïtilingom

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et al., 2010). As a result, wet deposition acts not only as a chemical transfer pathway but also as a biological vector, linking atmospheric microbial communities with ecosystem functioning, biogeochemical cycling, and even epidemiological processes (Joyce et al., 2019; Wiśniewska et al., 2022).

However, the efficiency of microbial transformation is strongly constrained by residence time. Most biologically mediated reactions are expected to occur within cloud droplets or fog, where aqueous lifetimes are sufficiently long to sustain metabolism, or after deposition to surface environments. In contrast, the brief lifetime of falling raindrops (typically minutes) limits in situ biological processing during precipitation, positioning rainwater primarily as an integrative transport medium rather than a dominant reaction environment.

3.3. Rainwater Acidity and Buffering

Because VOC oxidation strongly controls the production of organic acids, understanding rainwater acidity requires consideration of multiphase VOC chemistry alongside inorganic processes.

Under natural conditions, rainwater equilibrated with atmospheric CO_2 has a pH $\approx$ 5.6 due to carbonic acid (H_2CO_3) formation. Deviations from this value reflect the balance between acidic inputs and neutralizing agents (Charlson & Rodhe, 1982). Inorganic acidity is primarily driven by sulfuric (H_2SO_4) and nitric (HNO_3) acids formed from the oxidation of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) (Galloway et al., 1984; Pye et al., 2020). These strong acids dissociate extensively in aqueous phases, releasing protons and lowering pH.

Acidity is partially moderated by neutralization processes involving alkaline species such as NH_4^+, Ca^{2+}, Mg^{2+}, and mineral dust, collectively contributing to the acid-neutralizing capacity (ANC) of precipitation (Al-Momani et al., 1995; Glavas & Moschonas, 2002; Keresztesi et al., 2019, 2020; Khemani et al., 1989). Here, ANC refers to the capacity of alkaline species to consume free hydrogen ions generated by strong acids, thereby reducing precipitation acidity relative to that expected in the absence of neutralizing compounds. The efficiency of this neutralization varies regionally, depending on emission sources and the presence of dust and ammonia. For example, Saharan dust intrusions in southern Europe contribute significantly to ACN through the presence of calcium- and magnesium-rich carbonate minerals (Bandrés et al., 2026; Cerro et al., 2020; Pey et al., 2020).

Differences between cloud and rainwater pH reflect dilution, scavenging, and intra-droplet chemistry (Collett et al., 1993; Shah et al., 2020). Rainwater pH exhibits strong spatial and temporal variability, ranging from <4.5 in heavily polluted regions to >8 in dust- or ammonia-rich environments (Laouali et al., 2021; Prakash et al., 2023). Seasonal and regional differences are driven by shifts in emission sources, air-mass trajectories, and precipitation patterns (Keresztesi et al., 2020; Likens et al., 1996; Willey et al., 2006).

3.3.1. Contribution of VOC-Derived Organic Acids to Acidity

Organic acids derived from VOC oxidation (and also from direct vegetation emission) represent a significant and often dominant component of rainwater acidity, particularly outside heavily industrialized regions. Compounds such as formic, acetic, and oxalic acids are produced through both direct emissions and secondary formation via gas-phase and aqueous-phase oxidation of VOCs (Paulot et al., 2011).

In urban environments, organic acids typically contribute 16%–35% of precipitation acidity after partial neutralization by alkaline constituents, whereas in remote or biogenic regions they can account for up to 90% of total acidity (Andreae et al., 1988; Kawamura et al., 1996; Paulot et al., 2011; Peña et al., 2002). Their relative importance varies geographically, with organic acidity dominating in tropical and forested environments where biogenic emissions are abundant, while inorganic acids remain the primary contributors to precipitation acidity in industrialized regions (Cruz et al., 2019; Kassamba-Diaby et al., 2023; Peña et al., 2002; Shah et al., 2020; Sun et al., 2016).

Multiphase interactions between VOC oxidation products and inorganic species further modulate acidity. For example, organic acids can interact with sulfur and nitrogen chemistry, influence cloud-phase oxidation rates, and contribute to secondary organic aerosol formation. Long-term trends in organic acidity reflect changes in both VOC emissions and anthropogenic pollution controls, with decreases observed in regions where SO_2 and VOC emissions have declined (Willey et al., 2006).

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4. VOCs in Rainwater

Volatile organic compounds and their oxidation products are a major yet poorly constrained fraction of DOC in rainwater. Although early studies showed that VOCs can account for a substantial share of precipitation DOC (50% in North Carolina and up to 56% in São Paulo; Coelho et al., 2008; Willey et al., 2000), direct and systematic measurements remain scarce, leaving their sources, seasonality, and depositional pathways far less understood than their gas-phase chemistry. In this review, "rainwater VOCs" encompasses VOCs and SVOCs detected in precipitation. This includes compounds transferred directly from the gas phase via Henry's law partitioning, VOC-derived oxidation products formed through aqueous-phase processing, and species delivered through particle scavenging and aerosol washout (e.g., PAHs). Whilst cloud water, fog, and rainwater are chemically linked through multiphase atmospheric processing, they represent distinct aqueous compartments with different residence times and scavenging mechanisms. Cloud and fog droplets primarily reflect in situ aqueous-phase processing, whilst rainwater integrates both in-cloud chemistry and below-cloud scavenging during atmospheric transport.

Together, these pathways contribute to the organic carbon pool in precipitation, heavily influencing wet-deposition chemistry and impacts. Once dissolved, VOCs undergo aqueous-phase reactions that generate organic acids and secondary oxygenated products. These VOC-derived compounds often dominate rainwater acidity in forested, remote, and tropical regions (Andreae et al., 1988). Rainwater therefore functions as both a sink and a conveyor of labile organic carbon shaped by multiphase chemistry, highlighting the need for more extensive field data to resolve their concentrations, transformations, and biogeochemical significance.

4.1. Types of VOCs Detected in Rainwater

Targeted and untargeted analyses have identified the following VOCs, SVOCs, and VOC-derived compounds in rainwater, cloud water, fog, snow, or stormwater-associated precipitation (Table 1):

- *Low–molecular-weight organic acids (C_1–C_6) and oxygenated derivatives*: formic, acetic, propionic, pyruvic, lactic, glyoxylic, glycolic, oxalic, malonic, succinic, glutaric, adipic, phthalic, pinonic acids and long-chain dicarboxylic acids (C_7–C_{13}), are widely reported in rain and cloud water (Kawamura & Kaplan, 1983; Kieber et al., 2002; Shah et al., 2020; Sun et al., 2016; Vaïtilingom et al., 2010; Willey et al., 2000). Spanning a continuum from volatile species to low-volatility multifunctional oxidation products, they are a dominant organic fraction in precipitation, accounting for 14%–40% of rainwater DOC (Willey et al., 2000) and frequently driving acidity in remote and forested regions (Andreae et al., 1988; Willey et al., 2000). Higher-molecular-weight organic acids (e.g., fatty acids) are also present but are generally considered non-volatile (Seidl, 2000).
- *Aldehydes*, *ketones*, *carbonyls*, *alkanes and ethers* including formaldehyde, acetaldehyde, propanal, butanal, pentanal, hexanal, nonanal, decanal, benzaldehyde, acetone, 2-butanone, acrolein, glyoxal, methylglyoxal, glycolaldehyde, pinonaldehyde, acetamide, hexane, and gasoline additives such as methyl tert-butyl ether (MTBE), are widely detected in rain and cloud water (Chon et al., 2015; Dabrowska & Nawrocki, 2013; Godoy-Silva et al., 2017; Grosjean & Wright, 1983; Lopes & Bender, 1998; Munger et al., 1995; Nguyen et al., 2020; Polkowska et al., 2006; Steinberg & Kaplan, 1984). These species typically represent a small but highly reactive DOC fraction (Grosjean & Wright, 1983; Munger et al., 1995; Polkowska et al., 2006; Steinberg & Kaplan, 1984; Taguchi et al., 2012; Willey et al., 2000), are efficiently scavenged by cloud droplets, and often reflect secondary atmospheric oxidation processes (Levsen et al., 1993).
- *Alcohols* and small oxygenated VOCs including methanol, ethanol, propanol, isopropanol, butanol, methylfuran, and acetaldehyde-derived species have also been detected (Campos et al., 2007; Felix et al., 2014; Mullaugh et al., 2015; Muller et al., 2008).
- *Aromatic hydrocarbons*, *phenols and PAHs*: benzene, toluene, ethylbenzene and xylene (BTEX), trimethylbenzenes, benzoic acid, phthalimide, phthalic anhydride, 1,2-benzenedicarboxylic acids, benzonitrile, phenols (including cresols and substituted nitrophenols), and both low- and high-molecular-weight PAHs (e.g., naphthalene, methylnaphthalene, phenanthrene, fluoranthene, pyrene, benzo[a]pyrene) have been reported in rain and cloud water (Bianco, Nibert, et al., 2025; Chon et al., 2015; Dominutti et al., 2022; Konan et al., 2022; Levsen et al., 1993; Lopes & Bender, 1998; Mullaugh et al., 2015; Quaghebeur et al., 1983; Schummer et al., 2009; Šoštarić et al., 2017; Wang, Perroux, et al., 2020). PAHs illustrate the importance of the atmospheric volatility continuum: lower-molecular-weight compounds such as naphthalene occupy the

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Table 1
Volatile and Semi-Volatile Organic Compounds Reported in Rainwater and Cloud Water, Their Dominant Phase Association, and Representative Concentration Ranges

Compound class	Compounds reported in rainwater	Dominant phase in precipitation	Typical concentrations	Key references
Low–molecular-weight organic acids (VOC-derived DOC)	Formic, acetic, oxalic, malonic, succinic, …	Dissolved	1–5,000 μg L^{-1}; DOC: 0.1–10 mg C L^{-1}	Kawamura and Kaplan (1983), Kieber et al. (2002), Sun et al. (2016), Willey et al. (2000)
Aldehydes, ketones, and carbonyls	Formaldehyde, acetaldehyde, propanal, butanal, pentanal, hexanal, nonanal, decanal, benzaldehyde, acetone, 2-butanone, acrolein, glyoxal, methylglyoxal, glycolaldehyde, pinonaldehyde, acetamide, benzonitrile	Dissolved (gas scavenged)	0.1–100 μg L^{-1} (formaldehyde often 0.5–50 μg L^{-1})	Chon et al. (2015), Dabrowska and Nawrocki (2013), Grosjean and Wright (1983), Munger et al. (1995), Polkowska et al. (2006), Steinberg and Kaplan (1984)
Alcohols and small oxygenated VOCs	Methanol, ethanol, propanol, isopropanol, butanol, methylfuran	Dissolved	0.1–50 μg L^{-1} (methanol frequently dominant)	Felix et al. (2014), Mullaugh et al. (2015), Muller et al. (2008); Willey et al. (2019)
Aromatic hydrocarbons (BTEX and derivatives)	Benzene, toluene, ethylbenzene, o-, m-, p-xylene, trimethylbenzenes, naphthalene, methylnaphthalenes	Mixed (dissolved + particulate)	1–1,000 ng L^{-1} (occasionally up to μg L^{-1} in polluted regions)	Bąk et al. (2025), Garban et al. (2002), Mullaugh et al. (2015), Quaghebeur et al. (1983), Šoštarić et al. (2017)
Polycyclic aromatic hydrocarbons (PAHs)	Naphthalene, phenanthrene, fluoranthene, pyrene, benzo[a]pyrene, other LMW and HMW PAHs	Predominantly particulate	0.1–100 ng L^{-1} (LMW higher in dissolved, HMW particulate)	Birgül et al. (2011), Casas et al. (2021), Garban et al. (2002), He and Balasubramanian (2010), Konan et al. (2022)
Biogenic hydrocarbons and terpenoids	Isoprene, α-pinene, β-pinene, limonene; terpene oxidation products	Mixed (dissolved + gas-scavenged + particulate)	<1–10 ng L^{-1} (parent compounds); ~10–100 ng L^{-1} (oxidation products)	Dominutti et al. (2022), Wang, Perroux, et al. (2020)
Phenols and nitrophenols	Phenol, cresols, nitrophenol, substituted nitrophenols	Mixed (dissolved + particulate)	50–2000 ng L^{-1}	Bianco, Nibert, et al. (2025), Levsen et al. (1993), Schummer et al. (2009)
Volatile organohalogens (VOX)	Chloroform, carbon tetrachloride, dichloromethane, trichloroethene, tetrachloroethene, 1,1,1-trichloroethane, cis-1,2-dichloroethene, bromodichloromethane, dibromochloromethane, methyl iodide	Dissolved (gas scavenged)	1–100 ng L^{-1}	Gilfedder et al. (2007), Lopes and Bender (1998)
Fuel additives and industrial solvents	MTBE, TCE, PCE, methylene chloride, chloroform	Dissolved	10–500 ng L^{-1}	Lopes and Bender (1998), Mullaugh et al. (2015)
CUP/SVOCs	Atrazine, tebuconazole, neonicotinoids	Mixed	0.1 ng L^{-1} up to 2 μg L^{-1}	Bianco, Nibert, et al. (2025), Dias et al. (2025), Putri et al. (2025)
Persistent and semi-volatile organic pollutants	Organochlorine pesticides (HCHs, DDTs), PCBs, chlorinated dioxins and furans (PCDD/Fs)	Predominantly particulate	0.01–10 ng L^{-1}	Agrell et al. (2002), Casas et al. (2021), Noori et al. (2025)

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Table 1
Continued

Compound class	Compounds reported in rainwater	Dominant phase in precipitation	Typical concentrations	Key references
Untargeted/complex organic mixtures	Unresolved complex mixtures (UCM) of hydrocarbons; phthalates; oligoesters; organosulfates; nitrooxy-organosulfates; amines; azaarenes	Mixed (dissolved + particulate)	μg L^{-1} to mg L^{-1} (bulk DOM); individual compounds typically ng–μg L^{-1}	Altieri et al. (2009b), Chon et al. (2015), Kieber et al. (2002), Willey et al. (2000)

Note. VOCs in rainwater and cloud water refer to atmospherically volatile and semi-volatile organic compounds detected in precipitation, regardless of their dominant scavenging pathway. While many compounds are incorporated through gas–aqueous partitioning governed by Henry's law, others—particularly less soluble species such as aromatic hydrocarbons, phenols, PAHs, and semi-volatile organic pollutants—are transferred predominantly through particle scavenging and aerosol washout. For these compounds, rainwater concentrations may reflect particulate-associated inputs rather than direct gas dissolution and can exceed Henry's law predictions owing to aerosol dissolution, interfacial partitioning, or organic co-solvent effects. Thus, gas-scavenged VOCs represent only a subset of the total dissolved organic compounds detected in precipitation. Reported concentration ranges are compiled from multiple field studies and are intended to represent order-of-magnitude variability across environments rather than precise values from individual data sets. Typical values correspond to the most commonly reported concentrations under background or moderately polluted conditions, whereas maximum values represent elevated concentrations observed during pollution episodes, first-flush events, biomass-burning influence, or other extreme atmospheric conditions. All concentration ranges are derived directly from the cited literature and, where multiple studies report comparable values, represent aggregated envelopes supported by those data sets. Where available, values are based on recent observational studies (2015–2026). Earlier benchmark measurements are retained for compound classes lacking comprehensive modern data sets, particularly low-molecular-weight organic acids, and remain supported by more recent dissolved organic carbon (DOC) observations and modeling constraints. Reported concentrations may vary substantially with precipitation type (rain, fog, or cloud water), sampling strategy (event-based vs. bulk collection), site characteristics (remote, rural, urban, or industrial), and analytical methodology (targeted vs. untargeted approaches). Consequently, the reported ranges should be interpreted as indicative rather than universal values. Phase classifications ("dissolved," "particulate," and "mixed") denote the dominant association in precipitation samples but may vary according to compound volatility, atmospheric processing, and environmental conditions. Overall, recent analytical advances have largely confirmed previously reported concentration magnitudes while greatly expanding the diversity of compounds detected, from a relatively limited suite of oxygenated VOCs to a broader spectrum that includes VOCs, SVOCs, persistent organic pollutants (POPs), and multiphase transformation products. Additional information on concentration ranges is provided in Text S1 in Supporting Information S1.

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more volatile end of the PAH volatility continuum and can partition between the gas and aqueous phases, whereas higher-molecular-weight PAHs are predominantly SVOCs associated with atmospheric particles and are scavenged mainly through particulate wet deposition.

- *Biogenic hydrocarbons and terpenoids* such as isoprene, α-pinene, β-pinene, limonene and related terpene oxidation products are detected primarily in cloud water and precipitation influenced by vegetation (Dominutti et al., 2022; Spolnik et al., 2020; Wang, Perroux, et al., 2020).
- *Volatile organohalogens (VOX)*: chloroform, carbon tetrachloride, dichloromethane, trichloroethene, tetrachloroethene (PCE), 1,1,1-trichloroethane, cis-1,2-dichloroethene, bromodichloromethane, dibromochloromethane, methyl iodide (CH_3I) and related halogenated solvents occur at trace levels in precipitation and play roles in halogen cycles, photochemistry and oxidant regulation (Gilfedder et al., 2007; Kawamura & Kaplan, 1983; Lopes & Bender, 1998; Mullaugh et al., 2015).
- *Other VOC/SVOC species detected* include legacy organochlorine pesticides (e.g., HCHs, DDTs), CUPs, polychlorinated biphenyls (PCBs), chlorinated dioxins and furans (PCDD/Fs) (Agrell et al., 2002; Bianco, Nibert, et al., 2025; Dias et al., 2025; Leuenberger et al., 1988; Noori et al., 2025; Putri et al., 2025). Furthermore, untargeted analyses have revealed unresolved complex mixtures of hydrocarbons, phthalates, oligoesters (especially those formed via in-cloud processing (Altieri et al., 2008)), organosulfates, nitrooxy-organosulfates, amines (such as dimethylamine (Corral et al., 2022)), azaarenes, and hundreds of additional molecular structures (Altieri et al., 2009b, 2009a, 2012; Chon et al., 2015; Kawamura & Kaplan, 1983).

Despite this structural diversity, the existing literature is heavily skewed towards low-molecular-weight oxygenated VOCs, particularly short-chain carboxylic acids (e.g., formic and acetic acid) and other soluble compounds, reflecting both historical research priorities (e.g., acid deposition) and analytical feasibility. In contrast, hydrophobic or volatile species, such as BTEX, biogenic terpenes, or intermediate transformation products, are underrepresented due to analytical challenges and sampling losses. This introduces a significant uncertainty in global assessments of VOC wet deposition, potentially underestimating the role of hydrophobic and semi- and volatile compounds to multiphase atmospheric processes.

4.2. Sources and Variability of Rainwater VOCs

The abundance of cloud and rainborne VOCs reflects the interplay between primary emissions, secondary atmospheric formation, and multiphase processes such as gas–aqueous partitioning and in-cloud and below-cloud scavenging, modulated by air-mass history and precipitation characteristics (Campos et al., 2007; Willey et al., 2019).

Primary sources to rainwater include biogenic inputs from vegetation, soils, microbes, pollen, and spores (Coble et al., 1990; Milne & Zika, 1993), as well as marine organics from sea spray. Forested regions are major contributors of isoprenoids and other biogenic volatile organic compounds (BVOCs) (Seco et al., 2007; Šimpraga et al., 2019; Yáñez-Serrano et al., 2020, 2025), which undergo rapid oxidation to water-soluble organic acids and carbonyls (e.g., pinonaldehyde, glycolaldehyde, glyoxal, methylglyoxal) that readily incorporate into cloud droplets and rainwater (Altieri et al., 2009b; Kawamura et al., 2001; Satsumabayashi et al., 2001). Consequently both air mixing ratios and rainborne VOC and VOC-derived products concentrations peak during the growing season (Andreae et al., 1988; Dominutti et al., 2022; Green et al., 2025; Jardine et al., 2011; Siudek et al., 2015; Tripathy et al., 2026; Willey et al., 2000; Yáñez-Serrano et al., 2021). Emerging evidence suggests that climate-driven changes in vegetation phenology and composition may further increase BVOCs emissions in some regions, potentially altering the organic composition of precipitation (Green et al., 2025; Liptzin et al., 2022; Peñuelas & Llusià, 2003; Seco et al., 2015, 2022; Yáñez-Serrano et al., 2020, 2026).

Anthropogenic activities (primarily traffic, industrial emissions, and fossil-fuel combustion) also contribute substantially to rainwater VOCs (Rivera-Rivera et al., 2020). Urban and industrial environments are enriched in alcohols, aromatics, halogenated solvents, and fuel hydrocarbons, with concentrations influenced by local emissions, boundary-layer dynamics, and storm history (Campos et al., 2007; Felix et al., 2014; Mullaugh et al., 2015; In 't Veld et al., 2024). In regions using ethanol-based fuels, VOC contributions to rainwater DOC can be exceptionally high (Coelho et al., 2008). Biomass burning is another major source of large quantities labile organic carbon that can dominate both natural and anthropogenic components (Godoy-Silva et al., 2017; Tripathy et al., 2026), with specific fire conditions (e.g., smoldering or flameless combustion) enhancing VOC emissions (Garcia-Hurtado et al., 2014; Green et al., 2025).

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In addition to these primary inputs, secondary formation plays a critical role. Oxidation of VOCs and SVOCs in the gas phase or within cloud and rain droplets produces organic acids, aldehydes, peroxides, organosulfates, and HULIS, contributing to the molecular complexity of rainwater organics (Altieri et al., 2009b; Chebbi & Carlier, 1996). Secondary oxygenated VOC-derived compounds are ubiquitous in rainwater, often reflecting photochemical processing and in-cloud or below-cloud oxidation rather than direct emissions (Dabrowska & Nawrocki, 2013; Matsumoto et al., 2005). Highly soluble compounds dominate the dissolved organic fraction of precipitation, while less soluble VOCs typically contribute via their more water-soluble oxidation products. Seasonal variation is pronounced: cold-season precipitation and combustion plumes favor semi-volatile hydrocarbons and POPs, whereas "first-flush" rainfall following dry periods are often enriched in carbonyls and reactive oxygenated species (Birgül et al., 2011; Dabrowska & Nawrocki, 2013).

Global field observations demonstrate that rainwater acts as an integrative archive of atmospheric VOC emissions, chemical transformation and scavenging efficiencies. The spatial and seasonal variability reflects the sensitivity of rainwater VOC and derived compounds composition to ecosystem type, emissions and meteorology, reinforcing the need to interpret precipitation chemistry within a coupled atmosphere–biosphere framework.

4.3. Parameters Controlling VOCs in Rainwater

This section synthesizes the key chemical and physical controls on VOC partitioning into precipitation, emphasizing the mechanisms governing solubility, chemical transformations, scavenging efficiency, and the resulting impacts on rainwater chemistry.

4.3.1. Gas–Aqueous Partitioning, Solubility, and Physicochemical Rainwater Properties

Gas–aqueous partitioning controls the transfer of VOCs and SVOCs between atmosphere and condensed aqueous phases (cloud, fog, rain and aerosol liquid water) thereby regulating their processing and contribution to rainwater composition, acidity, and wet deposition (Sander, 2023). At thermodynamic equilibrium, the dissolution of a neutral gas into water is described by Henry's law:

$$C_{\mathrm{aq}} = H \cdot p_g$$

where C_{aq} (mol m^{-3}) is the aqueous concentration, p_g (Pa) is the gas-phase partial pressure, and H (mol m^{-3} Pa^{-1}) is the Henry's law constant (Sander, 2023). Higher H values correspond to higher solubility and more efficient gas uptake, allowing highly soluble species (e.g., formic and acetic acids, glyoxal, methylglyoxal, and aldehydes) to be rapidly scavenged during rainout and washout. Conversely, less soluble VOCs (e.g., isoprene, terpenes, benzene) enter the aqueous phase primarily through their oxidation products, which are incorporated after oxidative transformation (Ervens et al., 2011; Herrmann et al., 2015) or by changes in the physicochemical properties of rainwater (Šoštarić et al., 2017). Figure 2 depicts representative VOCs and VOC-derived products identified in cloud and rainwater across a range of Henry's law constants and volatilities within the Volatility Basis Set framework (Donahue et al., 2011), highlighting how physicochemical properties influence gas–aqueous partitioning, atmospheric transformation, and wet scavenging efficiency.

However, field studies consistently report higher-than-predicted VOC concentrations in rain, cloud water, fog, and dew relative to Henry's-law predictions (Coelho et al., 2008; Okochi et al., 2004; Sato et al., 2006; Šoštarić et al., 2016, 2017). Thus, the Henry's-law predictions often underestimate real aqueous partitioning for reactive organic compounds. The equilibrium is modulated in the atmospheric context by several processes and drivers:

- *pH and aqueous-phase ionization*: Reversible acid–base equilibria strongly modify partitioning by shifting the thermodynamic balance toward the dissolved phase. The pH exerts a stronger influence on ionizable compounds by enhancing effective solubility through dissociation. Dissociation increases the effective solubility of weak acids and bases beyond their neutral values, making uptake highly sensitive to droplet pH and buffering capacity (Franco et al., 2021; Sander, 2023). Acidic cloud-water conditions enhance the uptake of alkaline species while suppressing the solubility of weak organic acids. Reactions with oxidants or dissolved organic matter can transform volatile precursors into more soluble products, sustaining a continuous reactive uptake as observed for SO_2 hydration and oxidation to sulfate (Altieri et al., 2009b; Kieber et al., 1999; Muller et al., 2008; Sander, 2023; Southwell et al., 2010; Willey et al., 2012).

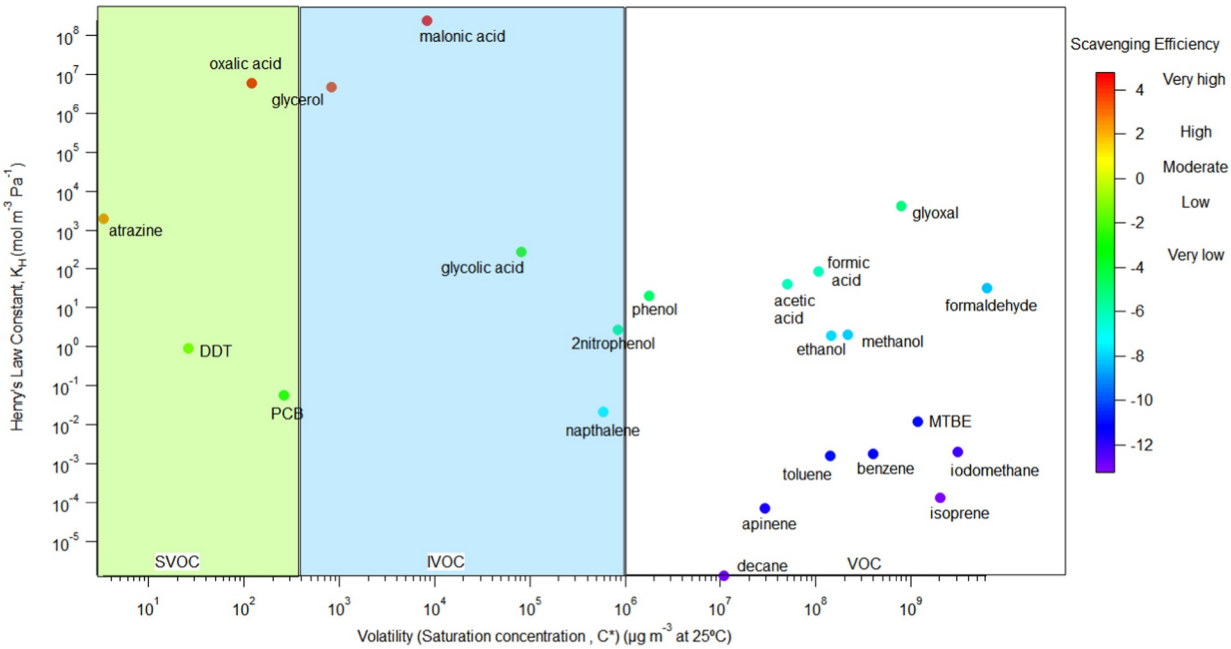

Figure 2. Conceptual relationship between volatility, aqueous solubility, and wet scavenging behavior for representative atmospheric organic compounds detected in cloud and rainwater. Compounds are positioned within the Volatility Basis Set (VBS) framework according to their effective saturation concentration and Henry's law constant, illustrating how physicochemical properties regulate gas–aqueous partitioning, atmospheric processing, and incorporation into precipitation. Highly soluble oxygenated compounds (e.g., formic acid, glyoxal, methylglyoxal) are efficiently scavenged into cloud and rain droplets, whereas less soluble hydrocarbons generally require atmospheric oxidation prior to significant aqueous uptake. Adapted from the VBS framework described in Donahue et al. (2011) and related atmospheric multiphase partitioning studies. Green shading stands for SVOC compounds, blue shading for IVOC (intermediate volatility) compounds and white shading for VOCs. See Text S2 in Supporting Information S1 for information on the data used for this figure.

- *Temperature*: Henry's constants decrease with increasing temperature, favoring volatilization and reducing aqueous concentrations. Conversely, lower temperatures enhance solubility and partitioning into droplets by strengthening hydrogen bonding and reducing acid dissociation, thereby enhancing uptake and raising pH. Temperature exerts a stronger influence on non-reactive species (Lopes & Bender, 1998; Stojić et al., 2019; Šoštarić et al., 2017).
- *Aqueous phase reactions*: many VOC oxidation products (i.e., VOC-derived products) undergo fast aqueous reactions (hydration, oligomerization, peroxidation) that consume dissolved gases and increase effective uptake from the gas phase, driving continuous chemical transformation (Iavorivska et al., 2016; Sato et al., 2006).

4.3.2. Droplet Chemistry: Inorganic Salts, Organics, and Surface Tension Effects

The microchemical environment of droplets is shaped by inorganic ions, organic acids, carbohydrates, and HULIS, many of which originate from VOC-derived products that constitute major components of cloud condensation nuclei, including SOA oligomers and organic acids (Altieri et al., 2009b). These constituents influence VOC solubility through co-solvent interactions and modifications to surface tension, with surface-active aerosols and VOCs reducing surface tension, facilitating droplet activation, and altering interfacial mass transport (Okochi et al., 2004; Sato et al., 2006). Organic-rich cloud water can therefore enhance uptake of moderately soluble VOCs, while salts modulate activity coefficients and stabilize specific ion–organic interactions (Allou et al., 2011; Tripathy et al., 2026). In addition, some VOC-derived compounds, such as formaldehyde, are produced within cloud droplets via aqueous-phase oxidation of precursors and can subsequently outgas, linking in-cloud chemistry with gas–aqueous exchange (Franco et al., 2021).

Salting-out and electrolyte effects. High concentrations of dissolved inorganic ions such as Na^+, K^+ or Cl^- lower Henry's constants, thereby reducing VOC solubility by the "salting-out" effect (Sander, 2023). At 35 g L^{-1} NaCl, Henry's constants for formaldehyde and benzaldehyde decrease by 27%–66% and 12%–21%, respectively (Allou et al., 2011). However, (Šoštarić et al., 2017) found enhanced TEX (toluene, ethylbenzene, xylenes) transfer to

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rainwater under high-salt conditions, suggesting local deviations due to co-varying meteorology or organic coatings.

Surface tension, *surfactants and organic matrices*. Rain, fog, and cloud samples may exhibit reduced surface tension relative to pure water, primarily due to surface-active organic compounds. Dissolved organic matter acts as a co-solvent, enhancing the apparent solubility and retention of hydrophobic VOCs in atmospheric waters (Okochi et al., 2004; Sato et al., 2006). HULIS are particularly effective surfactants, exhibiting surface activities several times greater than mono- and dicarboxylic acids and many neutral organics or polycarboxylic acids (Facchini et al., 2000). Organic films and interfacial surfactants influence aerosol and cloud-droplet chemistry by altering molecular accommodation, heterogeneous reactions, and non-ideal partitioning behavior (Nozière et al., 2014). Recent modeling using octanol–water partition coefficients (K_{ow}) further demonstrated that surfactant coatings can enhance the partitioning and retention of hydrophobic VOCs beyond predictions based solely on Henry's law equilibrium (Aiyuk et al., 2025). Organic macromolecules also modify droplet microenvironments, alter acid–base and redox equilibria, and facilitate secondary formation of oxygenated VOC-derived compounds (Altieri et al., 2009b; Seitzinger et al., 2003). For example, species like formaldehyde can be generated in situ via aqueous oxidation of precursors and subsequently outgas, establishing a dynamic bidirectional link between cloud chemistry and gas–aqueous exchange (Franco et al., 2021).

4.3.3. Microphysical and Meteorological Controls on Wet Deposition

Wet deposition efficiency of VOCs and VOC-derived compounds is governed by precipitation microphysics (i.e., droplet size, cloud depth), meteorological conditions (i.e., updraft velocity, atmospheric layering), and precipitation characteristics (i.e., type, intensity, duration, fall speed). All these variables determine gas–liquid partitioning, scavenging ratios, and depositional fluxes. Because VOCs and VOC-derived compounds span a wide range of solubilities and reactivities, their removal efficiencies vary strongly with droplet properties, atmospheric mixing, and storm dynamics, resulting in large spatial and temporal variability in rainwater composition.

Precipitation type and droplet size exert a primary control on VOC scavenging. Fog and cloud droplets, characterized by micrometer-scale sizes and long atmospheric residence times, scavenge VOCs more efficiently than rain, particularly for soluble compounds, for example, aldehydes (Levsen et al., 1993; Matsumoto et al., 2005). Scavenging rates depend on Henry's law constants and droplet-size distributions: large droplets preferentially remove low-solubility gases, whereas small droplets dominate uptake of highly soluble VOCs due to their greater surface-area-to-volume ratios (Bi & Isaacman-VanWertz, 2022; Hicks, 2005). For compounds with Henry's constants exceeding $\sim 10^3$ mol m^{-3} Pa^{-1}, wet-deposition timescales converge to ~4–6 hr, indicating rapid atmospheric removal largely independent of local microphysical variability (Bi & Isaacman-VanWertz, 2022).

Meteorological controls such as temperature, wind speed or humidity regulate VOC uptake by controlling gas–liquid contact time and solubility. Low wind speeds and weak turbulence enhance scavenging by increasing residence time near droplets, whereas high wind speeds disperse VOCs and reduce local uptake efficiency (Kalkan et al., 2025; Šoštarić et al., 2017). High temperatures decrease VOC solubility and suppress wet removal, especially for moderately soluble aromatics (Šoštarić et al., 2017). Field studies show that ambient gas-phase concentrations and air–rain temperature gradients are often stronger predictors of VOC partitioning than wind speed or ionic composition alone (Stojić et al., 2019; Šoštarić et al., 2017).

At regional and global scales, precipitation frequency and duration exert a stronger control on VOC wet removal than rainfall intensity, although intensity still modulates rainwater concentrations by balancing scavenging efficiency against dilution. Frequent, low-intensity precipitation reduces atmospheric gas more effectively than infrequent heavy storms; slower fall speeds and longer droplet residence times enhance scavenging (Fang et al., 2011; Mahowald et al., 2011; Wang et al., 2021; Yao et al., 2024), while frequent events repeatedly reset atmospheric concentrations, increasing overall removal efficiency (Bi & Isaacman-VanWertz, 2022). Such conditions favor aldehyde and carbonyl uptake, whereas high-intensity events often yield dilution-dominated signals (Dabrowska & Nawrocki, 2013; Matsumoto et al., 2005).

For certain VOCs including BTEX, intensity alone is a poor predictor of rainwater levels as atmospheric stability and air–raindrop contact time exert a stronger influence (Šoštarić et al., 2017). Ultrafast and short heavy-rainfall events (<2 hr) can still deliver disproportionately large wet-deposition fluxes—up to 11-fold higher than typical rainfall (Uchiyama et al., 2017)—but these pulses coincide with marked dilution of dissolved VOCs during peak

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rainfall rates (Matsumoto et al., 2005). Consequently, wet scavenging proceeds as intermittent yet highly efficient removal episodes rather than a continuous sink, highlighting the role of rainfall intermittency in controlling VOC atmospheric lifetimes (Bi & Isaacman-VanWertz, 2022).

Influence of early-washout dynamics. The initial phase of precipitation (e.g., first millimeters or first hour) typically exhibits the highest VOC and DOC concentrations, reflecting rapid below-cloud scavenging of soluble gases and aerosols at rainfall onset, followed by dilution and saturation limitations as the event progresses ("first-flush" effect; Avery et al., 2009; Campos et al., 2007; Dabrowska & Nawrocki, 2013; Godoy-Silva et al., 2017; Matsumoto et al., 2005). This is particularly evident after a long dry period. Sequential collection of precipitation captures these dynamics, revealing that the concentrations of many organic pollutants decrease exponentially throughout a single event, with the initial fractions containing a disproportionately large share of the deposited mass (Alastuey et al., 2001). Research indicates that 40%–80% of the total wet-only deposition for major ions can occur within the first 2 mm of precipitation (Alastuey et al., 2001) highlighting the importance of early-washout processes. Particulate-associated organic pollutants such as pesticides exhibit similar first-flush behavior. Their early washout effect is driven by rapid below-cloud scavenging of both gas-phase and particulate phases (Bianco, Nibert, et al., 2025; Siebers et al., 1994). Pesticides partition heavily into the particulate phase in continental regions (e.g., reaching up to 99% for certain triazines), making them highly susceptible to efficient removal at rainfall onset (Mayer et al., 2024). Capturing these early-washout patterns is critical for assessing the environmental fate of emerging contaminants, as their atmospheric transport and deposition depend strongly on multiphase partitioning and reactivity (Wang et al., 2023). Conversely, concentrations remaining elevated throughout an extended, high intensity event indicate a dominant contribution from in-cloud processes (Bianco, Nibert, et al., 2025; Godoy-Silva et al., 2017). Concentrations generally decline as atmospheric reservoirs are depleted, although interruptions in rainfall allow rapid VOC resupply and renewed concentration peaks when rain resumes (Taguchi et al., 2012). Prolonged rain events reflect a balance between washout and resupply from below-cloud layers. Local resupply mechanisms, including plant transpiration (Felix et al., 2014), in situ photochemistry (Kieber et al., 1999; Southwell et al., 2010) or BVOC oxidation bursts after rainfall (Machado et al., 2024), can sustain elevated concentrations of certain species (e.g., methanol, formaldehyde), which are subsequently scavenged by ongoing precipitation (Felix et al., 2014).

Role of air mass history and atmospheric transport. Rainwater VOC composition reflects integrated atmospheric processing along air-mass trajectories, including source regions, oxidation history, and aerosol loading (Avery et al., 2009; Sakihama et al., 2008). Long-range transport delivers oxidized VOCs and particle-associated organics into precipitation far from emission sources, while boundary-layer height, cloud-base altitude, and synoptic flow patterns modulate scavenging efficiency (Bi & Isaacman-VanWertz, 2022; Mullaugh et al., 2015). Together, these processes highlight rainwater as an integrative archive of atmospheric transport, chemistry, and removal pathways linking emissions to ecosystem inputs.

Influence of aerosols. Aerosols play a central role in shaping VOC and VOC-derived composition in rainwater by acting as reservoirs for semi-volatile organics and as substrates for heterogeneous and aqueous-phase chemistry, producing secondary organic material that can be efficiently scavenged by droplets (Altieri et al., 2009b; Hodzic et al., 2013). Many VOC-derived organic acids commonly found in precipitation (such as formic, acetic, oxalic, and glyoxylic acids) originate from both direct gas dissolution and in-cloud oxidation of carbonyl precursors, with multiphase reactions (e.g., hydration and oxidation of methylglyoxal) substantially enhancing their abundance and acidifying potential (Altieri et al., 2009b; Franco et al., 2021; Muller et al., 2008). Beyond gas–aqueous partitioning, aerosol washout represents a dominant delivery pathway for less soluble and strongly particle-associated compounds, including PAHs and highly chlorinated organics, whose presence in precipitation primarily reflects particulate scavenging rather than direct dissolution. Organic–inorganic particle mixtures influence cloud droplet activation, cloud water acidity, and multiphase pathways for sulfate formation, halogen cycling, and metal-catalyzed radical chemistry, thereby affecting both precipitation efficiency and rainwater composition. Aerosol composition further regulates VOC partitioning, primarily through absorptive partitioning and aqueous (heterogeneous) reactions, while adsorption to particle surfaces plays a more limited but sometimes significant role, particularly for hydrophobic or aromatic compounds. Organic-coated particles can enhance multiphase reactivity (Huang et al., 2023), while sulfate-rich aerosols promote the formation of organosulfates and oligomeric SOA (Brüggemann et al., 2020; Fan et al., 2022), which are efficiently scavenged by precipitation (Zhang et al., 2024). In contrast, urban aerosol, soot, and mineral dust can reduce aqueous BTEX concentrations by 10%–20% through adsorption, representing a secondary but measurable pathway under these conditions,

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which is amplified under high humidity (Kalkan et al., 2025). Particle-phase dominance is evident for PAHs and highly chlorinated PCDD/Fs, which exhibit large washout ratios and exceed dissolved concentrations in rain (Noori et al., 2025). The presence of combustion-derived ions (e.g., K^+, NO_2^-) and dust-associated metals further modulates acidity and catalytic pathways, influencing heterogeneous reactivity and the fate of DOC in precipitation (Başak et al., 2010; Cheng et al., 2021; Conko et al., 2004; Heimburger et al., 2013; Hsu et al., 2010; Stojić et al., 2019).

Trace metals and mineral solubility in rainwater. Rainwater acidity and ionic composition strongly regulate the solubility of mineral dust and trace metals, indirectly shaping VOC partitioning and transformation in the aqueous phase. Acidic rain enhances dissolution of elements such as Fe, Al, Mn, and Cu, increasing ionic strength and modifying the solubility and reactivity of VOC-derived compounds (Mahowald et al., 2005; von Glasow & Crutzen, 2003; Willey et al., 2006, 2012). Organic acids produced from VOC oxidation (particularly formate, acetate, and oxalate) further promote metal dissolution and stabilize dissolved metals through ligand complexation, whereas neutralization by ammonia or dust raises pH and suppresses uptake of weak organic acids (Willey et al., 2006). Global variability in rainwater pH (pH ∼ 4.5–8.5) therefore contributes to regional differences in VOC–metal interactions and wet deposition chemistry (Laouali et al., 2021; Prakash et al., 2023). Dissolved metals also influence aqueous radical chemistry and multiphase oxidation pathways that control VOC fate in precipitation. For example, a number of organic ligands derived from chromophoric dissolved organic matter (CDOM), humic-like substances, soil organic matter or biomass burning have a strong affinity for complexing trace metals with high stability constants, for example, Cu (log $K \approx 9$–14), maintaining free hydrated Cu^{2+} at low levels when ligands are in excess (Witt et al., 2007). Where Cu levels exceed ligand availability, weaker complexes and free Cu^{2+} activities dominate, which has important implications in terms of bioavailability and ecotoxicology (Witt et al., 2007) and atmospheric catalytic redox reactions (Weschler et al., 1986). Transition metals, particularly Fe, are key drivers of aqueous atmospheric oxidation chemistry in cloud and rain droplets through redox cycling and catalytic radical formation (Deguillaume et al., 2005). VOC-derived organic ligands (including organic acids and multifunctional oxygenated compounds) can strongly complex Fe(II)/Fe(III), thereby influencing Fe solubility, photoreduction pathways, and Fenton-like radical production. These interactions regulate the formation of oxidants such as ·OH, or $SO_4{\cdot}^-$ and connect VOC multiphase chemistry to broader oxidative processing in atmospheric waters (Willey et al., 2012). In dust-rich regions, low solubility of aluminosilicate-bound elements contrasts with enhanced solubility under acidic and pollutant-influenced conditions during transport. These interactions show the complex interplay between the roles of metals, inorganic chemistry, and VOC oxidation controlling rainwater composition (Cheng et al., 2021; Hsu et al., 2010; Jickells et al., 2016).

4.4. Contribution of VOCs and Organic Acids to Cloud and Rainwater Acidity

4.4.1. Global Importance and Pathways of Organic Acid Formation

Organic acids derived from VOCs oxidation (i.e., VOC-derived compounds), or directly emitted, are major contributors to rainwater acidity across a spectrum of environments, often rivalling or exceeding inorganic acids. Across ecosystems, these organic acids are major contributors to total free acidity, accounting for up to 90% in remote regions (Andreae et al., 1988), ∼50% in parts of Australia (Gillett et al., 1990), >40% in African tropical forests (Galy Lacaux et al., 2005; Vet et al., 2014) and forming the majority of acidity in some urban settings such as Los Angeles, where wet deposition of monocarboxylic acids and aldehydes exceeds several thousand tons annually (Kawamura et al., 2001). Formic and acetic acids are typically dominant and can contribute up to 35% of acidity in anthropogenically influenced regions (Keene & Galloway, 1984; Peña et al., 2002). Observational evidence confirms these patterns worldwide, with formate contributing ∼43% of acidity in Venezuelan savannah rainfall (Sanhueza et al., 1989), formic acid dominating acidity in northern Australia (Shah et al., 2020), and mixtures of formic, acetic, and oxalic acids controlling acidity in subtropical forests of China (Sun et al., 2016).

Although primary emissions exist, most light organic acids in precipitation and clouds are produced secondarily through multiphase oxidation of VOCs (therefore they are termed VOC-derived compounds in this review) (Blando & Turpin, 2000; Franco et al., 2021). Aqueous reactions of small carbonyls (particularly methylglyoxal and glyoxal) generate glyoxylic, pyruvic, oxalic, lactic, malonic, and succinic acids commonly detected in rainwater (Altieri et al., 2009b). Formaldehyde is especially influential because it rapidly hydrates to methanediol (formaldehyde glycol) in aqueous solution and is efficiently oxidized in atmospheric water droplets, producing

formic acid and other low-molecular-weight organic acids that contribute to rainwater acidity, with reported decreases of up to ~0.3 pH units. Methanediol can also react with O_3 in the aqueous phase, further contributing to cloud- and rainwater processing and the formation of oxygenated products (Polkowska et al., 2006). Laboratory and mechanistic studies further demonstrate that aqueous-phase oxidation pathways efficiently produce and transform low-molecular-weight carboxylic acids through radical-mediated reactions and multiphase processing in atmospheric waters (Charbouillot et al., 2012). Together with gas-to-droplet partitioning, these processes help explain why carboxylic acids observed in rainwater generally exceed direct emission sources (Kawamura et al., 2001) and why their atmospheric removal is dominated by wet and dry deposition (Chebbi & Carlier, 1996).

4.4.2. Anthropogenic Modulation of Acidity and Interactions With Sulfur Chemistry

Trends in rainwater VOC-derived DOC reflect human influence: reductions in anthropogenic VOC emissions, including reformulated gasoline use in the United States, have led to measurable decreases in formic, acetic, and oxalic acids since the late 1990s (Cao et al., 2025; Liptzin et al., 2022; Willey et al., 2006). Sulfur-containing VOCs also shape acidity. Dimethyl sulfide (DMS) and other sulfur VOCs are oxidized to methanesulfonic and sulfuric acids, which contribute (together with organic and nitric acids) to atmospheric and precipitation acidity (Taylor Barrie & Kiene Ronald, 1989). This acidity influences multiphase chemistry by modifying proton-catalyzed reactions and the partitioning and transformation of oxygenated organic compounds across atmospheric phases (Surratt et al., 2008). In contrast, cloud and rain droplets are generally more dilute, and while they contribute to the redistribution and processing of soluble species, they are typically less favorable environments for acid-catalyzed organosulfate formation.

4.5. Chemical Transformations of VOCs Inside Cloud Droplets

Once incorporated into droplets, VOCs undergo extensive aqueous-phase transformations that differ markedly from gas-phase pathways and strongly influence rainwater composition by sustaining rainwater acidity and producing secondary dissolved organic matter (Altieri et al., 2009b). Dissolved compounds react with oxidants such as OH^-, NO_3^-, and SO_4^{2-}, under photochemical or acid-catalyzed conditions (Herrmann et al., 2015), producing oxygenated organics, organic acids, peroxides, oligomers, organosulfates, and nitrooxy-organosulfates (Altieri et al., 2009b; Khare et al., 1999; Surratt et al., 2008). Because aqueous hydration suppresses fragmentation, oxidation generally retains carbon skeletons and favors functionalization into mono- and dicarboxylic acids rather than the smaller radical fragments characteristic of gas-phase oxidation (Ervens et al., 2013; Khare et al., 1999; Warneck, 2005). These reactions shape radical budgets and acidity: terpenes are transformed into aldehydes and organic acids (Amaladhasan et al., 2022; Franco et al., 2021; Peña et al., 2002), aldehydes yield glyoxylic and pyruvic acids (Khare et al., 1999), and methanol oxidation produces formic acid along with hydrated formaldehyde intermediates. Although the residence time of falling raindrops is relatively short (minutes to tens of minutes), rapid processes including dissolution, hydration, acid–base equilibria, and fast radical reactions can still modify VOC composition during atmospheric transport, particularly in-cloud or during early stages of precipitation formation where contact times are longer. In contrast, microbial transformations are expected to occur primarily after deposition or during extended aqueous residence in clouds, fog, or surface waters, rather than during the brief lifetime of falling raindrops (Amaladhasan et al., 2022; Franco et al., 2021; Khare et al., 1999; Peña et al., 2002).

4.5.1. Aqueous Oxidation and Acid-Generating Pathways

Aqueous-phase reactions of VOCs supply substrates that enhance formation of low-volatility acids central to rainwater acidity, including glyoxylic, pyruvic, and oxalic acids (Ervens et al., 2013; Franco et al., 2021; Khare et al., 1999; Peña et al., 2002). These transformations are initiated by oxidants derived largely from the photochemistry of dissolved species, specially the photogenerated hydroxyl radical, which drives the oxidation capacity in clouds during the day (Bianco et al., 2020), and by transition-metal catalysis (Herrmann et al., 2015), enabling continued acid production during cloud and rain droplet lifetimes. In this way, VOCs dissolved in droplets not only undergo oxidation themselves but also facilitate pathways that convert other VOC oxidation intermediates into acids, helping sustain acidity beyond what would be predicted from gas-phase oxidation alone.

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4.5.2. Formation of Aqueous Secondary Organic Material (aqSOA)

A key outcome of aqueous oxidation is the formation of secondary organic material (aqSOA). Dicarboxylic acids such as oxalic, malonic, and succinic acids (compounds with limited gas-phase sources and low volatility, Figure 2) are produced efficiently from droplet chemistry (Ervens et al., 2013). In addition, aqueous-phase reactions of small carbonyls such as glyoxal and methylglyoxal promote oligomerization, yielding low-volatility products that contribute substantially to aqSOA formation (Altieri et al., 2009b). Furthermore, organosulfates and nitrooxy-organosulfates are produced under acidic sulfate-rich conditions from precursors including isoprene and monoterpenes (Darer et al., 2011; Hyttinen et al., 2020; Liggio & Li, 2006; Satsumabayashi et al., 2001; Surratt et al., 2008). These acid-catalyzed reactions can be particularly efficient in acidic aerosol particles, as demonstrated by the formation of IEPOX-derived organosulfates (McNeill et al., 2012; Surratt et al., 2008). Cloud droplets and rainwater, although typically less acidic due to dilution, can act as media for transport, dilution, and further aqueous-phase processing, thereby linking particle-phase formation to wet deposition. Their presence in rainwater has been confirmed by ultra–high-resolution mass spectrometry (Altieri et al., 2009b). The abundance of organosulfates derived from monoterpenes depends on aerosol acidity or sulfate availability (Chan et al., 2011; Hyttinen et al., 2020), and they modulate surface tension, hygroscopicity, and CCN activity (Hansen et al., 2015), and can alter deliquescence transitions of salts such as NaCl (Estillore et al., 2016). Their atmospheric persistence and long-range transport demonstrate low volatility and chemical stability (Hyttinen et al., 2020; Nguyen et al., 2014), highlighting the role of multiphase processing and aqueous-phase chemistry in controlling the regional transport and fate of organic material.

4.5.3. Aqueous Chemistry of Isoprene and Monoterpenes

Even VOCs with low solubility, such as isoprene or monoterpenes, undergo aqueous-phase reactions that contribute significantly to rainwater composition. In droplets, isoprene reacts with nitrous acid (HONO) to generate C_5 nitro compounds (molecular weights 129 and 229) (Rudziński et al., 2016), and with sulfate radicals to form organosulfates (molecular weight 182), while gas-phase oxidation of isoprene produces methylglyoxal, pyruvic acid, and isoprene epoxydiols (IEPOX), which can partition into droplets and undergo further aqueous processing (Altieri et al., 2009b; Darer et al., 2011; Fu et al., 2008; Surratt et al., 2008) Once formed in the aerosol phase, IEPOX-derived organosulfates and other low-volatility oxidation products can subsequently be incorporated into cloud and rainwater through aerosol activation and wet scavengingx (Surratt et al., 2008), thereby linking aerosol-phase chemistry with precipitation composition. Organosulfate esters derived from isoprene, α-pinene, β-pinene, limonene, α-terpinene, and γ-terpinene have been detected in precipitation (Altieri et al., 2009b), and nitrooxy-organosulfates serve as tracers of formation under acidic, high-NO_x conditions (Altieri et al., 2009b). Monoterpene oxidation forms pinonaldehyde (Satsumabayashi et al., 2001) and subsequent organosulfates, reinforcing the role of biogenic precursors in rainwater composition (Liggio & Li, 2006; Matsunaga et al., 2007). Concentrations and temporal variations of glyoxal and methylglyoxal (key isoprene photooxidation products) trace biogenic influence on cloud processing and wet deposition (Pang et al., 2017). Collectively, these pathways demonstrate that aqueous reactions of VOCs, including terpenes, aldehydes, methanol, and their oxidation intermediates, are central to the formation of rainwater-borne secondary organics, the recycling of acidity, and the downward flux of oxidized carbon to surface ecosystems. Evidence of terpenes and their oxidation products in clouds has been documented (Bianco et al., 2019; Pailler et al., 2024).

4.5.4. Microbial Processing and Rainwater as a Source of Labile Carbon

Rainwater chemistry is further shaped by microbial and chemical transformations occurring both during atmospheric processing and after deposition. Cloud and rainwater host active microbial communities capable of degrading formate, acetate, and succinate, among others, although most microbial turnover occurs over timescales of days to weeks in cloud droplets, fog water, collectors, or surface waters rather than during the brief atmospheric lifetime of falling raindrops (Herlihy et al., 1987; Khaled et al., 2021; Vaïtilingom et al., 2010). Because falling raindrops typically persist in the atmosphere for only minutes to tens of minutes, rapid processes such as dissolution, acid–base equilibria, hydration, and fast radical reactions are expected to dominate during precipitation events. Nevertheless, rainwater delivers significant quantities of labile DOC (largely derived from VOC oxidation), of which more than 50% can be consumed within 1 week by microorganisms during incubation experiments (Avery et al., 2003; Godoy-Silva et al., 2017). Furthermore, nitrifying bacteria can also alter nitrogen speciation in cloud water (Hill et al., 2007; Mathonat et al., 2026). Such depositions influence soil microbial

activity, aquatic biogeochemistry, and coastal carbon budgets (Willey et al., 2006), highlighting rainwater as an efficient carrier of reactive organic carbon from the atmosphere to the biosphere.

5. Impacts of VOC Removal by Rainwater

Wet deposition acts as a key atmospheric route by which VOCs and SVOCs and associated pollutants are transferred from the atmosphere to the Earth's surface, linking atmospheric chemistry to terrestrial and aquatic environments. While the mechanistic controls on VOC scavenging (including gas–aqueous partitioning, cloud and raindrop microphysics, and in-drop chemical transformations) were addressed in Section 4, this section examines their broader implications for atmospheric cleansing, oxidative capacity, SOA formation, O_3 production, and ecosystem functioning. Rainwater integrates inputs over variable spatial scales and therefore reflects both local emissions and regional transport processes, making it a sensitive indicator of boundary-layer composition and pollution trajectories (Sakihama et al., 2008; Willey et al., 2019). As droplets incorporate and process compounds such as BTEX aromatics, isoprene-derived carbonyls like glyoxal and methylglyoxal, and a variety of monoterpene oxidation products, rainwater emerges not only as a depositional sink but also as a transient reaction medium.

The onset of precipitation rapidly removes readily scavenged VOCs, with initial rainwater fractions often exhibiting higher concentrations of dissolved species such as TEX hydrocarbons and biogenic carbonyls than later on within the same precipitation event, reflecting the efficient scavenging of pollutants accumulated in the atmosphere prior to rainfall (Avery et al., 2009; Campos et al., 2007; Stojić et al., 2019). Despite this efficient "first-flush" behavior, wet deposition typically represents only a small atmospheric sink—BTEX removal generally accounts for <0.1% of local emissions due to high volatility, low solubility, and rapid gas-phase oxidation (Mullaugh et al., 2015). However, while rain is a minor mass sink for hydrophobic VOCs (like Benzene), it is a major vector for their transfer to surface water where their toxicity matters. Enhanced uptake observed in polluted air masses likely reflects partitioning into organic aerosol coatings rather than increased intrinsic solubility (Okochi et al., 2004), reflecting the multiphase character of scavenging. Although limited as a quantitative sink for reactive carbon, VOC and VOC-derived compounds-rich rainfall remains central to understanding how atmospheric processing couples with deposition to influence oxidant budgets, radiative effects, nutrient and contaminant delivery, and ecosystem metabolism (Iavorivska et al., 2016; Sato et al., 2006).

5.1. Pollutant Removal, Transport, and Atmospheric Cleansing

Wet deposition removes VOCs from the atmosphere and transfers them to terrestrial and aquatic systems, making it a major pathway for environmental deposition of atmospheric pollutants (Galloway et al., 1984). POPs are efficiently scavenged, particularly by snow, allowing long-range transport and accumulation in remote and high-altitude environments (Casas et al., 2021). Anthropogenic compounds are scarce in pristine areas such as the Amazon, but increase in regions under the influence of biomass burning or industrial emissions (Andreae et al., 1990; Lara et al., 2001; Pauliquevis et al., 2012; Williams et al., 1997). Rainwater ethanol closely tracks atmospheric ethanol concentrations due to rapid gas–aqueous equilibration, illustrating how scavenging reflects transient boundary layer composition. Furthermore, as ethanol emissions rise due to biofuel use, these impacts become more regionally relevant (Willey et al., 2019). Washout can be a significant sink in polluted regions—toluene and xylene removal by precipitation underscores the need to consider rainfall as an exposure pathway when regulating emissions (Kalkan et al., 2025; Polkowska et al., 2005).

Rain also scavenges harmful atmospheric microorganisms, including cyanobacteria and microalgae (such *as Chlorococcum sp*., *Oocystis sp*., *Anabaena sp*., *Leptolyngbya sp*., *Nodularia sp*., *Pseudanabaena sp*., *Synechococcus sp*., *Synechocystis sp*., or *Gymnodinium sp*.) reducing airborne cell numbers by up to 87% following rainfall events (Wiśniewska et al., 2022). It is important to note that the microbial composition of rain and clouds is different. For instance higher abundance of *Staphylococcus*, *Corynebacterium* and *Kocuria* were found in clouds in comparison to corresponding precipitation, pointing out to the multiplication processes occurring within clouds (Péguilhan et al., 2023). Microbial wet deposition mitigates human inhalation exposure and links atmospheric biota to aquatic blooms in adjacent marine systems (Wiśniewska et al., 2022). Another example is how muddy rains act as an efficient vector for transport and dispersal of diverse and functionally significant bacterial communities (Navarro-Nieva et al., 2026). Collectively, these processes demonstrate that wet deposition acts both

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as a selective atmospheric cleansing mechanism and a pathway for redistributing pollutants and biological material to the Earth's surface.

The incorporation of reactive VOCs into rain and cloud droplets alters oxidative processes by interrupting gas-phase radical propagation and modifying aqueous redox cycling. The dissolution of carbonyls such as aldehydes and ketones suppresses gas-phase photolysis and initiates aqueous-phase pathways that produce unique compounds, including dicarboxylic acids, with no efficient gas-phase sources (Ervens, 2015; Ervens et al., 2013). Ethanol is particularly influential: it scavenges ·OH and $\cdot HO_2$ radicals in rainwater, decreasing in-drop oxidation rates and locally modifying oxidative capacity and multiphase chemistry (Kieber et al., 2013). Through effects on dissolved oxidants and chromophoric compounds, ethanol may also indirectly influence radiative transfer and light attenuation within droplets (Kieber et al., 2013). These modifications reflect a key atmospheric consequence of scavenging—removal not only of primary VOCs, but also of their oxidative potential.

Crucially, by removing reactive VOCs and oxygenated VOCs (OVOCs), including formaldehyde, acetaldehyde, methacrolein, ethanol, some terpenes and their oxidation products, before they undergo gas-phase oxidation (Bi & Isaacman-VanWertz, 2022; Hakkim et al., 2019), precipitation may reduce the availability of precursors for SOA formation and tropospheric O_3 production. This competition between atmospheric oxidation and wet deposition represents an important control on atmospheric organic carbon budgets: although many early-generation OVOCs react on timescales of hours, rapid scavenging during precipitation events can interrupt oxidation pathways and alter the production efficiency of SOA and O_3 (Bi & Isaacman-VanWertz, 2022). Aqueous reactions involving carbonyls, ammonia, SO_2, and NO_x further impact multiphase chemistry, affecting fog persistence and altering the composition of SOA and reactive nitrogen species during and after rainfall (Ervens, 2015; Ervens et al., 2013). Formaldehyde itself can be produced within cloud droplets through oxidation of precursors and subsequently outgas once droplets evaporate, illustrating that rainwater and cloud water function simultaneously as a sink and a temporary reservoir for reactive carbon (Franco et al., 2021). Although wet scavenging is often a minor sink for nonpolar, hydrophobic VOCs such as BTEX, it remains the dominant direct loss pathway for SOA in global models, removing up to 90% of particulate organic matter from the atmosphere (Tsigaridis et al., 2014).

Overall, the evidence indicates that scavenging of VOCs by rainwater alters atmospheric composition at multiple scales: selectively cleansing boundary-layer air, reshaping oxidant and radical budgets within droplets, limiting SOA and O_3 formation by interrupting precursor supply, and transferring reactive and labile carbon to surface ecosystems.

5.2. Ecological Impacts of VOCs Delivered to Terrestrial and Aquatic Environments by Rainwater

Rainwater is an efficient vector linking atmospheric VOC chemistry to terrestrial and aquatic ecosystems by delivering DOC, organic acids, oxidized VOC products (i.e., VOC-derived compounds), and trace toxic compounds to soils, vegetation, and surface waters. Through combined effects of acidity, labile carbon inputs, and chemical reactivity, wet deposition influences microbial activity, nutrient cycling, plant surface processes, and aquatic biogeochemistry. The magnitude and direction of these impacts depend on VOC identity and concentration, ecosystem buffering capacity, biological demand, and deposition intensity, underscoring the role of precipitation as an active mediator between atmospheric processes and ecosystem functioning.

5.2.1. Potential Impacts of Rainwater VOCs on Soils

Rainwater acidity, soil chemistry, and buffering capacity. Soil pH is a critical variable that controls a wide range of chemical, biological, and physical processes with multiple implications in the wider environment (Wei et al., 2019). Wet deposition of inorganic acid species such as H_2SO_4 and HNO_3 are the largest source of acidity in soils from industrial and urban areas (Payus et al., 2020). In contrast, in poorly buffered soils in remote, boreal, and tropical ecosystems, VOC-derived organic acids (primarily formic and acetic acids) are the dominant contributors to precipitation acidity, accounting for up to 80%–90% of the free acidity in rainwater (Andreae et al., 1988; Keene et al., 1983). However, the role of these organic acids as a driver of long-term soil acidification is limited because they are rapidly metabolized by soil microbes into weaker carbonic acid, often within 12 hr of deposition (Andreae et al., 1988). Consequently, persistent soil acidification in these regions is more likely driven by the input of inorganic species or internal processes like nitrogen cycling (Guo et al., 2010). When cumulative acidification does occur, it reduces the acid-neutralizing capacity of soils and decreases adsorption onto binding sites, thereby increasing the mobility of cations (Wei et al., 2019). This leads to the leaching of base cations and

micronutrients (e.g., Ca, Mg, K) and an increase in the solubility and bioavailability of toxic metals such as Al, Cd, or Pb (Driscoll et al., 2001; Likens et al., 1996). These changes can adversely affect soil microorganisms and the enzymatic processes central to carbon and nutrient cycling (Wang, Fang, et al., 2020; Zeng & Han, 2020). Persistent acidification-induced effects in soil biota may alter soil structure, health, and ecosystem resilience (Payus et al., 2020; Wang, Fang, et al., 2020). Furthermore, ecosystem recovery is often significantly delayed even after inorganic emissions decline due to the legacy depletion of base cation pools in the soil (Lawrence et al., 2015; Likens et al., 1996).

Effects of labile VOC-derived DOC inputs via rainwater. Soil rewetting is known to induce a rapid, short-lived pulse of CO_2 emissions in dry soils. This is commonly referred to as the *Birch effect* and it is triggered by the sudden activation of microbial activity and the decomposition of labile organic substrates accumulated during drought (Rossabi et al., 2018). This response may be further amplified by the presence of VOC-derived compounds dissolved in rainwater, providing immediately bioavailable C substrates to fuel microbial growth at the moment of rewetting. Rainwater therefore acts not only as a rewetting agent but also as a pathway for atmospherically derived labile carbon to soil surfaces. Recent evidence further suggests that rainwater can simultaneously deliver both the substrates and the microbial communities capable of metabolizing them. For example, "muddy rain" events have been shown to transport mineral dust and associated microbial consortia over long distances, including bacteria physically associated with clay particles that enhance their survival during atmospheric transport (Navarro-Nieva et al., 2026). These communities, often dominated by metabolically versatile taxa such as *Pseudomonadota*, are capable of utilizing simple VOC-derived compounds such as formate and acetate upon deposition. This co-delivery of labile DOC and functional microbial assemblages implies a synergistic interaction whereby rainwater supplies both the "fuel" (VOC-derived DOC) and the "biological machinery" required for its rapid transformation (Navarro-Nieva et al., 2026). Because low-molecular-weight VOCs and their oxidation products are metabolized rapidly, these C inputs can intensify microbial respiration thereby enhancing the decomposition of native soil organic carbon (a priming effect) during the *Birch* pulse (Yang et al., 2024). The response may be exacerbated in carbon-limited systems such as deserts (Lohse et al., 2008), alpine soils (Mladenov et al., 2012), karsts (Zeng & Han, 2020), and tropical forests (Veneklaas et al., 2002), where even small inputs of labile carbon can trigger large microbial responses. Greater DOC availability can shift microbial communities toward methylotrophs and specialized VOC degraders, altering nutrient mineralization and coupling carbon cycling with redox and trace-metal chemistry through DOC–metal complexation (Fang et al., 2008; Felix et al., 2014; Kolb, 2009; Wang, Fang, et al., 2020; Wu et al., 2016). In contrast, chronic acid and nitrogen deposition often suppress microbial biomass and mineralization, favoring accumulation of soil organic carbon and nutrients in more recalcitrant (non-bioavailable) pools, as observed in forest and paddy soils (Ouyang et al., 2008; Smith et al., 2013; Wang, Fang, et al., 2020).

Soil redox interactions and toxic VOCs/POPs. VOCs and their oxidation products can deplete O_2 supply in microsites within the interstices of soil particles where gas exchange is restricted, whilst accumulation of CO_2 derived from microbial respiration enhanced by labile C inputs may locally induce acidification. The pH and redox conditions in these microenvironments promote reductive dissolution of Mn and Fe oxy-hydroxides and a number of metals adsorbed on these surfaces (e.g., Cd, Pb), which are often released in their more readily bioavailable and toxic free ion (aqueous) forms (Izquierdo et al., 2017). Thus, rainwater VOCs can induce changes in metal speciation, radical chemistry, and regulate nutrient availability, with small pH shifts causing large changes in metal solubility and toxicity thresholds (Willey et al., 2006). Soil moisture and redox conditions regulate whether soils act as sinks or sources of VOCs (Pugliese et al., 2023). Wetting events enhance adsorption and microbial uptake of hydrophilic compounds but also trigger short-lived VOC emission pulses driven by microbial activity (Bachy et al., 2018; Li et al., 2016; Pugliese et al., 2023; Rossabi et al., 2018). Rewetting-induced VOC pulses (including methanol, acetone, sesquiterpenes, and monoterpenes) have been observed across forest ecosystems with soil water content, highlighting rainfall as a key control on soil–atmosphere VOC exchange (Bourtsoukidis et al., 2018; Holzinger et al., 2000; Mochizuki et al., 2014). These pulses are of biogeochemical relevance given their contribution to microbial carbon supply and ecological functions such as pathogen defense, and even enhance new particle nucleation (Machado et al., 2024; Marmulla & Harder, 2014; Minerdi et al., 2008). In addition, the co-transport of VOCs and SVOCs, including PAHs and pesticides that can accumulate in soils and can persist for decades, especially in cold or high-altitude regions where wet scavenging is highly effective, altering microbial communities, soil fauna, and plant health (Casas et al., 2021). In addition, such co-transport introduces chemical stressors that may select stress-tolerant or resistant microbial communities

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during atmospheric transport. As a result, deposited bioaerosols may already be preconditioned to withstand chemical stress and may carry functional traits, including those related to nutrient cycling or contaminant degradation, that can directly influence soil biogeochemical processes upon deposition (Navarro-Nieva et al., 2026). Together, these processes position VOCs and VOC-derived compounds in rainwater as important regulators of soil acidity, metal mobility, microbial dynamics, and long-term soil fertility.

5.2.2. Potential Impacts of Rainwater VOCs on Plants

Direct foliar exposure and rainwater acidity. VOC-containing rainwater directly wets leaf surfaces, enabling foliar uptake of water-soluble organics and acids through cuticles and stomata (Berry et al., 2019; Niinemets et al., 2014). Rainwater acidity can affect plant ecosystems through a combination of direct foliar damage and indirect soil-mediated processes. These effects include forest dieback, crop production decreases and biodiversity losses, with impacts strongly dependent on pH, species traits, and symbiotic interactions (Lara et al., 2001; Singh & Agrawal, 2004; Tatuśko-Krygier et al., 2023; Zheng et al., 2018). Acidic precipitation can erode cuticular waxes, deform stomata, disrupt chloroplasts and mitochondria, and reduce chlorophyll content and photosynthesis, with damage intensifying below pH ∼5 and varying strongly among species, cultivars, and plant functional types (Debnath et al., 2018; Ferenbaugh, 1976; Francisco Sant'Anna-Santos et al., 2006; Payus et al., 2020; Zhang et al., 2023). Chronic acid stress perturbs antioxidant defenses, nitrogen metabolism, and reproduction, leading to growth inhibition, reductions in flowering, and seedling establishment, chlorosis, necrosis, dehydration, wilting and premature senescence, pathogen infection and, ultimately, death. It can also cause alteration in gene expression or enhance the chance of invasion of alien plant species through allelopathy (Prakash et al., 2023). In contrast, moderate acidity can enhance growth in some species via nitrate fertilization (Ashenden & Bell, 1989; Dong et al., 2017; Lara et al., 2001; Medeiros et al., 2016; Shi et al., 2021; Tatuśko-Krygier et al., 2023; Wang, Fang, et al., 2020). Plant resistance varies widely, with woody species and ectomycorrhizal associations often being more tolerant, partly due to physiological defenses such as enhanced root exudation of organic acids that buffer acidity and chelate metals (Zhang et al., 2023; Zhou et al., 2020). Other plant resistance strategies could be rhizosphere-induced plant hormones, such as indoleacetic acids, to regulate plant growth and reproduction during acidic rainwater stress (Zhang et al., 2023).

Carbon and nutrient subsidies to the plant. Added nutrients and carbon delivered by rainwater (particularly VOC-derived DOC, nitrate, ammonium, and small oxygenated VOCs) can act as supplementary resources for plants and their associated phyllosphere and rhizosphere microbes. Under nutrient-limited conditions, these inputs may enhance plant nutrition and productivity by stimulating microbial mineralization, facilitating N uptake and, in some cases, providing directly assimilable carbon or signaling compounds via foliar uptake (Berry et al., 2019; Niinemets et al., 2014). However, sustained or excessive inputs can disrupt nutrient stoichiometry, promote eutrophication, and shift microbial communities on leaf surfaces and in soils, potentially reducing nutrient use efficiency and increasing plant stress, particularly in ecosystems already exposed to elevated N deposition or acidification (Fenn et al., 2003; Smith et al., 2013; Wang, Fang, et al., 2020). These carbon subsidies can indirectly influence plant health by altering pathogen–microbe competition and leaf surface chemistry, while bidirectional exchange of water-soluble VOCs between leaves and rainwater links plant metabolism with atmospheric chemistry (Niinemets et al., 2014).

Signaling interactions and toxicity. At low concentrations, some VOCs absorbed during wetting may function as metabolic intermediates or signaling and defense compounds, whereas at higher concentrations certain species (e.g., phenols and nitrophenols) are phytotoxic, inhibiting nutrient assimilation, transpiration, and growth and contributing to forest decline in polluted regions (Leuenberger et al., 1988; Schummer et al., 2009). Acid rain can further enhance plant susceptibility to metal toxicity by mobilizing Al, Cd, Pb Zn, and other cationic metals in soils, increasing uptake and stress in sensitive ecosystems (Tatuśko-Krygier et al., 2023). At the same time, shifts in the biogeochemical behavior of elements in the rhizosphere caused by soil acidification can compromise plant health by displacing essential cationic macronutrients (Ca, K, Mg) from exchange sites and immobilizing Al and P whilst increasing aqueous metal pools in soil pore water. Trace pollutants entering plant tissues following uptake and translocation are active in metabolic processes and can interfere in several physiological functions, inhibit root function or impair nutrient absorption (Kabata-Pendias, 2010). These biogeochemical shifts also disrupt microbial populations with beneficial roles including nitrogen-fixing bacteria and mycorrhizal fungi, further limiting nutrient availability. Overall, these changes reduce nutrient uptake efficiency and plant growth, particularly in acid-sensitive crops and forest species and/or stressed ecosystems (Tatuśko-Krygier et al., 2023).

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Removal of airborne pathogens and microalgae: Rainfall also provides a protective function by scavenging airborne microorganisms, reducing deposition of potentially harmful cyanobacteria and microalgae on plant surfaces by up to ~87% and reducing exposure of crops and wild plants to potentially toxic and allergenic taxa such as *Anabaena*, *Nodularia*, *Pseudanabaena*, and *Gymnodinium* (Wiśniewska et al., 2022). Together, these processes highlight rainwater as both a stressor and a regulator of plant–atmosphere–microbe interactions, with outcomes controlled by rainwater chemistry, species traits, and ecosystem buffering capacity.

5.2.3. Potential Impacts of Rainwater VOCs on Surface Waters (Freshwater and Marine)

Wet deposition of VOCs, DOC, organic acids, and associated pollutants represents an important pathway linking atmospheric chemistry to aquatic ecosystem functioning, especially when DOC in rainwater is much more bioavailable than that in river water (Avery et al., 2003). These inputs influence microbial productivity, acid–base balance, metal bioavailability, and contaminant exposure in both freshwater and marine systems. In open oceans, atmospheric deposition can provide an important external source of labile carbon and nutrients to surface waters, particularly in stratified or oligotrophic regions (Avery et al., 2003; Willey et al., 2000). Similarly, high-altitude oligotrophic lakes may be especially sensitive to atmospheric DOC and VOC inputs because of their low background organic carbon concentrations, limited terrestrial inputs, and strong dependence on atmospheric deposition, although direct evidence specifically linking rainborne VOCs to ecological responses in these systems remains limited (Mladenov et al., 2012).

Delivery of labile carbon to aquatic ecosystems. Rainwater supplies highly bioavailable VOC-derived DOC, including small organic acids and carbonyls, to lakes, rivers, and coastal waters, where it is rapidly metabolized by heterotrophic microbes (Avery et al., 2003; Godoy-Silva et al., 2017). In carbon-limited systems such as oligotrophic freshwater, and open-ocean environments, atmospheric VOC-derived DOC inputs can enhance microbial productivity, shift food webs toward bacterial dominance, and alter the rates and amounts of primary production, nutrient cycling and decomposition (Lohse et al., 2008; Mladenov et al., 2012; Payus et al., 2020; Willey et al., 2006; Xie et al., 2023). In marine systems, while labile fractions stimulate microbial respiration and may contribute to seasonal oxygen depletion, semi-labile and refractory DOC fractions can be exported to deeper waters and sediments, supporting long-term carbon sequestration via the biological carbon pump (Djaoudi et al., 2020; Xie, Gao, Liu, Yang, Lv, et al., 2022). In coastal and marine environments, rainwater introduces water-soluble VOCs (such as ethanol, or methanol), secondary organic compounds, and oxidized products (e.g., organosulfates and nitrooxy-organosulfates from BVOC oxidation) that can alter redox conditions and microbial turnover (Altieri et al., 2009b; Felix et al., 2014; Niinemets et al., 2014) influencing biogeochemical cycling and affecting the timing and magnitude of algal blooms. Atmospheric nitrogen deposition associated with VOC oxidation further supports primary production in N-limited marine waters, indirectly influencing carbon cycling and trophic state (Umezawa et al., 2021; Xie, Gao, Liu, Yang, Wang, et al., 2022). Changes in precipitation acidity also modulate metal solubility and carbonate chemistry, with implications for coastal productivity and calcifying organisms (Willey et al., 2006).

Effects on aquatic acid–base balance. Although inorganic acids derived from sulfate and nitrate remain the dominant contributors to precipitation acidity at regional and global scales, organic acids can represent a substantial fraction of free acidity in remote, forested, and tropical environments where biogenic emissions are high and anthropogenic sulfur inputs are comparatively low (Andreae et al., 1988; Sanhueza et al., 1991). In ecosystems receiving substantial organic acid deposition, these compounds can contribute to lower pH in poorly buffered lakes and streams, disrupting primary production, nutrient cycling, and organism survival (Andreae et al., 1988; Payus et al., 2020). Acidification enhances metal solubility and bioavailability (e.g., Al, Fe, Cd, Pb) increasing toxicity to fish, amphibians, and invertebrates and contributing to population losses in sensitive watersheds (Chen et al., 2022; Lawrence et al., 2015; Payus et al., 2020; Willey et al., 2006). Although declining sulfate deposition has reduced acid inputs in some regions (Willey et al., 2006), legacy depletion of base cations (e.g., Ca and Mg) delays chemical and biological recovery of surface waters (Lawrence et al., 2015; Likens et al., 1996).

Delivery of toxic compounds: Wet deposition efficiently transfers toxic VOCs and POPs (e.g., BTEX, PAHs, PCBs, pesticides) into surface waters, soils, and groundwater (Casas et al., 2021; Kalkan et al., 2025; Prakash et al., 2023; Zahed et al., 2009). Once deposited, these compounds can accumulate in sediments and biota, causing endocrine disruption, impaired reproduction, growth inhibition, and food-web transfer (Casas et al., 2021; Liggio

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et al., 2025). Halogenated VOCs and oxygenated compounds such as aldehydes further contribute to aquatic toxicity, odor problems in drinking-water sources, and increased health risks for aquatic organisms and humans (Chary & Fernandez-Alba, 2012; Dabrowska & Nawrocki, 2013; Kalkan et al., 2025). These findings highlight precipitation as a critical, yet often under-regulated, pathway for pollutant delivery to aquatic ecosystems.

5.2.4. Potential Impacts of Rainwater VOCs on Urban, Industrial, and Managed Environments

In urban and industrial environments, VOC- and acid-laden rainwater accelerates material degradation (e.g., stone weathering of buildings and monuments) and serves as an efficient pathway for transferring VOCs, BTEX, acids, and metal-associated pollutants from the atmosphere into soils, surface waters, vegetation, and groundwater (Payus et al., 2020; Zahed et al., 2009). Rainwater harvesting systems in these settings may accumulate BTEX, aldehydes, and trace metals, posing risks to drinking water, irrigation, hydroponics, and human health if untreated (Bąk et al., 2025; Friedt et al., 2025; Kalkan et al., 2025; Rivera-Rivera et al., 2020). In industrialized regions, wet deposition further enhances pollutant mobility and bioavailability, promotes soil acidification and nutrient leaching, and can remobilize legacy heavy-metal contamination, leading to persistent ecosystem degradation even after emissions decline (Tatuśko-Krygier et al., 2023). Collectively, these impacts highlight precipitation as an active exposure pathway that must be explicitly integrated into air-quality regulation and environmental risk assessment (Kalkan et al., 2025).

6. Current Methodological Techniques, Limitations, and Knowledge Gaps

6.1. Why Rainwater VOCs Remain Difficult to Quantify

Understanding VOCs (and VOC-derived compounds) in rainwater remains an emerging frontier in atmospheric chemistry. Progress in understanding rainborne VOCs and VOC-derived compounds has been constrained less by conceptual uncertainty than by major analytical and methodological limitations. In contrast to the extensive characterization of inorganic ions, metals, and particulate organics, dissolved VOCs have received limited attention, resulting in major uncertainties in source attribution, atmospheric fate, and wet-deposition fluxes.

One of the principal challenges is that VOCs span an exceptionally broad range of physicochemical properties. Their solubility, volatility, polarity, and chemical reactivity vary widely across compound classes, strongly influencing scavenging efficiency, gas–aqueous partitioning, and in-droplet transformation processes. Highly soluble oxygenated VOCs such as formaldehyde, methanol, and organic acids may partition efficiently into cloud and rain droplets, whereas less soluble hydrocarbons are less efficiently scavenged. At the same time, many VOCs undergo rapid aqueous-phase reactions including oxidation, hydration, oligomerization, and microbial degradation, meaning that measured rainwater composition may differ substantially from the original atmospheric composition at the time of scavenging.

These physicochemical characteristics create substantial analytical challenges. VOCs typically occur in rainwater at trace concentrations and can be lost or transformed during collection, storage, and analysis. Consequently, widely used precipitation chemistry protocols (developed primarily for ions and bulk DOC) often underestimate or entirely exclude volatile organic fractions from rainwater measurements through acidification, purging, or microbial degradation (Campos et al., 2007; Coelho et al., 2008), leading to systematic underestimation in historical data sets and biasing global rainwater DOC fluxes by excluding purgeable organic carbon (Avery et al., 2003, 2009).

The episodic and transient nature of precipitation further complicates VOC measurements. VOC concentrations are often highest during the initial stages of rainfall, when atmospheric washout is most efficient, yet many conventional collectors fail to adequately capture this “first flush” period. Integrated bulk sampling can therefore dilute short-lived concentration peaks and obscure scavenging dynamics. In addition, rainwater VOC concentrations are strongly influenced by precipitation intensity, droplet size distributions, air-mass origin, atmospheric oxidation state, aerosol loading, and local emission sources, generating large spatial and temporal variability that is difficult to constrain with sparse observational data sets.

Post-collection artifacts represent another major source of uncertainty. Volatilization, photochemical reactions, sorption to container walls, and microbial metabolism can substantially alter VOC concentrations within hours of sample collection, particularly for low–molecular-weight aldehydes, alcohols, and organic acids. Conventional DOC analytical procedures may further remove volatile fractions through acidification and purging steps prior to

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analysis, causing VOC-derived carbon to be systematically excluded from measurements of non-purgeable organic carbon (NPOC). As a result, historical rainwater DOC data sets likely underestimate total dissolved organic carbon in regions with substantial VOC emissions (Avery et al., 2003, 2009).

Together, these challenges help explain why VOCs and VOC-derived compounds remain poorly constrained relative to inorganic precipitation chemistry. Existing long-term monitoring networks were originally developed to quantify acid deposition, nutrients, and trace metals rather than reactive organic carbon, and therefore rarely include protocols specifically devised for volatile organic species. Consequently, rainborne VOCs remain substantially underrepresented in atmospheric observations, cloud-chemistry studies, and Earth system models despite their potentially important roles in atmospheric oxidation chemistry, secondary organic aerosol formation, wet-deposition fluxes, and ecosystem carbon cycling.

6.2. Sampling Constraints and Artifacts

6.2.1. Rainwater Collection Challenges

Reliable quantification of VOCs and VOC-derived compounds in rainwater depends critically on sample collection and processing. However, most precipitation collection systems currently used in atmospheric monitoring networks were developed for inorganic ions, nutrients, trace metals, and bulk dissolved organic carbon rather than for volatile and reactive organic compounds. As a result, rainwater VOC measurements are particularly vulnerable to artifacts associated with collection efficiency, volatilization, adsorption, microbial activity, and contamination, which can substantially bias measured concentrations and contribute to the large uncertainties surrounding atmospheric VOC scavenging and wet-deposition fluxes. Wet-only automatic collectors, such as the Aerochem Metrics (ACM) Model 301 (Avery et al., 1991, 2001; Keene & Galloway, 1984), and similar systems used in regional and global monitoring networks (e.g., NADP, EMEP), minimize contamination from dry deposition by opening only during precipitation events (Avery et al., 1991, 2001; Keene & Galloway, 1984; Laouali et al., 2012; Polkowska et al., 2011; Willey et al., 2006). Bulk collectors, in contrast, remain continuously open and integrate both wet and dry deposition, making them operationally simpler but more susceptible to contamination from aerosols, dust and dry-settled material.

Although these systems are highly effective for inorganic deposition studies, they present important limitations for VOC measurements. Many collectors fail to adequately capture the onset of precipitation, specifically the first millimeters of rainfall that often contain the highest concentrations of dissolved VOCs due to efficient below-cloud scavenging and washout processes (Campos et al., 2007). Thus, integrated storm sampling likely dilutes steep temporal concentration gradients and systematically underestimates the magnitude of initial VOC removal from the atmosphere. Because VOC scavenging is highly dynamic and non-linear, temporally integrated sampling approaches may obscure relationships between atmospheric composition, precipitation intensity, and rainwater chemistry.

Material selection also strongly influences sample integrity. Conventional collectors frequently contain polymeric components, tubing, lubricants, or sealants that can adsorb VOCs or release organic contaminants into collected samples. To minimize these effects, VOC-oriented sampling systems increasingly employ inert materials such as polytetrafluoroethylene (PTFE), borosilicate glass, stainless steel, polypropylene, or high-density polyethylene (HDPE) (Avery et al., 2009; Campos et al., 2007; Levsen et al., 1993). Additional precautions include acid-washed or prebaked collection vessels, ultrapure water rinsing, minimized headspace, rapid sample retrieval, and protection from direct sunlight.

Specialized sampling systems have also been developed for cloud water, fog, and dew, including Caltech Active Strand Cloudwater Collectors (CASCC) and related passive or active condensation samplers (Bianco, Nibert, et al., 2025; Demoz et al., 1996; Hutchings et al., 2008; Skarżyńska et al., 2006a, 2006b). These systems are particularly valuable because cloud and fog droplets may contain higher concentrations of dissolved VOCs and secondary organic products than rainwater due to enhanced aqueous-phase processing and reduced dilution.

6.2.2. Storage, Preservation, and Contamination Artifacts

Post-collection handling is one of the largest sources of uncertainty in rainwater VOC analysis. Because many VOCs are highly volatile, chemically reactive, and readily biodegradable, substantial compositional changes can occur during storage and transport, even over relatively short timescales. Volatilization losses are enhanced by

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sample headspace, permeable storage materials, elevated temperatures, and repeated container opening, whereas photochemical reactions and microbial metabolism can rapidly transform and probably also generate aldehydes, alcohols, organic acids, and other oxygenated VOCs (Herlihy et al., 1987; Kawamura & Kaplan, 1990; Keene et al., 1983).

Several studies have demonstrated that conventional preservation procedures developed for inorganic chemistry can inadvertently remove or alter VOCs. Acidification and purging steps commonly used in DOC analysis eliminate volatile fractions prior to quantification, effectively restricting many historical DOC measurements to non-purgeable organic carbon (NPOC) (Avery et al., 2003, 2009; Coelho et al., 2008). Similarly, refrigerated storage attenuates but does not fully prevent microbial degradation or volatilization losses (He & Balasubramanian, 2010), and some compounds such as toluene exhibit measurable instability within only a few days after collection (Mullaugh et al., 2015).

To reduce these artifacts, best-practice protocols increasingly emphasize immediate processing following sample collection, often within a few hours, particularly for aldehydes and low–molecular-weight organic acids (Altieri et al., 2009b; Guillemette et al., 2023; Taguchi et al., 2012). Samples are commonly stored in prebaked borosilicate glass vials with minimal headspace and preserved at temperatures ranging from −20 to −80°C to minimize volatilization and biological activity (Felix et al., 2014; Sun et al., 2016). Clean-laboratory handling procedures—including laminar-flow processing, solvent-rinsed materials, field blanks, and ultrapure water controls—are also essential because contamination levels negligible for ionic analyses may become significant for trace VOC measurements.

Together, these sampling and preservation artifacts substantially complicate interpretation of rainwater VOC data sets and contribute to poor comparability among studies. As a consequence, current estimates of VOC scavenging efficiencies, atmospheric deposition fluxes, and VOC-derived DOC inputs to ecosystems remain highly uncertain, underscoring the need for standardized protocols specifically tailored to volatile and reactive organic compounds in precipitation.

6.3. Analytical Constraints and Emerging Capabilities

Analytical limitations remain one of the principal reasons why VOCs and VOC-derived compounds are still poorly constrained in precipitation chemistry relative to inorganic species, having been largely underestimated or entirely excluded from precipitation measurements. Recent advances in molecular and real-time analytical techniques are beginning to reveal a much greater chemical complexity and dynamic behavior of rainwater organic matter than previously recognized. These emerging capabilities are increasingly enabling direct investigation of VOC scavenging, aqueous-phase transformations, and atmospheric carbon transfer processes that were previously inaccessible.

6.3.1. Conventional Rainwater Chemistry Approaches and Their Limitations

Conventional rainwater chemistry is typically characterized using analytical techniques optimized for stable inorganic solutes and bulk carbon measurements. Major ions are routinely quantified using ion chromatography (IC), while major and trace metals are commonly analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectroscopy (AAS), or flow injection analysis (FIA). These methods provide robust characterization of atmospheric acidity, nutrient deposition, mineral dust inputs, combustion products, and trace-metal transport, forming the foundation of long-term atmospheric deposition monitoring networks (Bandrés et al., 2026; Cerro et al., 2020; Galloway et al., 1993; Keene et al., 1986; Keresztesi et al., 2019, 2020; Pey et al., 2020; Szép et al., 2017, 2019).

Bulk DOC is conventionally quantified using TOC analyzers based on high-temperature catalytic oxidation or UV-persulfate oxidation. However, standard DOC protocols typically involve acidification and purging steps that remove volatile organic fractions prior to analysis (Avery et al., 2003, 2009; Campos et al., 2007; Coelho et al., 2008). As a result, historical rainwater DOC data sets likely underestimate total dissolved organic carbon in regions with substantial VOC emissions or strong aqueous-phase production of volatile oxygenated compounds.

These analytical frameworks were developed primarily in the context of acid rain, eutrophication, and inorganic deposition studies, and therefore remain poorly suited for chemically reactive and volatile organic species. Many atmospheric VOCs occur at ultra-trace concentrations, are highly polar or thermally unstable, and rapidly undergo

aqueous-phase reactions or biological degradation. Consequently, conventional precipitation chemistry measurements provide only limited insight into the molecular composition, transformation pathways, and atmospheric cycling of rainborne VOC-derived carbon.

6.3.2. Targeted VOC Techniques

To overcome these limitations, a range of targeted analytical techniques have been developed specifically for VOCs and VOC-derived compounds in rainwater. Gas chromatography–mass spectrometry (GC-MS), often coupled with purge-and-trap extraction, is one of the most widely used approaches for oxygenated VOCs, hydrocarbons, and aromatic compounds in precipitation samples (Campos et al., 2007). However, many VOCs require derivatization, pre-concentration, or matrix exchange prior to analysis because of their low concentrations, thermal lability, or poor chromatographic retention.

Solid-phase microextraction (SPME) and stir-bar sorptive extraction (SBSE) approaches have substantially improved pre-concentration efficiency for alcohols, aromatics, and carbonyl compounds, enabling sub-nanomolar detection limits under optimized conditions (Chary & Fernandez-Alba, 2012; Felli et al., 2026; Mullaugh et al., 2015). Carbonyl compounds are commonly stabilized through derivatization methods such as 4-Dinitrophenylhydrazine High Performance Liquid Chromatography DNPH-HPLC, 3-methyl-2- benzothiazolinone hydrazone (MBTH) spectrophotometry, or O-(2,3,4,5,6-Pentafluorobenzyl) hydroxylamine PFBHA-GC-MS, which convert reactive aldehydes and ketones into more stable derivatives suitable for quantification (Ervens et al., 2013; Pang et al., 2017; Steinberg & Kaplan, 1984; Taguchi et al., 2012). The reader is referred to Text S4 in Supporting Information S1 for extended information on the current state-of-the-art on rainborne and cloud borne VOC sampling and sample handling.

Despite these advances, targeted approaches still face substantial limitations. Analytical recoveries remain highly variable among compound classes, standardization is limited, and many methods remain labor-intensive and poorly comparable across studies. In addition, targeted analyses generally quantify only a restricted subset of compounds, leaving much of the chemically complex rainwater organic matrix unresolved. These limitations are particularly important because atmospheric oxidation continuously generates multifunctional compounds spanning a continuum from volatile precursors to dissolved and particulate organic matter.

6.3.3. Emerging Molecular and Real-Time Approaches

Recent advances in high-resolution molecular characterization and real-time atmospheric measurements are beginning to transform understanding of rainwater organic chemistry. Ultrahigh-resolution techniques such as Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS) and comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (GC × GC-TOF-MS) now enable molecular-level characterization of thousands of CHO, CHON, and organosulfur compounds within rainwater dissolved organic matter (Altieri et al., 2009b; Chen et al., 2016, 2022). These approaches have revealed that rainwater organic matter contains highly complex mixtures of secondary organic aerosol products, humic-like substances, organic acids, and multiphase oxidation products that were previously unresolved using bulk DOC methods.

At the same time, proton-transfer-reaction mass spectrometry (PTR-MS and PTR-TOF-MS) has enabled near real-time measurements of VOC partitioning and dissolution kinetics under controlled atmospheric and rainfall conditions (Šoštarić et al., 2016, 2017). Such experiments demonstrate that gas–aqueous partitioning often deviates substantially from equilibrium Henry's law predictions, particularly for aromatic hydrocarbons and multifunctional oxygenated VOCs. Emerging sensor technologies, including surface acoustic wave (SAW) sensors and dynamic dilution systems coupled to mass spectrometry, are further expanding capabilities for selective and high-frequency measurements of rainwater VOCs.

Collectively, these approaches are shifting rainwater chemistry from bulk compositional analysis toward process-oriented characterization of atmospheric reactive carbon cycling. Nevertheless, most techniques remain limited by high cost, low throughput, demanding sample handling requirements, and lack of harmonized protocols, restricting their widespread application in long-term atmospheric monitoring programs.

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6.4. Critical Knowledge Gaps and Future Measurement Priorities

Direct measurements of VOCs and VOC-derived compounds in rainwater remain exceptionally scarce. This scarcity of observations limits our ability to assess the relative importance of in-cloud versus below-cloud scavenging, distinguish episodic pollution events from background conditions, and quantify the role of wet deposition in regulating atmospheric oxidant budgets, SOA formation, and reactive carbon cycling. Most long-term precipitation networks focus on inorganic ions, while organic species (and VOCs in particular) are largely excluded (Vet et al., 2014). Despite recent analytical advances, less than 50% (Herckes et al., 2013; Iavorivska et al., 2016; Willey et al., 2000) or even less than 22% (Dominutti et al., 2022; Nibert et al., 2026) of DOC in cloud and rainwater has been chemically characterized, reflecting the molecular diversity and complexity of atmospheric organic matter (Altieri et al., 2009b). Global DOC fluxes are also likely underestimated because purgeable VOCs are not measured (Avery et al., 2003, 2009). Major unresolved questions include the magnitude of global VOC wet-deposition fluxes, the relative importance of in-cloud versus below-cloud scavenging, and the extent to which aqueous-phase reactions transform VOCs during atmospheric transport (Allou et al., 2011; Okochi et al., 2004; Safieddine & Heald, 2017; Sato et al., 2006). Scavenging ratios vary with precipitation microphysics, aerosol composition, and meteorological conditions, yet remain highly uncertain due to sparse and sometimes contradictory field observations. Global wet-deposition estimates for key compounds such as methanol still span more than an order of magnitude (Felix et al., 2014).

Significant uncertainty also surrounds the composition and reactivity of VOC-derived dissolved organic matter, particularly in tropical, marine, biomass-burning, and Southern Hemisphere environments where observations remain sparse (Godoy-Silva et al., 2017; Seitzinger et al., 2003). The chemical complexity of rainwater DOM—comprising thousands of compounds including organic acids and humic-like substances—further restricts characterization, even though these constituents strongly influence cloud pH and microphysics (Graber & Rudich, 2006; Shah et al., 2020).

These observational gaps propagate directly into both atmospheric processes understanding and modeling. Many VOCs lack reliable Henry's law constants, temperature dependencies, dissociation constants, and aqueous-phase reaction rates, preventing realistic simulation of gas–aqueous partitioning and in-droplet chemistry. Consequently, chemical transport models rarely include explicit VOC wet-deposition pathways and often oversimplify cloud water chemistry or neglect the roles of organic acids and dust alkalinity, leading to substantial biases in simulated precipitation chemistry (Pye et al., 2020; Shah et al., 2020). Wet scavenging therefore remains one of the largest unresolved uncertainties in atmospheric chemistry modeling (MacDonald et al., 2018; Neu & Prather, 2012; Safieddine & Heald, 2017; Seinfeld & Pandis, 2006).

Targeted modeling studies have demonstrated the value of improved representation of organic acid formation and transport, such as simulations linking VOC emissions to organic acids observed at remote sites like Whiteface Mountain, New York (Lawrence et al., 2024). The necessity of such models is further highlighted by a recent 7-year monitoring study (2018–2024) at the same site, which provides a comprehensive record of formate, acetate, and oxalate concentrations in cloud water, confirming their significant role in droplet acidity and the emergence of a 'new chemical regime' dominated by a shift in the composition of atmospheric moisture and cloud water (Tripathy et al., 2026).

Beyond atmospheric impacts, the ecological fate and biogeochemical significance of VOC-derived carbon following deposition also remain poorly constrained. Rainwater VOC-derived DOC may influence soil acidity, surface-water chemistry, microbial metabolism, and marine productivity, yet these ecosystem responses remain insufficiently understood (Zhang et al., 2023). These limitations have broader implications for carbon accounting, as current global carbon-cycle models remain unable to explain roughly 20% of atmospheric CO_2 variability. Addressing these gaps requires improved analytical standardization, event-resolved observations, and tighter coupling between atmospheric and ecosystem studies (Avery et al., 2009; Iavorivska et al., 2016; Pye et al., 2020; Shah et al., 2020).

7. Broader Implications for Biogeosciences

Given the breadth of potential atmosphere–biosphere interactions, this section prioritizes processes for which observational or mechanistic evidence exists, while distinguishing these from hypothesized effects that remain

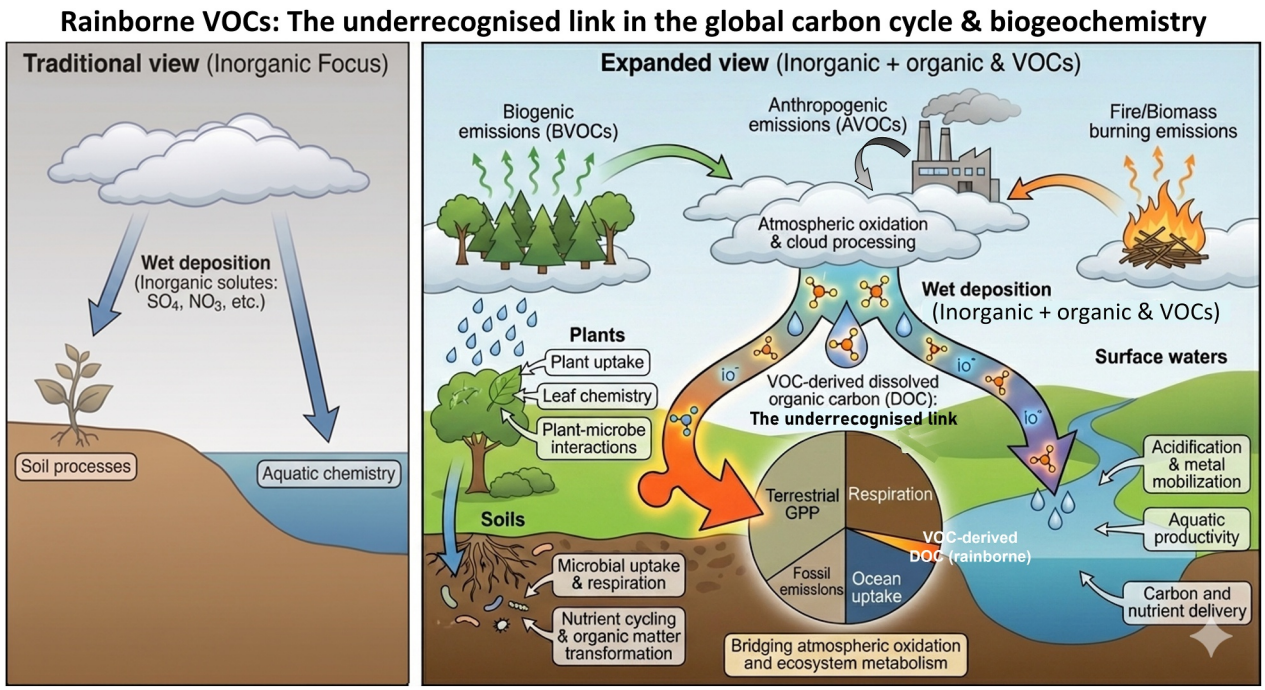

Figure 3. Diagram showing the potentially missing links of rainborne VOC to the carbon cycle. Rainborne VOCs: The missing link in the global carbon cycle and biogeochemistry. Gemini 3.0 Pro. https://gemini.google.com/share/b79d5f74f768.

insufficiently constrained. Atmospheric carbon budgets traditionally focus on major fluxes such as CO_2 exchange, particulate organic carbon transport, and bulk DOC deposition. However, the environmental fate of many water-soluble VOCs and VOC-derived oxidation products remains poorly constrained despite their widespread production through atmospheric oxidation processes. As a result, the transfer of this highly reactive organic carbon from the atmosphere to terrestrial and aquatic ecosystems is rarely considered explicitly in ecosystem carbon budgets. Rainborne VOCs and VOC-derived compounds therefore are a potentially quantitatively underconstrained pathway in carbon cycling that links atmospheric oxidation processes with terrestrial and aquatic metabolism.

Unlike bulk DOC, which encompasses a wide spectrum of reactivities, VOC-derived DOC represents a highly dynamic, chemically reactive, and rapidly bioavailable fraction that can disproportionately influence microbial activity, carbon turnover, and ecosystem feedbacks. By explicitly distinguishing VOC-derived carbon from more recalcitrant components of rainwater DOC, this section connects wet deposition to unresolved questions in terrestrial carbon budgeting and ecosystem-scale biogeochemistry. Wet deposition is a fundamental integrator of atmospheric chemistry, linking the atmosphere to soils, vegetation, surface waters, and human systems. While precipitation chemistry has historically been framed through the lens of inorganic solutes (e.g., sulfate and nitrate), growing evidence indicates that VOCs dissolved in precipitation are an overlooked but potentially consequential component of this linkage (Figure 3). Their removal from the atmosphere and delivery to terrestrial and aquatic ecosystems has implications for carbon cycling, biogeochemistry, ecosystem functioning, atmospheric reactivity, and global change processes.

Although relatively small compared to dominant terrestrial carbon fluxes, atmospheric deposition can still represent a meaningful external carbon subsidy, particularly in carbon-limited systems. VOC-derived compounds contribute to this flux as part of the most reactive fraction of dissolved organic carbon, especially in regions influenced by biomass burning, strong biogenic emissions, and rapid atmospheric oxidation. Low-molecular-weight oxygenated species (e.g., formic acid, acetic acid, formaldehyde, and acetaldehyde) are rapidly transformed or assimilated following deposition, in contrast to more refractory humic-like material, reinforcing their role as a fast-cycling carbon input to ecosystems.

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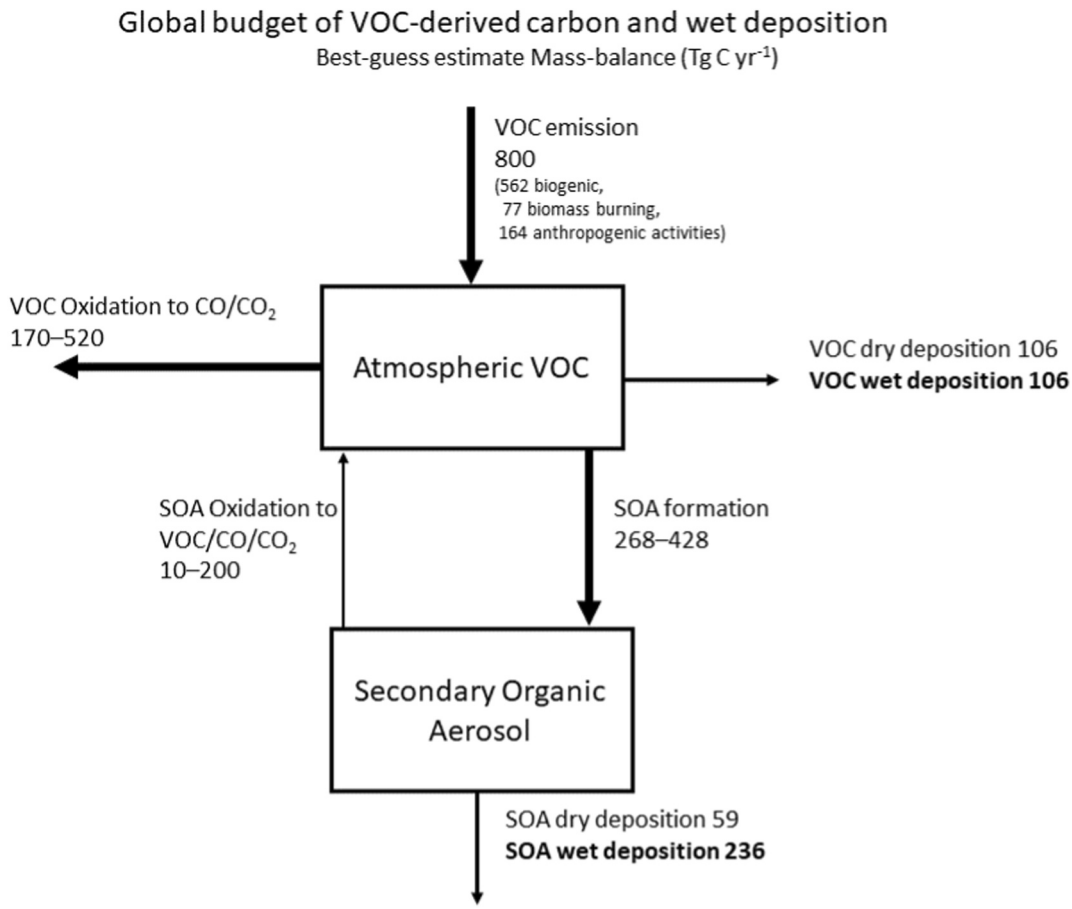

Figure 4. Best-estimate mass-balance framework for global atmospheric VOC and VOC-derived carbon, adapted from Goldstein and Galbally (2007) and updated with recent estimates. The framework follows carbon emitted as atmospheric VOCs through oxidation, gas-phase deposition, and formation of lower-volatility secondary organic aerosol (SOA), which is subsequently removed by deposition or atmospheric oxidation. The figure focuses on the VOC and VOC-derived carbon components relevant to this review and should not be interpreted as a complete budget of all atmospheric organic aerosol or total carbon in precipitation. The estimated ~460 Tg C yr^{-1} wet-deposition flux represents global DOC deposition, whereas the VOC and SOA components shown are inferred from the constraints and assumptions described in the text. Units = Tg C yr^{-1}.

These observations support the idea that rainborne VOC-derived carbon represents a dynamic and metabolically active component of atmospheric carbon transfer that remains underrepresented in current carbon-cycle frameworks.

7.1. Best-Guess Estimate Fluxes for Wet Deposition

VOCs are ultimately removed from the atmosphere through deposition, oxidation to CO and CO_2, or conversion into SOA, which itself is subsequently removed via deposition or oxidized back to more volatile products. To synthesize current understanding, we apply a conservation-of-mass framework based on Goldstein and Galbally (2007), to the global VOC-SOA budget (Figure 4). Within this framework, rainwater represents a major conduit for transferring atmospherically processed organic carbon to ecosystems, with global wet-deposition fluxes estimated at ~460 Tg C yr^{-1} (Cao et al., 2025). Organic carbon constitutes a large fraction of this flux and is often more labile than terrestrial or riverine DOC (Avery et al., 2003; Willey et al., 2000).

Global VOC emissions are constrained to approximately 800 Tg C yr^{-1}, based on updated estimates that combine biogenic (562 Tg C yr^{-1}), biomass burning (77 Tg C yr^{-1}), and anthropogenic sources (164 Tg C yr^{-1}) (Sfendla et al., 2026). See Text S3 in Supporting Information S1 for more information on the conversion from Tg yr^{-1} to Tg C yr^{-1}. Atmospheric processing pathways are quantified using observational and modeling constraints. Oxidation to CO and CO_2 accounts for 160–320 Tg C yr^{-1} (ca. 20%–40% of global emissions), consistent with

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global CO budget estimates (Granier et al., 2000). Gas-phase deposition contributes an additional ~212 Tg C yr^{-1}, inferred from wet deposition of DOC, assuming that 23% of wet-deposited DOC originates from gas-phase VOCs and that wet and dry deposition are of comparable magnitude (106 Tg C yr^{-1}). The remaining carbon must therefore be converted into lower-volatility products, implying SOA formation of approximately 268–428 Tg C yr^{-1} to close the VOC budget.

The atmospheric wet deposition of DOC (460 Tg C yr^{-1}; Cao et al., 2025) provides an important observational constraint on the organic carbon delivered through precipitation. Within this total, we estimate ~106 Tg C yr^{-1} can be associated with gas-phase VOC deposition, while the remaining dissolved organic carbon includes contributions from particle-associated organic carbon and other sources. Applying the assumptions described above, we estimate a wet-deposition flux of ~236 Tg C yr^{-1} for the SOA component. This value should therefore be regarded as an indirect, best-estimate constraint rather than a directly measured global SOA flux. Wet deposition is generally modeled to represent 70%–85% of total (wet plus dry) deposition of carbonaceous aerosols (Kanakidou et al., 2005). On this basis, we estimate that dry deposition contributes approximately 25% of the wet flux, yielding a total SOA deposition of about 295 Tg C yr^{-1}. In addition, oxidative fragmentation of SOA is estimated to return approximately 10–200 Tg C yr^{-1} to the gas phase, based on laboratory and modeling studies of aerosol aging (Kwan et al., 2006).

Taken together, gas-phase wet deposition of VOCs represents a 13.3% of total VOC emissions, whereas SOA particle-phase wet deposition represents a 30%. These constraints yield a consistent, though uncertain, mass balance for gas-phase VOCs and aerosol-phase carbon fluxes, emphasizing that these values are best-estimate approximations rather than tightly constrained quantities.

7.2. Rainborne VOCs and the Carbon Cycle

Rainwater serves as an important pathway for transferring atmospherically derived DOC to terrestrial and aquatic ecosystems. Global wet-deposition fluxes were estimated at ~430 Tg C yr^{-1} during the late 1990s—equivalent to ca. 9% of the fossil-fuel carbon emissions and cement production at that time (Willey et al., 2000). New estimates do not deviate much from this value (~460 Tg C yr^{-1}, from Cao et al., 2025). Organic carbon accounts for ~80% of total carbon deposited by rain, and much of this material is more labile and bioavailable than riverine DOC (Avery et al., 2003; Willey et al., 2000). Although atmospheric DOC deposition is small relative to major terrestrial carbon fluxes—typically 7.7–34 kg C ha^{-1} yr^{-1} compared with ecosystem gross primary productivity and respiration on the order of thousands of kg C ha^{-1} yr^{-1} (Fahey et al., 2005; Green et al., 2025; Liptzin et al., 2022; Tagesson et al., 2024)—it can nevertheless represent a meaningful external carbon subsidy that influences biogeochemical functioning. When combined with dissolved inorganic carbon inputs (~80 Tg C yr^{-1}), wet deposition has been suggested to contribute substantially to previously underestimated atmospheric carbon inputs to terrestrial ecosystems (Willey et al., 2000). Because VOCs and derived compounds are part of this labile DOC pool, their underestimation propagates uncertainty in carbon budgets and Earth system models, particularly in biomass-burning and tropical regions where rainwater delivers elevated, highly bioavailable organic carbon that can stimulate microbial metabolism and primary productivity (Godoy-Silva et al., 2017). Critically, VOCs constitute a chemically distinct and metabolically active subset of rainwater DOC. Low-molecular-weight oxygenated VOCs such as formaldehyde, acetaldehyde, formic acid, and acetic acid are rapidly assimilated or oxidized following deposition, in contrast to more aromatic or humic-like DOC components that persist longer in soils and waters. This high lability allows VOC-derived DOC to act as an immediate carbon and energy source, amplifying its biogeochemical significance relative to its mass contribution. In this sense, rainborne VOCs and VOC-derived compounds provide a mechanistic pathway through which atmospheric reactive carbon can enter ecosystems and contribute to the unexplained soil heterotrophic respiration variability or the unexpected aquatic productivity (Willey et al., 2000). Failure to resolve VOC-derived DOC separately from bulk DOC therefore obscures not only carbon flux magnitude but also carbon reactivity, masking a key linkage between atmospheric oxidation chemistry and ecosystem carbon processing.

7.3. Ecosystem Metabolism and Biogeochemical Cycling

The role of rainborne VOCs and VOC-derived compounds as a poorly acknowledged pathway linking atmospheric and ecosystem carbon cycling becomes especially evident when considering ecosystem metabolism. Because VOC-derived DOC is rapidly consumed, even modest deposition fluxes can trigger measurable

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biological responses in carbon-limited soils, surface waters, and plant-associated microbial communities. VOC wet deposition can stimulate or inhibit microbial activity in soils, surface waters, and plant-associated environments, thereby influencing nutrient transformations and trace-gas exchange. Because rainwater DOM composition varies strongly across space and time, ecological impacts are likely ecosystem-specific, with carbon-limited systems being particularly sensitive (Chen et al., 2022). In particular, VOC-derived compounds participate in elemental cycles, for example, reactions between iodine species and organic matter in precipitation form stable organo-iodine compounds, altering atmospheric oxidant budgets and potentially influencing iodine availability in terrestrial ecosystems (Gilfedder et al., 2007). Incubation and field studies indicate that a substantial fraction of rainwater organic carbon—dominated by VOC oxidation products—is consumed within days, demonstrating that VOC-derived DOC functions as a short-circuit in the carbon cycle, bypassing slow decomposition pathways and directly fueling microbial respiration and nutrient transformations. This rapid turnover contrasts with more recalcitrant DOC pools and helps explain how relatively small wet-deposition fluxes can exert outsized effects on ecosystem metabolism.

7.4. Atmosphere–Biosphere Interactions

Rainwater acts as a chemical archive of atmospheric processes, integrating emission variability, air-mass transport, and in-cloud chemistry. VOCs in precipitation capture both short-term pollution events and longer-term emission trends, offering a complementary monitoring medium to conventional air measurements—particularly where atmospheric observations are sparse (Kalkan et al., 2025). Upon deposition, VOCs may influence photochemistry and new-particle formation (Kulmala et al., 2013), SOA formation (Vaïtilingom et al., 2010), oxidative processes and surface-mediated reactions on leaves and soils. These interactions reinforce the concept that wet deposition is not merely a removal process, but also a chemically and biologically active interface between the atmosphere and biosphere. Together, these findings highlight that rainwater is not simply a carrier of dissolved compounds, but a coupled biological and chemical vector linking atmospheric processing with soil ecosystem function.

7.5. Climate Feedbacks and Global Change

Climate change is expected to increase biogenic VOC emissions (Peñuelas & Staudt, 2010), alter atmospheric chemical composition (Gaffney & Marley, 2003), modify precipitation patterns (IPCC, 2021), and influence cloud microphysics, all of which will directly affect VOC scavenging efficiency, wet-deposition fluxes, and rainwater chemistry. Mechanical stresses such as herbivory or pest damage can further stimulate BVOC emissions (Green et al., 2025), suggesting that disturbance events may contribute to elevated DOC deposition. Because VOC-derived DOC production is climate-sensitive and highly reactive upon deposition, it is a particularly responsive component of the carbon cycle under changing emission regimes and precipitation patterns. For example, following a high-wind event in 2013 damaging the forest canopy in parts of the Hubbard Brook Experimental Forest (US) (Battles et al., 2017), sustained increases in DOC concentrations in rainwater were documented (Green et al., 2025).

In a warming climate with shallower ocean mixed layers, atmospheric deposition of carbon- and nutrient-rich rainwater is also expected to exert stronger impacts on marine surface waters (Godoy-Silva et al., 2017), reinforcing the need to account for all forms of carbon in precipitation when developing reliable carbon flux models. These interactions underscore broader policy implications, and highlight that even relatively small but widespread fluxes of reactive VOCs may influence regional and global carbon budgets as climate and emission regimes continue to shift. These climate-driven shifts highlight rainborne VOCs and derived compounds as a significant, yet largely overlooked conduit through which atmospheric change is transmitted to terrestrial and aquatic carbon cycling, reinforcing their role as a quantitatively under-constrained pathway through which atmospheric reactive carbon is transferred to terrestrial and aquatic ecosystems.

7.6. Interdisciplinary Relevance and Societal Implications

Rainborne VOCs also carry implications for water quality, infrastructure, and ecosystem functioning and human health. Wet deposition introduces reactive and toxic organic atmospheric pollutants—including BTEX—and nutrients into surface waters and groundwater used for drinking and irrigation, with ecological and economic consequences (Kalkan et al., 2025; Polkowska et al., 2011). As rainwater harvesting expands in response to drought and urban water stress, understanding VOC contamination pathways, roof and tank effects, and treatment

efficacy (e.g., granular activated carbon) becomes increasingly important for sustainable water reuse (Bąk et al., 2025). More broadly, rainwater VOCs naturally bridge atmospheric chemistry, hydrology, microbial ecology, soil science, plant physiology, and Earth system modeling, creating opportunities for genuinely interdisciplinary research (Figure 4).

8. Future Perspectives: Pathways for Advancement

Future progress on rainborne VOCs relies on overcoming long-standing technical limitations rooted in the historical focus on inorganic solutes such as sulfate, nitrate, and ammonium due to concerns over acid rain, nutrient deposition, and inorganic pollution. Advancing the field now requires coordinated developments in observation, experimentation and modeling at the interface of atmospheric chemistry and ecosystem science.

A first priority is improving observational capacity. Automated, sequential precipitation collectors that target first-flush events and constructed from VOC-inert materials and operated under temperature-controlled conditions are needed to minimize volatilization losses and contamination. Standardized global protocols for VOC sampling, preservation, contamination control and reporting will also be essential for generating comparable global data sets across regions and monitoring networks. Box 1 proposes a standard operating procedure (SOP) for rainwater sampling. Paired atmospheric–precipitation measurements, in-cloud sampling, and coordinated inter-comparison efforts are particularly needed to resolve source attribution, seasonal variability, and depositional pathways.

Box 1. Toward a VOC-Specific Standard Operating Procedure (SOP) for Rainwater Measurements

Existing precipitation chemistry protocols developed within networks such as Global Atmosphere Watch (GAW) were primarily designed for inorganic solutes (e.g., sulfate, nitrate, ammonium) and are not fully optimized for the unique analytical challenges posed by volatile organic compounds (VOCs). Because VOC measurements are especially sensitive to volatilization, adsorption, contamination, and post-collection transformation, we propose the following minimum requirements as the basis for a VOC-specific standard operating procedure (SOP) for rainwater monitoring:

1. *VOC-inert collection systems*. Rainwater should be collected using pre-calcined glass, electropolished and passivated stainless steel, PTFE, or similarly inert materials to minimize adsorption, leaching, and contamination from reactive surfaces or polymers.
2. *Immediate sample stabilization*. Samples should be stabilized immediately after collection through cooling/freezing and, where analytically appropriate, acidification or biocide addition to suppress microbial degradation and post-collection chemical transformation.
3. *Zero-headspace storage and rapid processing*. Samples should be transferred into airtight containers without headspace (if freezing is not happening) and stored under refrigerated or frozen conditions to minimize volatilization losses and oxidative alteration prior to analysis.
4. *Sequential precipitation sampling*. Automated sequential collectors capable of isolating first-flush rainfall fractions should be prioritized over bulk-event collection because VOC concentrations and scavenging efficiencies vary strongly during storm evolution.

We propose these recommendations as an initial framework for harmonized VOC precipitation measurements within existing international atmospheric monitoring infrastructures, particularly ACTRIS and Global Atmosphere Watch. Coordinated protocol development, intercomparison exercises, and long-term implementation will be essential for generating globally comparable datasets capable of constraining VOC wet-deposition fluxes, multiphase atmospheric chemistry, and ecosystem impacts under changing climate and emission regimes.

Future work must also expand beyond the dominant focus on short-chain oxygenated compounds to include hydrophobic VOCs, aromatic hydrocarbons (e.g., BTEX), terpenoids, pesticides, and multiphase oxidation products, which remain substantially underrepresented in rainwater observations. Advances in analytical techniques, including cryogenic pre-concentration, purge-and-trap systems, dynamic dilution, SPME-GC–MS,

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PTR-MS (Šoštarić et al., 2016), GC × GC, Orbitrap MS, and FT-ICR-MS (Altieri et al., 2009b), are increasingly enabling speciated VOC measurements in precipitation. However, the high capital cost, operational complexity, and maintenance demands of these instruments remain a significant barrier to widespread implementation, particularly outside well-resourced laboratories. Addressing this challenge will require coordinated investment in shared facilities, development of cost-effective and field-deployable methods, and inter-laboratory calibration using certified reference materials to ensure data comparability.

A central research priority is resolving the chemical fate of VOCs during wet deposition. Key uncertainties? include the kinetics and products of oxidation, hydration, oligomerization, and incorporation into dissolved organic matter within cloud and rain droplets, as well as VOC reactivity during transport and after deposition. Addressing these gaps requires laboratory droplet experiments, in situ aircraft-based cloud sampling, and low-volume extraction of fog, drizzle, and small rain events to unravel multiphase pathways that shape secondary organic material and influence reactive carbon cycling. Quantifying regional and global VOC wet-deposition fluxes, particularly in the Global South and Southern Hemisphere (Godoy-Silva et al., 2017; Kieber et al., 2002), is equally critical. Coordinated atmospheric and precipitation measurements are needed to disentangle biogenic and anthropogenic sources (Green et al., 2025; Zhao et al., 2022) and to constrain droplet-scale transformation pathways by investigating VOC reactivity during transport and after deposition.

Understanding ecosystem responses to VOC-rich rainfall represents another major frontier. Microbiologists and soil biogeochemists must quantify the lability, uptake thresholds, and metabolic fate of deposited VOCs across contrasting soils and aquatic systems, while assessing impacts on nutrient cycling and trace-gas exchange, even at the cloud level (Ervens et al., 2025). Plant physiologists are needed to investigate foliar uptake, leaf-surface chemistry, and whole-plant responses under natural wetting conditions (Ossola et al., 2024). Hydrologists play a critical role in refining wet-deposition models and determining how rainfall intensity, duration, and cloud microphysics regulate VOC fluxes and redistribution across landscapes. Such issues gain urgency as warming, altered precipitation regimes, and rising biogenic and anthropogenic VOC emissions reshape atmospheric chemistry.

Finally, Earth system and chemical transport modelers are indispensable for integrating these advances into predictive frameworks. Explicit representation of VOC partitioning, droplet chemistry, realistic pH controls, and ecosystem feedbacks is required to reduce one of the largest remaining uncertainties in atmospheric chemistry and biogeochemical modeling (Neu & Prather, 2012; Seinfeld & Pandis, 2006; Shah et al., 2020). Because rainwater VOCs inherently link atmospheric oxidation, deposition, soil and plant responses, and biogeochemical fluxes, progress will require sustained interdisciplinary collaboration to achieve a comprehensive, mechanistic understanding of how wet-deposited VOC-derived DOC influences both atmospheric composition and ecosystem functioning under changing climate and emission regimes. Finally, as rainwater harvesting expands as a consequence of global change, recognizing and monitoring VOCs as contaminants becomes increasingly critical for agricultural reuse, drinking-water security, urban infrastructure planning, health-risk assessment, and future air-quality policy, making VOC-inclusive precipitation monitoring a likely component of emerging regulatory frameworks.

9. Conclusion—A New Frontier in Earth System Sciences

Rainwater has long been recognized as a conveyor linking the atmosphere to the Earth's surface, yet its dissolved VOCs have remained largely invisible to biogeosciences. Emerging evidence suggests that rainborne VOCs and VOC-derived compounds represent a missing link in carbon cycling (not as the entire missing sink, but as a mechanistic explanation for unexplained soil heterotrophic respiration variability or unexpected aquatic productivity), a modulator of atmospheric oxidizing capacity, and a driver of ecosystem metabolic responses. Their fluxes, transformations, and impacts remain poorly constrained—not because they are unimportant, but because their volatility, reactivity, and chemical diversity challenge conventional rainwater chemistry approaches. Studying VOCs and VOC-derived compounds in rainwater has become urgent because global change is simultaneously increasing atmospheric VOC loads, altering rainfall chemistry, and intensifying the ecological and societal relevance of rainwater. Because wet deposition simultaneously removes VOCs from the air and delivers them to ecosystems, it represents a dual-impact pathway central to pollution control, ecosystem health, and biogeochemical cycling. Yet removal efficiencies and ecological outcomes are not well understood due to

limited observational data sets, analytical challenges, and technological limitations of existing rainwater samplers.

Improved, speciated monitoring of VOCs is indispensable for capturing the full organic component of wet deposition and for resolving their roles in atmospheric oxidation, SOA formation, carbon cycling, and ecosystem inputs. By integrating improved sampling, advanced analytical tools, controlled experiments, and mechanistic modeling, the biogeosciences community can open a new research frontier at the interface of atmospheric chemistry, hydrology, and ecosystem science, and thus achieve a necessary step toward a more complete understanding of atmosphere–biosphere interactions. The historical neglect of rainborne VOCs has likely resulted in significant biases in global carbon budget models, incomplete understanding of ecosystem resilience to atmospheric change, and underestimation of certain contaminant exposure pathways. Addressing this omission is not merely an academic exercise but a critical step towards more accurate Earth system prediction and environmental management. Recognizing VOCs in rainwater challenges long-held assumptions about wet deposition and expands the scope of processes considered in global change research. Doing so holds clear potential for breakthroughs in predicting, managing, and adapting to environmental change in a warming and increasingly polluted world.

Abbreviations

AAS	Atomic Absorption Spectroscopy
ANC	Acid-neutralizing capacity
BTEX	Benzene, Toluene, Ethylbenzene, Xylene (Volatile aromatic hydrocarbons)
BVOC	Biogenic Volatile Organic Compounds
CCN	Cloud Condensation Nuclei
CDOM	Chromophoric Dissolved Organic Matter
CUPs	Currently Used Pesticides
DDS	Dynamic Dilution System
DDT	Dichlorodiphenyltrichloroethane
DNPH	4-Dinitrophenylhydrazine
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
DON	Dissolved Organic Nitrogen
FIA	Flow Injection Analyzer
FT-ICR-MS	Fourier Transform Ion Cyclotron Resonance Mass Spectrometry
GAW	Global Atmospheric Watch
GCxGC-TOF-MS	2D Gas Chromatography Time of Flight mass Spectrometer
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulfuric acid
HCH	Hexachlorocyclohexanes
HDPE	High-Density Polyethylene
HMW	High Molecular Weight
HNO_3	Nitric acid
HONO	Nitrous acid molecular formula

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HPLC	High Performance Liquid Chromatography
HULIS	Humic-like substances
IC	Inorganic Carbon
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP–OES	Inductively Coupled Plasma Optical Emission Spectroscopy
IEPOX	Isoprene Epoxidiols
LMW	Low Molecular Weight
MBTH	3-Methyl-2- benzothiazolinone hydrazone
MTBE	Methyl tert-butyl ether
NH_4	Ammonium
NO_x	Nitrogen oxides: nitric oxide (NO) and nitrogen dioxide (NO_2)
NPOC	Non-Purgeable Organic Carbon
O_3	Ozone
OPEs	Organophosphate esters
PAH	Polycyclic Aromatic Hydrocarbons
PCBs	Polychlorinated Biphenyls
PCDD/Fs	Polychlorinated dibenzo-p-dioxins and dibenzofurans
PCE	Tetrachloroethene
PFBHA	O-(2,3,4,5,6-Pentafluorobenzyl) hydroxylamine
PFAs	Per- and polyfluoroalkyl substances
PM	Particulate Matter
POC	Particulate Organic Carbon
POP	Persistent Organic Compounds
PRLIS	Protein-like substances
PTFE	Polytetrafluoroethylene
PTR-TOF-MS	Proton Transfer Reaction Time of Flight Mass Spectrometers
SAW	Surface Acoustic Wave sensors
SO_2	Sulfur dioxide
SOA	Secondary Organic Aerosol
SPME	Solid-Phase Microextraction
SVOC	Semi-Volatile Organic Compounds
TC	Total Carbon
TCE	Trichloroethylene
TEX	Toluene, Ethylbenzene, Xylenes
TOC	Total Organic Carbon
TON	Total Organic Nitrogen

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TPHP	Triphenyl Phosphate
TRYLIS	TRYptophan-LIke Substances
TYLIS	TYrosine-LIke Substances
UCM	Unresolved Complex Mixtures
VOC	Volatile Organic Compounds
VOX	Volatile Organohalogens
WSOC	Water-Soluble Organic Carbon

AI Tools Disclosure

Portions of this manuscript were refined for clarity and conciseness using an AI-assisted language model (ChatGPT, OpenAI, Gemini Pro and Copilot). All scientific content, interpretations, and conclusions were developed by the authors, who reviewed and approved the final text.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Availability Statement

Data were not used, nor created for this research.

Acknowledgments
This research was supported by the Spanish Ministry of Science and Innovation, the NextGenerationEU program of the European Union, the Spanish plan of recovery, transformation and resilience, and the Spanish Research Agency under the Consolidación Investigadora project (CNS2022-135757). AMYS also acknowledges La Caixa Foundation Junior Leader retaining and the support from her Ramon y Cajal grant (RYC2021-032519-I). Furthermore, it has also been supported by the Generalitat de Catalunya (AGAUR 2021 SGR 00447), and Departament de Territori, Habitatge i Transició Ecològica (DTER) of the Generalitat de Catalunya. AA acknowledges the project AIRPHONEMA PID2022-142160OB-I00 MCIN/AEI/10.13039/501100011033/FEDER EU. JP was supported by the Spanish Government Grant PID2022-140808NB-I00 funded by MCIN, AEI/10.13039/501100011033 European Union Next Generation EU/PRTR. RS acknowledges a Ramón y Cajal grant (RYC2020-029216-I) funded by MICIU/AEI/10.13039/501100011033 and by "ESF Investing in your future," and projects PID2021-122892NA-I00 and PID2024-162194OB-I00 funded by MICIU/AEI and by "ERDF A way of making Europe." JPey acknowledges his Grant PID2022-143146OB-I00 funded by MCIN, AEI/10.13039/501100011033 European Union Next Generation EU/PRTR. MI acknowledges her Grant PID2023-148914OB-I00 funded by MICIU/AEI/10.13039/501100011033 and by the European Union NextGenerationEU/PRTR.

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