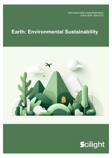
Earth: Environmental Sustainability
https://www.sciltp.com/journals/eesus



Article

Pollutants in Rainwater: Analytical Advances, Key Challenges, and Environmental Significance

Nina Felli, Massimo Giuseppe De Cesaris *, Lorenzo Antonelli, Giulia Bertini, Chiara Dal Bosco and Alessandra Gentili

Department of Chemistry, Sapienza University, P.le Aldo Moro 5, 00185 Rome, Italy
* Correspondence: massimogiuseppe.decesaris@uniroma1.it

How To Cite: Felli, N.; De Cesaris, M.G.; Antonelli, L.; et al. Pollutants in Rainwater: Analytical Advances, Key Challenges, and Environmental Significance. *Earth: Environmental Sustainability* **2026**, *2*(1), 37–55. https://doi.org/10.53941/eesus.2026.100004

Received: 20 October 2025
Revised: 14 January 2026
Accepted: 20 January 2026
Published: 28 January 2026

Abstract: Rainwater plays a key yet often underestimated role in the atmospheric transport and deposition of environmental contaminants, contributing to the dissemination of both traditional and emerging pollutants across urban, industrial, and remote areas. For the first time, rainwater as an analytical matrix is systematically addressed, providing a critical synthesis of the objectives, strategies, and methodological approaches required for a comprehensive investigation of atmospheric contamination mediated by precipitation. This review aims to provide a comprehensive overview of the major classes of contaminants detected in rainwater and to critically examine the analytical strategies currently employed for their determination at trace and ultra-trace levels. The manuscript discusses the most widely applied sample preparation techniques, with particular emphasis on solid-phase extraction using polymeric and mixed-mode sorbents, alongside complementary approaches such as liquid-liquid extraction, solid-phase microextraction, and treatments of the particulate fraction. Instrumental methodologies based on gas chromatography and high-performance liquid chromatography coupled with mass spectrometry are presented as the gold standard for multiresidue analysis of organic pollutants, while ion chromatography and ICP-MS are highlighted for inorganic and metal contamination profiling. The review highlights current trends, methodological strengths, and limitations in rainwater analysis. Overall, this work underscores the importance of integrated and robust analytical approaches to achieve a comprehensive assessment of rainwater contamination and identifies existing gaps in linking analytical data with atmospheric processes, source attribution, and health risk assessment, thereby reinforcing the relevance of rainwater monitoring in environmental and public health studies.

Keywords: rainwater contamination; emerging pollutants; atmospheric deposition; health implication; analytical chemistry

1. Introduction

In recent years, the issue of environmental contamination has attracted increasing attention from both the scientific community and the public opinion. The presence of chemical pollutants in environmental matrices, such as water, soil, air, and sediments, is now recognized as a serious global concern due to its direct impact on ecosystems and human health [1]. While traditional sources of contamination, such as industrial effluents, wastewater discharges, and stormwater runoff, have been extensively studied for their role in pollutant release and transport, the role of rainwater as a potential carrier of atmospheric pollutants remains underexplored and warrants further investigation [2]. Rainwater, in fact, plays a key role in the atmospheric transport of contaminants from polluted urban and industrial areas to remote or relatively pristine environments [3–5], even at considerable distances [6,7]. The composition of precipitation is mainly determined by atmospheric conditions, specifically by the type and concentration of both natural and anthropogenic pollutants present in the air. The amount and type of precipitation, along with wind direction and cloud height, also influence the chemical composition of precipitation. Through these processes, atmospheric pollutants are transported and deposited into water bodies and onto the soil [8]. The different types of precipitation, including direct rainfall, throughfall, and stemflow, contribute in varying ways to this transfer of pollutants. Throughfall, the portion of rainwater that passes through the forest canopy, differs chemically from direct rainfall due to canopy exchange processes, as well as the dissolution and washing off of aerosols and gaseous pollutants adsorbed onto leaves, branches, and bark [9]. Environmental pollutants originate from human activities, including industrial production, intensive agriculture, urban expansion, and the widespread use of synthetic materials and chemicals in everyday life, including sulfur, nitrogen, and carbon compounds, soot, and solid particulate matter. In industrialized areas, these are joined by by-products of industrial processes, incomplete combustion of fossil fuels, and typical emissions such as CO_2, NH_3, H_2S, nitrogen and sulfur oxides, heavy metals, and metal oxides [10]. Within the broad spectrum of environmental pollutants, in recent years, increasing concern has been directed toward emerging contaminants (ECs), reflecting the intensification of industrial production, agricultural practices, and the widespread use of synthetic chemicals [11]. In fact, ECs include pesticides, hydrocarbons, and various synthetic chemicals such as pharmaceutical residues, personal care products, endocrine-disrupting compounds, per- and polyfluoroalkyl substances (PFAS), microplastics [12], nanoplastics, cosmetics, surfactants, cleaning agents, industrial chemicals, food additives, packaging materials, metalloids, rare earth elements, nanomaterials, and even pathogens [13,14], whose environmental behavior, persistence, and toxicological impacts remain only partially understood [4,14]. Many ECs exhibit high chemical stability and resistance to degradation, enabling them to bioaccumulate and disperse over long distances, which makes detection and control difficult. Despite their increasing occurrence, most are still not subject to mandatory monitoring or disclosure in water supplies and wastewater systems. Their management is further complicated by complex environmental behavior, persistence at trace or ultra-trace levels, and potential for long-range transport. In addition, the absence of comprehensive regulations and the limited knowledge of their long-term impacts hinder effective strategies to limit their spread and mitigate associated risks [14]. The growing global population is driving a continuous increase in water demand for various human activities [8]. In regions with higher rainfall availability, this demand can be partly addressed through rainwater harvesting (RWH), which is emerging as a sustainable strategy to complement decentralized water supply systems and to provide drinking water even in remote communities lacking centralized infrastructure [15,16]. However, the direct consumption of untreated rainwater is discouraged, as precipitation can carry atmospheric pollutants and organic substances, while also being susceptible to biological contamination from animals [17]. Moreover, rainwater may disseminate pathogens and antibiotic resistance genes, highlighting the need for enhanced research and monitoring to fully assess its environmental implications.

Rainwater is generally regarded as a low-complexity environmental matrix, characterized by low organic content and limited matrix interferences [13]. The analytical challenge, however, mainly arises from the need to detect contaminants at ultra-trace levels, to perform multiresidue analyses, and to account for the wide diversity of physicochemical properties exhibited by rainwater-borne pollutants [18]. One of the most critical and analytically demanding aspects of such studies is the ability to provide a comprehensive snapshot of the contamination spectrum affecting this environmental compartment [19,20]. In this context, solid-phase extraction (SPE), particularly cartridge- or disk-based approaches employing polymeric sorbents with broad selectivity or mixed-mode functionalities, represents the most widely adopted and effective pretreatment strategy, as it enables high enrichment factors and simultaneous recovery of analytes spanning a wide polarity range. Complementary techniques, such as liquid-liquid extraction (LLE), solid-phase microextraction (SPME), and selective treatments of the particulate fraction are applied depending on the target analyte class, thereby allowing a more complete characterization of both dissolved and particulate-associated contaminants in rainwater. Regarding instrumental analysis, the techniques of choice are generally gas chromatography (GC) or high-performance liquid chromatography (HPLC) coupled with mass spectrometry (MS). These hyphenated platforms are widely regarded as the gold standard for multiresidue analysis at ultra-trace levels, owing to their high sensitivity, selectivity, and robustness. Ion chromatography (IC) remains highly relevant for the characterization of inorganic contaminants, particularly heavy metals, and is frequently coupled with elemental analysis by inductively coupled plasma mass spectrometry (ICP-MS) to define comprehensive metal contamination profiles. The interpretation of experimental data remains the most critical aspect of rainwater analysis, particularly when the objective is to elucidate local contamination sources and dispersion phenomena [4]. Integrated models capable of combining meteorological processes with analytical contamination data and health risk assessment are still limited, highlighting a significant gap in the comprehensive interpretation of rainwater monitoring results [13]. Understanding the complex dynamics of atmospheric pollution, its deposition through precipitation, and its subsequent impacts is essential for developing effective strategies to safeguard both ecosystems and human health from both traditional and ECs. This review provides a comprehensive overview of the major classes of environmental contaminants and the analytical approaches available for their detection, with particular attention to organic pollutants in rainwater as an often-overlooked pathway of transport and exposure. By examining current methodologies, recent innovations in sample preparation, and their contribution to greener analytical practices, we aim to address key challenges and environmental implications. Ultimately, this review emphasizes the critical role of rainwater monitoring in advancing our understanding of contaminant cycling and assessing ecological risks.

2. Organic and Inorganic Contaminants in Rainfall

2.1. Volatile and Semi-Volatile Organic Compounds

Atmospheric organic contaminants can be distinguished by their sources, environmental behaviour, and ecotoxicological impacts [21]. Among all, volatile and semi-volatile organic compounds (VOCs/SVOCs) represent a major class of atmospheric contaminants due to their high mobility, diverse chemical nature, and significant environmental and health implications [22]. This class encompasses a wide range of compounds, including aliphatic and aromatic hydrocarbons (e.g., benzene, toluene, xylenes), halogenated hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), oxygenated species such as aldehydes, ketones, and carboxylic acids, nitrogen-containing organics, phenols, and a variety of modern and legacy pesticides [23]. If VOCs are primarily emitted through anthropogenic activities, including vehicle exhaust, industrial processes, solvent usage, residential heating, and agricultural applications, SVOCs often originate from sources with lower volatility, such as surface coatings, plastics, and combustion residues [24]. However, regardless of their origin, their persistence, fate, and presence in rainwater strictly depend on the movement of air masses, climatic, seasonal, and daily variations, as well as the amount of solar radiation that favors their degradation [25].

For instance, D. Yao et al. quantified the total VOCs (TVOCs) in Beijing city, China, during spring months, detecting a TVOCs amount of 30.4 ± 17.0 $\mu g/m^3$ [26]. The TVOCs composition was dominated by alkanes (44.3%), followed by oxygenated VOCs (OVOCs) (17.4%), halogenated hydrocarbons (12.7%), aromatics (9.5%), alkenes (8.2%), acetylene (5.3%), and carbon disulfide (2.5%). The authors observed that the relative proportion of contaminants varied dramatically throughout the day, decreasing at night due to the reduction in human activities. Furthermore, they revealed the non-negligible contribution of the air mass of nearby cities and provinces to the total air mass composition over Beijing, highlighting how the movement of winds and air masses dramatically influences air quality.

In another study, Shi et al. investigated VOC concentrations in Kunming, China during both the dry and wet seasons, with particular focus on the rainy period [27]. Their findings showed that the environmental and health implications of VOCs/SVOCs depend not only on air mass mobility but also on precipitation events. Specifically, they reported that TVOCs concentrations during the rainy season were about 50% lower than in the dry season, due to the washing effect of intense rainfall. Both processes, atmospheric transport and precipitation, facilitate the displacement and deposition of contaminants into remote ecosystems, where they may accumulate in biota or enter human use, thereby posing tangible risks to human health [28].

As previously mentioned, a representative class of substances belonging to VOCs/SVOCs is represented by PAHs. PAHs, characterized by fused aromatic rings, are environmentally concerning due to their persistence, lipophilicity, and toxicological properties (mutagenic and carcinogenic) [29]. They are mainly produced by incomplete combustion of organic matter, with anthropogenic sources, such as vehicle emissions, residential heating, industrial processes, and waste incineration, representing the dominant contributors in urban and industrialized areas [30]. Natural sources, including forest fires, volcanic eruptions, and diagenetic processes in sediments, also contribute to atmospheric PAHs, but their relative contribution is typically lower in populated areas [31]. Once released, their atmospheric behavior depends on molecular weight (MW): lighter PAHs (2–3 rings) remain in the gas phase, while heavier ones (4–6 rings) adsorb onto particulate matter [32]. This partitioning governs their transport and fate, as particle-bound PAHs can undergo long-range atmospheric dispersion and deposit onto soils, waters, or snow through wet and dry deposition. Moreover, in the atmosphere they undergo photolysis and oxidation (e.g., by OH radicals or ozone (O_3)), leading to oxygenated derivatives and reactive intermediates that impact both air quality and secondary organic aerosol (SOA) formation.

Mu e coworker investigated the presence of 16 PAHs in Yitong River water after continuous rainfall events [33], detecting and quantifying 7 out of 16 PAHs especially with low MW, mainly composed of two to three rings, with total concentrations ranging 279.19–756.37 ng/L. Likewise, Nguyen et al., in a similar study conducted in Ulsan, South Korea, investigated the spatial distribution and temporal variation of PAHs observing how low MW are frequently encountered dissolved in the precipitation wet fraction, while higher MW are generally adsorbed on particulate matter [34]. Additionally, they observed that during the hotter month of the year the dissolved fraction increased due to the partial desorption of PAHs from the solid particles. Figure 1 schematically summarizes the phase distribution of VOC and SVOCs in atmosphere and their occurrence in precipitation events.

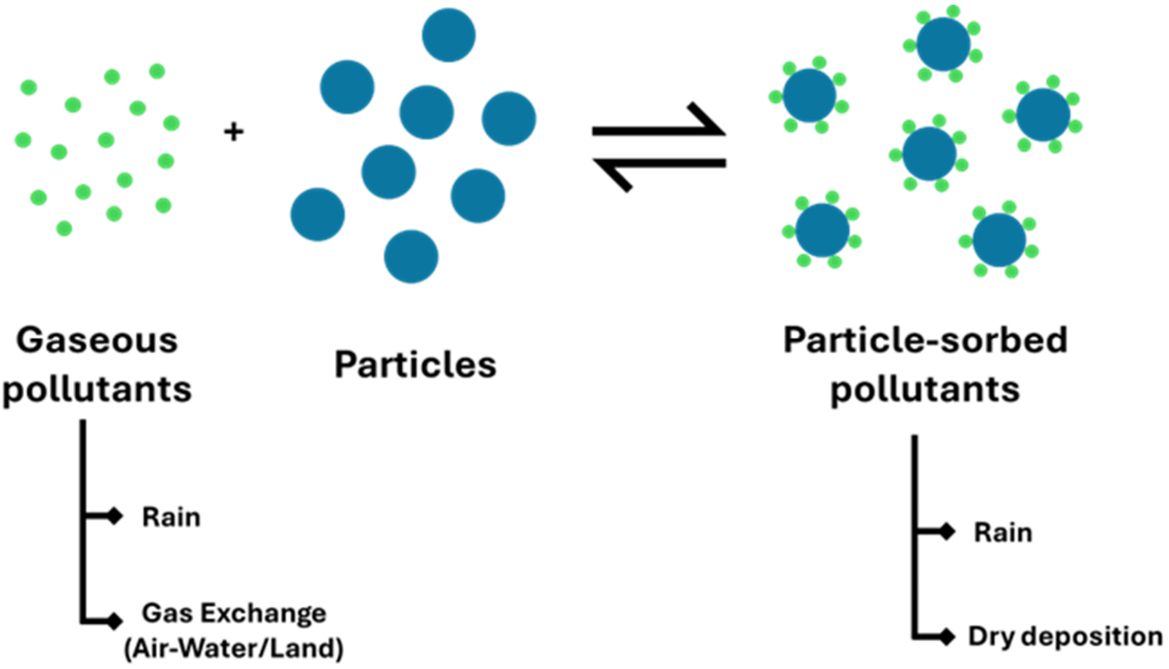


Figure 1. Schematic representation of the phase distribution of semivolatile pollutants and their occurrences in atmospheric events.

Overall, PAHs illustrate how VOCs and SVOCs combine persistence, mobility, and reactivity, connecting emission sources with atmospheric transport and transformation processes. Their tendency to partition between gas and particle phases, undergo chemical reactions, and deposit into diverse environmental compartments highlights the multiple pathways through which these compounds can accumulate, persist, and ultimately threaten both ecosystem integrity and human health.

2.1.1 Oxygenated Volatile Organic Compounds

Once released into the atmosphere, VOCs undergo a variety of physical and chemical processes, including oxidation and photolysis, giving rise to OVOCs. These compounds may have both primary and secondary origins: primary OVOCs are directly emitted from biogenic and anthropogenic sources such as vegetation, biomass burning, or fossil fuel combustion, whereas secondary OVOCs are predominantly formed through the atmospheric oxidation of hydrocarbons by oxidants such as OH radicals, O_3, and NO_3 radicals (Figure 2) [35,36]. Their formation and transformation play a pivotal role in tropospheric chemistry, contributing to O_3 generation, SOA production, and ultimately affecting air quality and climate and participating in processes that lead to acidification of precipitation [37]. Similar to VOCs/SVOC, OVOCs share chemical and physical properties such as partition between the gas phase and particulate matter, volatility, and stability, which affect atmospheric transportation and deposition [38]. Wet and dry deposition processes allow both local and regional dispersal, carrying these compounds to soils, surface waters, and vegetation as reported by Pfannerstill et al. [39]. The authors monitored the OVOCs reactivity during rain events, discovering them as the main contributors to OH reactivity, with short-term spikes driven by turbulence and possible re-volatilization from wet surfaces. Following precipitation, OH reactivity decreased by ~30%, primarily due to wet deposition removing water-soluble OVOCs and reduced plant emissions caused by lower temperature and irradiation [40].

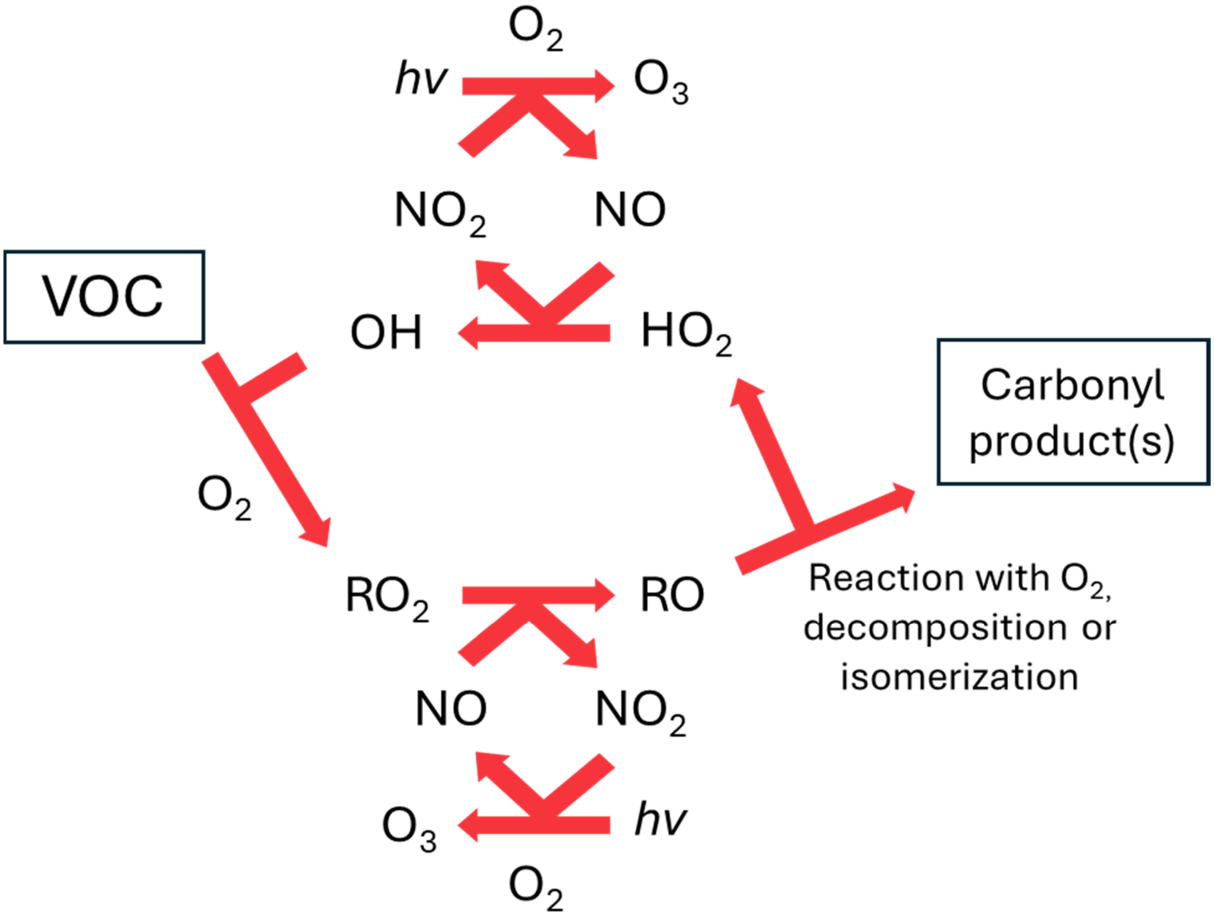


Figure 2. VOCs oxidation scheme and their contribution to O_3 pollution and OVOCs generation.

2.2. Persistent Organic Pollutants

Persistent organic pollutants (POPs) are highly stable, lipophilic organic compounds that resist environmental degradation and tend to bioaccumulate in living organisms, primarily emitted through anthropogenic activities [41]. POPs include polychlorinated biphenyls (PCBs), dioxins and furans (PCDD/Fs) [42] organophosphate esters (OPEs), organochloride pesticides (OCPs) such as DDT and lindane, polybrominated diphenyl ethers (PBDEs), and per- and PFAS. They are regulated under the Stockholm Convention, although the list of substances is continuously being updated due to increasing anthropogenic activity [43]. Similarly to the previous class, they can be transported over long distances by atmospheric events, reaching regions where they have never been produced or used, such as the Arctic [44] and Antarctic [45]. Many POPs are semi-volatile, allowing them to cycle between the gas phase and particle-bound phase which facilitates their global dispersion [46].

Luarte and coworkers demonstrate the important role of the low temperatures of Antarctica in the environmental fate of POPs, repressing re-volatilization processes and favoring cold trapping, deposition which limit any potential degradation [47]. In particular, they evaluated the atmospheric half life of some common POPs estimating times following the order: 4,4′ DDE (13.5 years) > 4,4′ DDD (12.8 years) > 4,4′ DDT (7.4 years) > 2,4′ DDE (6.4 years) > 2,4′ DDT (6.3 years) > α-HCH (6 years) > HCB (6 years) > γ-HCH (4.2 years). While for PCB congeners, they decreased in the following order: PCB 153 (7.6 years) > PCB 138 (6.5 years) > PCB 101 (4.7 years) > PCB 180 (4.6 years) > PCB 28 (4 years) > PCB 52 (3.7 years) > PCB 118 (3.6 years). Again, atmospheric wet events such as rain or snow play a pivotal role in the scavenging of atmospheric contaminants both adsorbed on particulates and in gas-phase. In particular, Figure 3 reports the meta-analyses conducted by Cacas et al. which depicts the coefficient partition rain/particulate ($\log K_{RP}$) of some common POPs.

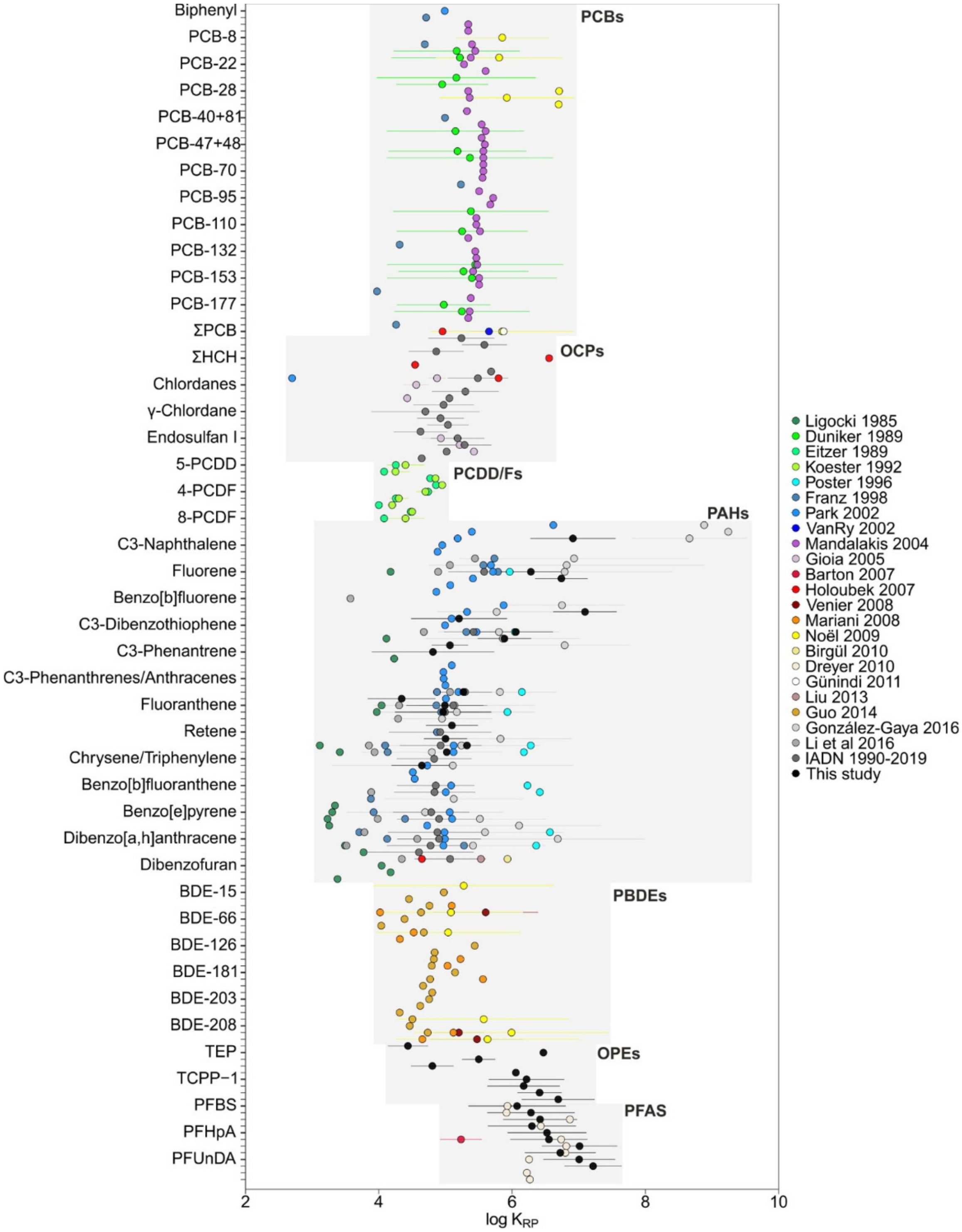


Figure 3. Meta-analysis of rain-air particulate partition constants (K_{RP}) for various families of organic pollutants. The results shown are the mean and the standard deviation of logK_{RP} (reproduced from [46]).

The value ranges from 2.6–11.5 with average value of 5.5 [46]. The highest values were observed for OPE (2.7–6.6), PFAS (3.6–8.8), PCB (4.0–7.0) and some high MW PAHs. When comparing these values across different environments, such as continental/urban versus coastal/open ocean regions, substantial differences were noted, with lower values typically found in continental and urban areas. The rain/gas phase partition coefficient (logK_{RG}) assessed and found to be generally lower than logK_{RP} ranging from 1.1 to 9.6, with a mean value of 4.4, and with higher value for high MW compounds. The authors also highlighted that precipitation scavenging, both by snow and rain, can amplify POPs deposition to a similar extent [46]. However, snow deposition is restricted to cold regions and/or winter periods, whereas rainfall occurs more broadly across seasons and climatic zones, making it the dominant mechanism for POPs removal from the atmosphere.

2.3. Inorganic Contaminants and Heavy Metals

Inorganic contaminants are worth mentioning as another critical component of atmospheric chemistry and environmental pollution, as they exert significant influences on air quality, cloud microphysics, acid deposition, and ecosystem health [48]. Among the most relevant species, the principal inorganic ions include nitrate (NO_3^-), sulfate (SO_4^{2-}), and ammonium (NH_4^+). These ions are ubiquitous in atmospheric waters and aerosols, often constituting a major fraction of fine particulate matter ($PM_{2.5}$) [47]. NO_3^- is predominantly formed through the atmospheric oxidation of nitrogen oxides (NO and NO_2) emitted from fossil fuel combustion, vehicular traffic, and biomass burning, while, SO_4^{2-} originates primarily from the oxidation of sulfur dioxide (SO_2), which is released during the combustion of coal and heavy oil, as well as from volcanic activity [49]. NH_4^+, in contrast, derives largely from agricultural sources, particularly volatilization of ammonia (NH_3) from livestock manure, synthetic fertilizers, and natural soil emissions [50]. The coexistence of these ions is strongly linked to the formation of secondary inorganic aerosols, contributing to regional haze, reduced visibility, and atmospheric acidity, which in turn affects precipitation chemistry and accelerates material degradation [51]. In addition to ionic species, heavy metals represent another common class of inorganic atmospheric contaminants with both soluble and particulate-bound forms influencing their transport, deposition, and bioavailability. Key metals of concern include lead (Pb), cadmium (Cd), zinc (Zn), copper (Cu), chromium (Cr), and mercury (Hg) [52]. These elements originate from diverse natural and anthropogenic sources such as gasoline, industrial processes, battery recycling, and metal smelting, fossil fuel combustion, metallurgical activities, waste incineration, and the abrasion of tires and brake linings in urban environments. The physicochemical form of these metals is of particular importance: water-soluble species exhibit higher mobility and ecological risk, as they can be readily incorporated into cloud droplets and rainwater, enhancing deposition fluxes [53]. An additional dimension to the behavior of inorganic contaminants in the atmosphere involves their interactions with organic compounds, which significantly influence both their physicochemical properties and their environmental fate [54]. Adsorption processes facilitate the attachment of inorganic species, particularly heavy metals (Pb, Cd, Zn, Cu, Cr, Hg), on organic aerosol surfaces. This interaction alters both the solubility and reactivity of the metals: while hydrophilic organic coatings may enhance dissolution and mobility, hydrophobic layers can stabilize metals in particulate form, extending their atmospheric residence time [55]. Furthermore, functional groups present in organic compounds (e.g., carboxyl, hydroxyl, phenolic groups) can act as chelating agents, forming stable metal-organic complexes that modify deposition pathways and influence bioavailability upon entering aquatic or terrestrial ecosystems [45]. From a deposition perspective, the coupling of inorganic and organic fractions in aerosols facilitates long-range atmospheric transport, as organic coatings can shield reactive inorganic cores from rapid scavenging or transformation. Once deposited, these mixed-phase particles contribute simultaneously to nutrient input (e.g., nitrogen and sulfur) and toxic metal contamination, exerting combined stress on [56]. This dual nature underscores the importance of considering inorganic-organic interactions when assessing the environmental and health impacts of atmospheric deposition. Particulate-bound metals, particularly those associated with fine and ultrafine particles, have in addition extended human health implications on the respiratory system.

2.4. Emerging Polar Contaminants

According to the scientific literature, the term “emerging contaminants” (ECs) is defined as synthetic or naturally occurring chemicals that are not commonly monitored in the environment, but have the potential to enter it and cause known or suspected adverse ecological and/or human health effects [4]. ECs are now detected not only in urban and agricultural areas but also in remote environments, reflecting intensified industrial production, widespread agricultural chemical use, and the pervasive application of synthetic compounds. As a result, numerous studies have investigated their occurrence, distribution, and analytical determination. ECs include a variety of substances such as modern agrochemicals, pharmaceuticals, personal care products, and industrial chemicals. Due to their chemical properties, ECs can reach all compartments, through their volatilization, aerosol formation or diffusive exchange process in the case of the atmosphere, dry and wet deposition in the case of soil and aqueous compartment, and through leaching and run off in the case of aqueous compartment [4]Additionally, many ECs exhibit high chemical stability and resistance to degradation, enabling them to bioaccumulate and disperse over long distances, which makes detection and control difficult. For example, Lee et al. [2] focused their attention on 26 emerging polar contaminants (EPCs) mainly associated with urban pollution sources in Northern Thailand. In particular, the presence of pharmaceuticals, industrial compounds, and agrochemicals at rural and remote sites suggested that rainfall may act as a vector for the long-range transport of these contaminants. To assess this contribution, concentrations of EPCs in rainwater and throughfall were compared with those measured in surface waters at remote locations. Among these, ten compounds were frequently detected. Notably, 4-nitrophenol showed the highest concentrations, with median values of 1431 ng L^{-1} in rainfall and 810 ng L^{-1} in throughfall and maximum concentrations exceeding 6.8 μg L^{-1}. Caffeine was also ubiquitous, with median concentrations of approximately 130–140 ng L^{-1} and detection frequencies up to 100%. tris(2-butoxyethyl) phosphate (TBEP) was commonly detected, reaching maximum concentrations of about 290 ng L^{-1}. Agrochemicals such as fenobucarb, atrazine, and 2,4-D were observed less frequently, with maximum concentrations of 342, 95, and 74 ng L^{-1}, respectively, and median values often below detection limits. These results provide quantitative evidence that atmospheric deposition via rainfall and throughfall represents a significant pathway for the dissemination of ECs from urban and agricultural source regions to remote aquatic environments. Alonso et al. [57] investigated the occurrence of the polar herbicides glyphosate (GLP) and atrazine (ATZ) in rainwater collected across agro-productive areas of the Pampas region in Argentina, highlighting the role of atmospheric transport and wet deposition in agricultural settings. Rainwater samples (n = 112) were collected throughout rainfall events at sites characterized by different land uses and analyzed by LC-MS. Both GLP and ATZ were detected in more than 80% of the rainwater samples, demonstrating substantial atmospheric transport and deposition in a region dominated by intensive agriculture. Specifically, GLP exhibited median-to-maximum concentrations ranging from approximately 1.24 to 67.3 μg L^{-1} in rainwater, and ATZ ranged from about 0.22 to 26.9 μg L^{-1}. The principal metabolite of GLP, aminomethylphosphonic acid (AMPA), was also present in rainwater at lower frequencies (~34% of samples) with concentrations between ~0.75 and 7.91 μg L^{-1}. These detected levels indicate that rainfall acts as an efficient wet deposition pathway for highly water-soluble herbicides, contributing significantly to their environmental redistribution and surface loading in agricultural landscapes. An interesting approach is proposed by Lamprea and colleagues [58]who demonstrated the ubiquitous presence of alkylphenols and bisphenol A (BPA) in urban materials and their extractable character with water simulating rainfall contact and runoff. Their experimental leaching tests demonstrated that BPA and nonylphenol (a representative alkylphenol) are ubiquitously present in construction and automotive materials and can be mobilized when exposed to water. The highest measured BPA emissions from materials such as polycarbonate, tires, and PVC ranged between approximately 10 ng $g^{-1}$and 300 ng g^{-1} of material when leached with water. Nonylphenol was leached in quantities of 1–10 ng g^{-1} from diverse urban substrates. In automotive fluids analyzed separately, BPA concentrations reached extremely high levels, up to 5.5 g L^{-1} in brake fluid, while nonylphenol was found at 2.3–2.9 mg L^{-1} in the same matrices. Although these fluid concentrations do not directly represent environmental rainwater levels, they reflect the high loading potential of polar contaminants in urban systems, especially when such fluids are washed off surfaces by rainfall and enter stormwater pathways. The study highlights how rain-induced contact with urban infrastructure and vehicle components can contribute to the environmental release and subsequent transport of EPCs like BPA and alkylphenols into runoff and receiving waters, reinforcing rain's role as a mediator of contaminant redistribution in urban landscapes.

3. Sample Management, Criticism in Analyses and Results Interpretation

3.1. Sample Collection, Management and Preservation

The accurate characterization of inorganic and organic compounds in precipitation critically depends on the reliability of sampling methods and the rigorous implementation of contamination control protocols [59]. Rainwater collection is generally carried out using either wet-only collectors or bulk collectors [60]. Wet-only collectors are automated systems that open exclusively during precipitation events, thereby minimizing contamination from dry deposition and ensuring that the collected sample accurately reflects the chemical composition of rainwater [61]. In contrast, bulk collectors remain open continuously, capturing both wet and dry depositions. While this approach allows for the assessment of total atmospheric inputs, it also complicates the interpretation of rain-specific processes. Advanced collectors often include temperature control and use inert materials (e.g., Teflon, polyethylene) to minimize chemical interactions between the sample and container surfaces [62]. From an operational perspective, wet-only and bulk collectors differ substantially not only in terms of sample representativeness, but also in the way sampling strategies can be implemented. Wet-only collectors, by opening exclusively during precipitation events, provide samples that are more directly attributable to in-cloud and below-cloud scavenging processes, thereby facilitating the interpretation of rainwater chemistry and source attribution. These systems are particularly well suited for event-based sampling, where individual precipitation events are collected and analyzed separately, as well as for fractional or first-flush approaches aimed at resolving intra-event variability and the enhanced contribution of atmospheric pollutants during the initial stages of rainfall [63]. However, their reliance on automated sensors and moving components increases maintenance demand and operational costs, especially in long-term monitoring programs. Bulk collectors, in contrast, offer a simpler and more cost-effective setup, enabling continuous exposure and making them suitable for time-based sampling strategies (e.g., weekly or monthly integrations) commonly adopted in long-term deposition studies. Nevertheless, the permanent exposure of bulk collectors to the atmosphere leads to the accumulation of dry deposition between precipitation events, which is subsequently dissolved during rainfall, potentially resulting in elevated solute concentrations and reduced specificity to rain-related processes. This phenomenon is particularly pronounced for species predominantly associated with particulate matter or dry deposition, such as trace metals (e.g., Pb, Zn, Cu) and ammonium, whose apparent concentrations in bulk samples tend to increase with longer integration times and extended contact with collector surfaces [64]. In addition, prolonged sample residence times in bulk collectors may promote physicochemical transformations, including adsorption-desorption processes, redox reactions, or pH-driven speciation changes, which can further complicate data interpretation. Conversely, wet-only sampling is generally more suitable for chemically reactive or less stable compounds, such as reduced nitrogen species and low-molecular-weight organic acids, whose concentration may be affected by volatilization, microbial activity, or photochemical degradation during extended exposure periods. As a result, differences between wet-only and bulk datasets are often amplified under low-frequency sampling regimes, whereas high-frequency collection and strict preservation protocols can partially mitigate these biases. Overall, the choice between wet-only and bulk sampling approaches should therefore be guided not only by the distinction between wet and total atmospheric deposition, but also by a critical evaluation of the chemical behavior, stability, and transformation potential of the target contaminants in relation to the adopted sampling strategy [62].

The implementation of standardized protocols is then essential to ensure data comparability across monitoring networks. These include specifications on collector design, sample volume requirements, and procedures for handling events of low precipitation. To prevent contamination, strict precautions are implemented: pre-cleaning of containers, immediate sample retrieval after precipitation events, and avoidance of direct handling with non-sterile equipment. Particular attention is also given to minimizing contact with atmospheric dust, insects, and plant debris, all of which may introduce trace metal or organic contaminants that could bias analytical results [65]. Field blanks and replicate sampling are often employed to evaluate background contamination and sampling precision. Post-collection treatment and preservation of rainwater samples are critical for maintaining the integrity of ionic and metallic constituents until laboratory analysis [66]. Given the low concentrations at which many analytes occur, even minor alterations during storage can significantly affect the accuracy of results. Immediately after collection, when necessary, samples are typically filtered (0.45 µm or smaller pore size) to separate dissolved and particulate fractions. With regard to filtration materials, careful selection is essential to prevent leaching or adsorption of target analytes. Among the most commonly used membranes are those made of polycarbonate and cellulose acetate.

Preservation strategies vary according to the analyte class. For cations and trace metals, acidification to $pH < 2$ with ultrapure nitric acid is routinely applied to prevent precipitation, adsorption onto container walls, and microbial activity [67]. In contrast, anions such as NO_3^- and SO_4^{2-} are generally stored without acidification to avoid chemical transformation. NH_4^+ requires particular attention as it is subject to volatilization and microbial conversion; therefore, rapid cooling to 4 °C and prompt analysis are recommended [68]. When organic fractions are analyzed together with inorganic species, freezing at −20 °C may be necessary to inhibit degradation processes [69,70].

Sample storage containers are commonly made of high-density polyethylene (HDPE) or Teflon to minimize analyte loss through wall adsorption. Glass is generally avoided for trace metal analysis due to the risk of leaching and adsorption [71]. Once stored, samples holding times prior to analysis should be kept to a minimum. International guidelines, in fact, generally recommend analyzing samples within one to two weeks for ionic species, and within a few days for more labile components such as NH_4^+ or organic carbon [67,71]. When longer storage is unavoidable, appropriate validation of stability, under chosen preservation conditions, must be performed [72]. Rigorous documentation, including chain-of-custody forms, sample metadata (time, duration, precipitation intensity, and meteorological conditions), and field notes on potential contamination events, is indispensable to ensure the reliability and traceability of the dataset [73]. Proper treatment and preservation practices not only safeguard the analytical accuracy but also enable robust interpretation of rainwater chemistry in relation to atmospheric processes and pollutant sources.

3.2. Sample Pre-Tratment

Given the wide diversity of chemical structures and properties among these contaminants, no single analytical approach can provide a universal solution [74]. Instead, tailored analytical strategies are required, combining careful sample preparation, rigorous clean-up procedures, and reliable instrumental platforms with the analytical requirement.

In the monitoring of precipitation, pre-concentration remains an essential step to reach analytical limits in the ng/L or even sub-ng/L range, as required by recent European guidelines for the surveillance of emerging pollutants in environmental waters [75]. Among extraction techniques, cartridge- or disk-based SPE remains the most widely employed approach due to its high enrichment factor, reproducibility, and compatibility with automated workflows [76]. The use of polymeric sorbents with broad selectivity (e.g., Oasis HLB, Strata-X), ion-exchange materials, and mixed sorbents enables efficient processing of large rainwater volumes and the simultaneous recovery of analytes spanning a wide range of polarities [33,77]. Polymeric phases with balanced hydrophilic and lipophilic properties are generally recommended for the retention of hydrophobic and moderately polar organic compounds, including PAHs, combustion-derived compounds, and pesticides, through non-specific interactions. In parallel, ion-exchange functionalities extend the applicability of the extraction to acidic and basic analytes, such as polar pesticides, organic acids, and fluorinated compounds, while cation-exchange phases allow the enrichment of dissolved trace metals. The combined use of these sorbents in mixed device, therefore, provides broad analytical coverage and reduces the need for multiple, compound-specific extraction procedures when characterizing rainwater contamination [78].

Alternatively, LLE remains a classical technique endorsed by European directives for hydrophobic and SVOC contaminants, including pesticides and PAHs.

Regarding trace heavy metal analyses, sequential extraction procedures are commonly applied to particulate matter to operationally discriminate metals associated with different solid-phase components. These approaches rely on a series of selective extraction steps performed under controlled chemical conditions, such as neutral salt solutions, weakly acidic buffers, reducing agents, and oxidizing reagents, to progressively release metals bound to distinct particulate fractions [79].

As a result, sequential extraction provides valuable information on metal partitioning, potential mobility, and environmental availability, although the extracted fractions are operationally defined and do not necessarily correspond to discrete chemical species [80].

Despite its simplicity, LLE often requires large amounts of solvent, offers limited selectivity, and performs poorly for highly polar compounds [79,81] The total metal content however, can be determined on dry particulate fraction collected from rainwater or atmospheric deposition samples. As metals are often strongly associated with or embedded within particulate matrices, acid digestion is performed to solubilize particle-bound metals, most frequently using nitric acid alone or in combination with oxidizing agents such as hydrogen peroxide [82]. Microwave-assisted (MAE) digestion is widely applied to enhance extraction efficiency, improve reproducibility, and reduce contamination risks. In cases where particles contain significant mineral or silicate components, more aggressive digestion mixtures may be employed to achieve near-total metal recovery [83].

Pressurized Liquid Extraction (PLE), is a more sustainable alternative to acid digestion employed for the treatment of solid materials such as filters or particulate matter collected from precipitation samples. Non-polar to moderately polar organic solvents such as hexane, dichloromethane, and acetone (or their mixtures like hexane:acetone or dichloromethane:acetone) can be used to extract hydrophobic and semi-volatile organics including PAHs, PCBs, pesticides, and other SVOC compounds. Polar solvents such as methanol, methanol-water mixtures and water-based or chemically modified aqueous solutions are applied for more polar organic contaminants to target labile metal fractions associated with particulate matter. Its high efficiency and reduced extraction times make it a valuable complementary technique for assessing the extraction of both organic contaminants, in a various range of polarity, and weak bonded metals from particulate fraction of atmospheric deposition [84].

Although miniaturized extraction techniques such as dispersive micro-SPE, micro-LLE, and derivatized SPME are increasingly being reported, their practical application in rainwater analysis remains limited. For volatile and semi-volatile species, SPME provides a solvent-free and miniaturized option, allowing extraction directly from the aqueous phase or headspace [85]. However, the limited capacity for analyte enrichment and sorbent-to-sorbent variability restricts their use mainly to qualitative screening or exploratory studies [81]. Table 1 reports some common extraction methods encountered in the literature applied for the enrichment of contaminants detected in rainwater in the last 5 years in multiple investigations.

Table 1. Representative examples of organic contaminants encountered in rainwater in different investigations.

Rainfall Event (Location)	Detected Organic Contaminants	Sampling/Extraction Method	Intrumentation	Detected Concentration (ng/L)	Reference
Thyfon rainfall (Changchun, China)	PAHs,	Passive sampling/C18 cartridge SPE	GC-MS	0.34–15.3 (on three precipitation events)	[33]
Rainwater (Isparta, Turkiye)	OPCs, PAHs	Passive sampling/Semi automated SPE system (C18 cartridge)	GC-MS	0.99–213 µg/L	[78]
Rainfall (Villiers-en-Bois, France)	Herbicides, fungicides and insecticides	Refrigerated collector/ Stir-bar SPE	GC-MS	0.5–170 (on multiple seasonal events)	[79]
Rainfall (Wisconsin, Upper Great Lakes Region, USA)	PFAS	NADP-NTN sampling protocol/SPE (Oasis WAX cartridge)	HPLC-MS/MS	0.7–6.1	[86]
Highway stormwater runoff (Treviso, Italy)	Microplastics, additives, plasticized, and polymers	Glass flasks/ Oleo-extraction, purification, and filtration	Micro-FTIR	12825 ± 157 to 96,425 ± 430 micro-litters/L	[12]
Determination of wet deposition flux (Bursca, Turkiye)	PCDDs and PCDFs	Wet deposition sampler/PLE	GC-HRMS	Wet deposition flux: Particulate (2030 ± 660 pg/m^2-day) and dissolved phase (397 ± 186 pg/m^2-day)	[42]

Abbreviations: NADP-NTN: National Atmospheric Deposition Program—National Trends Sites.

3.3. Instrumental Analyses

At the detection stage, advanced instrumentation plays a pivotal role in environmental monitoring. Chromatography, both gas (GC) and liquid (LC), coupled with MS systems remain the gold standards for organic pollutant analysis, offering sensitivity and selectivity [86,87]. These techniques are widely adopted for both targeted and non-targeted analyses, enabling the identification and quantification of a broad range of contaminants [88]. Compared to GC, LC provides broader applicability to polar and thermally labile compounds, whereas GC generally offers higher chromatographic efficiency and robustness for volatile and semi-volatile analytes [89]. Among the criticisms, LC-MS is more susceptible to matrix effects and ion suppression, which can reduce sensitivity and precision, especially in the analyses of polar analytes in complex environmental samples [76]. Additionally, the quantification of ECs may be constrained by the limited availability of reference standards, resulting from the complex environmental transformations of the primary chemical species. The absence of reference standards for many ECs can also limit structural confirmation and accurate quantification [90]. High-resolution mass spectrometry (HRMS) has revolutionized the field through non-target screening, broadening the analytical focus beyond known priority pollutants to include novel and unexpected compounds, while enabling the study of atmospheric dynamics and contaminant transformations [91]. However, despite its remarkable advantages, HRMS also poses significant challenges particularly in the interpretation of datasets which demands advanced algorithms, integrated analytical workflows, and expert evaluation to extract authentic molecular features from a multitude of artefacts and interferences [92]. For the quantification of inorganic constituents, particularly trace and ultra-trace metals, ICP-MS remains a benchmark technique, offering outstanding sensitivity, multi-element capability, and a broad linear dynamic range. In addition to its analytical versatility, ICP-MS enables isotopic analysis and source tracing, providing valuable insights into geochemical processes and environmental contamination pathways [93]. However, its performance can be affected by matrix-induced interferences, such as space-charge effects or polyatomic ion formation in high-salt or complex matrices, which may compromise signal accuracy and stability. Furthermore, the high operational costs, demanding maintenance requirements, and limited applicability to organic species, often requiring chemical derivatization or coupling with chromatographic separation, represent additional constraints [94].

IC is a robust and highly sensitive technique for the characterization of ionic contaminants in rainwater, offering high sensitivity and selectivity for a broad range of target analytes. It is particularly suited for the determination of major inorganic anions (e.g., Cl^-, NO_3^-, NO_2^-, SO_4^{2-}, PO_4^{3-}), cations (e.g., NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}), and low-molecular-weight organic acids such as formate (HCOO-) and acetate (CH_3COO-), which are key indicators of atmospheric processes and acid deposition [95]. When coupled with appropriate separation and detection strategies, IC can also be applied to selected metal species, especially those present as soluble ionic forms, although its capability for total heavy metal quantification remains limited compared to ICP-MS. The main advantages of IC over ICP-MS include minimal sample preparation, lower operational costs, and the ability to simultaneously resolve multiple anionic and cationic species while preserving their chemical speciation [95]. Conversely, ICP-MS provides superior sensitivity for trace and ultra-trace metals and broader elemental coverage but lacks intrinsic speciation capability and requires more complex instrumentation and sample handling. Accordingly, the integration of IC and ICP-MS provides complementary information on ionic speciation and trace metal abundance in rainwater, supporting both routine periodic monitoring and targeted investigations of contamination events.

Parallel to these high-end tools, more accessible techniques, such as ultraviolet-visible (UV-Vis) spectroscopy, fluorescence analysis [96], and electrochemical sensors [97,98], retain a crucial role in routine monitoring, rapid screening, and portable field applications, where cost and practicality outweigh ultimate sensitivity. These methods are particularly valuable for on-site assessments and real-time data acquisition. However, they generally provide lower sensitivity and selectivity than mass spectrometric techniques and may be influenced by interferences arising from the sample matrix.

In recent years, advances in environmental analytical science have promoted the adoption of integrated methodologies that go beyond bulk chemical measurements, incorporating particle-level techniques such as SEM-EDS and particle size analysis, together with atmospheric back-trajectory modeling. These approaches, increasingly applied in recent published studies, have improved the ability to link rainwater composition to local, regional, and long-range transport processes.

Several studies have demonstrated the effectiveness of combining sequential rainwater sampling, particle-level characterization techniques, and atmospheric back-trajectory modeling to elucidate the sources and transport pathways of contaminants deposited via precipitation. In this context, Berberler et al. [99] investigated sequential rain events in Bartın (Turkey), focusing on water-insoluble particulate matter together with major inorganic species. Rainwater samples were analyzed for pH and water-soluble ions (F^-, Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}), while insoluble particles were individually characterized using particle size distribution analysis and SEM-EDS. Particle sizes ranged from sub-micrometric to several hundred micrometers, and SEM-EDS revealed a heterogeneous mixture dominated by mineral dust particles (Si-, Al-, Ca-rich) and anthropogenic components containing Fe and Zn. By integrating these results with HYSPLIT backward trajectory analysis, the authors showed that long-range air masses contributed predominantly crustal and industrial particles, whereas locally influenced trajectories were associated with traffic- and construction-related sources, highlighting the importance of trajectory modeling for source apportionment beyond bulk chemistry.

Building on a similar experimental framework, Kilic and Kilic [78] extended this approach to sequential rainwater samples collected in Antalya (Turkey), combining SEM-EDS, particle size analysis, ion chromatography, and ICP-MS to characterize both insoluble and dissolved fractions. Particle size distributions covered a wide range, with maximum diameters reaching approximately 1500 µm, indicating efficient scavenging of coarse atmospheric particles during rainfall. SEM-EDS analyses again identified dominant Ca- and Si-rich mineral particles, alongside Fe- and Ti-bearing anthropogenic particles. The application of HYSPLIT back trajectories allowed the authors to associate enhanced coarse-particle deposition with continental and desert-influenced air masses, while marine trajectories were reflected by increased Na^+ and Cl^- concentrations in rainwater. This study further demonstrated how coupling single-particle analysis with trajectory modeling can disentangle the relative contributions of local, regional, and long-range sources to rainwater composition.

While the first two studies primarily addressed inorganic and particulate phases, Kilic and Pamukoglu [100] applied a comparable sequential sampling and modeling strategy to investigate organic contaminants in rainwater, focusing on 16 PAHs and 50 OCPs in Isparta Province. Following automated SPE, analytes were quantified by GC-MS, revealing widespread contamination. PAH concentrations spanned more than two orders of magnitude, from approximately 0.99 $\mu g\ L^{-1}$ for high MW compounds such as benzo[k]fluoranthene to 213 $\mu g\ L^{-1}$ for phenanthrene, indicating strong combustion-related inputs. Several legacy OCPs, including chlordecone and DDT derivatives, were also detected, confirming their atmospheric persistence. Importantly, HYSPLIT backward trajectory analysis linked elevated concentrations of both PAHs and OCPs to air masses originating from industrial and agricultural regions, providing clear evidence that long-range atmospheric transport significantly contributes to the wet deposition of organic pollutants.

Taken together, these studies demonstrate that the integration of SEM-based single-particle characterization, particle size analysis, targeted chemical measurements, and HYSPLIT trajectory modeling represents a robust and complementary approach for investigating the origin, transport, and deposition mechanisms of both particulate and molecular contaminants in rainwater.

3.4. Data Interpretation

The evolving landscape of environmental analytical chemistry reflects its intrinsically dynamic nature. The continuous emergence of new contaminants, increasingly stringent regulatory requirements, and ongoing advances in analytical instrumentation collectively underscore the need for flexible and adaptable methodologies [101]. In parallel, the interpretation of increasingly complex datasets has been substantially strengthened by the application of chemometric approaches and, more recently, machine learning algorithms. These tools enable advanced pattern recognition, source apportionment, and risk prioritization, and are no longer merely ancillary techniques but have become integral to the transformation of raw analytical data into meaningful environmental knowledge [102].

Within this context, recent developments in sample preparation, chromatographic separation, and mass spectrometric detection have significantly enhanced our ability to resolve and quantify the chemical complexity of atmospheric precipitation [103]. Of particular importance is the integration of non-target screening strategies, which has enabled the identification of transformation products, emerging contaminants (ECs), and chemical fingerprints that would otherwise remain undetected. This has fundamentally reshaped our understanding of atmospheric deposition, highlighting its dual role as both a sink and a vector in pollutant cycling [104]. Beyond their analytical relevance, these methodological advances provide essential evidence for source tracing, assessment of ecological and human exposure pathways, and the development of science-based regulatory frameworks. Consequently, progress in environmental analysis should be regarded not only as a technical achievement but as a cornerstone of effective environmental protection and sustainable policy.

The composition of rainwater contamination varies markedly across geographical regions and is largely governed by the nature of local emission sources, atmospheric transport processes driven by wind patterns, and the frequency and intensity of precipitation events. A fundamental distinction can be drawn between light, highly mobile species, such as small inorganic ions, and heavier organic compounds. The former tend to persist longer in the atmosphere and are therefore more susceptible to long-range transport, whereas the latter are more readily removed through wet and dry deposition and are typically detected in closer proximity to their emission sources [105].

At the global scale, extensive research has focused on nitrate- and sulfur-containing species in wet deposition, as these compounds constitute major contributors to rainwater contamination in urban environments. Emissions from domestic heating, vehicular traffic, and industrial activities are widely recognized as the primary sources of oxidized nitrogen and sulfur species in cities, frequently resulting in acidic precipitation. A long-term study conducted over more than 18 years in Mexico City revealed pronounced spatial and temporal gradients in rainwater chemistry, with central urban areas consistently exhibiting lower pH values and higher concentrations of acidic components compared to peripheral zones [106].

Conversely, rainwater collected in proximity to rural and agricultural areas often shows elevated levels of reduced nitrogen species, particularly ammonium, as well as increased concentrations of sodium and calcium ions. These latter components are commonly associated with soil resuspension and land-use practices [107]. Agricultural influence is further evidenced by the presence of pesticide active substances in precipitation. However, the atmospheric occurrence and subsequent incorporation of pesticides and other plant protection products into rainwater are generally restricted in both time and space. Detectable concentrations are typically limited to regions characterized by intensive agricultural activity and coincide with periods of peak application. This behavior is largely governed by the physicochemical properties of these compounds, as their relatively high molecular weight and low volatility promote rapid deposition, while the amounts scavenged by rainwater remain low. These patterns are clearly illustrated by the study of Scheyer et al., which examined pesticide distributions in rainwater from adjacent rural and urban areas, demonstrating a strong dependence on local usage practices [108].

More broadly, the presence of contaminants in precipitation reflects the spatial and temporal distribution of chemical species in the atmosphere. Seasonal variability plays a particularly important role, as demonstrated by Mullaugh et al. [109], who showed that the occurrence of volatile organic compounds (VOCs) in wet deposition over Wilmington, North Carolina (USA), is strongly influenced by seasonal emission dynamics and meteorological conditions. Taken together, these findings support the use of rainwater as a valuable environmental matrix for investigating the transport, persistence, and removal of atmospheric contaminants. The analysis of wet deposition therefore provides critical insights into source contributions, atmospheric processing, and the relative roles of local and long-range transport for both inorganic and organic pollutants.

4. Conclusions and Perspectives

Rainwater represents a dynamic sink and transfer pathway for a wide spectrum of atmospheric contaminants, ranging from VOCs and SVOCs to PAHs and POPs such as PCBs, OCPs, dioxins, brominated flame retardants, and per- and PFAS. These pollutants are released into the atmosphere through combustion processes, industrial activities, volatilization from soils and waters, and long-range transport. Once in the atmosphere, they undergo a range of physicochemical transformations, including oxidation, photolysis, and SOA formation, which influence their reactivity, solubility, and phase partitioning. Their subsequent removal occurs predominantly through wet deposition, by both in-cloud scavenging and below-cloud washout, processes whose efficiency depends on the physicochemical properties of the compounds as well as on meteorological factors such as rainfall intensity, droplet size distribution, and the trajectory of air masses. Intense rainfall events play a particularly important role in the transfer of contaminants from the atmosphere to terrestrial and aquatic environments. During episodes of heavy precipitation, both dissolved and particle-bound compounds are scavenged more efficiently, producing sudden pulses of contaminant input to receiving waters and soils. Several studies have shown that atmospheric concentrations of PAHs and related combustion products drop sharply during rainfall maxima, reflecting rapid removal, while deposition fluxes in rainwater increase by orders of magnitude compared with dry periods. These events can also promote the mobilization of oxygenated and nitrated PAH derivatives, which are often more toxic and bioavailable than their parent compounds, highlighting the ecological relevance of rainfall-driven deposition. However, the magnitude of these fluxes is highly variable, depending not only on precipitation characteristics but also on local emission sources and the chemical history of air masses, underscoring the need for monitoring strategies capable of capturing both long-term trends and event-based dynamics. Despite substantial advances, important gaps remain in the literature. Most investigations have focused on legacy pollutants such as PAHs, PCBs, and OCPs, while ECs, including PFAS, pharmaceuticals, personal care products, and novel flame retardants, have rarely been addressed in the context of rainwater. Their distinct physicochemical behavior, particularly polarity and persistence, calls for adapted sampling and analytical strategies. Moreover, very little is known about the role of convective storms and thunderstorms, despite their potential to significantly enhance deposition through strong updrafts, intense precipitation, and high electrical activity. The lack of systematic data on these processes limits our ability to predict contaminant fluxes in a changing climate, where extreme precipitation events are expected to increase in frequency and intensity. Addressing these knowledge gaps will require targeted monitoring campaigns, advanced analytical methods for ultra-trace detection, and closer integration of atmospheric chemistry, hydrology, and environmental sciences to fully understand the role of rainwater in the cycling and redistribution of organic pollutants.

Author Contributions

N.F.: Writing—original draft, Conceptualization, Visualization. M.G.D.C.: Writing—original draft, Conceptualization. L.A.: Writing—original draft, Data curation, Formal analysis. C.D.B.: Data curation, Methodology. G.B.: Data curation, Methodology. A.G.: Writing—review & editing, Supervision, Project administration. All authors have read and agreed to the published version of the manuscript.

Institutional Review Board Statement

Not applicable.

Informed Consent Statement

Not applicable.

Data Availability Statement

The data used for the writing of this review article are available online. The raw version of the work will be provided upon formal request to the corresponding author.

Conflicts of Interest

The authors declare no conflict of interest.

Use of AI and AI-Assisted Technologies

No AI tools were utilized for this paper.

References

1. Edo, G.I.; Itoje-akpokiniovo, L.O.; Obasohan, P.; et al. Impact of Environmental Pollution from Human Activities on Water, Air Quality and Climate Change. *Ecol. Front.* **2024**, *44*, 874–889. https://doi.org/10.1016/j.ecofro.2024.02.014.
2. Lee, T.H.Y.; Srinuansom, K.; Snyder, S.A.; et al. Atmosphere-Transported Emerging and Persistent Contaminants (EPCs) in Rainfall and Throughfall: Insights from a Rural Site in Northern Thailand. *Atmosphere* **2023**, *14*, 1603. https://doi.org/10.3390/atmos14111603.
3. Kim, S.K.; Kannan, K. Perfluorinated Acids in Air, Rain, Snow, Surface Runoff, and Lakes: Relative Importance of Pathways to Contamination of Urban Lakes. *Environ. Sci. Technol.* **2007**, *41*, 8328–8334. https://doi.org/10.1021/es072107t.

4. Barroso, P.J.; Santos, J.L.; Martín, J.; et al. Emerging Contaminants in the Atmosphere: Analysis, Occurrence and Future Challenges. *Crit. Rev. Environ. Sci. Technol.* **2019**, *49*, 104–171. https://doi.org/10.1080/10643389.2018.1540761.
5. Alfonso, M.B.; Arias, A.H.; Ronda, A.C.; et al. Continental Microplastics: Presence, Features, and Environmental Transport Pathways. *Sci. Total Environ.* **2021**, *799*, 149447. https://doi.org/10.1016/j.scitotenv.2021.149447.
6. Abbasi, T.; Abbasi, S.A. Sources of Pollution in Rooftop Rainwater Harvesting Systems and Their Control. *Crit. Rev. Environ. Sci. Technol.* **2011**, *41*, 2097–2167. https://doi.org/10.1080/10643389.2010.497438.
7. Pamuru, S.T.; Forgione, E.; Croft, K.; et al. Chemical Characterization of Urban Stormwater: Traditional and Emerging Contaminants. *Sci. Total Environ.* **2022**, *813*, 151887. https://doi.org/10.1016/j.scitotenv.2021.151887.
8. Polkowska, Z.; Astel, A.; Walna, B.; et al. Chemometric Analysis of Rainwater and Throughfall at Several Sites in Poland. *Atmos. Environ.* **2005**, *39*, 837–855. https://doi.org/10.1016/j.atmosenv.2004.10.026.
9. Zhang, S.; Yu, J.; Pan, T.; et al. Difference between Rainfall and Throughfall Chemistry for Different Forest Stands in the Qinling Mountains, China. *Hydrol. Res.* **2021**, *52*, 523–535. https://doi.org/10.2166/nh.2021.015.
10. Fayyazbakhsh, A.; Bell, M.L.; Zhu, X.; et al. Engine Emissions with Air Pollutants and Greenhouse Gases and Their Control Technologies. *J. Clean. Prod.* **2022**, *376*, 134260. https://doi.org/10.1016/j.jclepro.2022.134260.
11. Lucci, E.; Dal Bosco, C.; Antonelli, L.; et al. Enantioselective High-Performance Liquid Chromatographic Separations to Study Occurrence and Fate of Chiral Pesticides in Soil, Water, and Agricultural Products. *J. Chromatogr. A* **2022**, *1685*, 463595. https://doi.org/10.1016/j.chroma.2022.463595.
12. Rosso, B.; Corami, F.; Vezzaro, L.; et al. Quantification and Characterization of Additives, Plasticizers, and Small Microplastics (5–100 Mm) in Highway Stormwater Runoff. *J. Environ. Manage.* **2022**, *324*, 116348. https://doi.org/10.1016/j.jenvman.2022.116348.
13. Morin-Crini, N.; Lichtfouse, E.; Liu, G.; et al. Worldwide Cases of Water Pollution by Emerging Contaminants: A Review. *Environ. Chem. Lett.* **2022**, *20*, 2311–2338. https://doi.org/10.1007/s10311-022-01447-4.
14. Li, X.; Shen, X.; Jiang, W.; et al. Comprehensive Review of Emerging Contaminants: Detection Technologies, Environmental Impact, and Management Strategies. *Ecotoxicol. Environ. Saf.* **2024**, *278*, 116420. https://doi.org/10.1016/j.ecoenv.2024.116420.
15. Brião, V.B.; Cadore, J.S.; Graciola, S.; et al. Rainwater for Drinking Purposes: An Overview of Challenges and Perspectives. *Wiley Interdiscip. Rev. Water* **2024**, *11*, 1–18. https://doi.org/10.1002/wat2.1746.
16. Maniam, G.; Zakaria, N.A.; Leo, C.P.; et al. An Assessment of Technological Development and Applications of Decentralized Water Reuse: A Critical Review and Conceptual Framework. *Wiley Interdiscip. Rev. Water* **2022**, *9*, 1–31. https://doi.org/10.1002/wat2.1588.
17. Hamilton, K.; Reyneke, B.; Waso, M.; et al. A Global Review of the Microbiological Quality and Potential Health Risks Associated with Roof-Harvested Rainwater Tanks. *npj Clean Water* **2019**, *2*, 7. https://doi.org/10.1038/s41545-019-0030-5.
18. Philip, J.M.; Aravind, U.K.; Aravindakumar, C.T. Emerging Contaminants in Indian Environmental Matrices—A Review. *Chemosphere* **2018**, *190*, 307–326. https://doi.org/10.1016/j.chemosphere.2017.09.120.
19. Bossi, R.; Vorkamp, K.; Skov, H. Concentrations of Organochlorine Pesticides, Polybrominated Diphenyl Ethers and Perfluorinated Compounds in the Atmosphere of North Greenland. *Environ. Pollut.* **2016**, *217*, 4–10. https://doi.org/10.1016/j.envpol.2015.12.026.
20. Geissen, V.; Mol, H.; Klumpp, E.; et al. Emerging Pollutants in the Environment: A Challenge for Water Resource Management. *Int. Soil Water Conserv. Res.* **2015**, *3*, 57–65. https://doi.org/10.1016/j.iswcr.2015.03.002.
21. Balducci, C.; Perilli, M.; Romagnoli, P.; et al. New Developments on Emerging Organic Pollutants in the Atmosphere. *Environ. Sci. Pollut. Res.* **2012**, *19*, 1875–1884. https://doi.org/10.1007/s11356-012-0815-2.
22. Williams, J.; Koppmann, R. Volatile Organic Compounds in the Atmosphere: An Overview. In *Volatile Organic Compounds in the Atmosphere*; Koppmann, R., Ed.; Wiley: Chichester, UK, 2007.
23. Brüggemann, M.; Mayer, S.; Brown, D.; et al. Measuring Pesticides in the Atmosphere: Current Status, Emerging Trends and Future Perspectives. *Environ. Sci. Eur.* **2024**, *36*, 39. https://doi.org/10.1186/s12302-024-00870-4.
24. Hester, R.E.; Harrison, R. *Volatile Organic Compounds in the Atmosphereitle*; Royal Society of Chemistry: Cambridge, UK, 1995; ISBN 0-85404-215-6.
25. Zeng, J.; Han, G.; Wu, Q.; et al. Chemical Evolution of Rainfall in China's First Eco-Civilization Demonstration City: Implication for the Provenance Identification of Pollutants and Rainwater Acid Neutralization. *Sci. Total Environ.* **2024**, *910*, 168567. https://doi.org/10.1016/j.scitotenv.2023.168567.
26. Yao, D.; Tang, G.; Wang, Y.; et al. Significant Contribution of Spring Northwest Transport to Volatile Organic Compounds in Beijing. *J. Environ. Sci. China* **2021**, *104*, 169–181. https://doi.org/10.1016/j.jes.2020.11.023.
27. Shi, J.; Wang, Y.; Han, X.; et al. Differentiation Analysis of VOCs in Kunming during Rainy and Dry Seasons Based on Monitoring High Temporal Resolution. *Atmos. Pollut. Res.* **2024**, *15*, 101996. https://doi.org/10.1016/j.apr.2023.101996.

28. Liu, Y.; Yin, S.; Zhang, S.; et al. Drivers and Impacts of Decreasing Concentrations of Atmospheric Volatile Organic Compounds (VOCs) in Beijing during 2016–2020. *Sci. Total Environ.* **2024**, *906*, 167847. https://doi.org/10.1016/j.scitotenv.2023.167847.
29. Montano, L.; Baldini, G.M.; Piscopo, M.; et al. Polycyclic Aromatic Hydrocarbons (PAHs) in the Environment: Occupational Exposure, Health Risks and Fertility Implications. *Toxics* **2025**, *13*, 151. https://doi.org/10.3390/toxics13030151.
30. Li, Y.; Duan, X. Wet Deposition of Polycyclic Aromatic Hydrocarbons in a Remote Area of Central South China from 2014 to 2017. *Atmos. Sci. Lett.* **2024**, *25*, 1–12. https://doi.org/10.1002/asl.1201.
31. Paul, D. Boehm Polycyclic Aromatic Hydrocarbons (PAHs). In *Environmental Forensics Contaminant Specific Guide*; Morrison, R.D., Murphy, B.L., Eds.; Academic Press: Cambridge, MA, USA, 1964; pp. 313–337.
32. Fernández, P.; Grimalt, J.O.; Vilanova, R.M. Atmospheric Gas-Particle Partitioning of Polycyclic Aromatic Hydrocarbons in High Mountain Regions of Europe. *Environ. Sci. Technol.* **2002**, *36*, 1162–1168. https://doi.org/10.1021/es010190t.
33. Mu, G.; Bian, D.; Zou, M.; et al. Pollution and Risk Assessment of Polycyclic Aromatic Hydrocarbons in Urban Rivers in a Northeastern Chinese City: Implications for Continuous Rainfall Events. *Sustainability* **2023**, *15*, 5777. https://doi.org/10.3390/su15075777.
34. Nguyen, T.N.T.; Park, M.K.; Son, J.M.; et al. Spatial Distribution and Temporal Variation of Polycyclic Aromatic Hydrocarbons in Runoff and Surface Water. *Sci. Total Environ.* **2021**, *793*, 148339. https://doi.org/10.1016/j.scitotenv.2021.148339.
35. Wang, W.; Yuan, B.; Peng, Y.; et al. Direct Observations Indicate Photodegradable Oxygenated Volatile Organic Compounds (OVOCs) as Larger Contributors to Radicals and Ozone Production in the Atmosphere. *Atmos. Chem. Phys.* **2022**, *22*, 4117–4128. https://doi.org/10.5194/acp-22-4117-2022.
36. Xia, S.Y.; Wang, C.; Zhu, B.; et al. Long-Term Observations of Oxygenated Volatile Organic Compounds (OVOCs) in an Urban Atmosphere in Southern China, 2014–2019. *Environ. Pollut.* **2021**, *270*, 116301. https://doi.org/10.1016/j.envpol.2020.116301.
37. Liu, G.; Ma, X.; Li, W.; et al. Pollution Characteristics, Source Appointment and Environmental Effect of Oxygenated Volatile Organic Compounds in Guangdong-Hong Kong-Macao Greater Bay Area: Implication for Air Quality Management. *Sci. Total Environ.* **2024**, *919*, 170836. https://doi.org/10.1016/j.scitotenv.2024.170836.
38. Chen, D.; Xu, Y.; Xu, J.; et al. The Vertical Distribution of VOCs and Their Impact on the Environment: A Review. *Atmosphere* **2022**, *13*, 1940. https://doi.org/10.3390/atmos13121940.
39. Pfannerstill, E.Y.; Reijrink, N.G.; Edtbauer, A.; et al. Total OH Reactivity over the Amazon Rainforest: Variability with Temperature, Wind, Rain, Altitude, Time of Day, Season, and an Overall Budget Closure. *Atmos. Chem. Phys.* **2021**, *21*, 6231–6256. https://doi.org/10.5194/acp-21-6231-2021.
40. Hui, L.; Chen, Y.; Feng, X.; et al. The Critical Role of Oxygenated Volatile Organic Compounds (OVOCs) in Shaping Photochemical O_3 Chemistry and Control Strategy in a Subtropical Coastal Environment. *Atmos. Chem. Phys.* **2025**, *25*, 18355–18371.
41. Miglioranza, K.S.B.; Ondarza, P.M.; Grondona, S.I. et al. Persistent Organic Contaminants. In *Marine Analytical Chemistry*; Blasco, J., Tovar-Sánchez, A., Eds.; Springer International Publishing: Cham, Switzerland, 2022; pp. 275–306.
42. Noori, A.A.; Gülegen, B.; Birgül, A.; et al. Atmospheric Wet Deposition Monitoring of PCDD/Fs in an Urban Site: Fluxes, Rain Concentrations and Washout Ratios. *Environ. Pollut.* **2025**, *374*, 126224. https://doi.org/10.1016/j.envpol.2025.126224.
43. Ashraf, M.A. Persistent Organic Pollutants (POPs): A Global Issue, a Global Challenge. *Environ. Sci. Pollut. Res.* **2017**, *24*, 4223–4227. https://doi.org/10.1007/s11356-015-5225-9.
44. Muir, D.; Gunnarsdóttir, M.J.; Koziol, K.; et al. Local Sources versus Long-Range Transport of Organic Contaminants in the Arctic: Future Developments Related to Climate Change. *Environ. Sci. Adv.* **2025**, *4*, 355–408. https://doi.org/10.1039/d4va00240g.
45. Borghini, F.; Grimalt, J.O.; Sanchez-Hernandez, J.C.; et al. Organochlorine Pollutants in Soils and Mosses from Victoria Land (Antarctica). *Chemosphere* **2005**, *58*, 271–278. https://doi.org/10.1016/j.chemosphere.2004.07.025.
46. Casas, G.; Martinez-Varela, A.; Vila-Costa, M.; et al. Rain Amplification of Persistent Organic Pollutants. *Environ. Sci. Technol.* **2021**, *55*, 12961–12972. https://doi.org/10.1021/acs.est.1c03295.
47. Luarte, T.; Gómez-Aburto, V.A.; Poblete-Castro, I.; et al. Levels of Persistent Organic Pollutants (POPs) in the Antarctic Atmosphere over Time (1980 to 2021) and Estimation of Their Atmospheric Half-Lives. *Atmos. Chem. Phys.* **2023**, *23*, 8103–8118. https://doi.org/10.5194/acp-23-8103-2023.
48. Poissant, L.; Schmit, J.P.; Béron, P. Trace Inorganic Elements in Rainfall in the Montreal Island. *Atmos. Environ.* **1994**, *28*, 339–346. https://doi.org/10.1016/1352-2310(94)90109-0.

49. Villanueva, F.; Ródenas, M.; Ruus, A.; et al. Sampling and Analysis Techniques for Inorganic Air Pollutants in Indoor Air. *Appl. Spectrosc. Rev.* **2022**, *57*, 531–579. https://doi.org/10.1080/05704928.2021.2020807.
50. Sarkar, S.; Jaswal, A.; Singh, A. Sources of Inorganic Nonmetallic Contaminants (Synthetic Fertilizers, Pesticides) in Agricultural Soil and Their Impacts on the Adjacent Ecosystems. *Bioremediation Emerg. Contam. Soils* **2024**, 135–161. https://doi.org/10.1016/B978-0-443-13993-2.00007-4.
51. Srivastava, D.; Vu, T.V.; Tong, S.; et al.Formation of Secondary Organic Aerosols from Anthropogenic Precursors in Laboratory Studies. *npj Clim. Atmos. Sci.* **2022**, *5*, 22. https://doi.org/10.1038/s41612-022-00238-6.
52. Huston, R.; Chan, Y.C.; Gardner, T.; et al. Characterisation of Atmospheric Deposition as a Source of Contaminants in Urban Rainwater Tanks. *Water Res.* **2009**, *43*, 1630–1640. https://doi.org/10.1016/j.watres.2008.12.045.
53. Piwowarska, D.; Kiedrzyńska, E.; Jaszczyszyn, K. A Global Perspective on the Nature and Fate of Heavy Metals Polluting Water Ecosystems, and Their Impact and Remediation. *Crit. Rev. Environ. Sci. Technol.* **2024**, *54*, 1436–1458. https://doi.org/10.1080/10643389.2024.2317112.
54. Rudnicka-Kępa, P.; Zaborska, A. Sources, Fate and Distribution of Inorganic Contaminants in the Svalbard Area, Representative of a Typical Arctic Critical Environment—A Review. *Environ. Monit. Assess.* **2021**, *193*, 724. https://doi.org/10.1007/s10661-021-09305-6.
55. Cie’sla, M.; Gruca-Rokosz, R. Fate of Heavy Metals in Ecosystems of Dam Reservoirs: Transport, Distribution and Significance of the Origin of Organic Matter. *Environ. Pollut.* **2024**, *361*, 124811. https://doi.org/10.1016/j.envpol.2024.124811.
56. Wu, Y.S.; Osman, A.I.; Hosny, M.; et al. The Toxicity of Mercury and Its Chemical Compounds: Molecular Mechanisms and Environmental and Human Health Implications: A Comprehensive Review. *ACS Omega* **2024**, *9*, 5100–5126. https://doi.org/10.1021/acsomega.3c07047.
57. Alonso, L.L.; Demetrio, P.M.; Etchegoyen, M.A.; et al. Science of the Total Environment Glyphosate and Atrazine in Rainfall and Soils in Agroproductive Areas of the Pampas Region in Argentina. *Sci. Total Environ.* **2018**, *645*, 89–96. https://doi.org/10.1016/j.scitotenv.2018.07.134.
58. Lamprea, K.; Bressy, A.; Mirande-bret, C.; et al. Alkylphenol and Bisphenol A Contamination of Urban Runoff*:* An Evaluation of the Emission Potentials of Various Construction Materials and Automotive Supplies. *Environ Sci Pollut Res.***2018**, *25*, 21887–21900.
59. Costa, M.E.L.; Carvalho, D.J.; Koide, S. Assessment of Pollutants from Diffuse Pollution through the Correlation between Rainfall and Runoff Characteristics Using Emc and First Flush Analysis. *Water* **2021**, *13*, 2552. https://doi.org/10.3390/w13182552.
60. Suchara, I.; Florek, M.; Godzik, B.; et al. *Mapping of Main Sources of Pollutants and Their Transport in the Visegrad Space. Part I: Eight Toxic Metals.—Expert Group on Bio-Monitoring the Atmospheric Deposition Loads in the Visegrad Countries*; SILVA TAROUCA Research Institute for Landscape and Ornamental Gardening: Průhonice, Czech, 2007; ISBN 9788085116533.
61. Liyandeniya, A.; Priyantha, N.; Deeyamulla, M. Comparison of Chemical Composition of Wet-Only and Dry-Only Deposition at Peradeniya in Sri Lanka. *Res. Sq.* **2023**, 1–17. https://doi.org/10.21203/rs.3.rs-2779523/v1.
62. Stedman, J.R.; Heyes, C.J.; Irwin, J.G. A Comparison of Bulk and Wet-Only Precipitation Collectors at Rural Sites in the United Kingdom. *Water. Air. Soil Pollut.* **1990**, *52*, 377–395. https://doi.org/10.1007/BF00229445.
63. Cape, J.N.; van Dijk, N.; Tang, Y.S. Measurement of Dry Deposition to Bulk Precipitation Collectors Using a Novel Flushing Sampler. *J. Environ. Monit.* **2009**, *11*, 353–358. https://doi.org/10.1039/b813812e.
64. Chantara, S; Chunsuk, N. Comparison of Wet-Only and Bulk Deposition at Chiang Mai (Thailand) Based on Rainwater Chemical Composition. *Atmos. Environ.* **2008**, *42*, 5511–5518. https://doi.org/10.1016/j.atmosenv.2008.03.022.
65. Peden, M.E.; Skowron, L.M.; McGurk, F.M. *Sample Handling, Analysis and Storage Procedures*; UNT Digital Library: Denton, TX, USA, 1979; 71p.
66. Desboeufs, K.; Fu, F.; Bressac, M.; et al. Wet Deposition in the Remote Western and Central Mediterranean as a Source of Trace Metals to Surface Seawater. *Atmos. Chem. Phys.* **2022**, *22*, 2309–2332. https://doi.org/10.5194/acp-22-2309-2022.
67. EPA. *U.S. Method 1640: Determination of Trace Elements in Water*; EPA: Washington, DC, USA, 1997.
68. Zhang, H.; Zhao, Z.; Cai, A.; et al. Source Apportionment of Heavy Metals in Wet Deposition in a Typical Industry City Based on Multiple Models. *Atmosphere* **2022**, *13*, 1716. https://doi.org/10.3390/atmos13101716.
69. Fonvielle, J.A.; Felgate, S.L.; Tanentzap, A.J.; et al. Assessment of Sample Freezing as a Preservation Technique for Analysing the Molecular Composition of Dissolved Organic Matter in Aquatic Systems. *RSC Adv.* **2023**, *13*, 24594–24603. https://doi.org/10.1039/d3ra01349a.
70. Fourrier, P.; Dulaquais, G.; Riso, R. Influence of the Conservation Mode of Seawater for Dissolved Organic Carbon Analysis. *Mar. Environ. Res.* **2022**, *181*, 105754. https://doi.org/10.1016/j.marenvres.2022.105754.
71. ASTM. *ASTM D5012-20. Standard Practice for Preparation of Materials Used for the Collection and Preservation of Atmospheric Wet Deposition*; ASTM: West Conshohocken, PA, USA, 2020.

72. Amodio, M.; Catino, S.; Dambruoso, P.R.; et al. Atmospheric Deposition: Sampling Procedures, Analytical Methods, and Main Recent Findings from the Scientific Literature. *Adv. Meteorol.* **2014**, *2014*, 161730. https://doi.org/10.1155/2014/161730.
73. Vet, R.; Artz, R.S.; Carou, S.; et al. A Global Assessment of Precipitation Chemistry and Deposition of Sulfur, Nitrogen, Sea Salt, Base Cations, Organic Acids, Acidity and PH, and Phosphorus. *Atmos. Environ.* **2014**, *93*, 3–100. https://doi.org/10.1016/j.atmosenv.2013.10.060.
74. World Meteorological Organization. *Manual for the GAW Precipitation Chemistry Programme: Guidelines, Data Quality Objectives and Standard Operating Procedures*; World Meteorological Organization: Geneva, Switzerland, 2004; No. 160.
75. Zhang, Z.; Hibberd, A.; Zhou, J.L. Analysis of Emerging Contaminants in Sewage Effluent and River Water: Comparison between Spot and Passive Sampling. *Anal. Chim. Acta* **2008**, *607*, 37–44. https://doi.org/10.1016/j.aca.2007.11.024.
76. De Cesaris, M.G.; Felli, N.; Antonelli, L., E.L.; et al. Extraction of Organic Contaminants from Grab and Composite Water Samples. In *Sample Handling and Trace Analysis of Pollutants*; Barcelo, D., Pico, Y., Eds.; Elsevier: Amsterdam, The Netherlands, 2024; p. 822, ISBN 978-0-323-85601-0.
77. Fortuny, G.; Pineda, L.; Rúbies, A.; et al. Determination of 61 Organic Pollutants in Drinking Water by Solid Phase Extraction Followed by Liquid and Gas Chromatography Coupled to Tandem Mass Spectrometry: An Analytical Strategy for a Routine Laboratory. *Int. J. Environ. Anal. Chem.* **2013**, *93*, 707–726. https://doi.org/10.1080/03067319.2011.649745.
78. Kilic, S.; Kilic, M. Determination of Organic Pollutants and Pollution Sources in Sequentially Collected Rainwater Samples in Isparta Province. *Environ. Monit. Assess.* **2025**, *197*, 1–22. https://doi.org/10.1007/s10661-025-13872-3.
79. Décuq, C.; Bourdat-Deschamps, M.; Benoit, P.; et al. A Multiresidue Analytical Method on Air and Rainwater for Assessing Pesticide Atmospheric Contamination in Untreated Areas. *Sci. Total Environ.* **2022**, *823*, 153582. https://doi.org/10.1016/j.scitotenv.2022.153582.
80. Hollender, J.; Schymanski, E.L.; Ahrens, L.; et al. *NORMAN Guidance on Suspect and Non-Target Screening in Environmental Monitoring*; Springer: Berlin/Heidelberg, Germany, 2023; Volume 35, ISBN 1230202300779.
81. Sauret-Szczepanski, N.; Mirabel, P.; Wortham, H. Development of an SPME-GC-MS/MS Method for the Determination of Pesticides in Rainwater: Laboratory and Field Experiments. *Environ. Pollut.* **2006**, *139*, 133–142. https://doi.org/10.1016/j.envpol.2005.04.024.
82. Correa, M.A.; Franco, S.A.; Luisa, M.G.; et al. Characterization Methods of Ions and Metals in Particulate Matter Pollutants on $PM_{2.5}$ and PM_{10} Samples from Several Emission Sources. *Sustainability* **2023**, *15*, 4402. https://doi.org/10.3390/su15054402.
83. Garc, M.C.; Carlos, G.; Grindlay, G. Standardization of Microwave-Assisted Extraction Procedures for Characterizing Non-Labile Metallic Nanoparticles in Environmental Solid Samples by Means of Single Particle ICP-MS. *J. Anal. At. Spectrom.* **2024**, *39*, 1736–1740. https://doi.org/10.1039/d4ja00123k.
84. Clark, A.E.; Yoon, S.; Sheesley, R.J.; et al. Pressurized Liquid Extraction Technique for the Analysis of Pesticides, PCBs, PBDEs, OPEs, PAHs, Alkanes, Hopanes, and Steranes in Atmospheric Particulate Matter. *Chemosphere* **2015**, *137*, 33–44. https://doi.org/10.1016/j.chemosphere.2015.04.051.
85. Galindo-Miranda, J.M.; Guízar-González, C.; Becerril-Bravo, E.J.; et al. Occurrence of Emerging Contaminants in Environmental Surface Waters and Their Analytical Methodology—A Review. *Water Supply* **2019**, *19*, 1871–1884. https://doi.org/10.2166/ws.2019.087.
86. Pfotenhauer, D.; Sellers, E.; Olson, M.; et al. PFAS Concentrations and Deposition in Precipitation: An Intensive 5-Month Study at National Atmospheric Deposition Program—National Trends Sites (NADP-NTN) across Wisconsin, USA. *Atmos. Environ.* **2022**, *291*, 119368. https://doi.org/10.1016/j.atmosenv.2022.119368.
87. Felli, N.; Migneco, L.M.; Francolini, I.; et al. Hypercrosslinked β-Cyclodextrin Polymer for the Dispersive Solid-Phase Extraction of Organic Pollutants from Sea Water and Wastewater. *Talanta* **2025**, *290*, 1–9. https://doi.org/10.1016/j.talanta.2025.127773.
88. Felli, N.; Lorenzet, A.; Di, V.; et al. Cyclodextrin-Based Nanosponges for the Dispersive-Solid Phase Extraction of Pesticides from Environmental Waters. *Microchem. J.* **2024**, *207*, 112135.
89. Chambers, E.; Wagrowski-Diehl, D.M.; Lu, Z.; et al. Systematic and Comprehensive Strategy for Reducing Matrix Effects in LC/MS/MS Analyses. *J. Chromatogr. B Anal. Technol. Biomed. Life Sci.* **2007**, *852*, 22–34. https://doi.org/10.1016/j.jchromb.2006.12.030.
90. Williams, M.L.; Olomukoro, A.A.; Emmons, R.V.; et al. Matrix Effects Demystified: Strategies for Resolving Challenges in Analytical Separations of Complex Samples. *J. Sep. Sci.* **2023**, *46*, 2300571. https://doi.org/10.1002/jssc.202300571.
91. Zweigle, J.; Tisler, S.; Bevilacqua, M.; et al. Prioritization Strategies for Non-Target Screening in Environmental Samples by Chromatography—High-Resolution Mass Spectrometry: A Tutorial. *J. Chromatogr. A* **2025**, *1751*, 465944. https://doi.org/10.1016/j.chroma.2025.465944.

92. Anton Kaufmann, P.T. Capabilities and Limitations of High-Resolution Mass Spectrometry (HRMS): Time-of-Flight and Orbitrap^{TM}. In *Chemical Analysis of Non-Antimicrobial Veterinary Drug Residues in Food*; Kay, J.F., MacNeil, J.D., Wang, J., Eds.; John Wiley & Sons: Hoboken, NJ, USA, 2016.
93. Søndergaard, J.; Asmund, G.; Larsen, M.M. Trace Elements Determination in Seawater by ICP-MS with on-Line Pre-Concentration on a Chelex-100 Column Using a "standard" Instrument Setup. *MethodsX* **2015**, *2*, 323–330. https://doi.org/10.1016/j.mex.2015.06.003.
94. Dehouck, P.; Cordeiro, F.; Snell, J.; et al. State of the Art in the Determination of Trace Elements in Seawater: A Worldwide Proficiency Test. *Anal. Bioanal. Chem.* **2016**, *408*, 3223–3232. https://doi.org/10.1007/s00216-016-9390-6.
95. Ngere, J.B.; Ebrahimi, K.H.; Williams, R.; et al. Ion-Exchange Chromatography Coupled to Mass Spectrometry in Life Science, Environmental, and Medical Research. *Anal. Chem.* **2023**, *95*, 152–166. https://doi.org/10.1021/acs.analchem.2c04298.
96. Shi, Z.; Chow, C.W.K.; Fabris, R.; et al. Applications of Online UV-Vis Spectrophotometer for Drinking Water Quality Monitoring and Process Control: A Review. *Sensors* **2022**, *22*, 2987. https://doi.org/10.3390/s22082987.
97. Baranwal, J.; Barse, B.; Gatto, G.; et al. Electrochemical Sensors and Their Applications: A Review. *Chemosensors* **2022**, *10*, 363. https://doi.org/10.3390/chemosensors10090363.
98. Ejigu, A.; Tefera, M.; Guadie, A.; et al. A Review of Voltammetric Techniques for Sensitive Detection of Organophosphate Pesticides in Environmental Samples. *ACS Omega* **2025**, *10*, 29929–29949. https://doi.org/10.1021/acsomega.5c01514.
99. Karakas, D.; Berberler, E.; Ozel, H.U. Source Identification of Water-Insoluble Single Particulate Matters in Rain Sequences. *Atmos. Pollut. Res.* **2022**, *13*, 101499. https://doi.org/10.1016/j.apr.2022.101499.
100. Kilic, M.; Pamukoglu, M.Y. Characterization of Water-Insoluble Particulate Matters in Sequential Rain Samples Collected by a Novel Automatic Sampler in Antalya , Turkey. *Atmos. Pollut. Res.* **2023**, *14*, 101722. https://doi.org/10.1016/j.apr.2023.101722.
101. Foken, T.; Beyrich, F.; Wulfmeyer, V. Introduction to Atmospheric Measurements. In *Springer Handbook of Atmospheric Measurements*; Foken, T., Ed.; Springer: Berlin/Heidelberg, Germany, 2021.
102. Dupont, M.F.; Elbourne, A.; Cozzolino, D.; et al. Chemometrics for Environmental Monitoring: A Review. *Anal. Methods* **2020**, *12*, 4597–4620.
103. Cauteruccio, A.; Colli, M.; Stagnaro, M.; et al. In-Situ Precipitation Measurements. In *Springer Handbook of Atmospheric Measurements*; Foken, T., Ed.; Springer: Berlin/Heidelberg, Germany, 2021; pp. 359–400.
104. Latif, S.D.; Alyaa Binti Hazrin, N.; Hoon Koo, C.; et al. Assessing Rainfall Prediction Models: Exploring the Advantages of Machine Learning and Remote Sensing Approaches. *Alex. Eng. J.* **2023**, *82*, 16–25. https://doi.org/10.1016/j.aej.2023.09.060.
105. Nozie, B.; Kalberer, M.; Claeys, M.; et al. The Molecular Identi Fi Cation of Organic Compounds in the Atmosphere: State of the Art and Challenges. *Chem. Rev.* **2015**, *115*, 3919–3983. https://doi.org/10.1021/cr5003485.
106. Vega, E.; Wellens, A.; Alarcón, A.L.; et al. Spatiotemporal Variations in Chemical Composition of Wet Atmospheric Deposition in Mexico City. *Aerosol Air Qual. Res.* **2023**, *23*, 230023. https://doi.org/10.4209/aaqr.230023.
107. Mimura, A.M.S.; Almeida, J.M.; Vaz, F.A.S.; et al. Chemical Composition Monitoring of Tropical Rainwater during an Atypical Dry Year. *Atmos. Res.* **2016**, *169*, 391–399. https://doi.org/10.1016/j.atmosres.2015.11.001.
108. Scheyer, A.; Morville, S.; Mirabel, P.; et al. Pesticides Analysed in Rainwater in Alsace Region (Eastern France): Comparison between Urban and Rural Sites. *Atmos. Environ.* **2007**, *41*, 7241–7252. https://doi.org/10.1016/j.atmosenv.2007.05.025.
109. Mullaugh, K.M.; Hamilton, J.M.; Avery, G.B.; et al. Chemosphere Temporal and Spatial Variability of Trace Volatile Organic Compounds in Rainwater. *Chemosphere* **2015**, *134*, 203–209. https://doi.org/10.1016/j.chemosphere.2015.04.027.