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Automatic sequential rain sampling to study atmospheric particulate and dissolved wet deposition

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10 **Abstract.**

Wet deposition is a key mechanism influencing lifetime of particles in the atmosphere. It allows the deposition of particles via two distinct processes, washout and rainout. Wet deposition of particles is highly variable in space and time depending both on atmospheric aerosol loads and precipitation. This variability can be observed from an event to another as well as within an event. Studying the chemical composition of wet deposition can help us to understand the origin of the aerosols as well as the way they are deposited. Indeed, depending on their intrinsic properties, aerosols have specific chemical signatures. Sequential rain sampling provides a means to monitor the chemical composition of wet deposition throughout a rain event, trace its origin, and discuss the relative contribution of rainout and washout during a single event. In order to address these issues, an automatic sequential rain sampler was specifically developed to collect the rain in consecutive fractions. The sampler has a large sampling area (1 m²) and an automatic distribution system allowing the sampling of wet deposition with high temporal resolution to document intra-event deposition variability and a sufficient volume to analyze the dissolved and particulate phases of the rain. Two rain events collected in July 2021 and February 2022 in an urban site in the surroundings of the Paris agglomeration were studied. Our results allowed us to quantify how the total mass concentration decreases with the precipitation amount during a rain event until reaching a constant level. By combining elemental and ionic analysis, the evolution of particulate and dissolved major and trace element concentrations is documented for these two rainfall events. The particulate phase shows a higher decreasing trend than the dissolved one. Major elements such as Fe, Si and Al are predominantly in the particulate phase while trace metals (TMs), like Mn and Zn, are shared in both dissolved and particulate phases. However, each element shows an increasing ratio of its dissolved to total (dissolved + particulate) fraction as rainfall progresses, especially for TM. The study of dissolved compounds (SO₄²⁻, NH₄⁺ and NO₃⁻) confirms that concentrations are decreasing with rainfall depth but that the variations are influenced by changes in rainfall intensity. The rainout and washout relative contributions to wet deposition are discussed regarding the studied chemical species and the rain events.

Key Words

Wet deposition; Rain sequential sampling; Atmospheric aerosol; Ionic composition; Trace and major elements; Dissolved and particulate phases; rainout and washout

35 **1 Introduction**

Wet deposition is a set of physico-chemical processes allowing the removal of atmospheric aerosol particles by hydrometeor precipitation. As a key mechanism influencing the lifetime of particles in the atmosphere, wet deposition is a major process to be considered in order to describe particles concentrations (Textor et al., 2006), and hence their different impacts on air quality and climate. Moreover, by removing particles from the atmosphere to land and ocean surfaces, wet deposition constitutes an important input of chemical species for marine and terrestrial ecosystems (e.g., Wright et al., 2018), as major nutrients nitrogen (N) and phosphorus (P) (Galloway et al., 2008; Van Wambeke et al., 2021). Atmospheric wet inputs of trace metals (TMs) carried by aerosols are also known to affect marine ecosystem functioning, by delivering both essential (as Fe, Zn and Co; Mackey et al., 2012) or potentially toxic TMs (as Cu, Pb and Cd; Jordi et al., 2012; Paytan et al., 2009) to the ocean surface. Observations around the world have shown a strong spatial variation in the mass and chemical fluxes of wet deposition (e.g., Vet et al., 2014; Keresztesi et al., 2019) and hence on their environmental impacts. Besides total mass fluxes, understanding the dissolved and particulate partition of chemical species in the wet deposition fluxes is key for understanding the mechanism which determines their biogeochemical effects. Indeed, dissolved phase of deposition can be used as a proxy of bioavailability (Jickells et al., 2016; Fan et al., 2006).

50 The wet deposition process removes particles from the atmosphere using two distinct processes, the rainout and the washout (Pruppacher and Klett, 1996). The rainout corresponds to the in-cloud scavenging where either the aerosols act as a condensation nucleus for the hydrometeors making up the cloud, or are captured by droplets, already formed, by impaction (Seinfeld and Pandis, 2016). The washout refers to the below-cloud scavenging and correspond to the capture of particles by raindrops as they fall via, for example, impaction, interception and brownian diffusion mechanisms (Slinn, 1977). Wet deposition is therefore simultaneously influenced by cloud life cycle, through rainout process, and by local scavenging of atmospheric aerosols through washout processes (e.g., Bertrand et al., 2008). This can lead to an efficient removal of aerosol particles from the atmosphere in remote areas far from the source regions (e.g., Bergametti et al., 1989; Keene et al., 2015; Zhao et al., 2003), as well as in polluted areas (e.g., Kulshrestha et al., 2009; Tang et al., 2005). The contribution of rainout and washout to total wet deposition varies from one event to another as well as within an event. The partition between these processes depends on the studied environment (rural, urban...) and thus **on** the presence of local emissions (Aikawa et al., 2014; Ge et al., 2016), on meteorological characteristics such as rainfall amount, intensity and types (Ge et al., 2021; Bertrand et al., 2008) and on the vertical distribution of aerosols in the air column as a function of their loads and sizes (Lim et al., 1991; Bertrand et al., 2008). Modeling studies estimate aerosols wet deposition fluxes either by using theoretical or empirical scavenging coefficients to calculate rainout and/or washout contributions (Zhang and Vet, 2006; Gong et al., 2011) or by using

65 the washout ratio empirical concept (Duce et al., 1991). The dissolved and particulate partition of chemical species is mainly based on the solubility concept, which is fixed as a function of aerosol origin (Richon et al., 2018). Currently, large uncertainties remain in the modeling of aerosol wet deposition due to a lack of constraints on scavenging processes and a poor prediction of precipitation rates (Croft et al., 2010; Ryu and Min, 2022; Yang et al., 2015). In order to improve our understanding and representation of wet deposition in models, an effort has to be done to provide more in-situ deposition
70 measurements and to document its variability.

Wet deposition is usually studied at the event or weekly basis in order to monitor dissolved, particulate or total (dissolved + particulate) chemical composition and thus deposition fluxes over a long period (Castillo et al., 2017; Vincent et al., 2016). These measurements are needed to document the temporal variability of wet deposition. However, it has also been shown that
75 wet deposition is not constant during a rain event (e.g., Jaffrezo and Colin, 1988). The high intra-event variability of wet deposition can be linked to the evolution of the origin of the deposited particles as well as changes in the rainfall characteristics or in washout and rainout processes. For this purpose, it is necessary to continuously monitor the chemical composition of dissolved and particulate aerosols in wet deposition during a rainfall event. Some online measurements have been used to monitor the pH, conductivity and dissolved inorganic ions (Ames et al., 1987; Laquer, 1990). However, to study the chemical
80 composition evolution of both the dissolved and particulate concentrations, sequential sampling is the only method enabling the acquisition of successive rain fractions. It is of particular interest because of the dependence of wet deposition on the rainfall characteristics, such as its intensity, droplet sizes and distribution (e.g., González and Aristizábal, 2012), which also evolves during the event. For instance, several studies have highlighted the existence of the so-called dilution effect (e.g., Hicks and Shannon, 1979; Lindberg, 1982), i.e., the dependence of rain concentrations with the amount of precipitation.
85 Therefore, sequential collection allows documenting the evolution of chemical compound concentrations during a single rain event. Sequential sampling has been of great interest to study the evolution of acid deposition and their neutralization during rainfall since the '80s (e.g., Seymour et al., 1978; Burch et al., 1996; Aikawa and Hiraki, 2009; Chatterjee et al., 2010). Therefore, most of the studies in the literature were focusing on major elements and ions in the dissolved phase and only a few have investigated the evolution of TMs during a rainfall (Ambe and Nishikawa, 1986a; Luo, 2001; Shimamura et al., 2006;
90 Anil et al., 2017) or the relative distribution of particulate and dissolved phases to total rain concentrations (Ma, 2006; Kasahara et al., 1996).

Chemical composition of rainfall can change between the time of collection and the chemical analysis due to changes in the equilibrium between particulate and dissolved phases (e.g., Krupa, 2002). Therefore, rain is often filtered to enhance
95 preservation until analysis, and particulate phase is not systematically analyzed. However, it is necessary to have a complete description of rainfall (particulate and dissolved fractions), in order to have a complete documentation of scavenging processes as well as of chemical composition of wet deposition (e.g., Ambe and Nishikawa, 1986b; Krupa, 2002). Furthermore, it is necessary to monitor the total composition, i.e., both the particulate and dissolved phases in order to determine the sources of

the pollutants, for example by using enrichment factors (e.g., Desboeufs et al., 2022). Indeed, even if some markers are largely
100 in one phase or the other (e.g., Na, S in the dissolved; Al, Ti in the particulate), some elements such as K, P have a non-negligible share in both phases (e.g., Cheng et al., 2021).

The intra-event evolution of chemical composition of rain has been used to discuss the relative importance of the rainout and washout processes to total wet deposition (e.g., Aikawa and Hiraki, 2009; Báez et al., 1993; Celle-Jeanton et al., 2009; Ge et al., 2021). Indeed, one assumption used in the literature is that the first increments of the rain event are influenced by both
105 rainout and washout while the last fractions could be attributed to the scavenging by rainout only (Aikawa and Hiraki, 2009; Desboeufs et al., 2010; Germer et al., 2007; Karşı et al., 2018; Xu et al., 2017). Washout and rainout contributions to wet deposition may also reflect local sources (washout) and long-range transport (rainout). In addition, chemical composition as well as its evolution can be used to identify the anthropogenic and natural sources of atmospheric compounds and their evolution during wet deposition events (Keene et al., 1986; Safai et al., 2004; Cao et al., 2009).

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This study presents the development of an automatic sequential precipitation sampler in order to document the evolution of chemical composition both for the dissolved and particulate phases during the rainfall event. We focus on major elements (NO_3^- , NH_4^+ and SO_4^{2-}), source markers (Al, Si, Fe, Ti, Na^+ , Cl^-) and TMs (Zn, Mn). From two rain events collected in an urban area close to Paris, we investigate the temporal dynamic of deposition during rain events, the origin and partition between
115 dissolved and particulate phase of scavenged chemical species as well as the relative contribution of wet deposition processes (washout/rainout) in the total wet deposition.

2 Materials and Methods

2.1. Sampling site

The sampling of two rain events on 27 July 2021 (hereafter as R1) and 10 February 2022 (hereafter as R2) are done on the air
120 quality **study site** operated by the Interuniversity Laboratory of Atmospheric Systems (LISA) and located at the University of Paris Est Creteil (UPEC) in the south-east of the Paris agglomeration (48.79°N-2.44°E). This study site is co-located with the OASIS atmospheric observatory (Chelin et al., 2015). It is an urban environment close to multiple sources of pollution such as local industries and an incinerator (1 – 2 km), multiple highways (0.1 – 0.5 km), railway stations (0.8 km), and civil construction sites.

125 Wet deposition collection is performed with a sequential sampler developed specifically for this study concomitantly with measurement of meteorological parameters with instrumentation on the air quality measurement site.

2.2 Sequential rain sampler

The design of sequential rain sampler has to satisfy several requirements. In order to precisely document the evolution of concentrations during a rain event and to better understand it, the collection must be performed at high temporal resolution

130 (from a few seconds for convective rain rates to tens of minutes for very low drizzle). Secondly, in order to investigate the evolution of scavenging processes during the rain event, it is necessary to have information throughout the event until its end. For this purpose, a large sampling area should allow collecting numerous rain fractions with a high temporal resolution during one event. In addition, the sampling line and the distribution unit have to allow the collection of several successive fractions without mixing them. Then, as our objective is to document the chemical composition for both the dissolved and particulate
135 phase, the sampled rain volume needs to be at least equal to 50 mL to carry out a set of analyses. Moreover, TMs are expected to be present in very low concentrations at the end of the rain event. Therefore, it is critical to limit various chemical contamination for TMs measurements. Finally, it needs to be automated as much as possible so that it can be deployed in different environments and run with limited operator interventions.

A scheme of the sequential sampler developed at the LISA is presented in figure 1a. It is a 2 m high closed structure composed
140 of a Teflon pyramid funnel with a collection surface of 1 m² that allows sampling rainwater into 24 successive fractions (adjustable from 0.05 to 0.5 mm) with a high temporal resolution controlled by volume. The pyramid funnel is closed up with a cover which is removed manually at the onset of each rain event in order to avoid dry deposition in the sampler and to collect the first raindrops. During the sampling, the rainwater collected in the pyramid funnel flows into a separating funnel made with Teflon and connected via a polypropylene (PP) connector. The rain sequential sampling is managed by an optical level
145 sensor placed on the separating funnel (Fig. 1b). When a predefined range of rainwater volume is reached, the optical sensor triggers a peristaltic pump which empties the separating funnel (50 - 150 mL) into a sampling bottle in 4 s via the distribution unit. The distribution unit consists of two interlocking PP parts (Fig. 1c). The upper part is the rotating part of the unit (rotor) and has one port equipped with a PTFE connector for the transfer of rainwater from the peristaltic pump to the lower part of the distribution unit (stator). The latter has 24 holes with PTFE connectors for the distribution of rainwater to the sampling
150 bottles through PTFE tubes. All tubes are connected to the sampling bottles through a cap specially designed allowing the flow of rainwater (into the rain inlet) while pushing out the air of the bottle throughout the air outlet on which is placed a syringe filter of pore size 0.2 µm to avoid atmospheric particle contamination. The change of sampling bottles is assured by a control unit that successively serves 24 PP bottles (Fig. 1b). The control unit can be programmed to set beforehand the volume of each sampling position and to collect the rainfall automatically (Fig. S1 in supplements). The system unit controls if the programmed
155 volume in a sampling bottle is reached. When the latter is reached, the control unit note in a text file, the sampling line number, the date and hour and then triggers the stepper motor to rotate the rotor part by 15° to the next position. Once the rotation is complete, the collection bottle is closed by the rotor disc and rainwater cannot flow into it. The total volume of rainfall fractions collected sequentially can be up to 13 mm (+ field blank), the last position can be used for a larger volume collection of the end of the rain (2 mm of additional rainfall). The sampling device associated to the control unit allows us to adapt the collection
160 of rain and be able to sample several fractions of very light to very intense rainfall (up to 60 – 70 mm h⁻¹) with a minimum rainfall depth of 0.05 mm for each fraction without mixing.

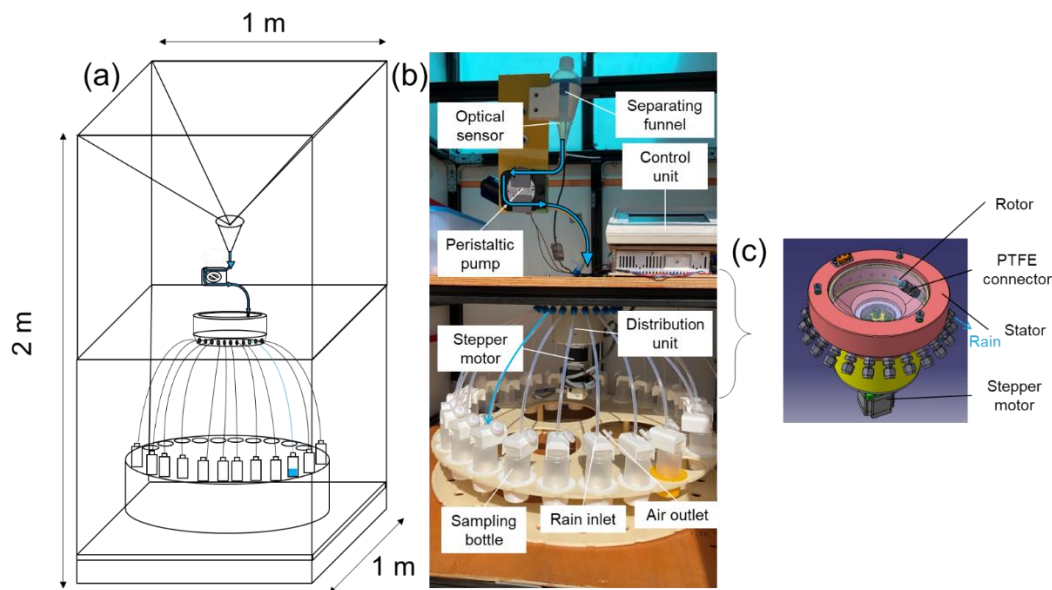


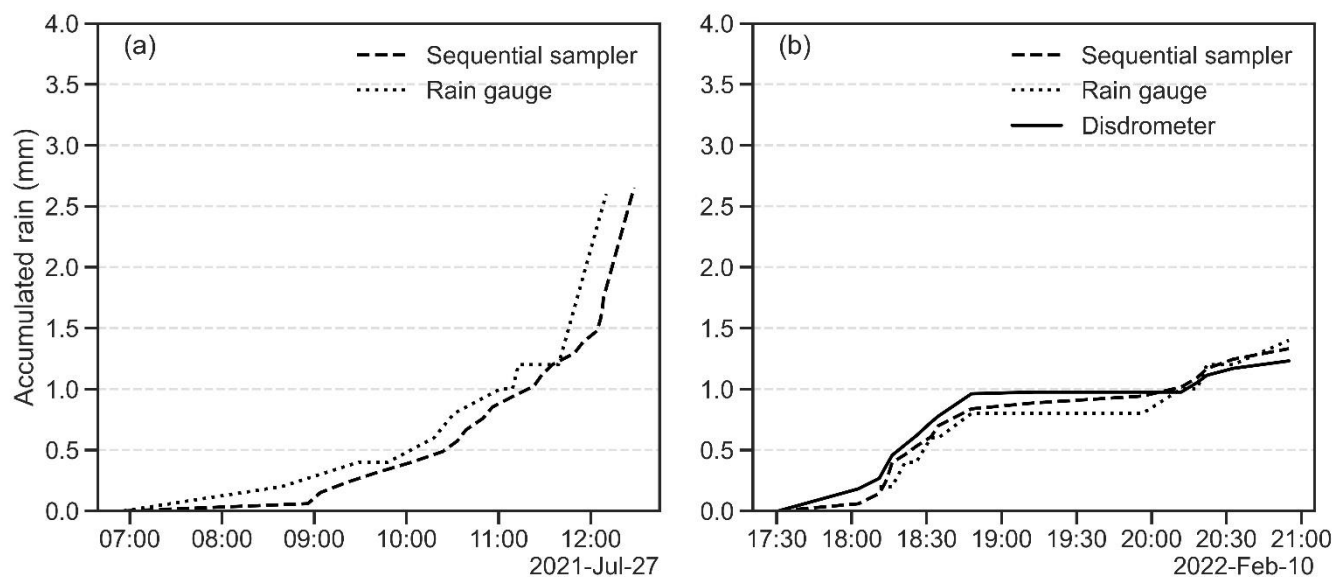
Figure 1. (a) Scheme of the rain sampler, (b) overview of the distribution system and (c) scheme of the distribution unit. Blue lines represent the rainfall runoff.

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2.3 Meteorological conditions

In order to characterize atmospheric conditions associated to rain events, meteorological measurements were done in the air quality station of the LISA. Rainfall was monitored using a Précis-Mécanique rain gauge model 3070A (0.2 mm precision). In parallel, other parameters characterizing the air masses at the site have been measured such as air temperature, relative humidity using instrumentation from Campbell Scientific© and are recorded with a time step of 1 min.

Since February 2022, an optical disdrometer OTT PARSIVEL® (PARTicle SIZE and VELOCITY) has been deployed to monitor rainfall with 0.001 mm h⁻¹ precision. In order to qualify how the sequential sampler collects the rain fraction, we compared the accumulated rain collected by this device with rainfall measured by the rain gauge for the first rain collected on July 27, 2021 (R1, Fig. 2a) and rainfall measured by the rain gauge and the disdrometer for the second rain collected on February 10, 2022 (R2, Fig. 2b). The three devices show similar temporal evolution of the accumulated rainfall for R1 and R2. The sequential sampler is able to correctly collect rain fractions for low rain intensity as well as for intense rain registered by the rain gauge and the disdrometer.



180 **Figure 2. Accumulated rain collected and measured as a function of time for two rain events (a) R1 event in July, (b) R2 event in February.**

In a complement to local wind measurements performed at the studied site, air masses' trajectories were computed using the HYSPLIT model (<http://ready.arl.noaa.gov/HYSPLIT.php>) (Draxler and Rolph, 2003). HYSPLIT forward and backward air mass simulations can be respectively used to study local to continental air mass dispersion and transport of atmospheric compounds (e.g., Celle-Jeanton et al., 2009; Bertrand et al., 2008; Calvo et al., 2012) and to identify the origin of air masses in order to identify sources of atmospheric substances, e.g., mineral dust, sea salt or anthropogenic (e.g., Vincent et al., 2016; Anil et al., 2017). Here, 48h backwards trajectories were computed by the HYSPLIT model, with GFS (0.25°, global), from the studied site (47.79°N – 2.44°W) at 0 m, 500 m and 1 000 m a.g.l. in order to have information about the origin of the air mass scavenged on the first kilometer of the atmospheric column for R1 on July 27, 2021, 06:00 and 12:00 GMT and R2 on February 10, 2022, 18:00 and 20:00 GMT.

2.4 Analytical and sampling protocols

The dissolved and particulate concentrations in the rainwater can vary over several orders of magnitude from hundreds of ppm to few ppb to tens of ppt according to the element (e.g., Lim et al., 1991; Ma, 2006). In order to quantify low concentration, especially for TMs, the chemical contamination along the sequential sampling line of the sampler needs to be limited and controlled. Following Laquer (1990) recommendation, surfaces materials in contact with rainwater (i.e., collection's and storage's surfaces) have to be chosen based on the chemical compound to be analyzed. In our case, the interest elements are metals and inorganic ions, so the device is made with Teflon, PP and Neoprene® (peristaltic pump tube), which are metal-free material (Method 1638, 1996). Sampling bottles and all contact surfaces underwent a drastic washing protocol. The latter

200 consisted in washing, several soaking (24h in Decon© 2% v/v, 24h in HCl 0.4M Normapur® then 7 days in HCl 0.4M Suprapur®, 24h then 7 days in ultrapure water (UPW, 18.2 MΩ.cm)) and repeated rinses with reverse osmosis-purified and ultrapure waters (UPW) in ISO 7 then ISO 5-controlled laboratory rooms, respectively.

Samples are pretreated and conditioned for ionic and elemental analysis as presented in figure 3 after the end of rainfall within 1 to 12 hours. Otherwise, they are kept in the dark at $T = 6^{\circ}\text{C}$, and treated within 24 hours. The treatment, filtration and
205 conditioning of the samples is carried out in an ISO 6-controlled laboratory room under a laminar flow hood (U15 filter) estimated ISO 3. For each sequential sample, pH measurements are done in a 5-10 mL aliquot using a pH meter (METTLER TOLEDO® Seven2Go).

The rest of the sample (60 to 145 mL depending on the collected fractions) is filtered through pre-cleaned Nuclepore® polycarbonate membranes with a porosity of $0.2\ \mu\text{m}$ to separate the particulate phase from the dissolved phase. The filters are
210 then dried under laminar flow hood then conditioned for 48h at a relative humidity of 45 – 50% and at a temperature between 20 and 25°C prior to weighing using a precision microbalance (METTLER TOLEDO® XPR26C, PRAMMICS Platform). Filtration is done from the last rain fractions to the first one in order not to risk any contamination of the less concentrated rainwater by the most polluted. Several rain sequential samples can be filtered on the same filter in order to accumulate sufficient material to obtain a mass on the filter with a confidence level of 95%. On the contrary, when particulate load is too
215 high, one rain fraction is filtered on several membranes. Uncertainties are calculated according to the propagation of the weighing uncertainty of the filters with a confidence level of 95%. Elemental composition (Al, Ba, Ca, Cr, Fe, K, Mg, Mn, Na, Ni, P, S, Si, Ti and Zn) of successive particulate fractions is obtained using X-ray fluorescence spectrometer (XRF, ZETIUM 4 kW, MalvernPanalytical®, PRAMMICS Platform). For dissolved phase, all the sequential samples are analyzed even if there are more fractions describing dissolved than particulate phases. Ten milliliters aliquot of the dissolved phase is
220 frozen until analysis of water-soluble major cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}) and anions (Cl^- , NO_3^- , PO_4^{3-} , SO_4^{2-}) by Ion Chromatography (Compact IC Flex, Metrohm®, PRAMMICS Platform). Organic ions (HCOO^- , CH_3COO^- , $\text{C}_2\text{H}_5\text{COO}^-$, MSA, C_2O_2^-) can also be measured, but are not presented here. Two 15 mL aliquots are acidified to $\text{pH} = 1$ with nitric acid (Suprapur®) and stored at 7°C protected from air and light until analysis by Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES, Spectro ARCOS Ametek®) of water-soluble Al, Ba, Ca, Cr, Fe, K, Mg, Mn, Na, Ni, P, S, Si, Ti and
225 Zn.

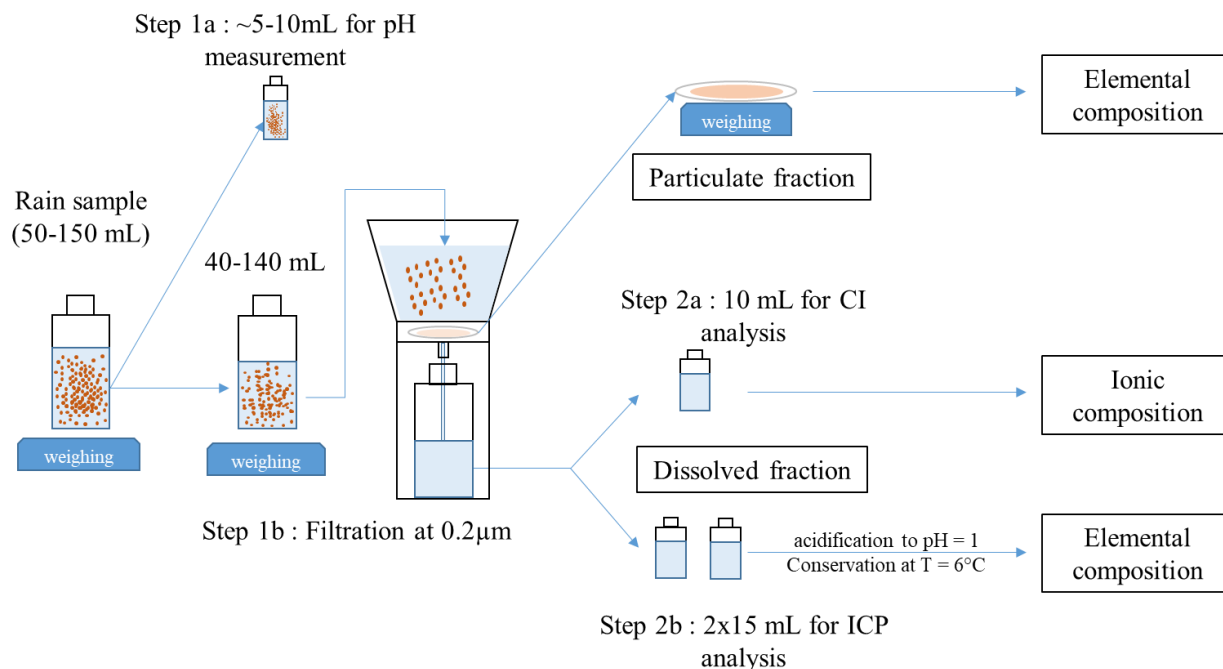


Figure 3. Scheme of sample treatment and chemical analysis followed for each of the rain samples collected during a rain event.

230 For XRF and ICP analysis, limits of detection (DL) are calculated as three times the standard deviation of laboratory analytical
 blanks, blank filters and acidified UPW, respectively (see table S2 in supplements). Uncertainties are defined as the standard
 deviation of analytical replicates. For IC, the quantification limit (QL) is determined empirically by comparing controls
 performed during the analysis and the calibration range. We assume the highest concentration for which there is a 10%
 difference with the calibration range is the QL. Then, DL is calculated as being equal to one third of the QL (see table S3 in
 235 supplements). Uncertainties are defined as the relative deviation of controls with calibration range. The detection limits allow
 us to determine the expected dissolved concentrations at the end of the rain with detection limits ranging from few ppb (for
 nutrients and major element) to several tens of ppt (TMs).

Based on preliminary tests for optimizing rinse (see text S4 in supplement), the funnel is rinsed using 500 mL UPW prior to
 the collection of rain. Field blanks are done by pouring UPW over the funnel after the rinsing of the collection system, before
 240 the onset of rainfall. The field blank values, if not below DL, represent in average less than 16.9 ppb (0.03 – 69.9ppb) compared
 to values obtained in the first 0.06 mm of rainfall up to 8 699 ppb for R1 and less than 41.2 ppb (0.1 – 358 ppb) compared to
 values obtained in the first 0.06 mm of rainfall up to 2 893 ppb for R2. However, the values obtained for the field blanks cannot
 be subtracted from each fraction as the successive fractions are not influenced the same way by initial sampling conditions.

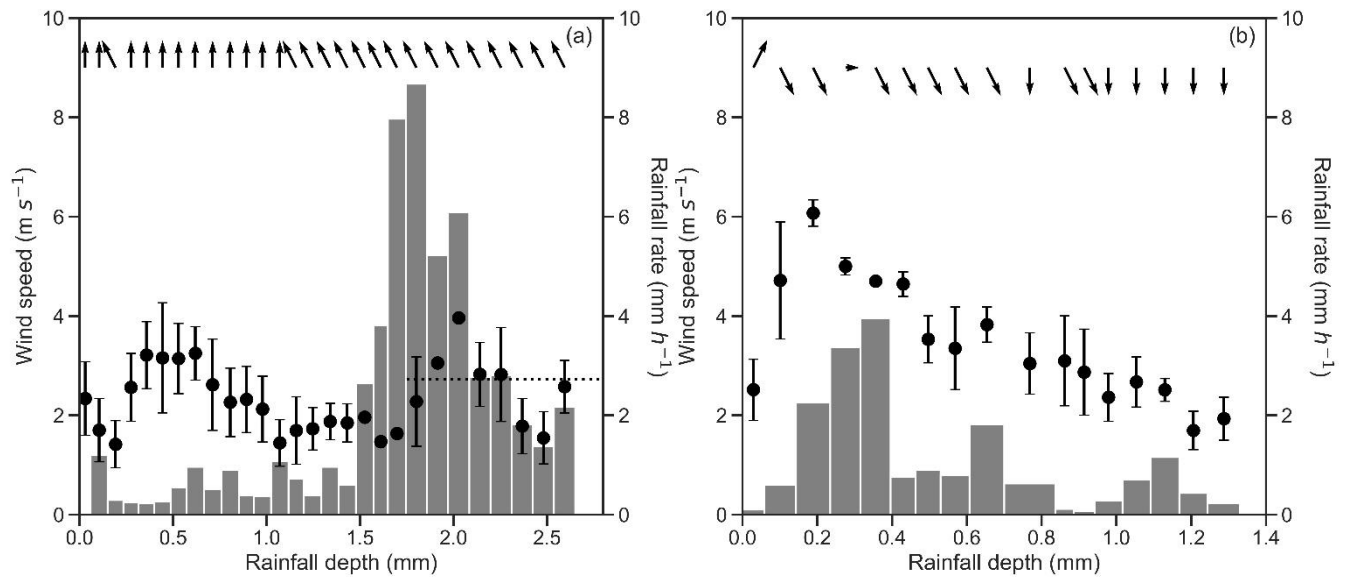
3 Results and discussion

245 3.1 Rain sequential sampling conditions

The R1 was collected from 06:55 GMT until 12:25 GMT on July 27, 2021, i.e., for 5 hours 30 min. The total rainfall was 2.65 mm, collected in 20 fractions between 0.06 and 0.1 mm, plus a last one being of 0.91 mm to collect the end of rain (Fig. 4a). The R2 was collected from 17:28 GMT until 20:55 GMT on February 10, 2022, i.e., for 3 hours 27 min, in 17 fractions between 0.05 and 0.14 mm for a total rainfall depth of 1.33 mm (Fig. 4b).

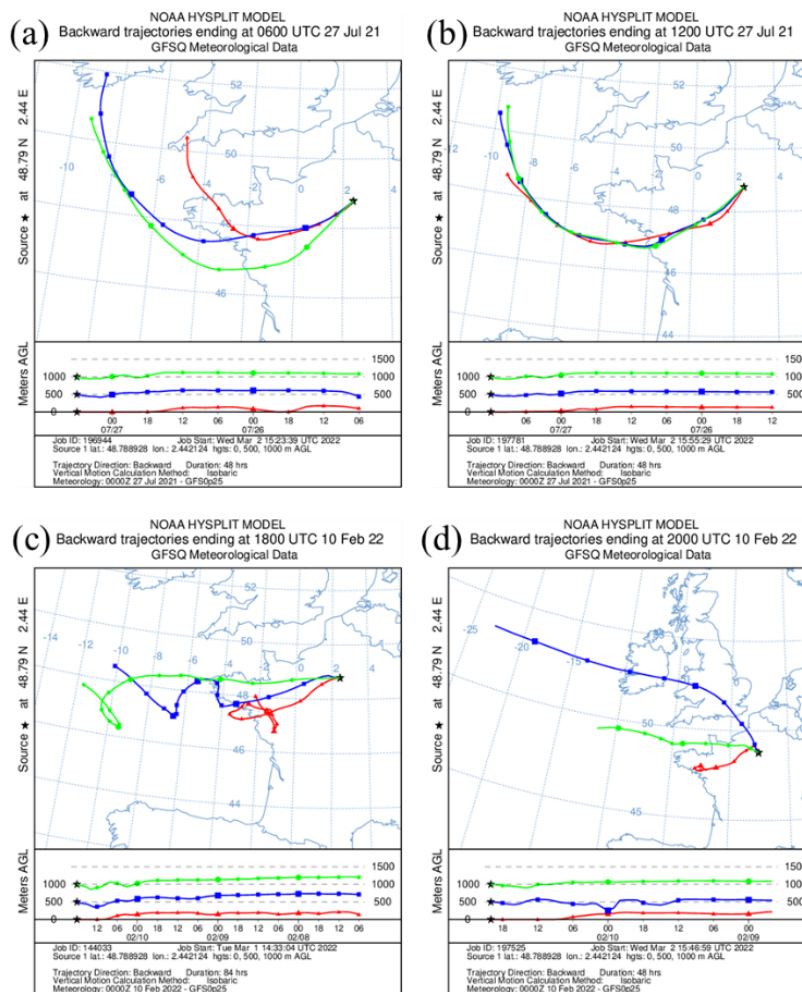
250 R1 wind speeds ranged from 0.5 to 5.0 m s⁻¹ (average = 2.4 ± 0.9 m s⁻¹) and were coming from south all along the event. Wind speeds during R2 were higher than during R1, ranging from 1.1 to 6.5 m s⁻¹ (average = 2.9 ± 1.1 m s⁻¹) and coming from west-south-west for the first collected fraction then north-north-west for the rest of sequential samples. On the contrary, the temporal dynamics of the rain pattern were very contrasted both during R1 and R2. For R1, rainfall intensity changed during the rain from 0.03 to 8.68 mm h⁻¹. For R2, intensity ranged from 0.03 to 2.25 mm h⁻¹. As sequential collection is based on volume, this illustrates the wide variation in collection time for each fraction (from 43s to 2 h).

R1 as well as R2 can be separated into four rainfall phases, based on rainfall regime (Fig. 4). Phase I of R1, between 0.06 – 0.49 mm, is characterized by a decreasing rainfall rate to 0.22 mm h⁻¹. Phase II, between 0.49 – 1.48 mm, is characterized a steady rainfall rate of 0.68 ± 0.26 mm h⁻¹, when the phase III, between 1.48 – 1.85 mm, is characterized by an increase of rainfall rates up to 8.68 mm h⁻¹ to finally decrease until the end of the event (phase IV). For R2, the phase I, between 0.00 – 260 0.40 mm, is characterized by an increasing rainfall rate from 0.10 to 3.95 mm h⁻¹. Phase II, between 0.40 – 0.61 mm, is characterized by constant rainfall rate of 0.82 ± 0.07 mm h⁻¹ and the phase III, between 0.61 – 0.94 mm, is characterized by a decreasing rainfall rate from 1.82 to 0.08 mm h⁻¹. The last phase IV presents a Gaussian distribution of rainfall rates with a maximum of 0.9 mm h⁻¹ around 1.17 mm. Based on the HYSPLIT 48h backwards trajectory calculation (Fig. 5), the origin of air masses scavenged by rain events were homogeneous on the precipitation period and came from the Atlantic Ocean for R1 and R2 events. Both local winds and the origin of air masses transporting aerosols were stable throughout both events.



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Figure 4. Evolution of mean wind speed (black dot, median wind direction (black arrows) and of rainfall rates (grey bar plot) as a function of rainfall depth during each sample of R1 (a) and R2 (b). The black dotted line corresponds to the mean rainfall rate of the last fraction of R1 during 1.75 – 2.65 mm (a). The tip of the arrow pointing in the direction (North upward and South down), while uncertainty bars correspond to standard deviation of wind speed during rain fractions' collection time. To give an example of how to read the figure, when the tip of the arrow is heading upwards, it means that the wind is coming from the south.



275 **Figure 5. 48 h Air mass backward trajectory arriving at Creteil, France, for R1 (a and b) and of R2 events (b and c) for air masses reaching 0 m, 500 m and 1000 m of altitude at the beginning (a et c) and the end (b and d) of rain events**

3.2 Intra-event variability of wet deposition

3.2.1 Total mass concentrations and chemical contributions

Particulate and dissolved mass concentrations as well as chemical contributions are represented as a function of rainfall depth
 280 for both R1 and R2 events (Fig. 6). The chemical composition of the two wet deposition events, described from the minimum, maximum and volume-weighted mean (VWM) values, is available in the supplement table S5. The 20 and 15 fractions of rain samples collected for R1 and R2 have been filtered on 8 and 5 filters, respectively. The mass concentrations of each rain fractions are obtained with a confidence level of 95% by weighting filters with the exception of the fraction 0.67 – 1.29 mm on the filter of R1. Therefore, no particulate mass concentration information between 0.67 and 1.29 mm of precipitation amount
 285 is presented.

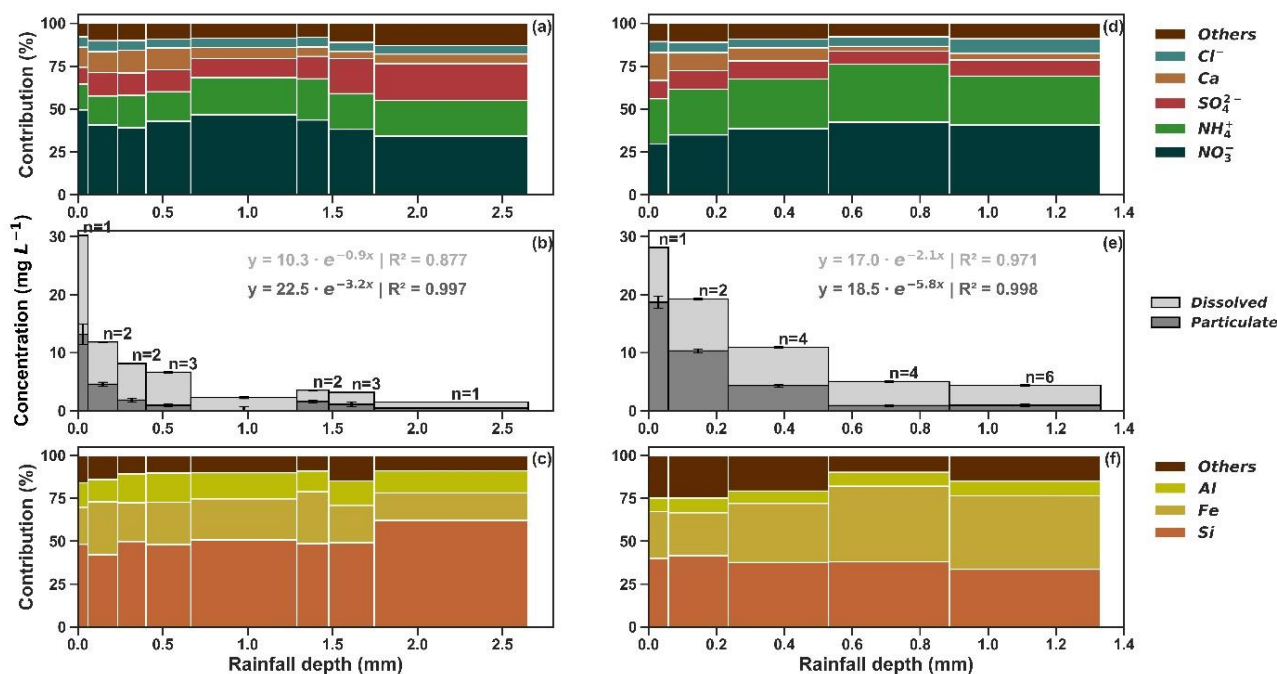


Figure 6. Evolution of total mass rain concentrations (in mg L⁻¹) for R1 (b) and R2 (e) and contributions (in %) of dissolved compounds (a and d) and particulate elements (c and f) with rainfall depth (mm). It must be noted that dissolved concentrations do not take into account organic carbon. Uncertainty bars are presented for dissolved and particulate phases. The number of fractions cumulated on each filter is noted next to each bar.

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Figure 6 emphasizes firstly that total mass concentrations decrease quickly with rainfall depth for both R1 and R2 until reaching constant values (Fig 6 b and e). The first sequential samples of R1 and R2 account for 14 to 16% of total mass fluxes while being responsible for only 2 to 4% (0.06 mm of rainfall depth) of the total rainfall amount of each event (Fig. 6 b-e). It must be noted that the particulate mass concentration increases for R1 between the 0.40 – 0.67 mm and the 1.29 – 1.48 mm rain fractions concomitantly with the increase of rainfall rates observed in figure 4b. For both events, the decreasing trend of the particulate phase concentration is more pronounced than the dissolved one. Indeed, 59 – 60% of the particulate and 30 – 41% of the dissolved mass fluxes occur during the first 15 – 18% of accumulated precipitation. In the literature, concentrations of particulate phases have been shown to follow a higher decreasing trend with precipitation amount than dissolved phase. This indicates that particulate components are more easily scavenged by raindrops (Kasahara et al., 1996; Ma, 2006).

In order to explore the decreasing pattern, we plotted an exponential fit ($y = a \cdot e^{-bx}$) of dissolved as well as particulate mass concentrations as a function of rainfall depth, y being the concentrations, x the rainfall depth and b the exponential decay parameter. Exponential fit parameters for dissolved and particulate phases evolution of both R1 and R2 events are shown on Figure 6 and described in the table 1. The decay of the particulate phase concentrations with rainfall depth is between 2.4 and 2.8 times greater than those of the dissolved phase. These equations support the fact that higher scavenging is observed at the beginning of rain events, with a most marked decreasing trend for the particulate phase.

Table 1. Exponential parameters of the dissolved and particulate mass concentrations evolution of R1 and R2

Event	Dissolved phase		Particulate phase	
	R1	$y = 10.3 \cdot e^{-0.9x}$	$R^2 = 0.877$	$y = 22.5 \cdot e^{-3.2x}$
R2	$y = 17.0 \cdot e^{-2.1x}$	$R^2 = 0.971$	$y = 18.5 \cdot e^{-5.8x}$	$R^2 = 0.998$

310 Figure 6 also emphasizes that the relative contribution of the different compounds in the dissolved and particulate phases is fairly similar in the two events. The stability of chemical contribution is consistent with the homogeneity of local wind direction and back trajectories (see 3.1.) during the rain events. Therefore, one can assume that the transported and scavenged air masses present a certain continuity throughout both rainfall events. Dissolved composition of rainwater is dominated by sulfate, nitrate and ammonium for both rain events. Their cumulated contribution is 74% for R1 and 79% for R2 of dissolved mass concentration measured in average (Figure 6a-c for R1 and figure 6d-f for R2). Even though air masses originate from the Atlantic Ocean, the influence of sea salt at the receptor site is low considering the low contribution of chloride and sodium in rain composition for both rainfalls (less than 7% for Cl in rain sequential samples). Thus, rain event composition seems to be mainly influenced by the scavenging of anthropogenic secondary inorganic aerosols such as ammonium nitrate and ammonium sulfate, or their gaseous precursors, NO_x, NH₃ or SO₂. Indeed, these compounds are resulting from the conversion of compounds related to anthropogenic activities such as fossil fuel emissions (conversion of NO_x into NO₃⁻ and SO₂ into SO₄²⁻) and agricultural emissions (NH₃ into NH₄⁺) and are mainly in the submicron particulate matter (PM₁). NH₄⁺ and NO₃⁻ VWM concentrations are 2.7 and 1.6 times higher for R2 than R1, respectively. Higher NH₄⁺ content could be attributed to higher urban emissions of NH₃ and to early nitrogen fertilizer applications in February (Airparif, 2021; Favez et al., 2021). Higher NO₃⁻ content can be due to lower winter temperatures that facilitate the formation of particulate nitrate (e.g., Cao et al., 2017; Schaap et al., 2004). The higher pH found in R2 (6.1 – 6.8) in comparison to R1 (4.9 – 6.1) (see supplement table S5) is in agreement with a pH neutralizing effect due to ammonium, previously observed in Paris (Beysens et al., 2017), which concentrations are inferior in R1 samples. Ammonium sulfate and ammonium nitrate aerosols are composed of mineral salts and are therefore highly soluble. Thus, dissolved concentrations are generally considered to represent total concentrations. The comparison between total S and SO₄²⁻ concentrations show that 94 to 97% of S is under sulfate form depending on the rainfall event, confirming that assumption.

330 Particulate phase is composed in the majority of Si, Fe and Al, representing more than 75% of the total elements that have been analyzed, whatever the rain sequential samples. The presence of construction sites (Si, Al) and highways (Fe) close to the receptor site may explain the high contribution observed for these elements, since these elements, as also Zn, Ba and Ti are known to be related with non-exhaust traffic emission as tire and brake wear or resuspended particles (e.g., Thorpe and Harrison, 2008; Pant and Harrison, 2013). Typically, these elements are associated with the mode of PM higher than 2.5 μm

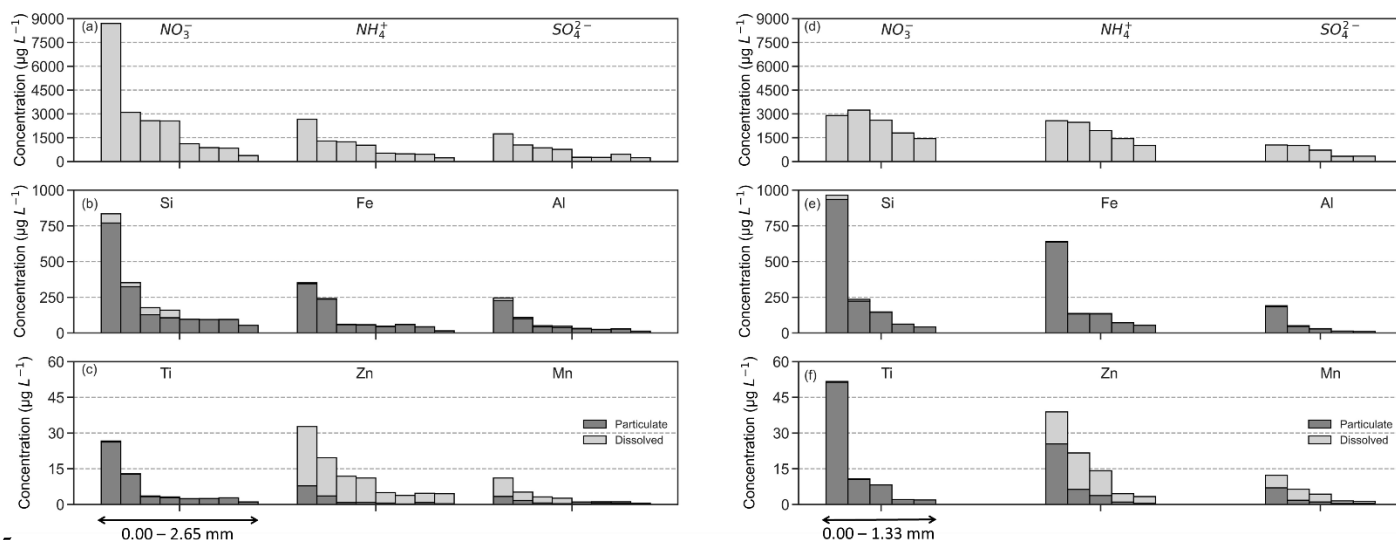
(Bukowiecki et al., 2009; Mamun et al., 2020). It is also interesting to note that Fe, Si, Al and Ti are predominantly found in the particulate phase of both rain events (see supplements table S5).

Among TMs, Ti is predominantly in the particulate phase whereas Zn and Mn are present in both the dissolved and particulate phase (these elements are part of ‘others’ class in fig. 6). Their contribution in the mass concentrations of each fraction, depending on the rain event, are ranging from 0.02 to 0.06% and for Mn and from 0.08 to 0.40% for Zn in the dissolved phase and from 0.10 to 0.39% for Mn, from 0.13 to 1.2% for Zn and from 1.2 to 2.2% for Ti, respectively in the particulate phase. Ti is mainly of crustal origin while Mn and Zn have various sources in the urban environment such as exhaust and non-exhaust emissions from road traffic, construction sites and incineration plants (e.g., Pant and Harrison, 2013; Sanderson et al., 2014; Citepa, 2022). However, due to the continuity of scavenged air masses, we estimate that their origins are stable all along the rainfall.

3.2.2. Chemical concentration evolution

Evolution with rainfall depth

The evolution of chemical concentrations is detailed in the figure 7 for major chemical species and TMs composing the rains. As it has been observed for mass concentrations, the major chemical species and TMs concentrations decrease quickly between the first sample and the next ones. Even if the general trend is a decrease of mass and chemical concentrations with rainfall depth, the decreasing patterns are both different from one rain to another but also from a chemical species to another. The final chemical concentrations are between 8 and 24 and between 2 and 27 times smaller than the values measured at the beginning of the rainfall R1 and R2, respectively.



355 **Figure 7. Evolution of concentrations of dissolved and particulate species in rainwater for R1 (a, b, c) and R2 (d, e, f) with rainfall depth. The dark gray area and light gray correspond to the particulate and dissolved phases, respectively. Each R1 bar corresponds to the fractions 0.00 – 0.06 mm, 0.06 – 0.23 mm, 0.23 – 0.40 mm, 0.40 – 0.67 mm, 0.67 – 1.29 mm, 1.29 – 1.48 mm, 1.48**

360 – 1.75 mm and 1.75 – 2.65 mm, respectively. Each R2 bar corresponds to the fractions 0.00 – 0.06 mm, 0.06 – 0.23 mm, 0.23 – 0.53 mm, 0.53 – 0.89 mm and 0.89 – 1.33 mm, respectively.

Figure 7 highlights a difference of scavenging of dissolved and particulate phases. The concentrations of elements mainly present in the particulate phase follow the same marked decreasing trend during the rain for both R1 and R2 (Al, Si, Fe and Ti in Fig. 7b and 7e). The general pattern for the concentrations evolution of soluble species differs between the two rains with
365 lower decrease observed for R2 (nitrate, ammonium and sulfate in Fig. 7a and 7d). Al, Si and Fe (which account for 73 to 90% of elemental composition of the particulate phase) are generally associated with PM higher than 2.5 μm (Bukowiecki et al., 2009; Mamun et al., 2020), while sulfate, nitrate and ammonium (depicting altogether for 69 to 86% of the dissolved phase mass according to rain events or fractions) are associated mainly with PM₁ fraction. The difference observed for the decays could be explained by the difference in particle sizes. Indeed, washout is a particle size-dependent process which shows a
370 minimum in the diameter range 0.2 - 2 μm (the so-called Greenfield Gap; Greenfield, 1957). Therefore, the largest particles (here Al, Si, Fe) are more easily removed and thus represent a larger fraction of the deposited particles at the beginning of the rainfall and a lowered proportion as the rainfall progresses, as also described by Karşı et al. (2018). The latter imply this overwhelming presence of smaller particles at the end of the rainfall event to a lower efficiency of the washout process to scavenge this range of particles, and a higher relative contribution of the rainout process in wet deposition.

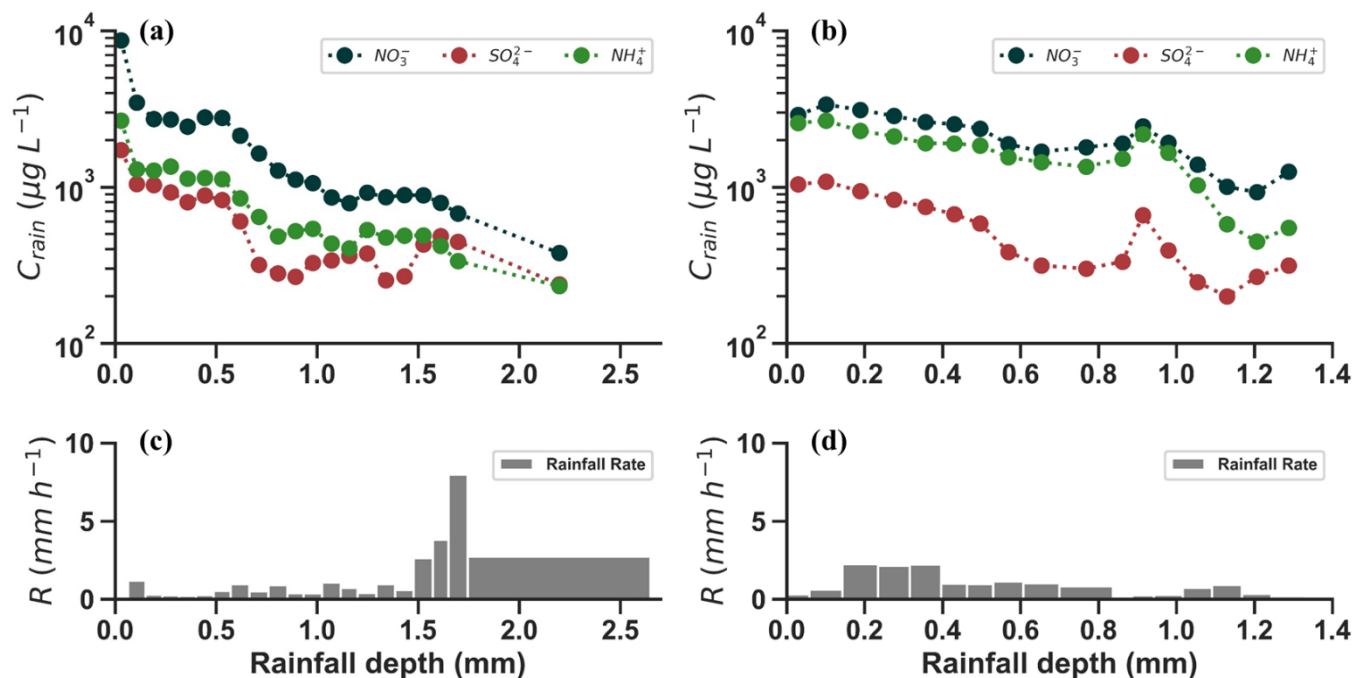
375 Figure 7 also illustrates that dissolved/total ratio of elements increases between the first and the last collected fractions. This ratio could be related to fractional solubility (hereafter referred as solubility) commonly used to understand dissolution processes. As an example, solubility increases during rainfalls for Mn (from 50 to 86% in R1 and from 43 to 62% in R2), Zn (from 76 to 93% in R1 and from 35 to 86% in R2) and Fe (from 2.1 to 10% for R1 and from 0.7 to 2.0% in R2).

Our results are consistent with a highest wet deposition at the beginning of the event due to the greater presence of particles in
380 the atmospheric column under the cloud. At the later stage of a rain event, the atmospheric column is depleted of aerosols, then, the wet deposition flux is limited and thereby causes a decrease in the observed average rain mass and chemical concentration of the event. As mentioned in the introduction, the mass and chemical concentrations patterns found in R1 and R2 could be related with evolution from first samples affected by both rainout and washout, whereas last samples correspond predominantly to scavenging by rainout (Aikawa and Hiraki, 2009; Desboeufs et al., 2010; Germer et al., 2007; Karşı et al.,
385 2018; Xu et al., 2017; Berberler et al., 2022). Our results support thus the fact that particulate phase, being deposited predominantly in the earlier stage of rain, is more likely to be scavenged by washout than rainout process.

Evolution with rainfall rate

Figure 8 illustrates the impact of changing rainfall regime on the sulfate, nitrate and ammonium (SNA) concentrations in the
390 rainwater with a higher time resolution than total concentrations. Evolution of SNA concentrations observed for R1 (Fig. 8a) is consistent with the evolution of total concentrations described figures 6 b and 7. However, for R2 (Fig. 8b), SNA concentrations show a decreasing trend at the beginning of the event (0.00 – 0.84 mm). This is followed by an increase in

concentrations when the rainfall rate is minimum (last moments of phase III, sect. 3.1). Then, as the rainfall rate increases, the decreasing trend is re-established until the rainfall rate decrease again.



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Figure 8. Evolution of sulfate, nitrate and ammonium (SNA) concentrations for (a) R1 and (b) R2; evolution of rainfall rate for R1 (c) and R2 (d) with rainfall depth (mm).

Disdrometer measurements (Fig. S6 in supplements) show an increase of the relative weight of smaller droplets concomitant with the increase of SNA concentrations observed between 0.8 and 0.9 mm (fig. 8b). On this basis, one can think that increases in SNA concentrations in rainwater during R2 may result from an increase in the scavenging efficiency, due to the smaller size of the rain droplets (Asman, 1980), or from an increase in droplet evaporation during their fall, leading to an increase in their concentrations (Huff and Stout, 1964; Baechmann et al., 1996a, b). In relation to this last hypothesis, we observed a decrease in surface relative humidity measured at our site. Additional ceilometer measurement made in Paris region (Haefelin et al., 2005) highlights the attenuation of the backscattered signal during the same time frame (Fig. S7 in supplements), which is consistent with a decrease of rainfall reaching the surface and hence evaporation of droplets.

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3.3. Rainout and washout deposition contributions

As mentioned, the patterns of mass and chemical concentrations are consistent with evolution from the combined rainout and washout process in the first samples, then a scavenging mainly due to rainout. However, the contribution of these processes seems to be different for a chemical species to another (e.g., Aikawa et al., 2014). In order to deconvolute the contribution of each process for each chemical species, we used here the set of dissolved samples for soluble species, which have a higher

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temporal resolution throughout both rainfall events than particulate samples (Fig. 8). We considered the total concentration (Fig. 9) for determining rainout and washout contributions of particulate elements and species shared in both particulate and dissolved phases.

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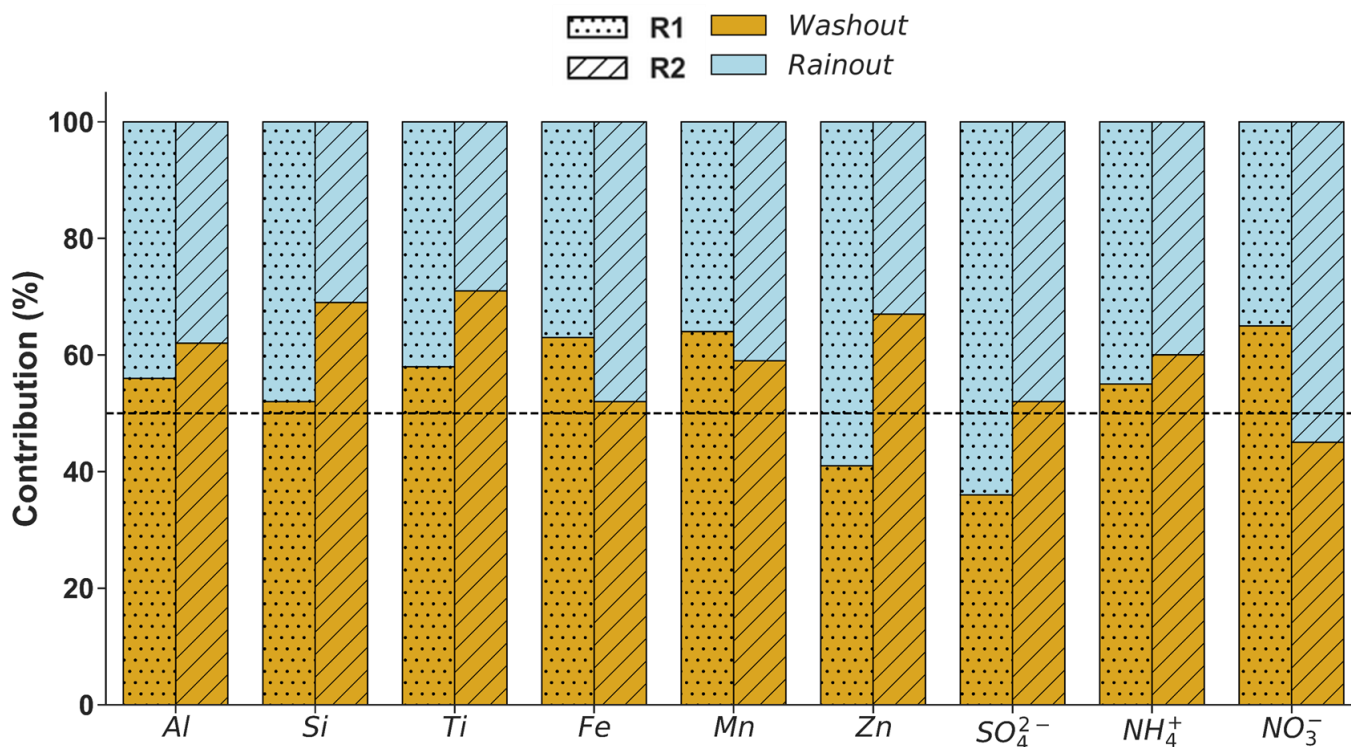
Chatterjee et al. (2010) as well as Karşı et al. (2018) have determined rainout and washout relative contributions on wet deposition of ionic species using sequential collection. On one hand, Chatterjee et al. (2010) defined two sub-events (named « below cloud » and « in-cloud » events) based on their respective evolution. The earlier stage of the precipitation where the concentrations decrease is higher being considered as below cloud event while the samples collected as the end of the rain event, where the decrease of concentrations shows a slower trend was considered as in-cloud event. On the other hand, Karşı et al. (2018) have used the average of at least the three lowest values as representative of the rainout droplet concentration, assumed to be representative of in-cloud concentrations prior any influence of washout. Then, rainout fluxes are compared to the total (rainout + washout) wet deposition fluxes to determine its relative contribution to wet deposition. Based on their approach, we determine in-cloud concentrations, $C_{rainout}$ ($\mu\text{g L}^{-1}$), for SNA, Fe, Si, Al, Ti, Zn and Mn using the VWM concentration of the constant level reached at the end of the rainfall for R1 (1.48 – 2.65 mm) and R2 (1.02 – 1.33 mm for SNA and 0.89 – 1.33 mm for other elements).

Values found for sulfate are similar for both events, between 259 and 287 $\mu\text{g L}^{-1}$, which is lower than in-cloud concentrations previously observed using sequential sampling in an urban environment in Japan and China (1 880 - 3 330 $\mu\text{g L}^{-1}$; Aikawa et al., 2014; Xu et al., 2017; Ge et al., 2021). This is consistent with higher levels of SO_2 emissions in Asia than in Europe (e.g., Zhong et al., 2020). Concerning nitrate and ammonium, we found in-cloud concentrations ~2.4 times higher for R2 (1 147 $\mu\text{g L}^{-1}$ and 645 $\mu\text{g L}^{-1}$, respectively) than for R1. These values are lower than values previously observed in urban environment in China (2 320 – 2 750 $\mu\text{g L}^{-1}$ and 1 390 – 2 510 $\mu\text{g L}^{-1}$ for nitrate and ammonium, respectively; Xu et al., 2017; Ge et al., 2021). However, nitrate in-cloud concentrations are higher than an urban environment in Austria (240 $\mu\text{g L}^{-1}$) (Monteiro et al., 2021). This illustrates therefore the various regional influences that can be observed in different urban environments.

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The first fractions of rainfall are influenced by both washout and rainout processes. It is therefore necessary to subtract rainout influence at the beginning of the event in order to determine their relative contributions to total wet deposition. To do so, once $C_{rainout}$ is obtained, we calculate the wet deposition fluxes due to the rainout process ($F_{rainout} (\mu\text{g m}^{-2}) = C_{rainout} \times P_{tot}$) according to what has been previously done in the literature (e.g., Aikawa and Hiraki, 2009; Ge et al., 2016; Xu et al., 2017), P_{tot} being the rainfall depth of the event, and subtract it to the accumulated wet deposition flux (F_{wet_dep} , $\mu\text{g m}^{-2}$).

We thus used the ratio $\frac{F_{rainout}}{F_{wet_dep}}$ (%) to estimate the wet deposition due to rainout process of Al, Si, Fe, Ti, Mn, Zn, SO_4^{2-} , NH_4^+ and NO_3^- for R1 and R2 (Figure 9).



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Figure 9. Rainout (light blue) and washout (orange) relative contribution for chemical species for R1 (dotted) and R2 (cross hatched). The dotted line corresponds to a relative contribution of 50%.

We observe variations in washout and rainout relative contributions of studied chemical species within each rain (Fig. 9). The washout process is predominant for Al and Si, which are present in the coarse fraction, yet it is more marked for R2 (62 – 450 69%) than R1 (52 – 57%). We observe as well the same behavior for smaller particles such as Ti (58 and 72% for R1 and R2, respectively). These elements are of crustal origin and the dominant washout contribution is similar to what has been observed for Ca in different environments (66 – 99%; Ge et al., 2016; Berberler et al., 2022). Fe and Mn are mainly scavenged by washout as well but, they have also anthropogenic sources. Indeed, enrichment factors (EF, Taylor and McLennan, 1985)

relative to the Earth's crust were calculated using their total concentrations as follows: $EF = \frac{([X]/[Al])_{\text{sample}}}{([X]/[Al])_{\text{crust}}}$, where $[X]/[Al]$ is

455 the ratio between the concentrations of an element X and Si in rainwater samples and in the upper continental crust. Fe is characterized by EF of 2 and 6 while Mn exhibits higher EF of 4 and 9, for R1 and R2, respectively. Washout contributions of Fe (62 vs. 52%) and Mn (64 vs. 59%) are more important for R1 than R2. Zn is an element with a well-marked anthropogenic source with EF of 226 and 396 for R1 and R2, respectively. Additional local emission of Zn in winter such as residential heating (oil and wood heating system; Citepa, 2022) can explain a higher washout relative contribution for R2 (67%) than R1 460 (41%). The same behavior is observed for SO₄²⁻, with a washout relative contribution of sulfate higher for R2 (52%) than R1 (38%) that can also be attributed to residential heating, explaining higher local emissions of SO₂ in the region in winter (oil

and wood heating system; Airparif, 2021; Favez et al., 2021). Ammonium is mainly deposited by washout for both events (55 – 60%). For nitrate, washout relative contribution is higher for R1 than R2 (65 vs. 45%) and could be due to a difference of the main nitrate form depending on the season (gaseous in summer vs. particulate in winter). Nevertheless, these chemical species are also influenced by the presence of the gaseous phase (SO_2 , NO_x and NH_3) which make the comparison with other particulate elements sensitive. Relative contributions of washout and rainout also differ in the literature. For example, the relative contribution of rainout for sulfate shows a large variability in the literature in studies for urban environment (e.g., 12% in China, Ge et al. 2016; 84% in Japan, Aikawa et al. 2014). Nitrates rainout contribution values found in the literature also exhibits a high level of variability for urban environments in China (39 – 41%, Xu et al., 2017), in Turkey (10 – 40%, Karşı et al., 2018; 2.2 – 31%, Berberler et al., 2022) and for urban and suburban environments in Japan (26 – 40%, Aikawa et al., 2014; Aikawa and Hiraki, 2009). Therefore, new observations performed in our study contributes to the documentation and quantification of large variability within a rain event.

Our results show that Al, Ti, Mn and NH_4^+ are in majority deposited via washout processes (57 – 62%, 52 – 69%, 58 – 72%, 59 – 64% and 55 – 60%, respectively) for both R1 and R2 events (Fig. 9). However, the predominance of rainout to total wet deposition depends on the rain event for Zn, NO_3^- and SO_4^{2-} (33 – 59%, 35 – 55% and 48 – 62%, respectively) for both rain events. In contrast, washout processes are predominant during R1 for Fe (64%) and R2 for Si (69%) while wet deposition is approximately due to rainout (48%) and washout (52%) processes equally during R2 for Fe and R1 for Si. Therefore, our study shows a more pronounced local contribution of NH_4^+ , Al, Ti and Mn for both rain events, while the contribution of the local and medium to long-range of other species in wet deposition (Zn, Fe, Si, NO_3^- and SO_4^{2-}) differs according to the event.

4. Conclusion

The sequential sampler developed in this study allows investigating the time evolution of chemical composition of wet deposition throughout a rainfall event, down to trace levels. It has a large collection area and an automatic distribution system ensuring a high temporal resolution to analyze both dissolved and particulate phases as well as major and trace species in elemental and ionic compositions of rainfall.

The chemical compositions of rainfall are consistent with the specificity of air quality in Paris and its region. The dominant dissolved species are inorganic ions (SNA: sulfate, nitrate and ammonium). It is interesting to note that Al, Fe, Si and Ti are overwhelmingly present in the particulate phase of rain, even in this urban environment, while Trace Metals (TMs) such as Mn and Zn are present in both the dissolved and particulate phases. For these elements, we observed an increasing dissolved/total ratio as the rainfall progress. This intra-event evolution probably involves the effect of dissolution time into rain droplets (in relation with washout or rainout scavenging) and the evolution of the nature of scavenged particles. The time resolution of rainfall composition allows determining washout and rainout relative contribution to total wet deposition for

SNA, some insoluble elements (Si, Al, Fe and Ti) as well as TMs for both events. Our results show that Al, Fe, Si, Ti, Mn and
495 NH_4^+ are in majority deposited via washout processes while the predominance of rainout or washout processes to the wet
deposition of Zn, NO_3^- and SO_4^{2-} depends on the rain event.

The sequential sampling allows us to study the link between deposition fluxes and rainfall pattern. The total mass
concentrations of rain sharply decrease in the beginning of rainfall so that around 15% of the total mass of wet deposition
fluxes is deposited within the first 4% of rainfall depth, whatever the intensity pattern of rainfall. Mass concentrations
500 throughout rainfall events are not only dependent on rainfall depth, but also to the variation of the rainfall rate regime within
the rain event. Indeed, we observed for both rain events an increasing sulfate, nitrates and ammonium concentrations in the
dissolved phase correlated with rainfall rates decrease and with an increase of the relative weight of smaller droplets. This
increase may result from either an increase in the scavenging efficiency or from an increase in droplet evaporation during their
fall.

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In order to link the evolution of dissolved to total ratio with these scavenging processes, concomitant measurements on
atmospheric aerosols (e.g., homogeneity of the air column, aerosol chemical content and particle size distribution) and
meteorological parameters (e.g., cloud base height, droplet size distribution and rainfall rate) during the rain sampling need to
be planned in future experiments.

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