Rainwater sequential sampler: assessing intra-event water composition variability

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Abstract—Rainwater sequential sampler instruments can be very useful in characterizing the variability in rainwater composition, which can occur over relatively short time periods. The main aim of this study was to develop a low-cost volume-based sequential rain sampler for the assessment of variations in the chemical composition of rainwater during individual rain events in one place. In order to evaluate the performance of the apparatus a few tests were conducted under field conditions in Coimbra (Portugal). Rainy periods were analysed in relation to the following physicochemical parameters: electrical conductivity, pH, turbidity, nitrates, sulphates and chloride. The results showed that the rainwater composition varied over time; moreover, some parameters were found to be highest at the beginning of the rainy period, followed by a rapid decline of the initial value and then remained approximately constant. The findings suggest that the rainwater sequential sampler is a low-cost solution tool that can be useful for non-continuous assessment of intra-event rainwater composition variability.

Index Terms—Rainwater sampler, rainwater composition, equipment design.

I Introduction

Rain is a scavenging agent for pollutants present in the atmosphere (e.g. [1]) creating a potential of contamination for terrestrial and aquatic ecosystems. Collecting rainwater sequentially is crucial to understand the variability in rainwater composition during rain events.

The rainwater composition is related to the atmospheric composition. For example, in rural areas that are located far from cities and industrial pollution and are not so much affected by the transport of pollutants, the rainwater is expected to be low polluted, as the air is mostly clean. On the contrary, urban areas are typically marked by intense traffic and industry can produce pollutants that are "washed out" from the atmosphere during rainfall events (e.g. [2]).

A wide variety of sequential rain samplers have been proposed: manual sampling (e.g. [3]); linked collection vessels (e.g. [4]); automatic sequential samplers (e.g. [5]); and continuous monitors (e.g. [6]). In addition, a classification of sequential rain samplers can be defined by the way the rain is fractionated, i.e. by volume (e.g. [7]) or at fixed time intervals (e.g. [8]). The method used to collect the rainwater might affect the results (e.g. [9]).

The variability in different rainwater components has been explored in relation to, for example, the rainfall event intensity and depth, the season when it occurs, and the antecedent dry periods (e.g. [10], [11], [12]). Some of the studies on rainwater chemical composition use daily or lower time resolutions (e.g. [13], [14]). However, as pointed out by Raynor and Hayes [15], and Seymour and Stout[16] short-period samples (e.g. hourly) can provide crucial information, because the rainwater composition and the meteorological conditions (e.g. wind patterns, temperature, humidity) often change significantly over time during an event, and important relationships might be masked by inadequate temporal resolution of the observations.

The aim of this research was to present a volume-based sequential rain sampler that can be adapted for low or high volume resolution (by using sampling-bottles with different capacities). The equipment was designed to attain: low manufacturing cost, set-up and maintenance easiness, and no power requirements. It was tested under field conditions in Coimbra (Portugal).

II Rainwater sequential sampler

A Design of the equipment

The intra-event variability of rainwater quality can be explored by collecting sequential samples of rainwater (with an appropriate resolution) during the event. In this study a volume-based sequential rain sampler was designed (Figure 1, see also the photograph of the equipment in Figure 2c). The components of this equipment are:

i) Rainwater collection: a knife-edge collector ring; an aluminium funnel with an aperture diameter of 0.358 m; a flexible hose that connects the funnel to a flume; an adjustable support which keeps the funnel at an height of 1.5 m above the ground; and a support for the flume.

ii) The sampler: an acrylic flume with 11 openings (regularly spaced at 100 mm) where bottles are attached; and 11 polypropylene bottles to collect/store the rainwater samples.

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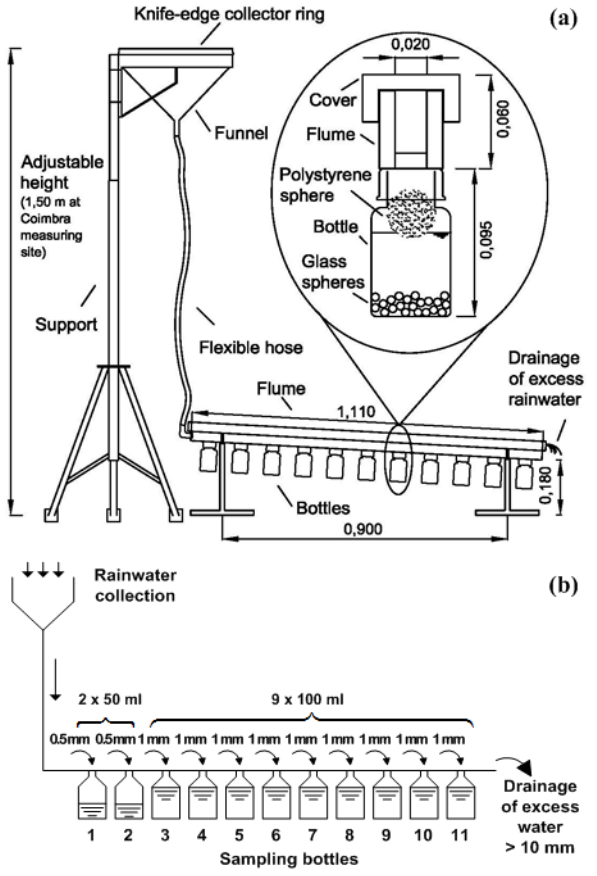

Figure 1 (a) Setup of the rainwater sequential sampler. Distances are in meters; (b) Hydraulic scheme of the rainwater sampling

This study was performed in a way to provide a continuous storage of rainwater until a maximum of 10 mm of cumulative rainfall depth. For that purpose, and taking into account the funnel aperture/collecting area, i.e. around 0.1 m^2, a maximum of 1000 ml of rainwater were collected (using a total of 11 individual samples): 50 ml (0.5 mm) for the first two bottles and 100 ml (1 mm) for each of the other bottles (Figure 1b); after all the bottles are filled the additional rain is disregarded. The first two bottles were used to better capture the eventual stronger variation on rainwater composition at the beginning of the events. Because all the sampling bottles attached in the equipment have 100 ml capacity, the volume collected in each bottle was adjusted by placing small glass spheres in the bottle (Figure 1a); i.e. the first two bottles were filled with small glass spheres until the empty space left were enough for storing a maximum of 50 ml of rainwater. There was also some concern regarding mixing the rainwater from earlier samples and the following ones. Therefore, each bottle also contains a large polystyrene sphere which seals it once it is filled and prevents the inflow of additional rainwater; as entrapped air was present surrounding the float sphere and the water level, the inexistence of rainwater mixing between individual samples was confirmed. This sealing also protects samples from contamination.

B Advantages and disadvantages of the equipment

The sequential rainwater samplers found in the literature vary in complexity, but the manual collection of rainwater is

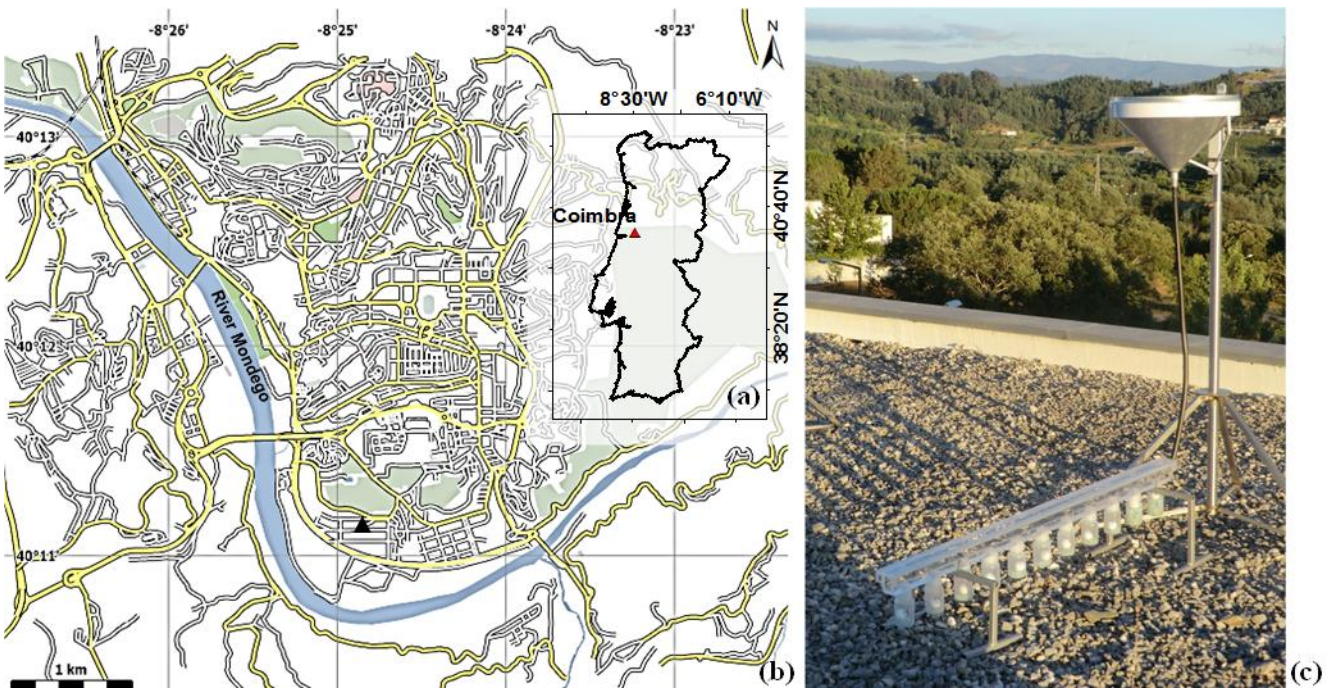

Figure 2 (a) Location of Coimbra in mainland Portugal; (b) Location of the study site in the city of Coimbra (black triangle); (c) Photograph of the equipment

the simplest and least expensive method in terms of equipment requirements (e.g. [3] and [17]). However, the long term availability of an operator to carry out the experiments makes this procedure difficult to implement. The sampler present in this study has low manufacturing costs and the bottles are filled in sequence by gravitational flow. Indeed, the samplers based on linked collection vessels, such as the present, have a simple construction (e.g. [4]).

Since these samplers are designed to operate unattended, the number of samples that can be collected is an important specification to consider. The number of sampling bottles typically used in linked collection vessels is five or less [18], this equipment is prepared to attach 11 samples.

Depending on the number of samples and the purpose of the analysis, the collection of samples can be based on time or on precipitation volume; automatic sequential samplers are usually able to sample at unit times but in that case some extra care should be taken to avoid incomplete record of the event, for example, if a sample container is not big enough, the excess of water will overflow before the next container is in position to fill.

The total amount of rainfall collected by the present sampler can be easily adapted to different measuring schemes by using bottles with different volume capacities, i.e., decreasing or increasing the sampling volume resolution.

In addition to the assessment of the intra-event water composition variability, if one wants to register the intensity and duration of the rain event, it is necessary to complement the measurements using a recording rain-gauge (e.g. tipping-bucket rain-gauge), which would obviously involve extra costs and power requirements.

This equipment only provides an unrefrigerated collection of samples; some other devices store the samples under refrigeration conditions, see e.g. [19]. For studies aiming at analysing rainwater composition in terms of stable chemical species, the samples can be removed immediately after the end of the event, which guarantee their physicochemical integrity. Nevertheless, this sampler is easily transported to the field and it does not require power. The equipment also has low maintenance requirements (it can be easily cleaned with distilled water).

TABLE 1
Description of the rainy periods sampled.

Rainy periods	Date (day-month-year) (h.min)	Antecedent dry period (h)	Total rain amount (mm)	Total duration (min)	Shortest sampling duration* (min)	Longest sampling duration** (min)	Mean rain intensity (mm h^{-1})	Maximum rain intensity (mm h^{-1})	Mass-weighted mean drop diameter, D_m (mm)
1	01-09-2011 17.23–20.20	8	10	178	7	51	3.4	10.2	1.76
2	02-11-2011 8.08 – 9.36	33.4	10	89	1	49	6.8	69.8	2.11
3	11-11-2011 6.31– 10.30	43.5	10	240	7	58	2.5	13.6	1.48
4	23-09-2012 3.04 – 6.13	120	6	190	2	134	1.9	63	1.64

**The "shortest sampling duration" is the minimum interval needed to fill a sampling bottle.*
***The "longest sampling duration" is the maximum interval needed to fill a sampling bottle.*

III TESTING THE SAMPLER

A Measuring site

The sequential rain sampler was tested in the field in the city of Coimbra (Portugal), which is located in the valley of Mondego River, and it is at approximately 50 km from the Atlantic coast (Figure 2). The sampler was installed on the flat roof of the building of the Department of Civil Engineering of the University of Coimbra (with geographic coordinates 40º11'08"N and 08º24'52"W).

B Data acquisition

The dataset analysed comprises four rainy periods (Table 1), which were selected based on the following criteria: i) a

TABLE 2
Description of rainwater parameters for the four rainy periods: I (Rainfall intensity), D_m (Mass-weighted mean drop diameter), EC (Electrical conductivity), Tr (Turbidity), Cl^- (Chloride), SO_4^{2-} (Sulphates), and NO_3^- (Nitrates), used to test the sampler.

Samples number	Rainfall amount (mm)	01-09-2011					02-11-2011					11-11-2011					23-09-2012							
		I (mm h^{-1})	D_m (mm)	Tr (FNU)	EC (µS cm^{-1})	pH	I (mm h^{-1})	D_m (mm)	Tr (FNU)	EC (µS cm^{-1})	pH	I (mm h^{-1})	D_m (mm)	Tr (FNU)	EC (µS cm^{-1})	pH	I (mm h^{-1})	D_m (mm)	Tr (FNU)	EC (µS cm^{-1})	pH	Cl^- (mg L^{-1})	SO_4^{2-} (mg L^{-1})	NO_3^- (mg L^{-1})
1	0.5	0.5	1.38	1.76	48.0	6.73	0.5	2.06	3.79	35.2	7.05	0.5	1.02	2.90	21.2	6.41	0.8	1.42	3.73	75.3	7.34	13.0	0.24	0.04
2	0.5	3.4	1.70	1.14	30.4	6.62	1.4	1.88	3.02	33.0	7.06	3.8	1.62	1.49	11.9	6.79	18.2	2.22	1.40	21.3	7.53	4.1	7.47	0.65
3	1.0	3.7	1.96	0.74	8.4	6.82	19.2	1.92	1.70	9.6	6.98	4.0	2.20	0.74	5.8	6.88	14.3	1.82	1.09	10.8	7.53	2.4	0.17	0.00
4	1.0	7.8	2.21	0.48	5.5	7.20	49.6	2.25	1.07	6.6	6.91	3.6	1.18	0.90	6.0	6.84	12.9	1.73	0.91	7.8	7.40	4.1	2.65	2.71
5	1.0	7.7	1.91	0.47	5.2	7.26	39.8	2.09	0.68	5.4	7.00	2.8	1.22	0.88	6.3	6.75	12.2	1.91	0.95	7.3	7.43	4.1	32.03*	2.00
6	1.0	3.9	1.69	0.57	5.4	7.14	35.6	1.79	0.67	4.2	7.17	2.4	1.18	0.83	4.5	6.84	3.6	1.20	0.65	9.1	7.02	5.9	3.46	0.05
7	1.0	2.4	1.57	0.39	5.2	7.06	69.1	2.53	0.61	3.6	7.10	2.1	1.27	0.76	3.3	7.02	0.5	1.05	0.56	15.8	7.18	2.4	5.14	0.01
8	1.0	4.6	1.69	0.46	5.1	6.96	69.8	2.56	0.65	3.1	6.98	1.4	0.95	0.59	2.8	7.30								
9	1.0	6.2	1.77	0.22	9.9	6.51	32.9	2.14	0.61	2.9	7.10	8.5	1.53	0.47	2.2	6.98								
10	1.0	8.0	1.78	0.39	7.7	6.43	33.3	1.95	0.49	2.7	6.93	7.9	2.10	0.53	2.2	6.86								
11	1.0	4.6	1.63	0.53	11.8	6.50	14.2	1.70	0.42	3.1	7.10	7.6	2.02	0.74	3.3	6.74								
Mean		3.4	-	0.65	12.96	6.84	6.8	-	1.25	9.95	7.03	2.5	-	0.98	6.32	6.86	1.9	-	1.33	21.06	7.35	5.14	3.19	0.78
Coef. of variation		0.80	-	0.67	1.06	0.04	2.16	-	0.91	1.22	0.01	1.03	-	0.70	0.90	0.03	2.27	-	0.83	1.16	0.03	0.71	0.89	1.43

**Apparent anomalous value; it was ignored in the analysis.*

minimum rainfall amount of 6 mm (to provide at least 7 sampling bottles); ii) a minimum of 6 hours of dry period prior to sampling (dry period means here that the rain intensity was lower than 0.05 mm h^{-1}).

In relation to the procedure for collection and analysis of rainwater samples: all the components of the rain sampling equipment were pre-washed with distilled water; the sampling bottles were removed immediately after being filled.

The electrical conductivity (EC), pH and turbidity of rainwater were measured immediately upon completing the removal of samples, using the following portable instruments: HI9033 Multi-range EC meter, HI8314 pH/ORP/Temperature meter, and the HI93125 Turbidity meter, all of them manufactured by Hanna Instruments.

In addition to the electrical conductivity, pH and turbidity measurements, the sampled rainwater from rainy period 4 (23-09-2012) was frozen and transported to an analytical laboratory for analysing nitrates, sulphates, and chloride. The concentrations of sulphates and nitrates were measured by ion chromatography, and the chloride was determined by the Mohr Method.

Although under certain conditions the chemical composition of the rainwater (e.g. pH) can change between the time from filling the first bottle and the time of sampling collection, it is believed that such time period is not long enough to influence the concentration of the major inorganic ions in the dissolved fraction (e.g. [20]).

The rain intensity was measured by a laser disdrometer ("Laser Precipitation Monitor" from Thies Clima) installed next to the sequential rain sampler. This instrument also yields the number of raindrops over 21 size classes and 20 fall speed classes. The precipitation data temporal resolution is one-minute and the depth resolution is 0.001 mm.

The variability in rainwater composition was explored in relation to the distribution of raindrop sizes. The laser disdrometer provided each minute a two dimensional matrix with the count of drops in each size and fall speed classes; the matrices were added over the sampling period to obtain one single matrix, which was used for determining the mass-weighted mean drop diameter (D_m).

The D_m allows the quantification of the overall distribution of raindrop sizes and is obtained by (e.g. [21]):

$$D_m = \frac{\sum_{i=1}^{21} D_i^4 N(D_i) \Delta D_i}{\sum_{i=1}^{21} D_i^3 N(D_i) \Delta D_i} \quad (1)$$

where D_i [mm] is the central diameter of the size class i (21 classes) and $N(D_i)$ [mm^{-1} m^{-3}] is the expected number of drops, with diameters between D and $D+\Delta D$, present per unit volume of air.

The $N(D_i)$ [$mm^{-1}m^{-3}$] defined in the Eq. (1) is obtained by (e.g. [22]):

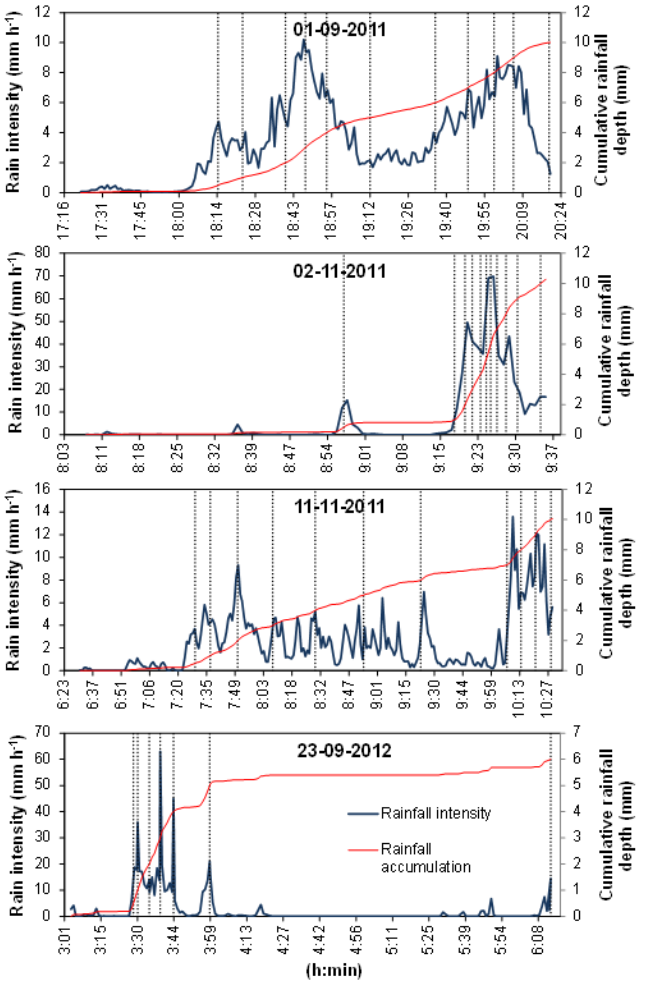

Figure 3 Hyetographs of the four rainy periods (see Table 1). Time needed to fill each sampling bottle is represented on the hyetographs (time between two vertical dotted lines)

$$N(D_i) = \frac{1}{A \Delta t \Delta D_i} \sum_{j=1}^{20} \frac{n_{ij}}{v_j} \quad (2)$$

where n_{ij} is the number of detected raindrops in the size class i and fall speed class j (20 classes), which is measured during the time period Δt [s] taken to fill the sampling bottles, v_j [m s^{-1}] is the fall speed at the middle of the fall speed class j, A [m^2] is the detection area and ΔD_i [mm] is the width of the size class i.

C Data analysis

Figure 3 shows the hyetographs of the four rainy periods investigated (see also Table 1). The total amount of rainwater collected in each rainy period was 10 mm, with the exception of rainy period 4 (23-09-2012), which accumulated 6 mm. The time taken to fill all the sampling-bottles for the four rainy periods varied from 89 min (rainy period 2) to 240 min (rainy period 3). The time needed to fill each sampling bottle is also represented in Figure 3; the highest difference in sampling duration was observed for the rainy period 4 (23-09-2012), ranging from 2 to 134 min.

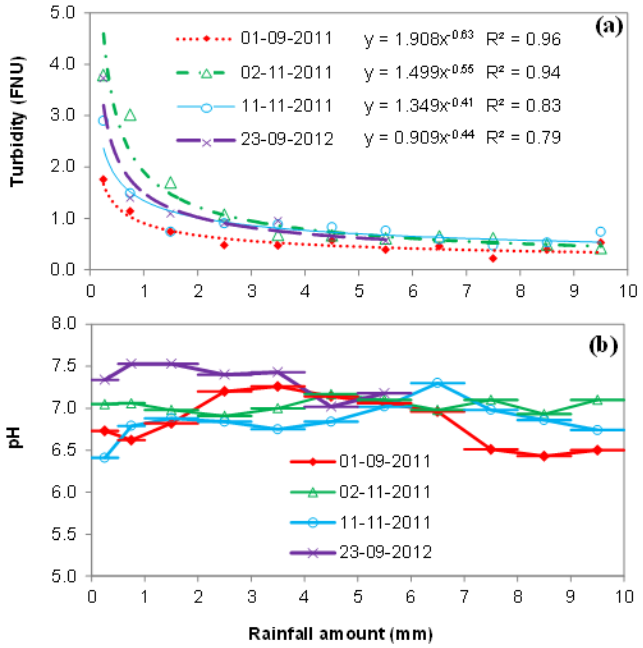

Figure 4 (a) Turbidity measured for each sample collected during the four rainy periods. Power laws are fitted to the data; (b) pH measured in the rainwater samples collected during the four rainy periods

The mean intensity for the four rainy periods varied between 1.9 mm h^{-1} (rainy period 4) and 6.8 mm h^{-1} (rainy period 2). The mass-weighted mean drop diameter (D_m) ranged from 1.48 to 2.11 mm (Table 1). The highest D_m was observed in rainy period 2 (02-11-2011), which was expected since the highest mean and maximum intensity was found for this sampling period, and bigger drops are typically more abundant in high rain rate episodes.

The physical and chemical parameters that characterize the rainwater of the rainy periods investigated using the rainwater sequential sampler are given in Table 2.

Empirical turbidity time variation was represented in Figure 4a for the four rainy periods investigated. The turbidity of the rainwater reduced over time; a power law fitted well the data. The results suggest the suitability of high resolution sampling – in particular, the 2 first bottles with 0.5 mm of rain each – to assess the intra-event rainwater composition; in case e.g. 3-mm sampling-bottles were used, the rapid decline of turbidity in the beginning of this particular event would be unnoticed. This variability in rain turbidity is consistent with several studies that report the presence of higher concentration of suspended matter during the beginning of rainfall and decrease throughout the rain event, which is likely to result from "washout" processes (e.g. [23]).

The rainwater sequential sampling also permitted to identify the pH fluctuations during the rainy periods (Figure 4b). For the four rainy periods investigated, the samples pH values ranged between 6.4 and 7.5. The mean (± standard deviation) for each rainy period was 6.8 (± 0.3), 7.0 (± 0.1), 6.8 (± 0.2), and 7.3 (± 0.2) for rainy periods 1 to 4, respectively.

Figure 5 shows the evolution of the electrical conductivity of the rainwater during the four rainy periods. They all show the occurrence of higher electrical conductivity at the beginning of rainfall and a rapid decreased in the first millimetre of rain. Nevertheless, it is possible to observe some differences between the studied rainy periods. For example, the rainy period 4 (23-09-2012) reached the highest electrical conductivity, 75 µS cm^{-1}, which might be explained by the corresponding longest antecedent dry period, ~ 5 days (see Table 1). This relationship is usually described in the literature, for example Nyika et al. [24] observed that the rainwater samples had higher electrical conductivity when there was no rainfall on the days before the rainwater collection, in comparison with the samples taken after a rainy day.

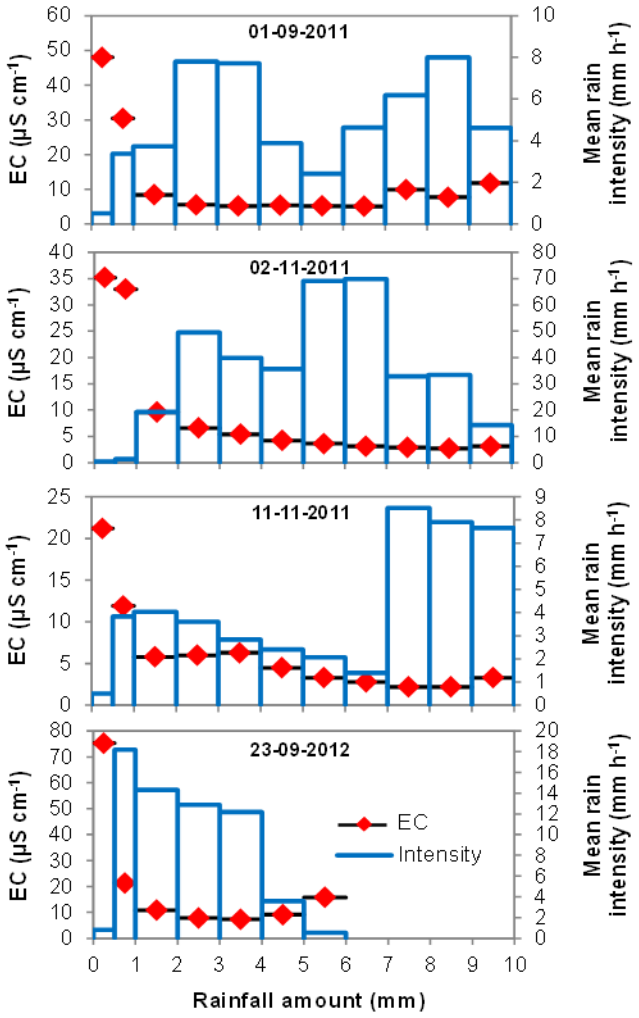

Figure 5 Electrical conductivity (EC) measured in each sample during the four rainy periods. Rainfall intensity was averaged over each sampling interval

The Figure 6a shows the variations of concentrations of chloride, sulphates and nitrates for the rainy period 4 (23-09-2012). The chloride concentration was higher in the first 0.5 mm and, after that, the concentration fluctuated between 2 and 6 mg L^{-1} (see also Table 2). The rainwater sequential samples have concentrations of sulphates between 0.2 and 7.5 mg L^{-1}, with a mean value of 3.2 mg L^{-1}. In relation to

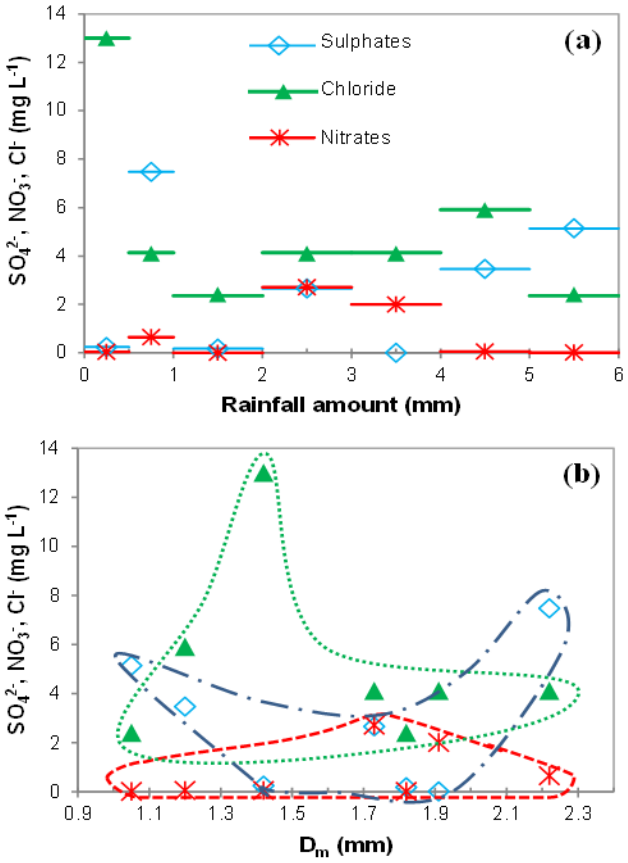

Figure 6 (a) Concentrations of chloride, sulphates and nitrates during the rainy period 4 (23-09-2012); (b) Concentrations of chloride, sulphates and nitrates plotted against the mass-weighted mean drop diameter (Dm).

the nitrates, the mean concentration recorded was 0.8 mg L^{-1}; and 2.71 mg L^{-1} was the maximum value detected, which corresponds to the sample filled at the time of maximum rain intensity (~ 63 mm h^{-1}), see Figure 3.

The relationship between the processes of removal of pollutants from the atmosphere and raindrop sizes has been studied for a long time. For example, Levine and Schwartz [25] stated that the removal of HNO_3 vapour depend on raindrop size, with the smaller drops (< 1 mm) having the greatest contribution to the washout scavenging. In addition, Ebert et al. [26] establish different relationships between scavenged particle sizes (0.19 - 1.8 µm) and the most effective raindrop diameter. In Figure 6b the mass-weighted mean drop diameter (D_m) is plotted against the concentrations of chloride, sulphates and nitrates measured in the rainy period 4 (23-09-2012), apparently showing no clear relationship. The variation of D_m, ranging from 1.05 to 2.22 mm, seems to have a different effect on rainwater composition depending on the ionic species. For example, the highest concentrations of sulphates (7.5 and 5.1 mg L^{-1}) were observed for the extreme (highest and lowest) values of D_m (2.22 and 1.05 mm, respectively) (see also Table 2). But the small sample size analysed does not allow any inference of relations between the relevant variables, which in any case was not the main goal of this work.

IV CONCLUSION

This study proposed a rainwater sequential sampler that can be useful as a low-cost solution to explore rainwater composition variations during a rainfall event. Because of the simplicity of its design, the apparatus can be easily adapted to include different sample volumes and total amount of sampled rainfall. A drawback is that in order to register the intensity and duration of the rain event it is necessary to use in addition a recording rain gauge.

Sequential samples of rain were collected in Coimbra (Portugal) during four rainy periods to test the performance of the equipment. The higher resolution of the initial rainwater samples (2 bottles with 0.5 mm of rainwater each whereas all other bottles have 1 mm) allowed the detection of higher values of some parameters followed by a rapid decline. Results suggest that the volume resolution of the device is able to assess rainwater composition variability during a rain event, but if necessary this can be easily adapted to specific requirements.

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