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ORIGINAL PAPER

Analysis and sampling of atmospheric particles of precipitation sub-events in Istanbul, Turkey

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Abstract

The scavenging of atmospheric particles from the atmosphere is known to be efficiently carried out by the below-cloud scavenging process. To examine this process, a total of 51 sub-event samplings was carried out in 10 precipitations during a 129-day sampling period. $PM_{2.5}$ samples were also collected simultaneously. The concentrations of Na, Mg, K, Ca, Al, Cu, Mn, and Fe were determined in the sub-events as well as in $PM_{2.5}$ samples, and the pH values were also measured. The observed volumeweighted mean pH values of the precipitation sub-events were between 6.58 and 8.32, with an average value of 7.28. It was observed that the element with the highest average volumeweighted mean concentration value in precipitation was Na. Among the elements in $PM_{2.5}$ particles, K had the highest concentration value. Next, the scavenging ratios of the elements were calculated in the precipitations that occurred. According to the averages of scavenging ratios of precipitations, it was determined that the element with the highest scavenging ratio was Na and the element with the lowest scavenging ratio was Fe. In addition, scavenging indexes were also determined in precipitations events. Variations in the scavenging properties of the elements were observed in each sub-event. The novelty of this study is that it is the first study carried out in Istanbul and even Turkey in terms of calculating scavenging indexes in sub-event sampling. Although this study is local, however, the importance of studies like this should not be ignored in terms of testing different air quality models.

Keywords $PM_{2.5}$ · Rainwater · Scavenging index · Scavenging ratio · Sub-event

Introduction

The atmosphere contains suspended solids and liquid particles along with gases, originating from natural and anthropogenic sources (Jacobson 2002). Particles that enter the atmosphere from the land through wind movements including from deserts, because of wildfires, and sea salt particles released by the breaking of ocean waves, are of natural origin. The gases and particles emitted into the atmosphere by combustion and other human activities are of anthropogenic origin. All these particles are then settled down on the earth's surface by wet and dry deposition (Al-Khashman 2005; Zheng et al. 2005).

Wet deposition occurs through the two main scavenging mechanisms: In cloud and below cloud scavenging (Minoura and Iwasaka 1997; Seinfeld and Pandis 2006). In practice, it has been reported that small parts of fine particles originate from the condensation of the vapor, while small pieces of coarse particles consist of dust, fly ash, and mechanically produced aerosols (Seinfeld 1975). Soil erosion by wind is another important source of dust (Borrelli et al. 2021). To capture the pollutant gas molecules, they can pass to the liquid–vapor interface after first passing from the atmosphere to the liquid surface. In the last stage, the liquid moves towards its inner surface. The presence of dissolved gas molecules creates a gas concentration in the liquid. Thus, gas

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molecules will tend to return to the atmosphere by removing from the liquid and leaving the mechanism it has acquired (Hales 1972). Cloud droplets result from aerosol particles acting as cloud condensation nuclei, as well as dissolution of soluble species transferred from the gas phase. The liquid phase of clouds, which affects the life cycle of many important atmospheric compounds, is a particularly reactive medium (Baray et al. 2020). Small particles scavenged by water droplets in the cloud then fall to the earth with precipitation. Larger particles can be removed from the atmosphere with the same process or the direct below-cloud process of falling raindrops (Seinfeld 1975). The sources of these particle depositions can be both local and global, depending on the trajectory of global precipitation systems that carry and deposit the particles far from their point of origin (Bergametti et al. 1989; Kubilay and Saydam 1995; Güllü et al. 1998; Kabatas et al. 2018; Lee et al. 2020).

It is known that atmospheric particles are scavenged by rain and is known to be an important way to scavenge the atmosphere (Bourcier et al. 2012). The below cloud scavenging process plays a vital role in removing and depositing larger atmospheric particles, usually found closer to the surface (Andronache 2003). Akkoyunlu and Tayanç (2008) reported coarse particles close to the surface in the atmosphere may contain high amounts of cations and that such particles are scavenged more efficiently by precipitation than fine particles. They stated that fine particles are considered to be important sources of precipitation acidity and that these particles can be found in the high troposphere (as well as in the lower atmosphere) and can also be removed from the atmosphere by rain and washout processes. It has been noted that during the processing time during a storm, the concentration of large particles in the atmosphere is reduced by scavenging, resulting in a progressive decrease in the concentrations of suspended large particles compared to small acidic particles. It has been stated that smaller amounts of larger particles are transferred to the droplets, causing a decrease in cation levels and also the development of more acidic wet deposition. In a study performed by Akkoyunlu et al. (2013), the average concentrations of K^+, Ca^{2+}, Mg^{2+}, and Na^+ ions were measured to be 0.77, 0.98, 1.32, and 5.16 mg L^{-1}. Because of the wash-out effect on the atmospheric particles, the average concentrations of all ions except the Mg^{2+} ion in the initial stage, which includes the first 5 sequential samples, were higher than those in the last stage. It was stated that the ratios of the mean concentration values of K^+, Ca^{2+}, Mg^{2+}, and Na^+ ions taken in the first stage to those in the last stage of the rain event were calculated as 1.73, 1.54, 0.75, and 1.77, respectively. In addition, it was stated that an inverse relationship was observed between the rain density and the ion concentration. Wang et al. (2021) stated that there is a positive correlation between below-cloud isotopic variation and air temperature, and a negative correlation with relative humidity. It is also explained that in general, the below-cloud effect evaporation on precipitation isotopes in semi-arid and arid regions of China is much greater than in humid and semi-humid regions. Lin et al. (2021) simultaneously sampled daily $PM_{2.5}$ and precipitation samples. Their results indicate that $PM_{2.5}$ concentrations reached the highest value in winter and had the lowest value in summer. It was stated that NH_4^+ and SO_4^{2-} ions are the two most abundant ions in precipitation, and after these ions, the most abundant ions in precipitation are Ca^{2+} and NO_3^- ions. Seasonal patterns of major inorganic ions in precipitation were explained to be similar to $PM_{2.5}$, with the lowest concentrations in summer and highest concentrations in winter. The mean scavenging ratios were 364, 394, 445, 454, and 456, for NH_4^+, K^+, NO_3^-, SO_4^{2-}, and Cl^-, and 18, 116, and 353, for gas NH_3, SO_2, and HNO_3, respectively.

Sub-event sampling can be performed using manual or automatic sequential precipitation sampling devices. Precipitation samples taken at regular intervals from the beginning to the end of precipitation in the sampling of sub-events in precipitation are examined. An important advantage of sub-event sampling over wet-only, bulk, and dry deposition sampling is that more detailed information is obtained for precipitation as more samples are collected in sub-event sampling. An important disadvantage of sub-event sampling is that the autosampler is expensive and the cost increases due to the large number of samples to be analyzed. If sub-event sampling is to be performed manually, equipment costs will be cheaper, but the person collecting the samples will need to change the collection container at appropriate times. In this study, sub-events sampling was carried out using an automatic sequential precipitation sampler (Akkoyunlu et al. 2013).

It has been shown that pollutants are effectively removed from the atmosphere by precipitation scavenging. In Northern Europe, significant radioactivity pollution in the wet deposition occured after the Chernobyl event (Jylhä 1991). It has been noted that wet deposition velocities are typically much higher than dry deposition velocities (Slinn 1984). There are studies that include precipitation scavenging in real-time modeling of atmospheric transport for hazardous materials. However, real-time rain data are limited for testing precipitation scavenging modelings (Loosmore and Cederwall 2004). This study provides real-time precipitation data to test such modelings. Directly measured scavenging indexes in field observations provide a better understanding of aerosol removal processes from the atmosphere.

In this study carried out in Istanbul (30 September 2015–05 February 2016), 51 sub-events samples were collected during 10 precipitations. Concentrations of elements were determined in sub-events and $PM_{2.5}$ samples. The pH values of sub-events in precipitations were measured. In order to examine the scavenging properties of the elements, scavenging ratios and scavenging indexes were calculated separately for each sub-event. This study is the first study in Turkey in which scavenging indexes are calculated in sub-event sampling. It has been observed that the calculated scavenging ratios can be a useful indicator of scavenging efficiency.

Materials and methods

Study area

Istanbul is located in the Marmara Region of Turkey. Istanbul is one of the most important megapolises in the world. It is located between 28° 01' and 29° 55' E longitudes and 41° 33' and 40° 28' N latitudes. Administratively, Istanbul has 39 districts. Fourteen of these districts are on the Anatolian side and 25 are on the European side (İÇDR 2020). It is Turkey's largest city in terms of population with approximately 16 million people (TSI 2021). Located at the point where the Asian and European continents are separated by a narrow sea passage, it is established on two continents and has the distinction of being the only city in the world with a sea through it. Istanbul, which has an important history, has been and still continues to be an important trade center due to its establishment in this strategic region where the sea and the land are combined.

It is not possible to evaluate the climate type of Istanbul in a specific climate type. Due to its geographical location and physical geographical features, Istanbul has different climatic characteristics than the climate of many settlements located at the same latitude. In Istanbul, different climatic conditions occur in the winter and summer seasons (İÇDR 2020). During the measurement period between 1929 and 2020, the annual number of precipitation days in Istanbul is 125.1. The average number of precipitation days is higher in December and January than in other months. The average number of precipitation days in these months is 16.6. The annual total precipitation amount is 690.5 mm. The annual average temperature is 16.2 °C (TSMS 2021). The sampling station is located on the campus of Marmara University in Goztepe in the Kadikoy district. The coordinates of the sampling station are 40° 59′ 14" N and 29° 03′ 14" E (Fig. 1). Approximately half of the campus area where sampling is carried out is a green field. The nearest building to the measurement point is approximately 20 m away. Natural gas is used for heating purposes in the buildings on campus and the surrounding area. There are no industrial facilities around the campus. During the study period, 10 precipitations were sampled on 30 September 2015, 06 October 2015, 22–25 October 2015, 29 November 2015, 16 December 2015, 29–31 December 2015, 08 January 2016, 12–13 January 2016, 17 January 2016, and 05 February 2016. The number of sub-events in the precipitations on these dates are 3, 3, 10, 3, 3, 13, 3, 5, 3, and 5, respectively.

Sampling procedure

During the sampling period, sub-event and particulate matter ($PM_{2.5}$) sampling were carried out. In 10 precipitations, 51 sub-event samples were collected. 8 out of 10 precipitations occurred only in the form of rain. The other 2 precipitations first started as rain and then continued as snow. Sub-event sampling was carried out by applying certain techniques and procedures with an automatic sequential precipitation sampler. In this study, precipitations occurring during the study period were collected with a computer-controlled sequential rain sampler. This device has two main components, mechanical and electronic. The mechanical part of this device includes a metallic body, a set of solenoid valves, a rain gauge, and 100 mL polyethylene sample bottles. In the electronics part, there are various electronic components, sensors, ICs, and relays. A computer is used as the main controller of the system. The system is controlled by commands generated through the MATLAB programming language, and also volume and the sequential sampling period can be changed. Human errors are kept to a minimum as the system is controlled by a computer were collected with a computer-controlled sequential rain sampler (Akkoyunlu et al. 2013).

Precipitation samples taken into sterile 50 mL falcon tubes were transferred to another sterile 50 mL falcon tubes by filtering through blue band filter paper in the laboratory medium. After these processes, the analysis of elements was performed using 8 different concentrations of calibration standards from a 1000 ppm multielement ICP (Merck) stock solution. $PM_{2.5}$ samples were collected with Zambelli ISO PLUS 6000 instrument. This device is a low volume sampler and operates at a flow rate of 1 m^3 h^{-1}. Teflon filters with 2 µm pore size and 47 mm diameter were used in the sampling of particulate matter. The sampling of $PM_{2.5}$ particles was performed according to the "40 CFR Part 50" standards (U.S. EPA 2006). Filters were placed in Teflon vessels cleaned with ultrapure water to make them ready for analysis in the Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Spectro Blue) device using a microwave sample preparation device (Berghof—MWS2). 5 mL of ultrapure H_2SO_4 and 5 mL of $HClO_4$ were added to them. Teflon vessels were sealed according to the instrument procedure and placed in the microwave oven for thawing. The device was heated to 145 °C for 10 min. Then it was kept for 10 min at 165 °C and finally at 175 °C for 20 min. After the process was finished, Teflon vessels were opened, filtered into 50 mL falcon tubes, made up to 50 mL with ultrapure water, and made ready for elemental analysis in the ICP-OES. The concentrations of Na, Mg, K, Ca, Al, Cu, Mn, and Fe elements in sub-events and $PM_{2.5}$ samples were determined using the ICP-OES device (Summak et al.

Fig. 1 Location of the study area

2018). Measures have been taken to prevent contamination of sub-event samples and $PM_{2.5}$ samples both in the laboratory and in the field. The surface of the funnel and the polyethylene containers were cleaned and dried regularly before installation. After each sub-event, the cleaning process was repeated, and the used polyethylene containers were replaced with the other cleaned polyethylene containers. The pH measurement of the samples collected after each precipitation was carried out immediately. Hanna Portable Water pH Meter device was used for pH measurements. Calibration of the pH meter device was performed before each measurement using a standard buffer solution of 4.00 and 7.00, respectively. Data quality and control procedures were carried out for the measurements.

Volume weighted mean, scavenging ratio and scavenging index

The volume-weighted mean (VWM) concentration of elements in sub-event samples in precipitations has been calculated (Koelliker et al. 2004).

$$C = \frac{\sum C_i . V_i}{\sum V_i} \quad (1)$$

where, C_i is the concentration in each sample and V_i is volumes in each sample. The calculation was applied to all the samples of the same precipitation in order to see the decrease in concentration concerning an increase in the volume.

Calculation of scavenging ratios based on the assumption that the concentration of a component in precipitation is related to its concentration in the air has been performed using the formula given below (Kasper-Giebl et al. 1999).

$$\omega_v = C_p . \rho_w / C_a \quad (2)$$

where, C_p is the concentration of a component in precipitation,C_a is the concentration of the same component in air, and ρ_w is the density of rain. The scavenging ratios of Na, Mg, K, Ca, Al, Cu, Mn, and Fe elements in each sub-event were calculated. After calculating the scavenging ratios for each event, the mean value of all the events combined has been determined.

Shimamura et al. (2006) approached the scavenging process with the power law.

$$C = a R_t^{-b} \quad (3)$$

where C is the concentration of an element in the precipitation, R_t is rainfall depth, a and b are the empirical constants. The scavenging index (b), on the other hand, represents the degree of scavenging efficiency. In this study, scavenging indexes were determined by using the precipitation amount (mL) in volume instead of rainfall depth (mm).

Results and discussion

pH analysis

The 10 precipitations were sampled on 30 September 2015, 06 October 2015, 22–25 October 2015, 29 November 2015, 16 December 2015, 29–31 December 2015, 08 January 2016, 12–13 January 2016, 17 January 2016, and 05 February 2016 during the study period. In the precipitation events that took place on these dates, 51 sub-events samplings were carried out. The number of sub-events occurring on these dates was 3, 3, 10, 3, 3, 13, 3, 5, 3, and 5, respectively. Average VWM-pH values of precipitations occurred on 30 September 2015, 06 October 2015, 22–25 October 2015, 29 November 2015, 16 December 2015, 29–31 December 2015, 08 January 2016, 12–13 January 2016, 17 January 2016, and 05 February 2016 were 6.66, 6.97, 7.42, 7.09, 7.51, 7.58, 7.14, 7.24, 7.46, and 6.82, respectively (Fig. 2). While the lowest VWM-pH value (6.58) was detected in the 2nd sub-event in the precipitation that took place on 30 September 2015 in 51 sub-event samples out of 10 precipitations sampled, the highest VWM-pH value (8.32) was determined in the 2nd sub-event in the precipitation that took place on

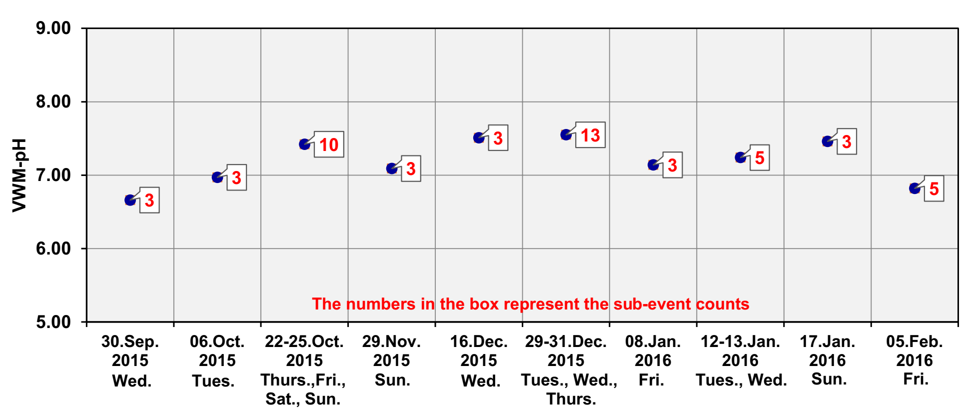

Fig. 2 Average VWM-pH values of sub-events in precipitations

29–31 December 2015 (Table 1). The average VWM-pH of 51 sub-event samples was 7.28.

Sub-events in precipitations were all alkaline. It was seen that the average pH values of sub-events were higher than in previous studies performed in Istanbul (Gülsoy et al. 1999; Tuncer et al. 2001; Okay et al. 2002; Akkoyunlu and Tayanç 2003; Uygur et al. 2010). Calcium is one of the main neutralizing agents of acidity and it is widely accepted that the main source of calcium is expected to be soil with rich $CaCO_3$ content (Al-Momani et al. 1995; Okay et al. 2002; Akkkoyunlu and Tayanç 2003; Dueñas et al. 2012). Limestone is one of the most important components of the land in Turkey, and therefore the possibility of $CaCO_3$ particles into the troposphere is high during stormy periods (Al-Momani et al. 1995; Okay et al. 2002; Akkoyunlu et al. 2003). Consistent with previous studies, it was observed that the pH values of the samples belonging to the sub-events were higher in the first samples than the pH values in the series (Akkoyunlu et al. 2003; Akkoyunlu and Tayanç 2008). The high pH of samples in the initial stage of precipitation can be explained by the more efficient removal of coarse dust particles from the atmosphere.

Concentrations of elements in precipitations and $PM_{2.5}$

When the average VWM values of the elements were compared in the precipitations during the sampling period, the Ca element has the highest average VWM value (13.359 mg L^{-1}) in the precipitation that took place on 16 December 2015. This element has the lowest average VWM value (1.084 mg L^{-1}) in the precipitation on 29 November 2015. The element with the lowest average VWM value (0.0028 mg L^{-1}) among the elements was Mn in the precipitation that took place on 30 September 2015. The order of magnitude of the average VWM values of the elements in precipitations was Na ˃ Ca ˃ K ˃ Mg ˃ Fe ˃ Al ˃ Cu ˃ Mn. The values of these elements were 3.761 ˃ 3.542 ˃ 1.485 ˃ 0.426 ˃ 0.012 ˃ 0.007 ˃ 0.006 ˃ 0.004 mgL^{-1}, respectively (Fig. 3).

Concentration values of Na, Mg, K, Ca, Al, Cu, Mn, and Fe elements in $PM_{2.5}$ samples have been determined. Average concentration values of these elements in $PM_{2.5}$ samples were 0.170, 0.037, 0.295, 0.184, 0.072, 0.030, 0.005, and 0.325 mg L^{-1}, respectively. It was K (the precipitation on 22–25 October 2015) with the highest concentration value (0.966 mg L^{-1}) among the elements in $PM_{2.5}$ particles. The element with the lowest concentration value (0.0020 mg L^{-1}) was Mn (the precipitation on 06 October 2015) (Fig. 4).

The results showed that Na, K, Mg, and Ca elements have higher concentration values in precipitation than in $PM_{2.5}$ samples. In addition, it was seen that other elements Al, Cu, Mn, and Fe elements have lower concentration values in precipitation than $PM_{2.5}$ samples. Small particles are scavenged by water droplets in the cloud and then fall with precipitation. Larger particles can be removed from the atmosphere by the same process or by the direct washout process of falling raindrops. Particles fall to the surface faster than gases unless the wind speed is high (Jacobson 2002). The precipitation scavenging process is crucial for cleaning the atmospheric pollutants (Wallace and Hobbs 2006). As a result of the absence of precipitation for a long time, particle deposition occurs in the atmosphere. These particles are scavenged away in the first sub-events by precipitation. Precipitation scavenges, especially the particles more effectively than gases. The extra gases coming to the sampling region are not expected to be scavenged as much as the particles. Extra particles may have arrived at the sampling site. These particles may have changed the concentration during the precipitation. However, air pollution during traffic hours had no effect on precipitation chemistry. This may be because motor vehicles emit more gas than particulate.

Scavenging ratios in precipitations

Scavenging ratios were calculated for the elements Na, Mg, K, Ca, Al, Cu, Mn, and Fe analyzed in sub-events. The average scavenging ratios of the measured elements in precipitations were shown in Fig. 5. The resultant scavenging ratios show that the naturally occurring elements have higher scavenging ratios, meaning that rainwater scavenges the atmosphere from these elements more efficiently.

In precipitations, the highest average scavenging ratios among the elements were obtained for Na, Ca, Mg, and K elements, respectively. Na and Mg are considered to be sea-salt components and show higher scavenging ratios. High scavenging ratios for Na and Mg are also reported in the Bay of Bengal in India and in Vitoria, Spain (Kulshrestha et al. 2009; Encinas et al. 2004). The scavenging ratios are highly dependent on the variations in origin of air masses at cloud forming levels and on the surface. The backward trajectories run for these precipitations show different points of origin for the air masses that influence the precipitation chemistry of the sampling region. There can be large variations in scavenging ratios from event to event. These variations can be attributed to the different sources of air masses and clouds. Ca is the main crustal element and is found at $CaCO_3$ forms in soil. The $CaCO_3$ is a prominent component of soils in Turkey, therefore, during dry and windy conditions some part of it is blown away and remains suspended in the air and ultimately affecting the rainwater chemistry (Okay et al. 2002; Akkoyunlu et al. 2003; Oruc et al. 2021).

Okay et al. (2002) stated in their study carried out in Istanbul that the high non-sea salt fractions of calcium reveal the importance of $CaCO_3$ as a source, and that the enrichment factors for soil and sea also show strong effects of $CaCO_3$ on precipitation composition. In another study

Table 1 The pH and VWM values (mg L^{-1}) of elements in each sub-event in precipitations

Date	Sub-events	pH	Na	Mg	K	Ca	Al	Cu	Mn	Fe
30.Sep.2015	1	6.60	9.5640	1.1923	0.6353	2.8256	0.0064	0.0067	0.0038	0.0164
	2	6.58	2.6640	0.4279	0.3247	1.3179	0.0065	0.0056	0.0019	0.0113
	3	6.81	9.4980	1.1692	0.9345	2.1549	0.0102	0.0079	0.0027	0.0154
06.Oct.2015	1	7.38	9.3650	1.3946	1.0597	5.5765	0.0057	0.0150	0.0075	0.0116
	2	6.87	0.7960	0.3194	0.2578	1.9912	0.0061	0.0068	0.0029	0.0102
	3	6.65	0.5390	0.0964	0.1117	0.5848	0.0075	0.0056	0.0032	0.0114
22–25.Oct.2015	1	6.99	8.8470	0.7851	4.5680	8.2369	0.0055	0.0119	0.0114	0.0105
	2	7.14	6.4140	0.3461	3.3955	4.2406	0.0075	0.0069	0.0087	0.0122
	3	7.12	4.9830	0.1700	2.8162	2.1078	0.0068	0.0057	0.0052	0.0116
	4	7.22	0.8140	0.3453	1.2860	2.6446	0.0050	0.0063	0.0046	0.0102
	5	7.30	3.0440	0.4261	8.8855	1.7878	0.0057	0.0049	0.0033	0.0099
	6	7.33	0.9950	0.2259	4.7711	0.7960	0.0060	0.0055	0.0034	0.0101
	7	7.72	2.8020	0.4266	1.8230	2.1520	0.0055	0.0059	0.0028	0.0112
	8	7.68	2.0240	0.3529	1.0452	1.4311	0.0055	0.0053	0.0031	0.0102
	9	7.85	0.8360	0.1350	0.6852	0.4409	0.0052	0.0051	0.0022	0.0097
	10	7.82	0.6980	0.1601	0.9301	0.4993	0.0050	0.0058	0.0018	0.0096
29.Nov.2015	1	6.99	5.3950	0.5902	0.9545	2.1025	0.0051	0.0053	0.0049	0.0100
	2	7.30	1.2890	0.1128	1.2455	0.5533	0.0051	0.0053	0.0025	0.0105
	3	6.99	3.2450	0.1145	6.4952	0.5975	0.0061	0.0098	0.0018	0.0115
16.Dec.2015	1	7.38	3.2110	0.4164	1.3106	11.2545	0.0067	0.0080	0.0034	0.0116
	2	7.60	4.8060	0.7965	0.9803	19.6788	0.0114	0.0056	0.0031	0.0106
	3	7.54	3.6940	0.4864	1.2193	9.1438	0.0065	0.0048	0.0067	0.0112
29–31.Dec.2015	1	7.59	45.7090	1.3167	4.5224	5.1454	0.0447	0.0078	0.0019	0.0470
	2	8.32	6.3560	0.7778	1.1105	8.1016	0.0068	0.0031	0.0016	0.0104
	3	7.83	6.3460	0.6549	0.9435	3.5957	0.0065	0.0036	0.0022	0.0116
	4	7.74	6.2570	0.7943	1.0926	5.4902	0.0080	0.0032	0.0020	0.0132
	5	7.38	6.0070	0.6313	2.6833	6.9478	0.0090	0.0039	0.0064	0.0108
	6	7.29	18.7980	0.8228	2.0366	2.5128	0.0166	0.0060	0.0014	0.0245
	7	7.67	3.9890	0.3472	5.2544	5.2092	0.0062	0.0027	0.0013	0.0107
	8	7.56	3.4190	0.4004	1.8184	7.8209	0.0052	0.0023	0.0014	0.0105
	9	8.01	3.4070	0.4190	2.2920	9.4503	0.0084	0.0030	0.0033	0.0125
	10	7.42	1.9660	0.1483	0.7501	3.4436	0.0060	0.0032	0.0025	0.0109
	11	7.22	2.9190	1.2449	0.6051	5.8291	0.0125	0.0022	0.0013	0.0160
	12	7.21	2.9810	0.2833	0.4617	5.9659	0.0211	0.0020	0.0028	0.0194
	13	7.28	7.8030	0.8279	0.8006	10.6605	0.0062	0.0049	0.0119	0.0111
08.Jan.2016	1	7.10	2.9160	0.2889	0.4112	1.7450	0.0098	0.0037	0.0043	0.0110
	2	6.99	1.6500	0.2480	0.4046	1.8917	0.0064	0.0040	0.0073	0.0101
	3	7.32	1.3450	0.1689	0.9469	1.8553	0.0048	0.0032	0.0049	0.0093
12–13.Jan.2016	1	7.20	4.1470	0.4186	1.1344	1.9935	0.0060	0.0057	0.0066	0.0102
	2	7.28	4.8330	0.5710	0.8727	3.2899	0.0057	0.0048	0.0046	0.0103
	3	7.33	4.4600	0.5417	0.7350	2.5272	0.0058	0.0038	0.0074	0.0113
	4	7.29	2.3230	0.2904	0.8475	1.5888	0.0053	0.0045	0.0045	0.0104
	5	7.12	1.2090	0.1361	0.4624	0.7028	0.0053	0.0045	0.0029	0.0108
17.Jan.2016	1	7.54	1.3200	0.1644	1.6818	2.1832	0.0060	0.0086	0.0054	0.0112
	2	7.51	0.6320	0.0565	0.8413	0.3623	0.0056	0.0047	0.0026	0.0123
	3	7.32	1.0330	0.0830	3.9043	0.9293	0.0058	0.0050	0.0024	0.0103

Table 1 (continued)

Date	Sub-events	pH	Na	Mg	K	Ca	Al	Cu	Mn	Fe
05.Feb.2016	1	7.00	3.4490	0.4761	0.8078	9.2337	0.0064	0.0046	0.0095	0.0108
	2	6.92	0.9410	0.1813	0.5318	5.8973	0.0069	0.0036	0.0034	0.0118
	3	6.77	0.4410	0.0543	0.2847	0.8813	0.0050	0.0034	0.0028	0.0101
	4	6.72	0.5150	0.0834	0.1758	1.1057	0.0058	0.0032	0.0029	0.0098
	5	6.68	1.1050	0.1778	0.7759	1.1785	0.0050	0.0046	0.0023	0.0101

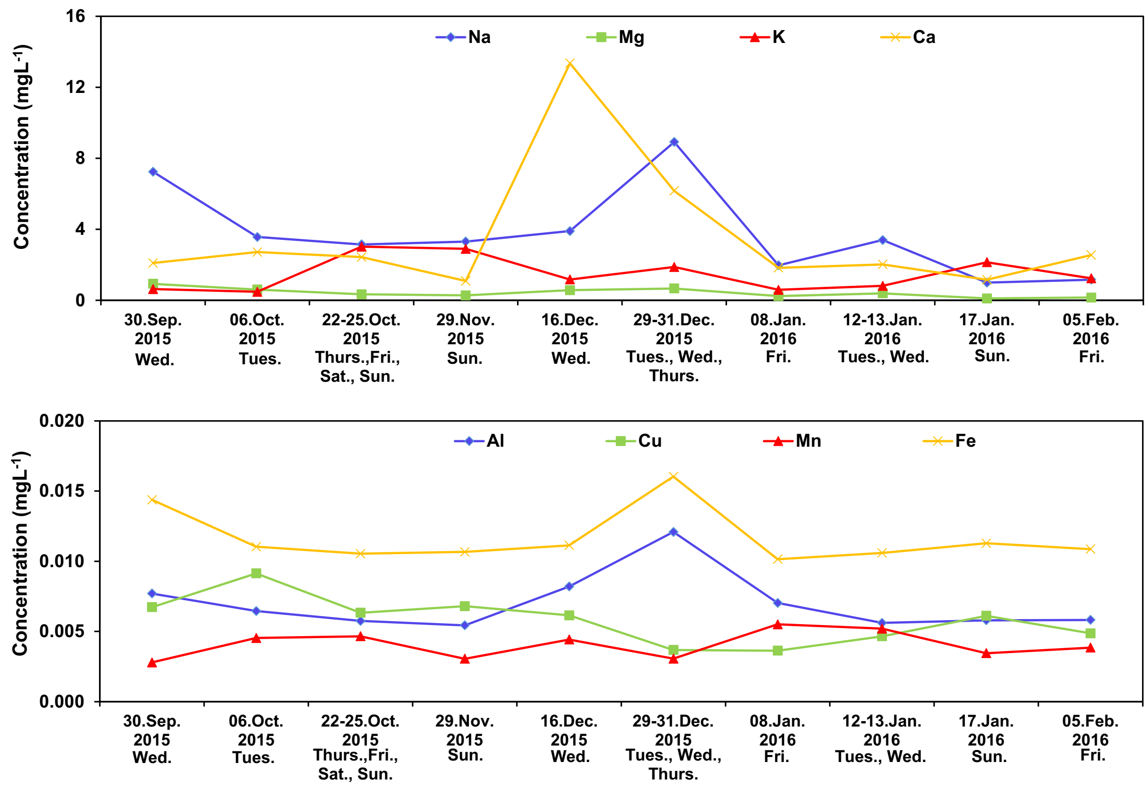

Fig. 3 Average VWM values of elements in sub-events in precipitations

carried out in Istanbul, it was stated that the main reason for not having high acidity in the precipitations that occurred could be attributed to the high calcium concentration (Akkoyunlu et al. 2003). Na has the highest value in samples, followed by Ca. This situation also suggests that below cloud scavenging is an effective process of removal for Ca. Mn has been showed a high scavenging ratio. This situation may be because of the reason that it reacts with water and dissolves in dilute acids. One of the most abundant metals in the soil, Mn occurs as oxides and hydroxides and is known to cycle through various oxidation states (McKenzie 1989). It was noted that the particles contributed higher than gases to the total wet deposition, with the particle ions showing higher scavenging ratios than their gaseous precursors. It was stated that scavenging rates for the gaseous species studied differed greatly, possibly related to their different solubility in the air or their lifetime. It has been explained that the main sources and chemical processes contribute to the ambient concentrations of some chemical species and thus may have significantly reduced the scavenging ratio, for example in the case of NH_3. It is stated that the obtained scavenging ratio data can be used to improve the estimation of particle concentrations during rainy periods using air quality models (Lin et al. 2021). Oduber et al. (2021) stated that scavenging ratios show that coarse particles derived from the soil are effectively removed due to increasing precipitation intensities, while for fine particles this process is more effective in long and continuous rainfall. They also stated for ammonium, it increased due to the inclusion of NH_4^+ in the gas phase to the drop.

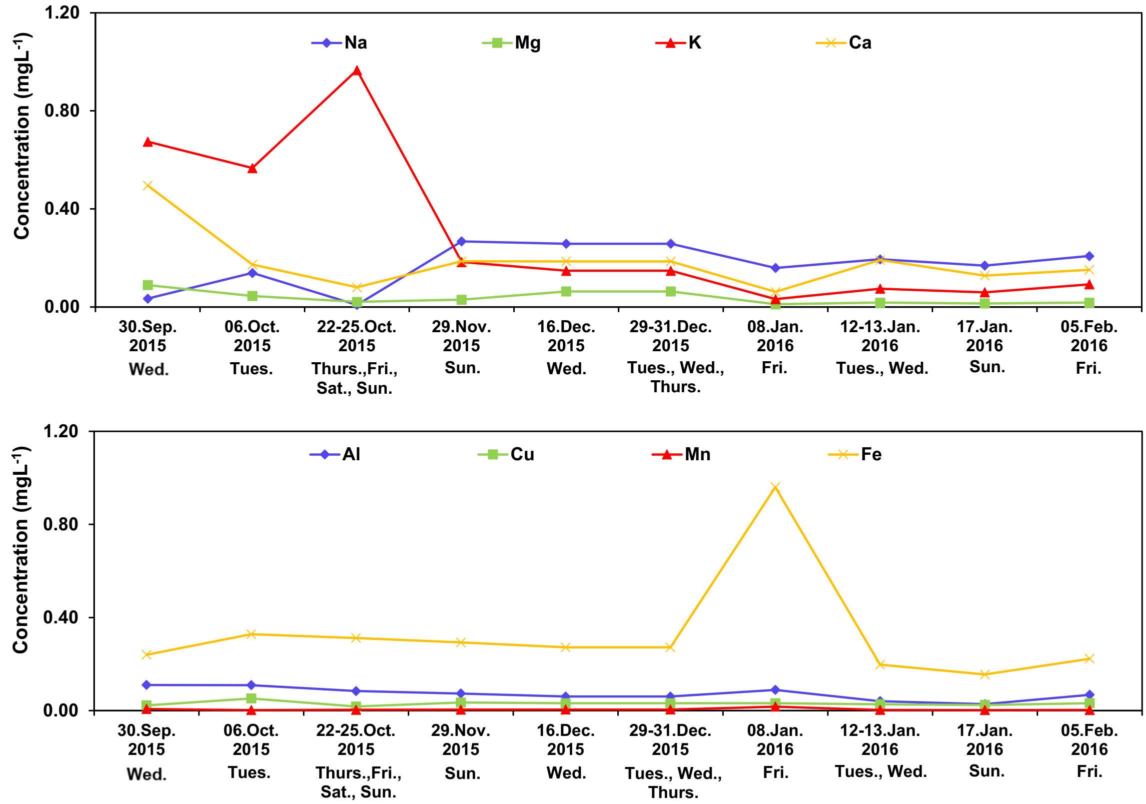

Fig. 4 Average concentration values of elements in $PM_{2.5}$ samples

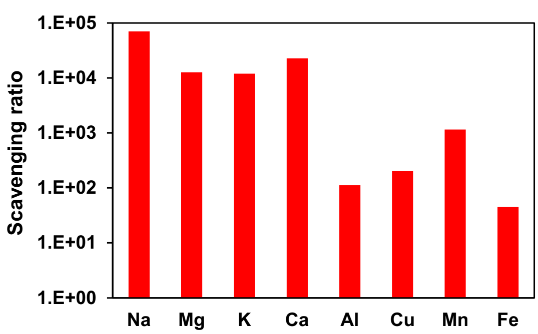

Fig. 5 Average scavenging ratios of the measured elements in precipitations

Scavenging indexes in precipitations

The scavenging index of elements for each sub-event was calculated and presented in Figs. 6 and 7. It is shown in Fig. 6 that the concentration of Na decreases with an increasing amount of precipitation. There was a different scavenging property of each precipitation. Some uncertainties have been observed in some events. It was observed that the concentration increased rather than decreased during the 16 December 2015 precipitation (Fig. 6). However, the uncertainty for Na was observed in only one event in precipitations. Like Na, Mg, also showed variation in scavenging properties for each sub-event. In most of the sub-events, decrease in concentrations with respect to rainfall amount was observed during precipitation. There was uncertainty in only two sub-events, namely 16 December 2015 and 08 January 2016, and in these sub-events, there was an increase trend according to the rainfall amount rather than a decrease in concentrations. K also showed similar trends like Na and Mg. But unlike Na and Mg, the numbers of sub-events with uncertainties were higher for K. The number of these sub-events is three and their dates are 29 November 2015, 08 January 2016, and 17 January 2016. This situation can be explained by the fact that the atmospheric conditions do not remain similar during the rain event. During the precipitation some other sources can affect the K concentration. In two of these uncertain events the concentration has decreased initially but then observed sudden peaks again indicating the influence of other air masses which enter the atmosphere at that point.

In the study conducted by Akkoyunlu and Tayanç (2008), it was stated that the pH and ion concentrations in the first sub-events were generally higher for all four precipitations than in the other sub-event samples, respectively. It was stated that the reason for this was the strong initial wash-out of the atmosphere by raindrops. It was stated by Zhou et al. (2021) that the higher the rain intensity, the higher the

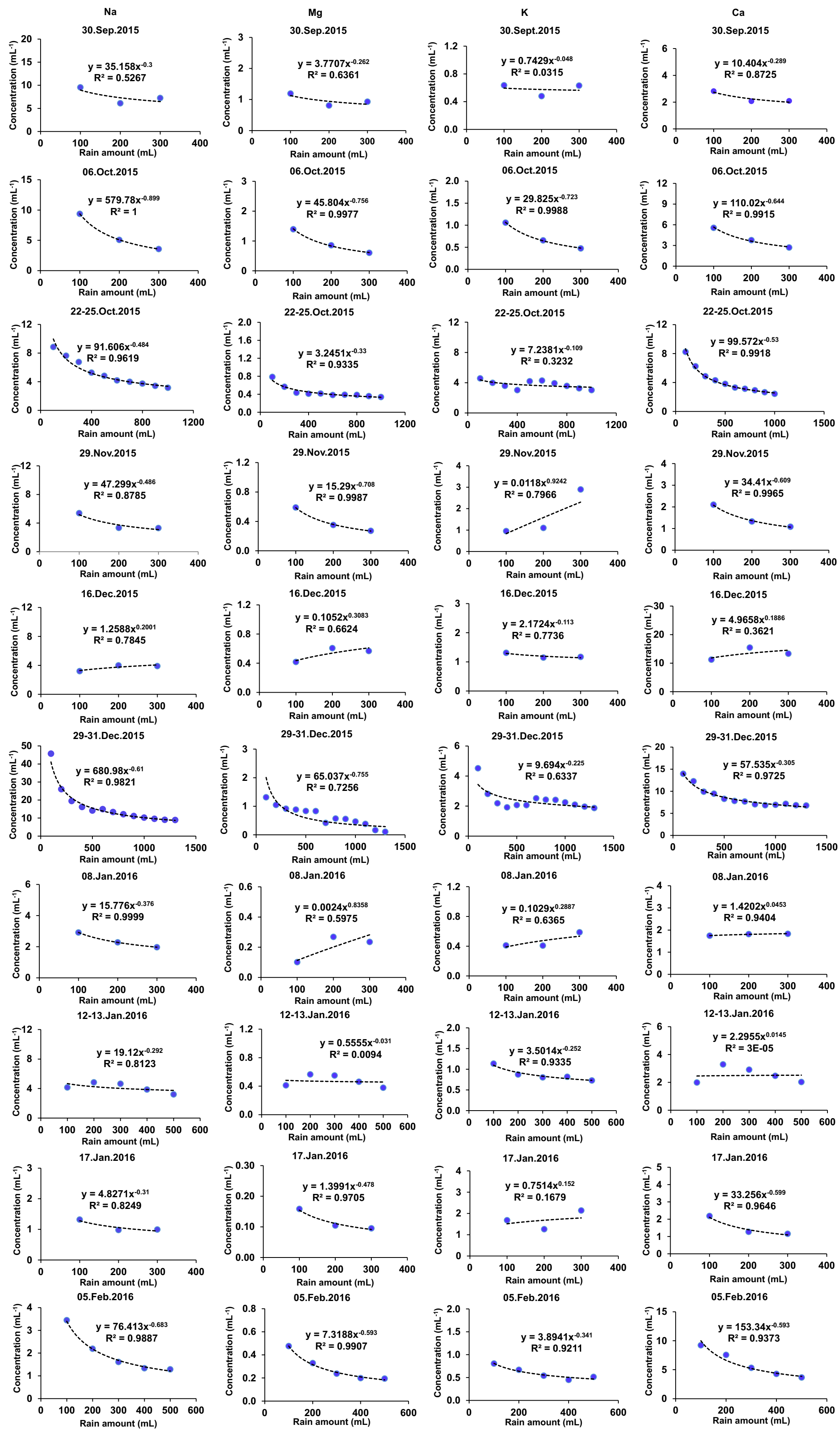

Fig. 6 Scavenging indexes in precipitations (Na, Mg, K, Ca)

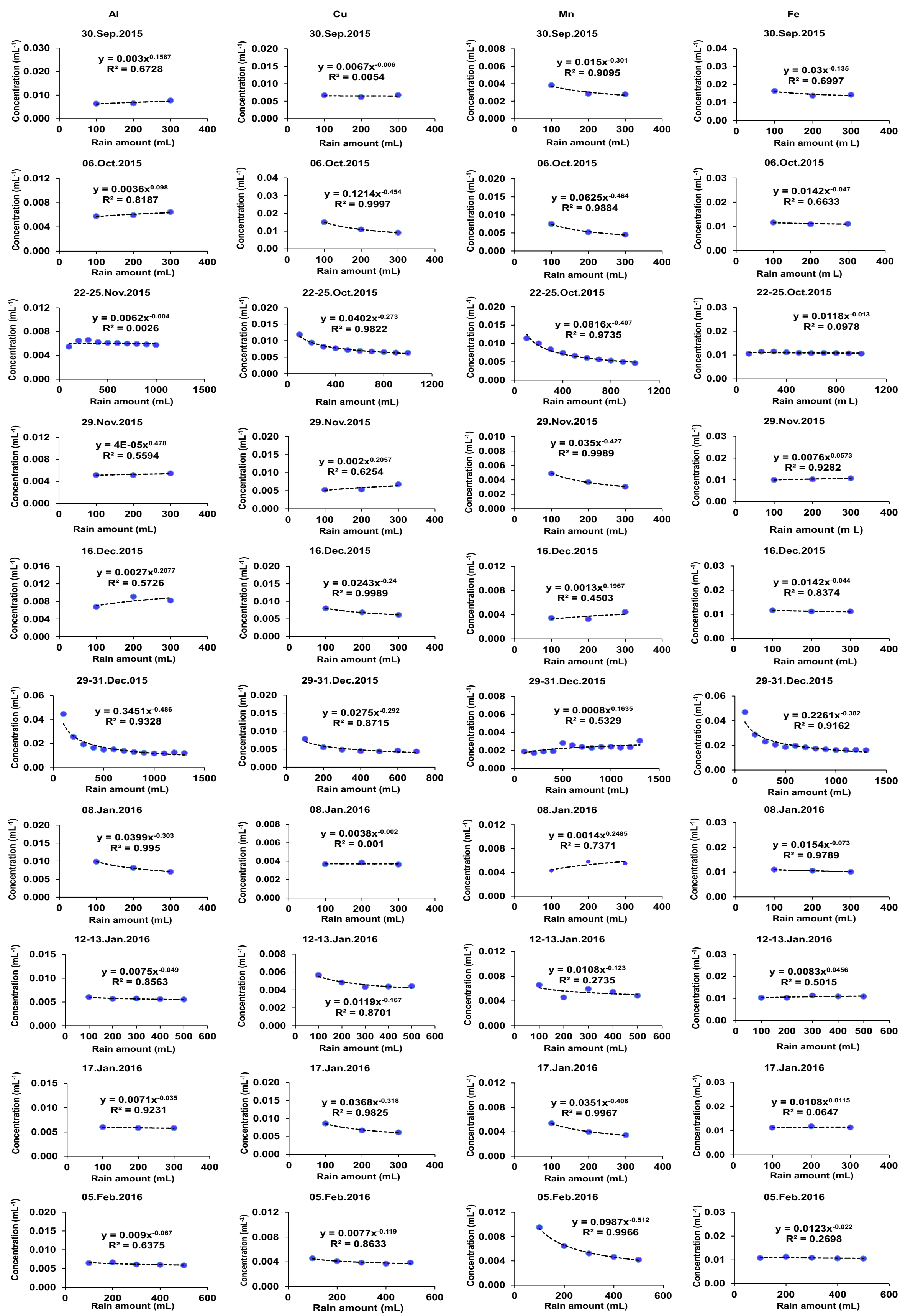

Fig. 7 Scavenging indexes in precipitation events (Al, Cu, Mn, Fe)

scavenging efficiency will be. It was predicted by Izhar et al. (2020) that the mass-scavenging efficiency of water-soluble components elicits their effectiveness to act as condensation nuclei. They stated that the results showed higher scavenging efficiency of the crustal-oriented components. Then they explained that secondary components and biomass burning species have high scavenging efficiency. Ca showed the good scavenging property in most of the precipitations. Just like Na it also has one event with uncertainties, where the concentrations of Ca increased with increasing precipitation amount instead of decreasing. The event with uncertainty is of 16 December 2015 precipitation event (Fig. 6).

Al showed less scavenging property as compared to the elements including Na, Ca, Mg, and K. The numbers of uncertain events were higher for this element with a total of four events. The other six rain events showed a somehow good decreasing trend for Al with respect to rainfall amount. This may be because of the fact that rain does not scavenge Al very efficiently as compared to Na, Ca, Mg, and K. The number of uncertain events where Cu increased in concentration versus the precipitation event was only two. Like all other analyzed elements, the scavenging properties of Cu varied according to the situation. During these precipitations, which took place on 29 November 2015 and 08 January 2016, concentration values showed an increasing trend rather than decreasing. Mn showed a decreasing trend of concentration with respect to rainfall amount. Mn also showed uncertainty in three of the events calculated as like K. The reason for these discrepancies can be the variations in the atmospheric conditions and the air masses which affects the element concentration. But the reasons associated with the uncertainty are not limited to these reasons there can also be other reasons as well. And it's been observed that these elements are not scavenged very efficiently by rain as compared to the Na, Mg, and Ca. The concentrations of Fe in the rain events were observed to be very low as like concentrations of Al, Mn, and Cu elements. Fe also showed varying scavenging properties for each event. Some of the events showed uncertainties in the concentrations of Fe during the course of rainfall events. The local sources of Fe might have affected the concentrations when there was no precipitation during the sub-events.

Conclusion

To examine the below-cloud scavenging process in Istanbul, one of the most important megapolises of the world, sequential precipitation samples were collected between 30 September 2015 and 05 February 2016. Fifty-one sub-event sampling was carried out in 10 precipitations during the sampling period. Sub-event sampling can be performed by using manual or automatic sequential precipitation sampling devices. It is thought that the use of automatic sampling systems instead of manual sampling systems in sub-event sampling will provide more reliable values. In this study, all the sub-events in the sampled precipitations were alkaline. It was determined that the elements with the highest concentration values in the precipitation and $PM_{2.5}$ samples were Na and Fe, respectively. It was clear from the obtained scavenging ratios that the elements show different scavenging ratios for each event. It was determined that Ca showed good scavenging properties in most of the precipitation events. The reason for this may be that the atmospheric source of Ca is dust particles formed as a result of wind erosion and these dust particles contain coarse particles with high scavenging indexes. It was determined that the Al element showed fewer scavenging properties than Na, Ca, Mg, and K elements. It was observed that the number of precipitation events in which Al showed fewer scavenging properties than these elements was four. In the other six precipitation events, a decrease was observed in the concentrations according to the precipitation amount during the precipitation. The reason for this may be that rain does not scavenge Al very efficiently compared to these elements. It was observed that the concentration values of Mn element decreased according to the rainfall amount during the precipitation. In addition, it was determined that this element had uncertainty in three events. Among the reasons for this difference may be variations in atmospheric conditions and air masses that affect element concentration.

This study is the first study conducted in Turkey in terms of calculating scavenging indexes in sub-event sampling. Since the amount of particulate matter has an impact on atmospheric temperature and short-term climate change, therefore, the scavenging ratios of atmospheric particles can be used in short-term climate change models. In terms of identifying local and global pollutant sources and understanding the operation of the in-cloud and below-cloud scavenging mechanism, examining the ion concentration in the subevent sampling may be more useful than examining the ion concentration in the wet and bulk deposition sampling. It is believed that this study will contribute to the advancement of the current state of knowledge about scavenging ratios and scavenging indexes in sub-events.

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Declaration

Conflict of interest The authors declare that they have no conflict of interest.

References

Akkoyunlu BO, Tayanç M (2003) Analyses of wet and bulk deposition in four different regions of Istanbul. Turkey Atmos Environ 37(25):3571–3579. https://doi.org/10.1016/S1352-2310(03)00349-2

Akkoyunlu BO, Tayanç M (2008) Four storms with sub-events: sampling and analysis. Environ Int 34(5):606–612. https://doi.org/10.1016/j.envint.2007.12.019

Akkoyunlu BO, Tayanç M, Karaca M (2003) Study of bulk and subevent wet deposition in Gebze, Turkey. Water Air Soil Pollut: Focus 3:135–149. https://doi.org/10.1023/A:1026057229263

Akkoyunlu BO, Dogruel M, Tayanc M, Oruc I (2013) Design and construction of a computer controlled automatic sequential rain sampler. Biotechnol Biotechnol Equip 27(3):3890–3895. https://doi.org/10.5504/BBEQ.2013.0016

Al-Khashman OA (2005) Study of chemical composition in wet atmospheric precipitation in Eshidiya area. Jordan Atmos Environ 39(33):6175–6183. https://doi.org/10.1016/j.atmosenv.2005.06.056

Al-Momani IF, Tuncel S, Eler Ü, Örtel E, Sirin G, Tuncel G (1995) Major ion composition of wet and dry deposition in the eastern Mediterranean basin. Sci Total Environ 164(1):75–85. https://doi.org/10.1016/0048-9697(95)04468-G

Andronache C (2003) Estimated variability of below-cloud aerosol removal by rainfall for observed aerosol size distributions. Atmospheric Chem Phys 3:131–143. https://doi.org/10.5194/acp-3-131-2003

Baray J-L, Deguillaume L, Colomb A, Sellegri K, Freney E, Rose C, Van Baelen J, Pichon J-M, Picard D, Fréville P, Bouvier L, Ribeiro M, Amato P, Banson S, Bianco A, Borbon A, Bourcier L, Bras Y, Brigante M, Cacault P, Chauvigné A, Charbouillot T, Chaumerliac N, Delort A-M, Delmotte M, Dupuy R, Farah A, Febvre G, Flossmann A, Gourbeyre C, Hervier C, Hervo M, Huret N, Joly M, Kazan V, Lopez M, Mailhot G, Marinoni A, Masson O, Montoux N, Parazols M, Peyrin F, Pointin Y, Ramonet M, Rocco M, Sancelme M, Sauvage S, Schmidt M, Tison E, Vaïtilingom M, Villani P, Wang M, Yver-Kwok C, Laj P (2020) Cézeaux-Aulnat-Opme-Puy De Dôme: a multi-site for the long-term survey of the tropospheric composition and climate change. Atmos Meas Tech 13:3413–3445. https://doi.org/10.5194/amt-13-3413-2020

Bergametti G, Dutot A-L, Buat-MéNard P, Losno R, Remoudaki E (1989) Seasonal variability of the elemental composition of atmospheric aerosol particles over the northwestern Mediterranean. Tellus B Chem Phys Meteorol 41(3):353–361. https://doi.org/10.3402/tellusb.v41i3.15092

Borrelli P, Alewell C, Alvarez P, Anache JAA, Baartman J, Ballabio C, Bezak N, Biddoccu M, Cerdà A, Chalise D, Chen S, Chen W, De Girolamo AM, Gessesse GD, Deumlich D, Diodato N, Efthimiou N, Erpul G, Fiener P, Freppaz M, Gentile F, Gericke A, Haregeweyn N, Hu B, Jeanneau A, Kaffas K, Kiani-Harchegani M, Villuendas IL, Li C, Lombardo L, López-Vicente M, Lucas-Borja ME, Märker M, Matthews F, Miao C, Mikoš M, Modugno S, Möller M, Naipal V, Nearing M, Owusu S, Panday D, Patault E, Patriche CV, Poggio L, Portes R, Quijano L, Rahdari MR, Renima M, Ricci GF, Rodrigo-Comino J, Saia S, Samani AN, Schillaci C, Syrris V, Spinola Kim HS., DN, Oliveira PT, Teng H, Thapa R, Vantas K, Vieira D, Yang JE, Yin S, Zema DA, Zhao G, Panagos P, (2021) Soil erosion modelling: a global review and statistical analysis. Sci Total Environ 780:146494

Bourcier L, Masson O, Laj P, Chausse P, Pichon JM, Paulat P, Bertrand G, Sellegri K (2012) A new method for assessing the aerosol to rain chemical composition relationships. Atmos Res 118:295–303. https://doi.org/10.1016/j.atmosres.2012.07.020

Dueñas C, Fernández MC, Gordo E, Cañete S, Pérez M (2012) Chemical and radioactive composition of bulk deposition in Málaga (Spain). Atmos Environ 62:1–8. https://doi.org/10.1016/j.atmosenv.2012.07.073

Encinas D, Calzada I, Casado H (2004) Scavenging ratios in an urban area in the Spanish Basque Country. Aerosol Sci Technol 38(7):685–691. https://doi.org/10.1080/02786820490460716

Epa US (2006) 40 CFR Part 50. National ambient air quality standards for particulate matter. Final Rule Fed Reg 71:61144–61233

Güllü GH, Ölmez İ, Aygün S, Tuncel G (1998) Atmospheric trace element concentrations over the eastern Mediterranean Sea: factors affecting temporal variability. J Geophys Res Atmos 103(D17):21943–21954. https://doi.org/10.1029/98JD01358

Gülsoy G, Tayanç M, Ertürk F (1999) Chemical analyses of the major ions in the precipitation of İstanbul. Turkey Environ Pollut 105(2):273–280. https://doi.org/10.1016/S0269-7491(98)00186-9

Hales JM (1972) Fundamentals of the theory of gas scavenging by rain. Atmos Environ 6(9):635–659. https://doi.org/10.1016/0004-6981(72)90023-6

İÇDR (2020) İstanbul İli 2019 yılı Çevre Durum Raporu, T.C. İstanbul Valiliği Çevre ve Şehircilik İl Müdürlüğü. https://webdosya.csb.gov.tr/db/ced/icerikler/-stanbul_2019_-cdr_son-20201015102245.pdf

Izhar S, Gupta T, Panday AK (2020) Scavenging efficiency of water soluble inorganic and organic aerosols by fog droplets in the Indo Gangetic Plain. Atmos Res 235:104767. https://doi.org/10.1016/j.atmosres.2019.104767

Jacobson MZ (2002) Atmospheric pollution: history, science, and regulation. Cambridge University Press, Cambridge

Jylhä K (1991) Empirical scavenging coefficients of radioactive substances released from Chernobyl. Atmos Environ A Gen Top 25(2):263–270. https://doi.org/10.1016/0960-1686(91)90297-K

Kabatas B, Pierce RB, Unal A, Rogal MJ, Lenzen A (2018) April 2008 Saharan dust event: Its contribution to PM_{10} concentrations over the Anatolian Peninsula and relation with synoptic conditions. Sci Total Environ 633:317–328. https://doi.org/10.1016/j.scitotenv.2018.03.150

Kasper-Giebl A, Kalina MF, Puxbaum H (1999) Scavenging ratios for sulfate, ammonium and nitrate determined at Mt. Sonnblick (3106m a.s.l.). Atmos Environ 33(6):895–906. Doi: https://doi.org/10.1016/S1352-2310(98)00279-9

Koelliker Y, Totten LA, Gigliotti CL, Offenberg JH, Reinfelder JR, Zhuang Y, Eisenreich SJ (2004) Atmospheric wet deposition of total phosphorus in New Jersey. Water Air Soil Pollut 154:139–150. https://doi.org/10.1023/B:WATE.0000022952.12577.c5

Kubilay N, Saydam AC (1995) Trace elements in atmospheric particulates over the Eastern Mediterranean; concentrations, sources, and temporal variability. Atmos Environ 29(17):2289–2300. https://doi.org/10.1016/1352-2310(95)00101-4

Kulshrestha UC, Reddy LAK, Satyanarayana J, Kulshrestha MJ (2009) Real-time wet scavenging of major chemical constituents of aerosols and role of rain intensity in Indian region. Atmos Environ 43(32):5123–5127. https://doi.org/10.1016/j.atmosenv.2009.07.025

Lee G, Ho C-H, Chang L-S, Kim J, Kim M-K, Kim S-J (2020) Dominance of large-scale atmospheric circulations in long-term variations of winter PM_{10} concentrations over East Asia. Atmos Res 238:104871. https://doi.org/10.1016/j.atmosres.2020.104871

Lin C, Huo T, Yang F, Wang B, Chen Y, Wang H (2021) Characteristics of water-soluble inorganic ions in aerosol and precipitation and their scavenging ratios in an urban environment in Southwest China. Aerosol Air Qual Res 21(5):200513. https://doi.org/10.4209/aaqr.200513

Loosmore GA, Cederwall RT (2004) Precipitation scavenging of atmospheric aerosols for emergency response applications:

testing an updated model with new real-time data. Atmos Environ 38(7):993–1003. https://doi.org/10.1016/j.atmosenv.2003.10.055
McKenzie RM (1989) Manganese oxides and hydroxides. In: Dixon JB, Weed SB (eds) Minerals in soil environments, 2nd edn. SSSA, Madison, pp 439–465
Minoura H, Iwasaka Y (1997) Ion concentration changes observed in drizzling rains. Atmos Res 45(3):165–182. https://doi.org/10.1016/S0169-8095(97)00041-0
Oduber F, Calvo AI, Blanco-Alegre C, Castro A, Alves C, Cerqueira M, Lucarelli F, Nava S, Calzolai G, Martin-Villacorta J, Esteves V, Fraile R (2021) Towards a model for aerosol removal by rain scavenging: the role of physical-chemical characteristics of raindrops. Water Res 190:116758. https://doi.org/10.1016/j.watres.2020.116758
Okay C, Akkoyunlu BO, Tayanç M (2002) Composition of wet deposition in Kaynarca. Turkey Environ Pollut 118(3):401–410. https://doi.org/10.1016/S0269-7491(01)00292-5
Oruc I, Georgieva E, Hristova E, Velchev K, Demir G, Akkoyunlu BO (2021) Wet deposition in the cross-border region between Turkey and Bulgaria: chemical analysis in view of cyclone paths. Bull Environ Contam Toxicol 106:812–818. https://doi.org/10.1007/s00128-021-03210-x
Seinfeld JH (1975) Air pollution physical and chemical fundamentals. McGraw-Hill Inc, New York
Seinfeld JH, Pandis SN (2006) Atmospheric chemistry and physics: from air pollution to climate change, 2nd edn. Wiley, Hoboken
Shimamura T, Wada T, Iwashita M, Takaku Y, Ohashi H (2006) Scavenging properties of major and trace species in rainfall collected in urban and suburban Tokyo. Atmos Environ 40(22):4220–4227. https://doi.org/10.1016/j.atmosenv.2006.03.010
Slinn WGN (1984) Precipitation scavenging. In: Randerson D (ed) Atmospheric Science and Power Production. OSTI, Oak Ridge, pp 466–532
Summak G, Ozdemir H, Oruc I, Kuzu L, Saral A, Demir G (2018) Statistical evaluation and predicting the possible sources of particulate matter in a Mediterranean metropolitan city. Glob Nest J 20(2):173–180. https://doi.org/10.30955/gnj.002333
TSI (2021) Turkish Statistical Institute. https://www.tuik.gov.tr/
TSMS (2021) Turkish State Meteorological Service. https://www.mgm.gov.tr/eng/forecast-cities.aspx
Tuncer B, Bayar B, Yeşilyurt C, Tuncel G (2001) Ionic composition of precipitation at the Central Anatolia (Turkey). Atmos Environ 35(34):5989–6002. https://doi.org/10.1016/S1352-2310(01)00396-X
Uygur N, Karaca F, Alagha O (2010) Prediction of sources of metal pollution in rainwater in Istanbul, Turkey using factor analysis and long-range transport models. Atmos Res 95(1):55–64. https://doi.org/10.1016/j.atmosres.2009.08.007
Wallace JM, Hobbs PV (2006) Atmospheric science: an introductory survey, 2nd edn. Academic Press Inc., Amsterdam
Wang S, Jiao R, Zhang M, Crawford J, Hughes CE, Chen F (2021) Changes in below-cloud evaporation affect precipitation isotopes during five decades of warming across China. J Geophys Res Atmos. https://doi.org/10.1029/2020JD033075
Zheng M, Guo Z, Fang M, Rahn KA, Kester DR (2005) Dry and wet deposition of elements in Hong Kong. Mar Chem 97(1–2):124–139. https://doi.org/10.1016/j.marchem.2005.05.007
Zhou B, Liu D, Yan W (2021) A simple new method for calculating precipitation scavenging effect on particulate matter: based on five-year data in Eastern China. Atmosphere 12:759. https://doi.org/10.3390/atmos12060759